



Étude de liants de coordination pour électrodes négatives au silicium de batteries lithium-ion

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Étude de liants de coordination pour électrodes négatives au silicium de batteries lithium-ion

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À ma famille,

Mes amis de toujours,

Et aux personnes formidables rencontrées pendant ces quatre années,

En France et au Québec.

Résumé en français

Ce résumé s'appuie sur le manuscrit de thèse et l'exposé oral de la soutenance. Il ne contient pas de références bibliographiques, elles sont toutefois disséminées dans les différentes parties du manuscrit

Les sociétés sont très dépendantes des énergies fossiles que sont le gaz, le pétrole et le charbon, car elles représentent environ 80% de la consommation d'énergie mondiale. Or, celles-ci sont majoritairement à l'origine du dérèglement climatique actuel, car leur utilisation comme source d'énergie (par combustion) dégage des gaz à effet de serre. Il faut donc les remplacer par d'autres sources, elles décarbonées, et qui sont majoritairement électriques. Pour cela les usages anciennement basés sur les énergies fossiles, tel que le transport routier, doivent être électrifiés. Par exemple, pour que la voiture électrique soit massivement adoptée par les consommateurs, le pack batterie doit posséder une densité d'énergie d'environ 350 Wh.kg^{-1} (pour l'autonomie), à un prix de $125 \$.\text{KWh}^{-1}$. Or, les performances des batteries Li-ion, qui sont les systèmes électrochimiques actuels les plus denses en énergie, sont autour de 150 Wh.kg^{-1} pour un prix à plusieurs centaines de $\$. \text{KWh}^{-1}$. Avant d'envisager quels leviers exploiter pour améliorer les performances d'une batterie et en réduire le coût, il faut en analyser les constituants et leur fonctionnement.

Une batterie Li-ion est un système de conversion puis de stockage de l'énergie électrique. Elle est constituée entre autres de deux électrodes, contenant chacune un matériau actif, qui est le lieu des réactions électrochimiques réversibles (donc du stockage de l'énergie) faisant intervenir des ions lithium. Les électrodes présentent aussi une porosité (remplie d'électrolyte permettant la diffusion des Li^+), et contiennent des particules d'additifs conducteur électrique et enfin un liant qui assure la cohésion des particules entre elles et avec le collecteur de courant (sur lequel la matière de l'électrode est déposée). Ainsi, une stratégie pour augmenter la densité d'énergie d'une batterie est d'utiliser de nouveaux matériaux actifs capables de stocker plus de Li.

Cette thèse est axée sur l'électrode négative, dont le principal matériau pour batterie Li-ion est le graphite, déjà commercialisé au prix de 8 à 13 $\$. \text{kg}^{-1}$. Il possède une capacité spécifique d'environ 370 mAh.g^{-1} , pour une expansion volumique de seulement 10 %. L'objectif de la thèse est de le remplacer par le silicium dont le prix pourrait être réduit à seulement quelques $\$. \text{kg}^{-1}$, et dont la capacité spécifique est 10 fois supérieure à celle du graphite. Concrètement, cela permet d'augmenter de 25 à 50 % la densité d'énergie d'une batterie dans des conditions réalistes, mais aussi de réduire de 40 % le coût du KWh à densité d'énergie équivalente avec les batteries déjà existantes. Toutefois, l'expansion volumique des particules de Si lors de la lithiation peut atteindre 280 %, ce qui est à l'origine de nombreuses problématiques.

Les premières d'entre elles sont intrinsèques au Si. Lors de la lithiation les particules se déforment et les contraintes associées entraînent leur fracturation. Les fragments ainsi créés se retrouvent isolés électriquement dans l'électrode. Néanmoins, il existe un diamètre critique en dessous duquel les particules ne se fracturent plus. La seconde problématique a lieu lors de la delithiation avec le passage de particules denses à poreuses. Malheureusement, cette évolution morphologique ne peut être évitée qu'en sous-exploitant les capacités du Si, ce qui n'est pas envisageable dans une optique d'amélioration des performances des batteries Li-ion.

Les autres problématiques sont extrinsèques au Si, avec tout d'abord la formation de la couche de passivation à l'interface avec l'électrolyte ou SEI. Elle est constituée des produits de dégradation de l'électrolyte qui est instable au potentiel de travail de l'électrode négative. Plus précisément, l'électrolyte se réduit et les produits de dégradation insolubles se déposent à la surface des particules, puis forment une couche de passivation qui stabilise l'interface entre le Si et l'électrolyte. Toutefois, avec les variations de volume successives des particules de Si, la SEI est déstabilisée et donc s'accumule au cours du cyclage, empêchant le bon fonctionnement de l'électrode. À noter que la fracture des particules et leur nanoporosification exacerbent la formation de SEI. La dernière problématique est la fracturation de l'électrode associée à sa déformation macroscopique. Les fractures peuvent se faire à l'interface avec le collecteur de courant (délamination) ou dans le revêtement de l'électrode (craquelures). Pour y répondre rentrons dans le cœur du sujet de cette thèse : le liant, garant de l'intégrité mécanique de l'électrode. Les liants classiquement utilisés pour les électrodes de Si sont les poly(acide carboxylique), polymères présentant des fonctions acides carboxyliques le long de leur chaîne. Un exemple type est la carboxyméthyle cellulose, car elle peut former des liaisons, et donc s'accrocher, avec tous les éléments de l'électrode. Dans le détail les poly(acide carboxylique) peuvent former des liaisons hydrogène et/ou covalentes (silyl-ester) avec le Si, les particules d'additif conducteur carboné et le liant (et de coordination avec le collecteur de courant en cuivre). Les premières sont très faibles en termes de force de liaison mais totalement réversibles alors que les secondes sont très fortes et renforcent l'électrode, mais ne sont pas réparables après rupture. Il existe cependant un bon compromis entre force de liaison et réversibilité : les liaisons de coordination, qui n'ont été que très peu étudiées dans le cadre des liants pour électrode à base de Si.

Une liaison de coordination c'est une liaison intermoléculaire de type iono-covalente entre un cation métallique et un ligand organique. Par exemple, les poly(acide carboxylique) peuvent former des complexes entre les carboxylates et des cations multivalents. Ainsi, le liant va être réticulé et devrait théoriquement mieux dissiper les contraintes lors de sollicitations mécaniques. Il devrait aussi être plus cohésif, et potentiellement auto-réparant. Mais tout ceci reste à investiguer. Pour les liants de coordination à base de poly(acide carboxylique) (le système d'intérêt de cette thèse), il existe dans la

littérature principalement des études sur les couples alginate et cation divalent, tel que le Cu, le calcium, le fer ou le nickel, avec une augmentation significative de la rétention de capacité des électrodes au cours du cyclage. Les auteurs expliquent systématiquement que l'impact de la coordination sur les propriétés mécaniques et parfois sur la formation de la SEI, est à l'origine de l'augmentation des performances. Toutefois, dans ces études les électrodes contiennent généralement peu de Si par unité de surface ce qui veut dire que les sollicitations mécaniques restent faibles. De plus, une fois coordonné le liant à base d'alginate forme un gel très fort ce qui le rend difficile à manipuler et donc pas nécessairement extrapolable à des procédés de mise en forme industriels. Dans notre équipe, c'est le couple CMC-Cu(II) qui a montré une forte amélioration de la rétention de capacité des électrodes.

Cette preuve de concept est le point de départ de la thèse dont les objectifs sont de :

- Généraliser l'utilisation de la CMC à d'autres cations et particulièrement le zinc et de montrer la formation des liaisons de coordination, grâce notamment aux techniques spectroscopiques;
- Rendre la méthode de réticulation industrialisable, le liant facilement manipulable et vérifier sa distribution/conformation sur les particules de Si grâce à de la microscopie haute résolution;
- Caractériser finement les propriétés mécaniques des électrodes et suivre leur comportement *in-situ* avec des techniques *operandi*;
- Ne pas négliger la formation de la SEI, identifiée comme un axe d'amélioration des électrodes dans la littérature.

Tout en évaluant les performances électrochimiques des électrodes, à un grammage surfacique en Si significatif. L'analyse d'autres paramètres d'intérêts qui relèvent plus de l'ingénierie est aussi présentée.

La première partie des résultats expérimentaux est dédiée à la caractérisation des liaisons de coordination. Tout d'abord, les solutions de liant se préparent en dissolvant de la NaCMC dans une solution tampon à pH 3, ce qui favorise la formation des liaisons silyl-esters. Ce dernier est constitué d'acide citrique et d'hydroxyde de potassium/sodium. Puis, de l'eau ultrapure est ajoutée pour contrôler la concentration du liant. À ce stade c'est le liant de référence, donc non coordonné, qui est obtenu. Enfin, le liant de coordination est formé avec l'ajout d'un précurseur de cation divalent à cette solution. Ce résumé concerne seulement la formulation ZnSO₄ et sa référence sans Zn. La rhéologie montre une plus forte viscosité du liant de coordination par rapport à celui de référence à bas gradient de cisaillement, c'est-à-dire au repos. De plus, sur les courbes de module de stockage et de perte en fonction de la déformation, le premier est supérieur au second pour le liant de coordination, ce qui indique un état de gel physique. À l'inverse, le liant de référence se comporte comme un liquide. Ces deux caractérisations montre qu'il y a formation d'un réseau tridimensionnel dans tout le volume de

liant grâce aux liaisons de coordination en solution entre le Zn et la CMC. Ensuite, la spectroscopie infrarouge sur des échantillons de liant secs montre qu'il y a un décalage en nombre d'onde pour les vibrations asymétrique et symétrique des carboxylates entre les deux formulations. Ces vibrations sont sensibles à l'environnement chimique des carboxylates et le décalage avec l'ajout du précurseur de Zn montre la formation de carboxylates de Zn. Toutefois, la complexité du liant, avec ces deux molécules pouvant former des carboxylates et ses trois cations, empêche une analyse plus fine. Pour cela, de la spectroscopie de résonance magnétique nucléaire de l'oxygène 17 a été réalisé sur des échantillons de liant secs grâce à de l'acide citrique enrichi à 40 % en ^{17}O uniquement sur les fonctions acides carboxyliques. Le spectre obtenu est large et peu défini, ne permettant pas d'obtenir plus d'information sur les liaisons de coordination. Toutefois, l'asymétrie du pic montre une distribution de gradient de champ électrique, ce qui semble indiquer une dispersion homogène de l'acide citrique dans le liant.

Ensuite, les électrodes se préparent en mélangeant le Si avec du graphène (l'additif conducteur électrique) et la solution de liant, respectivement en proportion 70:10:20 % (à sec), puis en enduisant l'encre obtenue sur un collecteur de courant en Cu. Ensuite, des électrodes sont prélevées et séchées avant d'être transféré en boîte à gant. Seules les électrodes de $1,75 \text{ mg}_{\text{Si}}.\text{cm}^{-2}$ sont sélectionnées pour le cyclage. De la NMR du carbone 13 a été réalisé sur de la poudre d'électrode. Le spectre obtenu est large et peu défini, ne permettant pas d'obtenir des informations fines sur les liaisons de coordination. Cependant, le pic est décalé vers les plus petits déplacements chimiques lorsque le liant est plus acide (*i.e.* la formulation ZnSO_4), ce qui est potentiellement révélateur de la formation des liaisons silyl-esters entre le liant et la surface du Si. Du reste, l'observation d'un échantillon d'électrode (sans graphène) contenant le liant de référence, par microscope électronique à transmission et à balayage couplé à la spectroscopie de rayons X à dispersion d'énergie, montre que le liant couvre les particules de Si et fait la jonction entre-elles. La conclusion est identique pour un échantillon d'électrode contenant le liant de coordination (observé dans les mêmes conditions). De plus, le Zn est distribué de manière homogène dans la phase de liant (et aucune particule riche en Zn n'est observable).

Pour conclure, si l'on schématise grossièrement l'état du liant de coordination dans l'électrode, il recouvre les particules grâce aux accroches des liaisons silyl-ester et hydrogène présentes entre la surface du Si et la CMC et l'acide citrique. Le liant assure aussi la jonction entre les particules de Si, notamment grâce aux liaisons de coordination connectant les molécules d'acide citrique et de CMC entre-elles.

La deuxième partie des résultats expérimentaux est dédiée à la caractérisation des propriétés mécaniques des électrodes et de leur comportement en cyclage. Tout d'abord, des tests de nano-indentation effectués sur des électrodes sèches montre que les valeurs de duretés et de module

élastique sont multipliées par deux environ pour les électrodes contenant le liant de coordination. Ce qui indique que ce dernier renforce effectivement le film d'électrode. De plus, lorsque ces tests sont réalisés sur des électrodes imprégnées de propylène carbonate pour imiter l'électrolyte, alors les propriétés mécaniques de l'électrode de référence sont divisées par deux environ alors que celles de l'électrode contenant le liant de coordination reste inchangées. Donc, ce dernier préserve ses propriétés dans les conditions d'opération de la batterie, ce qui peut s'expliquer par une plus faible imprégnation du liant réticulé par le solvant d'électrolyte, car moins mobile. Ensuite, des tests de rayure dans le film d'électrode avec une pointe chargée ont été effectués, afin d'évaluer la cohésion et l'adhésion du film d'électrode. Ces dernières sont plus élevées pour les électrodes formulées avec le liant de coordination, ce qui étaye les résultats obtenus par nano-indentation.

Ensuite, les batteries sont assemblées en boîte à gant dans des cellules Swagelok et en configuration demi-cellule, selon l'état de l'art. L'électrolyte utilisé est du LP30 plus 10 % massique de FEC. Le cyclage est réalisé en mode galvanostatique, dans la gamme de potentiel : 1 à 0,005 V versus Li^+/Li^0 ; les conditions de cyclage sont un premier cycle à C/40, puis 5 cycles à C/20 et enfin le reste à C/10. Les résultats électrochimiques montrent que la rétention de capacité après 60 cycles est augmentée de plus de 750 mAh.g^{-1} pour les électrodes contenant le liant de coordination, pour atteindre environ 2520 mAh.g^{-1} . Il est possible de suivre le comportement mécanique des électrodes lors du cyclage par dilatométrie operando, système permettant de mesurer leur variation d'épaisseur. Pour l'électrode de référence, après seulement quelques heures de cyclage, la variation d'épaisseur de l'électrode dépasse l'expansion théorique pour atteindre environ 220 %. Une analyse post-mortem de cette électrode montre le gondolement du film qui s'est détaché du collecteur de courant. Ce gondolement est un mécanisme de rupture qui a lieu lors de la lithiation et est probablement à l'origine de l'importante variation d'épaisseur mesuré par dilatométrie. Pour l'électrode contenant le liant de coordination, cyclée dans les mêmes conditions, la variation d'épaisseur est globalement fidèle à l'expansion théorique. La réticulation du liant permet donc de contenir l'expansion volumique de l'électrode. Afin, de comprendre l'influence respective de la CMC et de l'acide citrique sur l'augmentation des performances, ce dernier a été remplacé par une molécule tampon non complexante vis-à-vis des métaux (avec un pK_{a1} similaire), le PIPPS. Lorsque la substitution est effectuée pour la formulation de liant de référence, la rétention de capacité s'effondre après seulement quelques dizaines de cycle. Ainsi, l'acide citrique est nécessaire à la bonne cyclabilité du Si pour nos formulations de liant. En partant de cette formulation de référence contenant le PIPPS, avec l'ajout de ZnSO_4 la rétention de capacité s'améliore, indiquant le rôle crucial de la coordination de la CMC. Il faut toutefois revenir à la formulation de liant de coordination avec de l'acide citrique pour retrouver une rétention

de capacité maximal. De sorte que la coordination de l'acide citrique, au même titre que la CMC, a un rôle prépondérant dans la rétention de capacité des électrodes.

Pour conclure, la formation d'un réseau de réticulation formé de carboxylates de Zn de CMC et d'acide citrique permet d'augmenter les propriétés mécaniques du film d'électrode et donc d'améliorer son comportement mécanique lors du cyclage. Ainsi, les électrodes contenant le liant de coordination donnent les meilleures performances électrochimiques.

La troisième partie des résultats expérimentaux est dédiée à la caractérisation de la SEI des électrodes après 1 cycle. La SEI de nos électrodes se compose de LiF et d'espèces type $\text{Li}_x\text{PO}_y\text{F}_z$ qui en composent la partie inorganique. Le reste est composé de molécules organiques contenant du Li, qui ne sont pas clairement identifiables. Ces informations sont obtenues grâce à la NMR du fluor 19 et du ^7Li . Des observations par STEM-EDX sur un échantillon d'électrode contenant du liant de référence, qui n'a pas été exposé à l'air, montre que la SEI inorganique est disséminée, poreuse et relativement épaisse. Malheureusement, la partie organique de la SEI n'est pas différenciable du liant. Sur l'échantillon d'électrode contenant le liant de coordination (analysé dans les mêmes conditions que le précédent), la SEI inorganique est plus dense et relativement plus fine que celle de l'électrode contenant le liant référence. De plus, celle-ci ne recouvre que les zones où le liant de coordination est relativement absent, ce qui indique, dans une certaine mesure, que la surface de Si recouverte de liant de coordination n'induit pas de dégradation de l'électrolyte. Ensuite, la NMR du ^{19}F et du ^7Li a permis la quantification de certaines espèces de la SEI (en plus de leur identification comme expliqué précédemment). À noter que, les électrodes sont débarrassées de tout électrolyte résiduel éventuellement présent dans leur porosité après le cyclage (et ce, sans pratiquer de rinçage avec un solvant). Les résultats indiquent des différences subtiles dans les quantités de SEI entre les deux formulations. Cependant, ce qui est surtout remarquable pour les électrodes contenant le liant de référence c'est la quantité deux fois supérieure de LiPF_6 (le sel d'électrolyte), parfois même présent dans un état solvato. Or ceci ne semble envisageable que pour une SEI avec une forte porosité fermée, ce qui vient étayer les observations d'une SEI plus dense pour les électrodes contenant le liant de coordination.

Pour récapituler, le liant de coordination protège dans une certaine mesure de la dégradation de l'électrolyte sur les surfaces de Si couverte, et lorsque la SEI (inorganique) se forme, elle apparaît plus dense. Finalement, pour les électrodes contenant le liant de coordination, ces deux paramètres ont très probablement une incidence positive sur le cyclage.

La quatrième partie des résultats expérimentaux porte sur des paramètres étudiés qui relèvent plus de l'ingénierie. Dans un premier temps, l'influence du précurseur de Zn a été évaluée en comparant un liant de coordination formulé avec du ZnSO_4 vs. du ZnO . L'intérêt de ce dernier est de

simplifier la formulation en se débarrassant du contre-ion, mais aussi d'augmenter de quelques pourcents la fraction massique de Si dans les électrodes. La rétention de capacité des électrodes de la formulation contenant du ZnO est nettement supérieure à celle des électrodes de sa formulation de référence et est similaire à celles contenant du ZnSO₄ après 60 cycles. Par contre, les caractérisations par rhéologie et spectroscopie infrarouge semblent indiquer que la coordination du liant avec le Zn est différente, sans doute du fait du pH de mise en œuvre différent. L'influence du collecteur de courant en cuivre a aussi été étudiée, avec la comparaison entre un collecteur laminé à froid, un recuit et un texturé. Des observations au MEB révèlent que les craquelures de l'électrode sont différentes selon le collecteur utilisé pour la formulation de référence, alors qu'elles ne varient pas pour la formulation contenant le liant de coordination. Il semblerait donc que, la formulation de référence soit plus sensible aux paramètres du collecteur de courant comme sa limite d'élasticité ou encore sa rugosité. Ces dernières étant respectivement plus faible et plus forte pour les collecteurs de courant, par rapport à celui laminé à froid, comme l'ont montré des mesures de nano-indentation et profilométrie, respectivement. Au final, l'utilisation des collecteurs recuit et texturé permettent d'augmenter la rétention de capacité des électrodes de la formulation de référence, mais pas de celles à base de liant coordonnés. En effet, ces dernières sont plus cohésives et ont une meilleure accroche avec le collecteur de courant, la ou la formulation de référence se délamine probablement plus facilement. Le dernier paramètre à avoir été investigué est la fraction de solide, c'est à dire la quantité de matière sèche dans l'encre d'électrode. Augmenter la fraction de solide de quelques pourcents a permis d'améliorer la rétention de capacité des deux formulations, notamment avec l'emploi d'un collecteur de courant en Cu laminé à froid, mais de manière plus significative pour le liant de référence. Une analyse thermogravimétrique montre que la répartition du liant dans l'électrode dépend de la fraction de solide. En particulier, l'ab/adsorption du liant à la surface des particules de Si est plus importante lors de la formulation de l'encre.

Pour conclure, cette étude a démontré qu'il y a bien coordination de la CMC et de l'acide citrique par le Zn. Les électrodes formulées avec un liant réticulé présentent des propriétés mécaniques améliorées, ainsi que la formation d'une SEI de bonne qualité. Ces paramètres sont à l'origine des meilleures performances électrochimiques observées en cyclage. Enfin, les 3 derniers paramètres analysés donnent systématiquement des performances supérieures pour les électrodes contenant le liant de coordination, ce qui témoigne de la robustesse de cette approche.

Pour ouvrir ce travail de recherche, il serait intéressant de se tourner vers des techniques *operandi* et *in-situ* entrevues durant cette thèse. Par exemple, la microscopie optique *operando* qui permet de voir la formation et l'évolution des craquelures, mais qui dans sa version actuelle souffre de problématiques techniques toutefois solvables en s'inspirant de la littérature. Il y a aussi la tomographie

aux rayons X qui permet de segmenter les différentes phases (gaz, électrolyte, matière(s)) d'une électrode et d'en suivre l'évolution lors du cyclage. Enfin, les autres perspectives portent sur la chimie, avec la possibilité d'utiliser la dialyse pour échanger le Na de la NaCMC par du Zn, ce qui permettrait de simplifier la formulation. Il est aussi possible d'étendre notre approche, en utilisant des cations trivalents comme le Fe ou l'aluminium, ou encore d'utiliser des molécules de liant différentes, comme l'acide tanique qui est un polyphénol pouvant former des phénolates, ou l'acide polyacrylique qui est lui aussi un poly(acide carboxylique) pouvant former des carboxylates.

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Liste des abréviations

ACE : additif conducteur électrique	Alg : alginate
a-Si : silicium amorphe	B : grande base
b : petite base	BSE : électrons rétrodiffusés
C : capacité	CE : efficacité coulombique
CMC : carboxyméthylcellulose	C-rate : régime de charge/décharge
c-Si : silicium cristallin	D.S. : degré de substitution de la CMC
d_{50} : diamètre médian	DMC : carbonate de diméthyle
d_{moy} : diamètre moyen	d_{pointe} : diamètre de la pointe
DRX : diffraction des rayons X	e^- : électron
e : épaisseur	EC : carbonate d'éthylène
EDX : spectroscopie de rayons X à dispersion d'énergie	EE : efficacité énergétique
EIS : spectroscopie d'impédance électrochimique	$E_{K\alpha}$: énergie de radiation $K\alpha$ de l'Al
e_{moy} : épaisseur moyenne	F : constante de Faraday
f_b : force de liaison	FEC : carbonate de fluoroéthylène
FIB : faisceau d'ions focalisés	FTIR : spectroscopie infrarouge à transformée de Fourier
G' : module de stockage	G'' : module de perte
GES : gaz à effet de serre	h : hauteur
HAADF : champ sombre annulaire à grand angle	HOMO : plus haute orbitale moléculaire occupée
I : courant	IR : infrarouge
L : largeur	l : longueur
LCO : $LiCoO_2$	LIB : batteries lithium-ion
$LiPF_6$: hexafluorophosphate de lithium	LP30 : 1 mol.L ⁻¹ $LiPF_6$ dans EC:DMC 1:1 v:v
LTO : $Li_4Ti_5O_{12}$ titanate de lithium	LUMO : plus basse orbitale moléculaire inoccupée
LVDT : transformateur différentiel linéaire variable	M : métal
MA : matière active	MAS : rotation à angle magique
MH : hydruure métallique	m_{sec} : masse des composants secs
Mw : masse molaire	Mylar : polyéthylène téréphtalate

NCA : $\text{LiNi}_{0,8}\text{Co}_{0,15}\text{Al}_{0,05}\text{O}_2$

NMR : résonance magnétique nucléaire

P : pression

PC : carbonate de propylène

PEO : oxyde de polyéthylène

PP : polypropylène

PVDF : polyfluorure de vinylidène

RF : radiofréquence

SE : électrons secondaires

SEM : microscopie électronique à balayage

S_{spe} : surface spécifique

T : température

TEM : microscope électronique à transmission

TGA : analyse thermogravimétrique

v : vitesse

V_l : volume de liant

w_{eq} : épaisseur équivalente de liant

α : angle

Δ_m : incertitude sur la masse

Δx : nombre d' e^- dans réaction électrochimique

λ : longueur d'onde

ρ : masse volumique

ρ_l : densité surfacique de liant

σ_{e^-} : conductivité électrique effective

σ_{ACE}^{eq} : conductivité électrique équivalente de l'ACE

σ_{Li^+} : conductivité ionique effective du Li^+

φ : fraction volumique

NMC : $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$

OCV : tension de circuit ouvert

PAA : acide polyacrylique

PEDOT PSS : poly(3,4-éthylènedioxythiophène)

poly(styrène sulfonate)

pH : potentiel hydrogène

P_t : taux de désordre turbostratique

r : résistivité

S : surface

SEI : interface d'électrolyte solide

SF : fraction de solide

STEM : TEM à balayage

t : temps

T_f : température de fusion

V : volume

V_c : tension d'une cellule

w : distance entre les particules

XPS : spectroscopie photoélectroniqueX

Δ_e : incertitude sur l'épaisseur

ΔV : expansion volumique

ϑ : angle de diffraction

$\lambda_{K\alpha 1}$: longueur d'onde de radiation $K\alpha 1$ du Cu

$\rho_{\text{H}_2\text{O}}$: masse volumique de l'eau

σ_{ACE} : conductivité électrique de l'ACE

$\sigma_{\text{Electrolyte}}$: conductivité du Li^+ de l'électrolyte

σ_{int} : résistance mécanique à l'interface

τ : tortuosité

1. Contextualisation

Les premières batteries lithium-ion (LIB) ont été commercialisées par Sony en 1991. Leur cellule se base sur le couple de matériaux LiCoO_2 (LCO) et le coke de pétrole¹⁻³, comme matériaux d'électrode positive et négative, respectivement. Cette cellule a une densité d'énergie d'environ 80 Wh.kg^{-1} ^{2,3}, ce qui est relativement élevé par rapport aux autres technologies contemporaines (Ni/Cd et Ni/MH *i.e.* hydrure métallique, voir Figure i.1). Cela a permis d'accompagner, voire de permettre la croissance rapide du marché de l'électronique portable^{2,3}. L'impact certain sur le monde de cette technologie a valu aux chercheurs Goodenough J. B., Whittingham M. S. et Yoshino A., le Prix Nobel de Chimie en 2019 pour leurs travaux sur le développement des LIB².

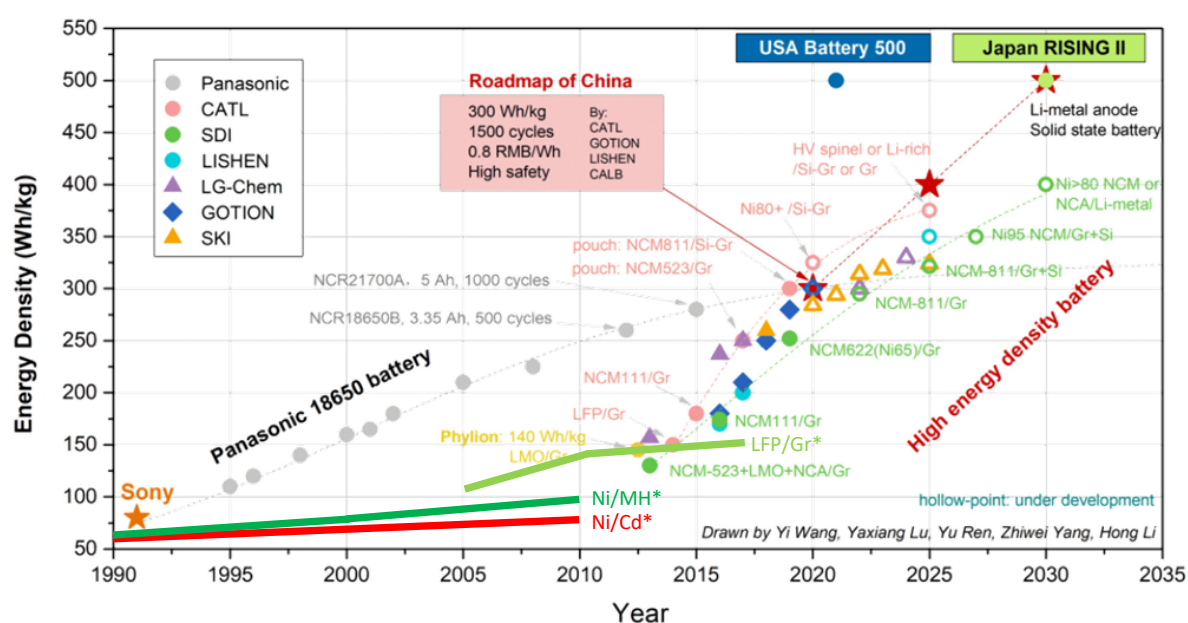


Figure i.1 Évolution de la densité d'énergie (Wh.kg^{-1}) de technologies (couple électrodes : positive/négative) de LIB (sauf Ni/Cd et Ni/MH). Cette figure est adaptée de Winter M., et al³ pour les technologies marquées d'un astérisque et de la « roadmap battery 2030+ »⁴ pour le reste.

Depuis l'émergence des LIB les matériaux d'électrodes utilisés commercialement ont relativement peu évolué. Par exemple, les rares matériaux d'électrodes négatives (hors graphite) à avoir été intégrés dans des batteries commercialisées sont le lithium métal et le titanate de lithium (LTO). Toutefois, l'emploi du premier pose des problèmes de sécurité et le second induit une densité d'énergie relativement faible¹ (vs. graphite), de telle sorte que leur emploi reste marginal. Quant aux matériaux d'électrode positive, ce sont majoritairement des dérivés iso-structuraux du LCO où le Co a été substitué partiellement ou totalement par d'autres métaux de transitions¹, tel que le $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$ (NMC) et le $\text{LiNi}_{0,8}\text{Co}_{0,15}\text{Al}_{0,05}\text{O}_2$ (NCA). Les meilleures cellules actuelles possèdent une densité d'énergie proche

de 300 Wh.kg⁻¹ en se basent sur le couple LiNi_{0,8}Mn_{0,1}Co_{0,1}O₂/graphite (comme présentée Figure I.1) et la marge d'amélioration est limitée.

Cependant, avec la volonté d'électrifier les usages utilisant des énergies fossiles non renouvelables et émettrices de gaz à effets de serre (GES), comme le pétrole, le gaz ou le charbon, des exigences plus importantes sont apparues pour les LIB. Par exemple, pour que l'installation des voitures électriques sur le marché automobile (qui a déjà commencée) se fasse pleinement, le département de l'énergie des États-Unis d'Amérique et le Consortium sur les Batteries Avancées⁵ estiment que les cellules doivent posséder une densité d'énergie d'environ 350 Wh.kg⁻¹ (pour l'autonomie) et le coût du pack de batteries doit être inférieur à 125 \$.kWh⁻¹⁵. Hors actuellement, c'est approximativement le coût du kWh⁻¹ pour les cellules lithium-ion⁵, et l'intégration des cellules dans le pack contenant aussi d'autres systèmes¹ augmente le coût. La nécessité d'augmenter la densité d'énergie des batteries peut être nuancée. En effet, le Shift Project estime que les automobiles (20 % des émissions de GES en France⁶) devraient être utilisées pour la mobilité courte distance, soit entre 15 et 80 km⁶. Au-delà, le train est préférable. Cette estimation s'articule autour d'un plan permettant une décarbonation suffisante des secteurs de l'économie française, en phase avec l'Accord de Paris sur le climat (soit une limitation de 1,5 à 2 °C du réchauffement planétaire global). À noter qu'en 2017, les modèles d'automobiles électriques les moins performant proposaient déjà une autonomie de 130 km^{5,7}. D'ailleurs, les auteurs préconisent de plafonner à 50-60 kWh l'énergie totale du pack batterie (en 2017, seul le constructeur tesla proposait des modèles avec une densité d'énergie supérieure^{5,7}). Ainsi, pour ce qui est de l'automobile, le coût devrait être le facteur le plus déterminant. Par contre, le transport de fret (9 % des émissions de GES en France⁶) par camion, où l'électrification permet de diviser par 5 l'équivalent CO₂ sur l'ensemble du cycle de vie⁶ (vs. véhicule thermique), devrait pouvoir tirer parti d'une plus grande autonomie.

Un autre exemple plus exigeant pour les LIB concerne leur utilisation dans les logements (12 % des émissions de GES en France⁶). Elles peuvent être chargées la nuit, lorsque la demande sur le réseau électrique est en période creuse (avec parfois des tarifs préférentiels), puis déchargées le jour, lorsque la pression sur le réseau est forte. Cela pourrait aider à décarboner la production de chaleur dans les logements, car environ 50 % d'entre eux en France sont basés sur le fioul domestique ou le gaz naturel pour le chauffage⁶. Les LIB Powerwall 2 de Tesla par exemple, stockent une énergie de 13,5 kWh⁸, ce qui n'est pas négligeable par rapport à la consommation journalière en chauffage d'un logement français. En effet, celle-ci s'élève à approximativement 31 kWh, en se basant sur les chiffres suivants : 30,2 millions de résidences principales⁹, 487 TWh de consommation énergétique pour ce secteur¹⁰ et environ 70 % de l'énergie consommée sert au chauffage¹¹. De plus, Rodrigues S. et al¹² ont montré que ces systèmes souffraient surtout d'un coût d'investissement élevé, dans les endroits où ils ne sont pas

déjà économiquement viables. Donc, une augmentation de la densité d'énergie et une réduction des coûts des cellules lithium-ion serait aussi favorable pour cette application.

Enfin, le stockage d'énergie par batteries peut pallier l'intermittence des sources de production d'énergie renouvelable. En effet, l'énergie est stockée lorsque la source produit plus d'énergie que nécessaire, puis restituée au réseau simultanément à celle produite par la source, quand cette dernière ne suffit plus. Pour ces applications, c'est principalement le coût qui est pénalisant au déploiement des batteries¹.

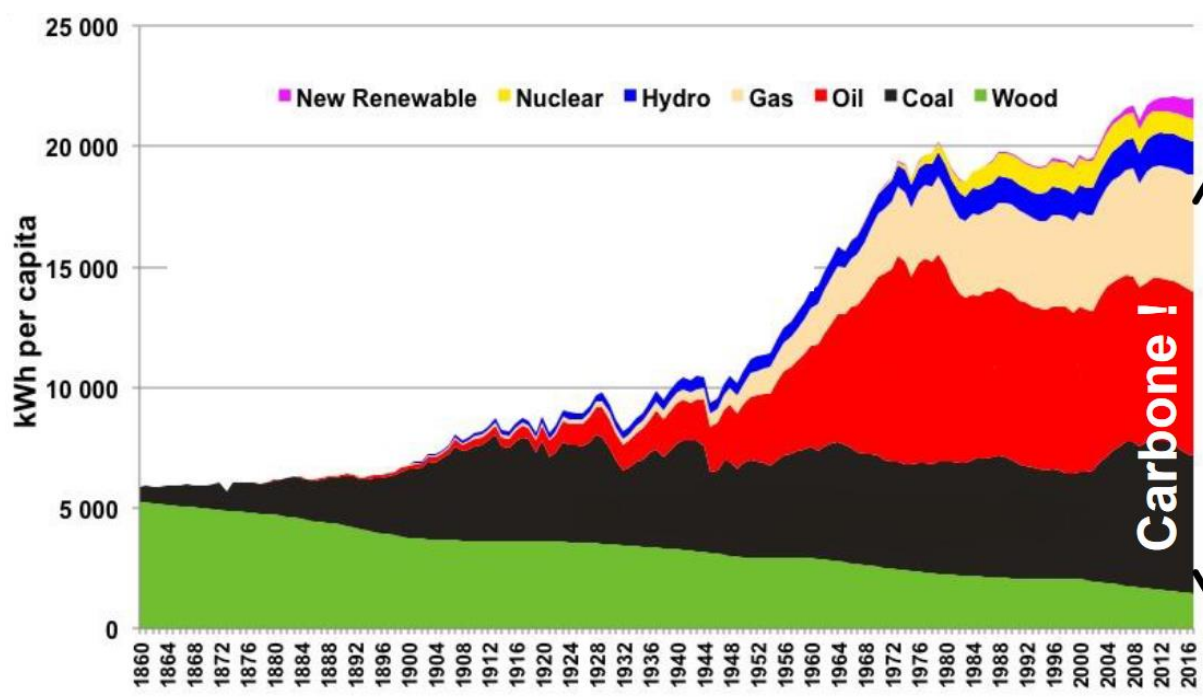


Figure i.2 Évolution de la quantité d'énergie consommée par habitant dans le monde, pour l'ensemble des sources d'énergie¹¹.

Il faut cependant garder en mémoire qu'une batterie n'est qu'un système de stockage et de conversion de l'énergie. Donc, tous les usages où les batteries sont et seront utilisées nécessitent un système de production d'électricité qui n'émet pas de GES pour qu'il y ait réellement un impact sur ceux-ci. Cependant, en 2016, environ 80 % de l'énergie mondiale consommée par personne a un bilan carbone non nul, comme le montre la Figure i.2. Il est donc très probable que les futurs LIB ne seront pas la panacée pour réduire les émissions planétaires de GES.

Quoi qu'il en soit, pour répondre aux problématiques de densité d'énergie et de coût des LIB, il est nécessaire de développer de nouveaux matériaux actifs plus performants. Le silicium est employable à l'électrode négative en remplacement du graphite. Dans des conditions réalistes et face à une électrode positive de LCO, l'utilisation d'une électrode négative (porosité fixée à 40 %) contenant du

silicium à la place du graphite permettrait d'accroître la densité d'énergie d'environ 25 %¹³. Ces calculs sont réalisés en considérant un empilement d'électrodes, donc l'amélioration au niveau de la cellule est moindre. D'autres calculs réalisés estiment qu'un couple NCA/Si ou NMC/Si augmenterait la densité d'énergie des cellules d'approximativement 50 %¹⁴ et réduirait directement le coût au kWh d'approximativement 30 à 40 %¹⁴. La réduction des coûts peut aussi se faire sur le matériau en lui-même. Le prix du graphite se situe entre 8 et 13 \$.kg⁻¹, selon qu'il est d'origine naturel (c'est-à-dire miné) ou d'origine synthétique⁵, respectivement. Le prix du silicium va dépendre de son origine et de la méthode de synthèse. S'il est obtenu par voie plasma et donc à partir de gaz, son coût sera supérieur au graphite. En effet, les réactifs sont relativement chers, soit environ 15 et 210 \$.kg⁻¹ pour le trichlorosilane et le silane¹⁵, respectivement. Toutefois, s'il est synthétisé par mécano-synthèse, du silicium métallurgique ou provenant des déchets de l'industrie photovoltaïque pourrait être utilisé¹⁶. Dans ce cas, le prix des précurseurs est seulement de 1 à 3 \$.kg⁻¹ ^{17,18}.

Ainsi, l'objectif est d'utiliser du silicium préparé par mécano-synthèse comme matériau d'électrode négative. Les LIB auront alors une densité d'énergie plus importante, un coût réduit et une empreinte environnemental plus faible (grâce à l'économie de matière à densité d'énergie équivalente avec une cellule contenant du graphite¹⁴, ce qui est primordial pour la durabilité des ressources⁶). Cependant, le silicium voit son volume multiplié par 3 lors de la charge (voir Figure i.3) et inversement lors de la décharge de la batterie. L'utilisation d'un liant permet de maintenir la cohésion de l'électrode. Cependant, les liants communément utilisés (par exemple le polyfluorure de vinylidène, PVDF) ne supportent pas l'intensité des contraintes/déformations qu'engendrent l'expansion et la contraction du silicium. Les électrodes s'en retrouvent fragmentées et/ou délaminées, ce qui réduit significativement leurs performances.



Figure i.3 Schéma de l'expansion volumique lors de la lithiation du silicium (pas à l'échelle).

Cette thèse porte sur l'étude de polymères dits de coordination comme liant pour électrodes négatives au silicium, afin de remédier (entre autres) à leur dégradation mécanique. Les liants de coordination sont une famille de polymères réticulés grâce à des liaisons intermoléculaires. Ici, ce sont plus précisément des liaisons de coordination entre un cation métallique M(II) et des fonctions carboxylates qui sont exploitées. Le liant de coordination s'obtient par simple mélange entre un

poly(acide carboxylique), la carboxyméthylcellulose (CMC) (liant classique pour les électrodes de silicium) et une source de $M(II)$, tel que le $ZnSO_4$.

La thèse s'articule autour d'un premier chapitre, qui porte principalement sur l'état de l'art des électrodes au silicium, leurs problématiques et l'impact des liants (particulièrement de coordination) sur celles-ci. Le deuxième chapitre présente les matériaux, les moyens de leur mise en œuvre et les techniques utilisées pour leurs caractérisations. Enfin, les résultats expérimentaux sous la forme d'articles constituent le troisième chapitre, avec notamment la caractérisation de la physico-chimie du liant de coordination, des propriétés mécaniques de ces électrodes et de leur impact sur les performances électrochimiques.

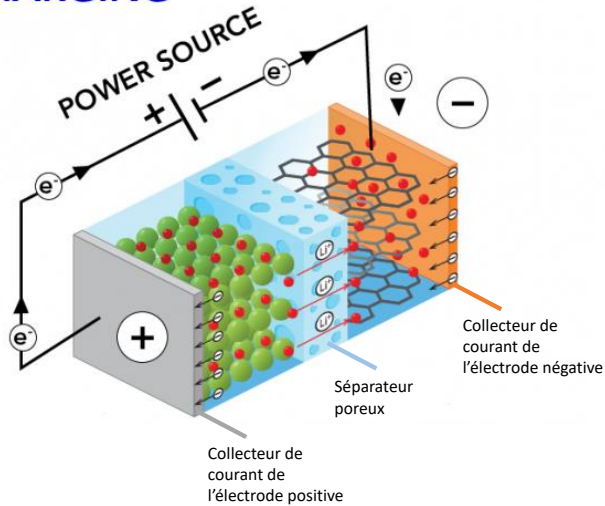
2. Chapitre 1 : Bibliographie

2.1. Fonctionnement d'une batterie Li-ion

Une batterie est un système de conversion et de stockage d'énergie. En effet, de l'énergie électrique est convertie en énergie chimique et inversement (c'est cette réversibilité qui la distingue d'une pile), grâce aux réactions électrochimiques ayant lieu aux deux électrodes. Lors de la décharge, l'électrode négative est oxydée (réaction anodique), c'est-à-dire que des électrons sont produits par la réaction électrochimique. Ceux-ci circulent à travers le circuit électrique externe (fournissant un travail électrique exploitable), car l'électrolyte qui imprègne l'ensemble de la cellule n'est pas conducteur. Tandis que, l'électrode positive est réduite (réaction cathodique), donc des électrons sont consommés dans la réaction électrochimique. Lors de la charge, ce sont les réactions inverses qui se produisent aux électrodes et le sens du courant est inversé.

La Figure I.1 illustre une décharge et charge appliquées à une LIB, dont les éléments et matériaux employés uniquement dans des cellules commerciales seront présentés succinctement dans le prochain paragraphe. Seuls les matériaux d'électrode négative seront détaillés, car notre étude porte sur le silicium qui est un matériau de cette famille.

CHARGING



DISCHARGING

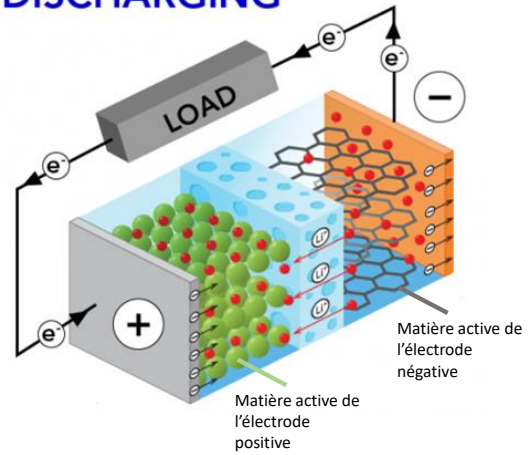


Figure I.1 Schéma simplifié d'une batterie¹⁹.

Les matériaux d'électrodes positives fonctionnent tous sur le mécanisme d'intercalation du Li^+ dans leur structure. Cette dernière est rendue possible grâce aux structures lamellaires des matériaux LCO, NMC et NCA, ou encore les structures présentant des tunnels de type spinelle ou olivine du LiMn_2O_4 et du LiFePO_4 , respectivement¹.

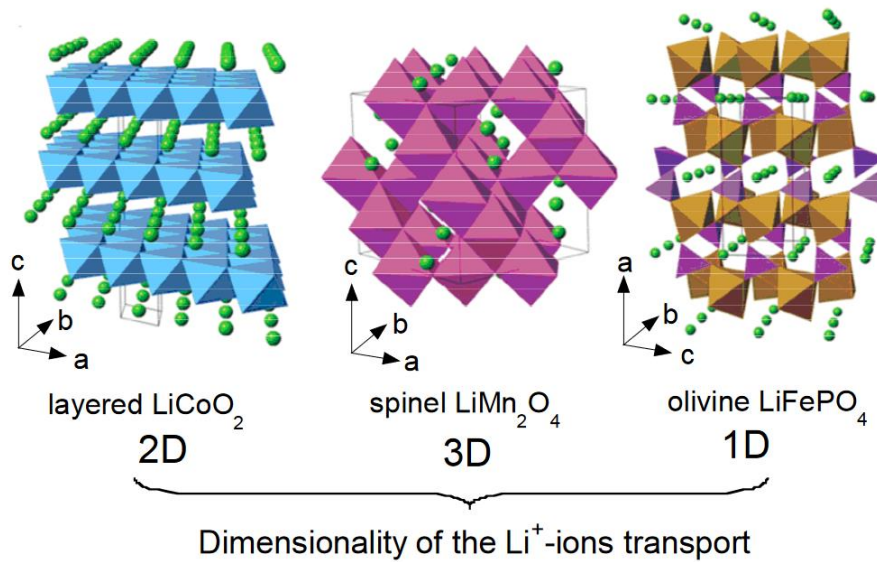
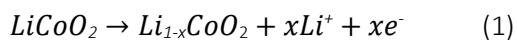


Figure I.2 Structures cristallines des matériaux d'intercalation d'électrode positive²⁰.

Lors de la charge, la réaction électrochimique du LCO (par exemple) suit l'éq. (1) :



Les ions Li^+ désinsérés se retrouvent dans l'électrolyte qui permet leur diffusion jusqu'à l'électrode négative, de telle sorte que le courant électrique dans le circuit est contrebalancé par ce courant ionique. L'électrolyte est composé d'un solvant organique dans lequel est dissout un sel de lithium. Par exemple, l'hexafluorophosphate de lithium (LiPF_6) dissout dans un mélange de carbonate d'éthylène (EC) et de carbonate de diméthyle (DMC) est un électrolyte classique. Le DMC permet d'obtenir un mélange liquide car l'EC ne l'est pas à température ambiante, sa température de fusion étant de $36\text{ }^\circ\text{C}$ ¹. Un séparateur est employé pour empêcher le contact physique et donc le court-circuit entre les deux électrodes, tout en présentant une microporosité pour être perméable à l'électrolyte. Les matériaux de choix sont généralement les polyoléfines telles que le polypropylène (PP). Enfin, les matériaux d'électrodes sont soutenus par des collecteurs de courant qui doivent être inerte au potentiel de travail des matériaux actifs des électrodes. Ainsi, le cuivre et l'aluminium sont principalement utilisés pour l'électrode négative et positive, respectivement.

2.2. Matériaux d'électrode négative

2.2.1. Matériaux d'intercalation

Le graphite est le premier matériau d'électrode négative de LIB à avoir été intégré dans une cellule commerciale³ et reste celui qui est le plus utilisé de nos jours. Le graphite est un empilement de feuillets de graphène, c'est-à-dire un plan d'atomes de carbone liés formant des motifs hexagonaux, selon une structure hexagonale ABA¹. Lors de la lithiation, les ions Li^+ s'intercalent entre les feuillets avec dans un premier temps un ordonnancement aléatoire : l'étape 1L. Ensuite, la lithiation se poursuit avec un état de remplissage successif d'une 1 couche sur 4 (étape 4) puis sur 3 (étape 3) etc... jusqu'à ce que l'ensemble des couches soient lithiées (étape 1). Toutefois, les mécanismes structuraux de la lithiation du graphite ne sont pas encore complètement compris et le modèle de Rüdorff et Hofmann présenté Figure I.3 est probablement erroné²¹ (notamment le passage de l'étape 3 à 2 qui serait plus plausible selon le modèle de Daumas et Herold²¹). La Figure I.3 illustre aussi les tensions de lithiation et de délithiation du graphite selon les étapes. Son potentiel moyen de fonctionnement se situe autour de $0,15\text{ V}$ (vs. Li^+/Li^0) et sa capacité spécifique maximale est de 372 mAh.g^{-1} , correspondant à une stœchiométrie LiC_6 .

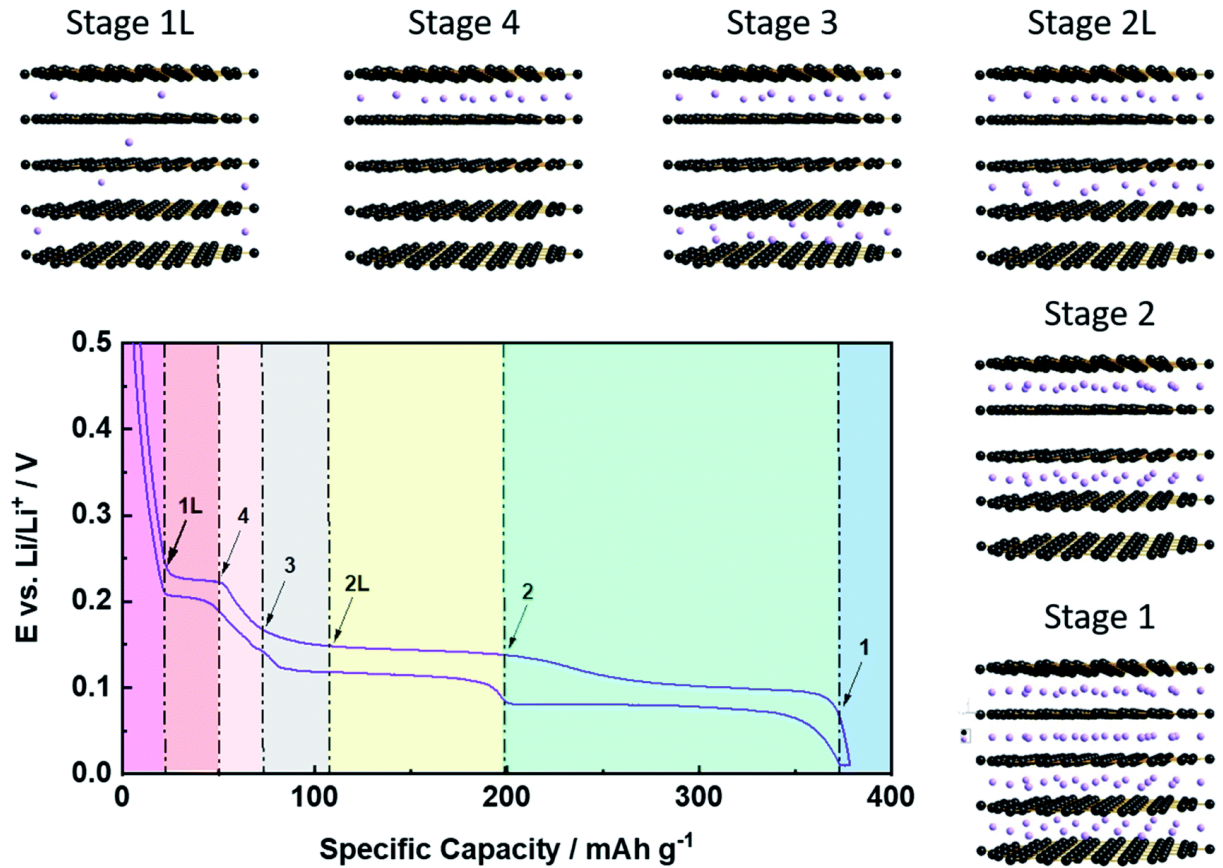


Figure 1.3 Illustration des différentes étapes de lithiation du graphite (selon le modèle de Rüdorff et Hofmann) et du profil en tension correspondant²¹.

Cependant, les couches de graphène peuvent être désordonnées de telle sorte qu'elles sont décalées ou pivotées entre elles, tout en restant parallèles. Dans ce cas, le graphite est dit turbostratique et la lithiation de ces couches n'est pas possible. Le taux de lithiation maximal est donc proportionnel à la quantité de désordre (P_t) dans le matériau, ce qui impacte la capacité du graphite selon l'éq. (2) :

$$C_{\text{graphite}} = 372 \times (1 - P_t) \text{ (mAh.g}^{-1}\text{)} \quad (2)$$

Cette relation de proportionnalité entre P_t et C_{graphite} est observée expérimentalement, comme l'illustre la Figure 1.4a, avec des électrodes contenant du graphite à taux de désordre variable.

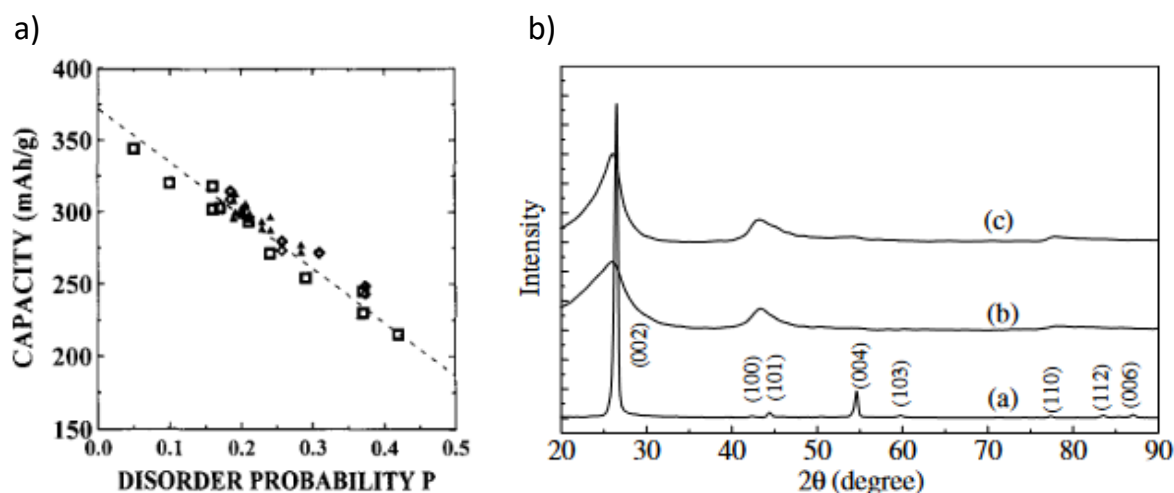


Figure 1.4 (a) Capacité spécifique délivrée par des électrodes contenant du graphite en fonction du taux de couches désordonnées dans ce dernier²²; (b) Diffractogrammes de graphite ordonné (structure hexagonal, courbe « a ») et de graphite turbostratique (courbe « b » et « c »)²³.

Les défauts d'alignement du graphite turbostratique entraîne des différences structurales et notamment un élargissement entre les feuillets de graphène²⁴. Ces différences sont observables par diffraction des rayons X (DRX) et comme le montre les diffractogrammes du graphite ordonné et turbostratique présentés Figure 1.4b. Il est alors possible de quantifier P_t à partir du diffractogramme d'une poudre de graphite, soit en se basant sur le décalage du pic (002)²⁵, soit en réalisant un affinement structural²⁶. Un traitement thermique à haute température permet d'augmenter la proportion de graphite ordonné en réduisant la quantité de défauts¹.

Le LTO est aussi un matériau d'intercalation grâce aux tunnels de sa structure spinelle. Son potentiel moyen de fonctionnement se situe autour de 1,55 V (vs. Li^+/Li^0) et sa capacité spécifique maximale est de 170 mAh.g⁻¹ pour une stoechiométrie $\text{Li}_{7/3}\text{Ti}_{5/3}\text{O}_4$ ¹.

Les structures de ces matériaux leur fournissent des avantages considérables. En effet, l'intercalation/désintercalation du lithium se fait dans des sites vacants²⁰ (et sans rupture/formation de liaisons chimiques) et induit très peu de variation structurales. Par exemple, lors de lithiation la distance entre les feuillets de graphène augmente de 35 Å, ce qui n'induit qu'une expansion volumique des particules d'environ 10 %²¹. Ainsi, la diffusion du lithium dans ces matériaux est rarement limitante et leur rétention de capacité au cours du cyclage est notable.

2.2.2. Matériaux d'alliage et de conversion

La formation de matériaux d'alliage se base sur un autre mécanisme de lithiation, qui contrairement au matériaux d'intercalation nécessite la rupture des liaisons du matériau actif, ainsi que

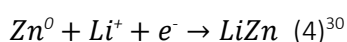
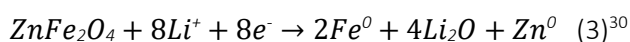
son amorphisation^{27,28}. Ces matériaux ne sont donc pas limités dans leur réaction avec le lithium aux simples sites d'insertion²⁷. En conséquence, les stœchiométries de lithiation sont plus importantes que dans les matériaux d'intercalation et les capacités qui en découlent aussi. Le Tableau I.1 illustre ces deux caractéristiques pour quelques matériaux d'alliage. Des informations plus exhaustives et pour d'autres matériaux sont disponibles dans la revue d'Obrovac M. N. et Chevrier V. L.¹³.

Table I.1 Caractéristiques électrochimiques de certains matériaux d'alliage avec lithium¹³.

Matériaux	Stœchiométrie	Capacité spécifique (mAh.g ⁻¹)	Expansion volumique (%)	Capacité volumique (mAh.cm ⁻³)	Potentiel de délithiation (V)
Mg	Li _{1.95} Mg	2150	125	1658	0,0325
Al	LiAl	993	90	1411	0,38
Si	Li _{3.75} Si	3579	280	2194	0,4

Comme pour les matériaux d'intercalation, la lithiation entraîne une expansion volumique linéaire (loi de Vegard), mais elle est nettement plus importante pour les matériaux d'alliage avec environ + 8,9 mL.mol⁻¹ de lithium (vs. 4,2 mL.mol⁻¹ pour le graphite). Cependant, ce facteur couplé au fait que les matériaux forment des alliages avec une stœchiométrie riche en lithium engendre des fortes expansions volumiques. Le Tableau I.1 montre que celles-ci peuvent atteindre plusieurs centaines de pourcent, comme dans le cas du silicium, réduisant considérablement la capacité volumique disponible. L'expansion volumique est au cœur de plusieurs des problématiques des matériaux d'alliage et elles seront détaillées dans le chapitre sur le silicium. Néanmoins, le faible potentiel de délithiation de certains matériaux et leur importante capacité spécifique, particulièrement dans le cas du silicium, en font des matériaux de choix pour augmenter la densité d'énergie des LIB.

Les matériaux d'alliage contiennent parfois des phases inactives, par exemple au sein d'une même particule. Lorsque l'élément actif est fortement lié à la phase inactive, celle-ci reste totalement spectatrice. À l'inverse si l'élément actif n'est pas fortement lié, il peut y avoir réaction de conversion²⁹, par exemple selon l'éq. (3), puis réaction d'alliage de l'élément actif selon l'éq. (4) :



Lors de la délithiation, les liaisons du matériau actif (ici Zn) se reforment mais il conserve un état amorphe, tandis que la matière inactive (ici Fe⁰) reste spectatrice.

La réaction de conversion a l'avantage de réduire le potentiel moyen de fonctionnement par rapport au simple matériau d'alliage²⁹ et de réduire son expansion volumique, grâce à la matière

inactive. Cependant, la réaction de conversion s'accompagne généralement aussi d'une expansion volumique, qui additionnée à celle de la réaction d'alliage peut dépasser l'expansion volumique de l'élément pur. Par exemple, les réactions (3) et (4) engendrent respectivement une expansion de 93 %_v et de 20 %_v³⁰. Donc, l'expansion de la réaction d'alliage est bien inférieure au 98 %_v d'expansion de LiZn²⁹, mais au total la réaction (3) plus (4) la dépasse. Autres points négatifs : la formation de Li₂O induit une forte capacité irréversible au premier cycle et la capacité spécifique du matériau est réduite par la présence de la matière inactive.

2.2.3. Lithium métallique

Le lithium sous forme métallique est le premier matériau d'électrode négative de LIB à avoir été développé³. Mais, il n'a pas pu être imposé comme matériau de référence malgré sa capacité spécifique de 3860 mAh.g⁻¹ et son potentiel moyen de fonctionnement de 0 V (vs. Li⁺/Li⁰). L'un des problèmes majeurs est la formation des « dendrites » lors de la charge de la batterie. Ces structures, visibles Figure I.5a et I.5b, se forment au niveau des hétérogénéités de surface, c'est-à-dire là où la densité de courant est plus élevée³¹. Étant elles-mêmes des zones de dépôt privilégiées du lithium, leur croissance atteint facilement l'électrode positive, provoquant le court-circuit de la batterie.

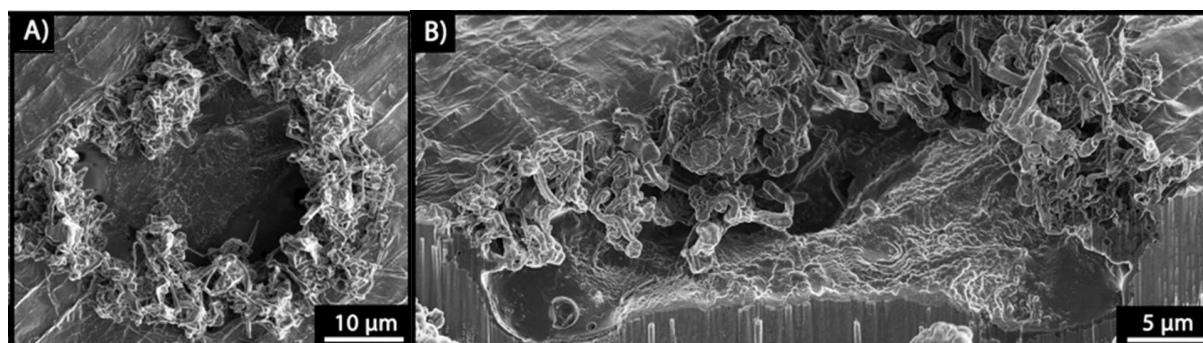


Figure I.5 Observations de dendrites formées par électro-dépôt à la surface d'une électrode négative de lithium métallique³¹ : (a) Vue de dessus; (b) Coupe transversale.

L'emploi de lithium métallique comme électrode négative dans des batteries commerciales à principalement vu le jour couplé avec un électrolyte solide à base de polymère. Ces batteries nécessitent d'être chauffées à plus de 60 °C pour obtenir une diffusivité des ions Li⁺ dans l'électrolyte suffisante, tout en réduisant la formation des dendrites³.

2.3. Grandeurs électrochimiques

Les performances d'une batterie sont décrites par un certain nombre de grandeurs électrochimiques, qui sont détaillées dans les sous-chapitres suivants.

2.3.1. La capacité

Elle définit la quantité de charge électrique qu'un matériau peut délivrer/stocker lors d'une réaction électrochimique. La valeur théorique est généralement normalisée par unité de masse ou de volume de matière active, tel que l'éq. (5) ou (6), respectivement et se mesure lors d'un test galvanostatique selon l'éq. (7) :

$$C = \frac{F \times \Delta x}{3,6 \times Mw} (\text{mAh.g}^{-1}) \quad (5)$$

$$C = \frac{F \times \Delta x}{3,6 \times Mw} \frac{\rho}{\Delta V} (\text{mAh.cm}^{-3}) \quad (6)$$

$$C = I \times t (\text{mAh}) \quad (7)$$

Avec C la capacité, F la constante de Faraday égale à 96485 C.mol^{-1} , Δx ($\text{mol.e}^{-}.\text{mol}^{-1}$) le nombre d'électrons impliqué dans la réaction et Mw (g.mol^{-1}) la masse molaire du matériau. Dans l'éq. (6), ρ (g.cm^{-3}) représente la masse volumique et ΔV l'expansion volumique du matériau (par exemple $\Delta V = 1,1$ pour les 10 % d'expansion volumique du graphite). Enfin, I (mA) est égale au courant imposé lors du test galvanostatique et t (h) est le temps de charge ou de décharge.

2.3.2. Le régime de charge/décharge (C-rate)

Il correspond au temps nécessaire pour stocker/fournir la capacité théorique d'un matériau pour un courant donné et se définit tel que l'éq. (8) :

$$C\text{-rate} = \frac{C}{I} \quad (8)$$

Par exemple, des $C\text{-rate}$ de $C/100$ et de $2C$ signifient que la charge ou la décharge est accomplie théoriquement en 100 h et 30 min, respectivement.

2.3.3. Énergie et puissance

L'énergie d'une batterie est la quantité de travail électrique qu'elle peut fournir et se calcule selon l'éq. (9) :

$$E = \int_0^{\Delta t} I \times V_c(t) dt (\text{Wh}) \quad (9)^{32}$$

$$E = C \times V_c \quad (10)$$

Avec $V_c(t)$ (V) la tension de la cellule à l'instant t (h) et I (A) le courant. L'éq. (10) est une formule simplifiée de l'énergie utilisant C (Ah). L'énergie est presque systématiquement normalisée par la masse ou le volume de la cellule pour être comparable avec d'autres systèmes, on parle alors de densité

d'énergie. Enfin, la puissance d'une batterie est égale à son énergie divisée par le temps nécessaire pour la décharge.

2.3.4. Tension et polarisation

La tension d'une cellule dépend de la différence de potentiel entre les matériaux des deux électrodes, mais aussi de trois autres facteurs de polarisation :

- La polarisation d'activation aux deux électrodes, qui dicte la réaction électrochimique à la surface de la matière active (transfert de charge)¹;
- La polarisation de concentration aux deux électrodes, qui vient des différences de concentration du aux transferts de masse¹;
- La polarisation ohmique, qui dépend de l'impédance totale (résistances électrique et ionique) de la batterie et du courant, suivant la loi d'Ohm.

De telle sorte que lors de la décharge ces facteurs diminuent la tension de la cellule, ce qui réduit la quantité d'énergie exploitable.

2.3.5. Les efficacités

Il en existe deux types, l'efficacité coulombique (CE) et l'efficacité énergétique (EE). La première détermine avec quelle efficacité les charges électriques stockées lors de la charge sont restituées lors de la décharge et se calcule selon l'éq. (11) :

$$CE = \frac{C_{Décharge}}{C_{Charge}} \times 100 (\%) \quad (11)$$

La seconde illustre avec quelle efficacité l'énergie stockée lors de la charge est restitué lors de la décharge et se calcule selon l'éq. (12) :

$$EE = \frac{E_{Décharge}}{E_{Charge}} \times 100 (\%) \quad (12)$$

Comme expliqué précédemment les polarisations affectent les tensions des deux électrodes, et au final augmentent l'énergie nécessaire pour la charge et baissent l'énergie fournie lors de la décharge de la batterie. De telle sorte que $EE < CE < 100 \%$, comme l'illustre la Figure I.6.

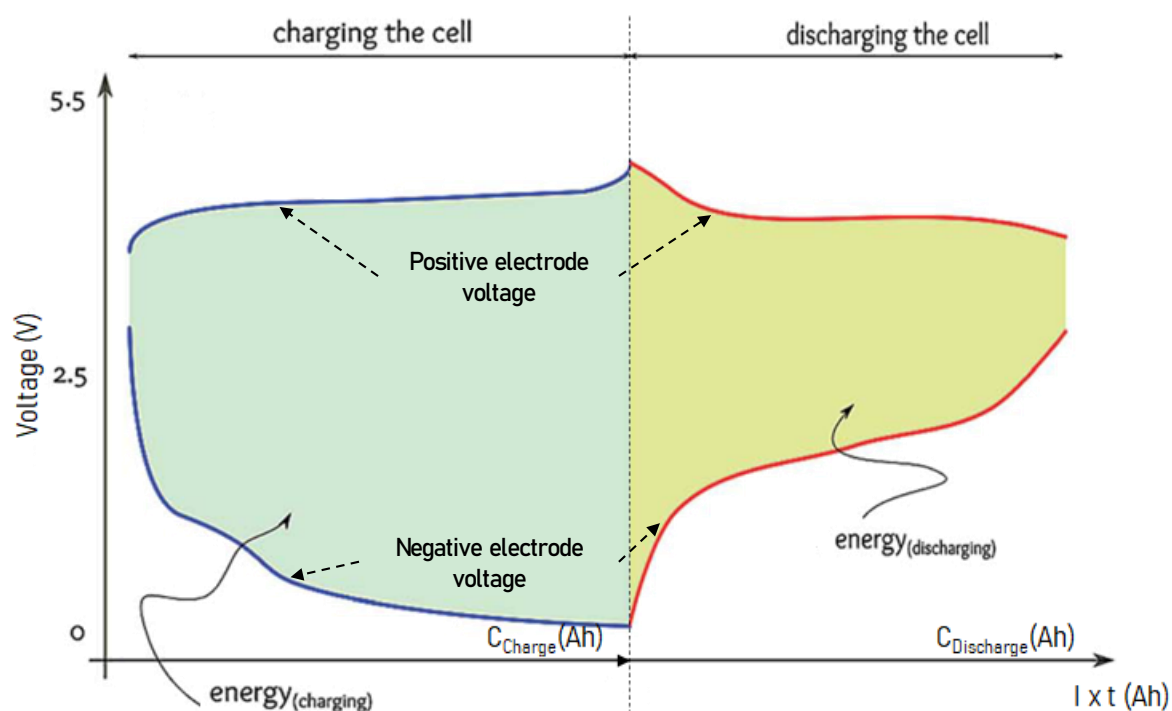


Figure 1.6 Schéma de l'évolution de la tension des deux électrodes au cours d'une charge et décharge galvanostatique. Cette figure est adaptée de Eftekhari A.³³

2.4. L'interface d'électrolyte solide (SEI)

Lors de la charge de la batterie le potentiel électrochimique des deux électrodes évolue. Lorsque celui de l'électrode négative dépasse l'énergie de la plus basse orbitale moléculaire inoccupée (LUMO) des espèces au contact de l'électrode, celles-ci se réduisent³². À l'opposé, si le potentiel électrochimique de l'électrode positive passe en dessous de l'énergie de la plus haute orbitale moléculaire occupée (HOMO), les espèces s'oxydent³². Cela vaut pour tous les éléments de l'électrode composite comme par exemple le liant, mais cela vaut aussi pour l'électrolyte. Lorsque c'est ce dernier qui se dégrade, les espèces solubles dans l'électrolyte s'y dispersent et d'autres précipitent à la surface de l'électrode. Les dépôts qui se font à l'électrode négative constituent la SEI et ses propriétés physico-chimiques influent sur le comportement des électrodes composites lors du cyclage. Cette couche est isolante électrique et sa croissance lors du cyclage aboutit à la passivation de la surface de l'électrode³⁴ vis-à-vis de l'électrolyte.

La formulation de l'électrolyte est très importante, car la chimie de la SEI est dictée en grande partie par la composition de la couche de solvation du Li^+ ³⁵. En conséquence, l'objectif de ce sous-chapitre est de détailler la composition et les propriétés de la SEI produite par la dégradation de l'électrolyte utilisé pour cette thèse. Ce dernier est composé de 1 mol.L^{-1} de LiPF_6 dissout dans un mélange d'EC et de DMC en proportion 1:1 v:v et porte le nom de LP30, auquel du carbonate de

fluoroéthylène (FEC) est ajouté comme additif à hauteur de 10 %_m. Les molécules de l'électrolyte sont présentées Figure I.7. Le Li⁺ privilégie l'EC puis le DMC et enfin le FEC³⁵ pour sa solvation, mais ce dernier devrait tout de même être réduit préférentiellement. En effet, avec cette quantité il devrait participer de manière non négligeable à la couche de solvation. De plus, son potentiel de réduction est plus élevé que celui des autres solvants, avec dans l'ordre décroissant FEC > EC > DMC, car les carbonates cycliques ont plus d'affinité électronique que les linéaires et la fluoration décale l'énergie du LUMO et du HOMO vers le bas³⁵. Les potentiels de réduction des complexes Li⁺-solvant ont été obtenus par calcul quantique pour ces molécules³⁵. Ainsi, les potentiels de réduction sont 0,9 V pour Li⁺(FEC), 0,48 à 0,61 V pour Li⁺(EC), 0,22 à 0,4 et 0,6 V pour Li⁺(DMC)_{cis-cis} et Li⁺(DMC)_{trans-cis}, respectivement³⁵ (potentiel vs. Li⁺/Li⁰). Cependant, d'autres valeurs expérimentales et théoriques de potentiel sont données dans la littérature : dans une revue récente Wang A., et al³⁶ rapportent des valeurs allant de 0,8 à 1,36 V pour l'EC et 0,7 V pour le FEC, ou encore 0,8 V pour l'EC et 1,4 V pour le FEC³⁷ (potentiel vs. Li⁺/Li⁰).

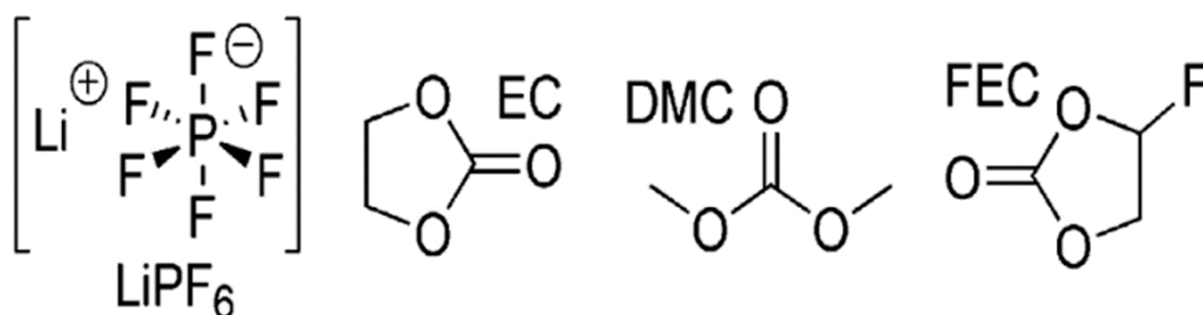


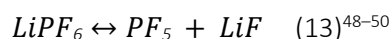
Figure I.7 Molécules composant l'électrolyte utilisé pour cette thèse.

Les chemins réactionnels pour la décomposition d'une même molécule peuvent être variés. Ainsi, pour le FEC, il y a surtout deux mécanismes souvent concomitants, la défluoration et l'ouverture du cycle³⁷, faisant intervenir un ou deux électrons³⁸. Sans rentrer dans le détail des mécanismes réactionnels qui ont été étudiés expérimentalement^{39,40}, modélisés³⁸ et comparés³⁷ pour les électrodes de silicium, les produits de dégradation du FEC qui forment la SEI sont principalement des polymères linéaires mais fortement réticulés de type oxyde de polyéthylène (PEO) et polycarbonates, et du LiF.

Pour l'EC, le mécanisme réactionnel est l'ouverture du cycle, faisant intervenir un³⁷ ou deux³⁶ électrons (ils seraient favorisés respectivement, à forte et faible concentration en EC). Les produits de dégradations de l'EC qui forment la SEI sont principalement le dicarbonate d'éthylène de dilithium (Li₂EDC) qui peut ensuite se décomposer en Li₂CO₃, oxalate et alcoolate de lithium. Des oligomères et un peu de polymères de type PEO linéaire rentrent aussi dans la composition de la SEI avec l'EC³⁷. À noter que le Li₂CO₃ ne serait pas stable au contact du Li_xSi et se décomposerait en Li₂O (avec dégagement de CO₂), qui lui serait instable au contact du silicium et formerait des silicates de lithium.

Pour résumer, le FEC sert de molécule sacrificielle dans l'électrolyte LP30 pour que ses produits de dégradation soient privilégiés à ceux de l'EC ou du DMC dans la SEI. Lorsque que le FEC est utilisé, le LiF occupe une place importante dans la composition de la SEI et ses bénéfices sont multiples. D'abord son épaisseur critique pour empêcher la conduction électronique par effet tunnel et plus faible que celle du Li_2CO_3 par exemple³⁴, et donc son effet passivant est plus fort. De plus, les particules de LiF servent aussi probablement de points d'accroche/de charge pour la matrice organique⁴¹. De manière générale, la SEI comprenant les produits de dégradation du FEC possède un module élastique plus élevé⁴² et la forte réticulation de la partie organique confère à celle-ci un caractère élastomère⁴³. Ces composés et le LiF sont insolubles, et ne se décomposent pas lors de la délithiation^{3,15,16} contrairement à une fraction de la SEI organique non polymérisé et au Li_2O ^{42,44}. Ceci réduit nettement la respiration de la SEI et participe donc à sa stabilité^{42,43}. La couche formée est aussi plus couvrante⁴³⁻⁴⁵, pas nécessairement plus fine⁴⁴, mais plus dense⁴⁶. De plus, la SEI avec le FEC possède une meilleure conduction ionique^{37,40} et par extension une résistance d'interface plus faible⁴². Enfin, l'ensemble de ces propriétés de la SEI obtenue par la dégradation du FEC permettent d'atténuer significativement les pertes de performances électrochimiques des électrodes de silicium^{42,43,45,47}. Néanmoins, la dégradation de l'électrolyte reste une problématique majeure.

Le sel de l'électrolyte LiPF_6 peut aussi se dégrader en se dissociant suivant l'éq. (13) :



Le PF_5 est très réactif avec les molécules de solvant organique et leurs produits de dégradation⁴⁸. Avec les premières il va créer des adduits³⁶ (réaction acide-base de Lewis avec la paire libre de l'oxygène des carbonates l'EC et le DMC⁴⁹). Avec les seconds le PF_5 va produire systématiquement du LiF, mais aussi d'autres molécules fluorées⁴⁸ (entre autres) qui peuvent elles-mêmes se dégrader pour aboutir à des molécules du type $\text{Li}_x\text{PO}_y\text{F}_z$ ⁴².

Mais surtout, le LiPF_6 et le PF_5 réagissent avec l'eau pour systématiquement produire du HF ^{37,49}. Celui-ci peut attaquer le Li_2O et le Li_2CO_3 et produire entre autres du LiF et de l'eau^{37,51}. À noter que le HF peut aussi réagir avec la couche d'oxyde du silicium pour former du SiO_xF_y ($y \leq 3$)^{37,49}. Le principal problème du LiPF_6 est donc la présence de boucles de rétroaction entre ses produits de dégradations successives⁵⁰.

2.5. Le silicium

2.5.1. Généralités

Le silicium possède une capacité spécifique et volumique respectivement, 10 et 3 fois supérieure à celle du graphite et son potentiel de délithiation est de 0,4 V (vs. Li^+/Li^0). Ainsi, une

électrode de graphite remplacée par une électrode au silicium dans des conditions réalistes¹³ augmenterait la densité d'énergie d'une LIB d'environ 25 %.

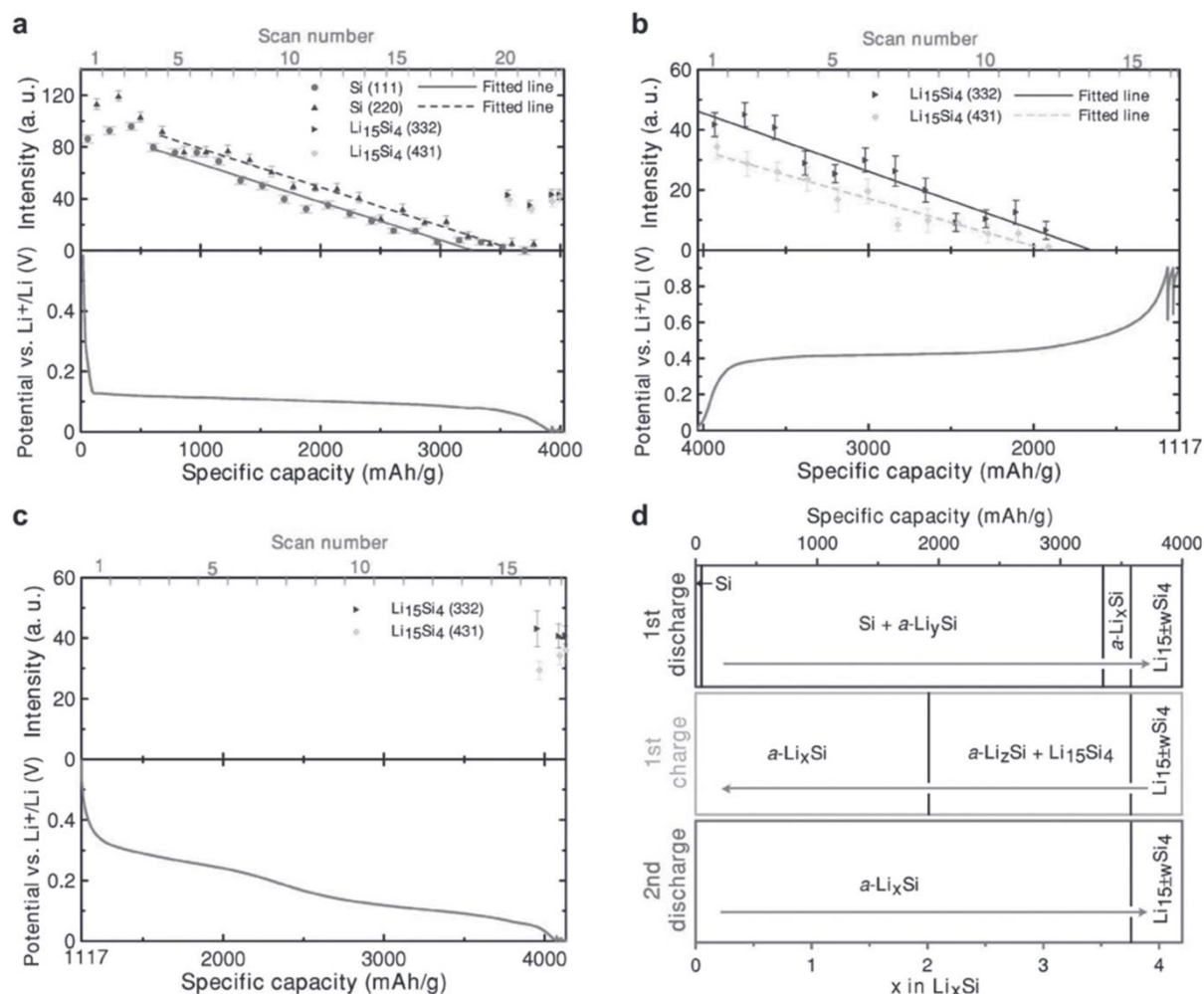


Figure I.8 Mesures DRX et cyclage galvanostatique ($C/100$) couplées sur une électrode de silicium²⁸, en haut les intensités des pics de Bragg et en bas le profil en tension: (a) Première lithiation (c-Si); (b) Première délithiation du silicium; (c) Deuxième lithiation du silicium (a-Si); (d) Model décrivant l'évolution de la structure du silicium lors du cyclage.

La lithiation du silicium cristallin (c-Si) commence à 170 mV (vs. Li⁺/Li⁰) et suit un mécanisme biphasé, ce qui donne à la courbe de tension l'allure d'un plateau avec une légère pente, tel que le montre la Figure I.8a¹³. Dans la particule, un front de réaction à l'échelle du nanomètre sépare le cœur cristallin de la phase Li_xSi amorphe ($x = 3,4 \pm 0,2$), qui constitue la coquille²⁸. Une telle concentration en lithium est nécessaire pour fragiliser suffisamment les liaisons du c-Si et entraîner sa lithiation²⁸. La poursuite de la lithiation diminue la taille du cœur cristallin comme l'illustre la baisse de l'intensité des pics de Bragg du c-Si Figure I.8a. La lithiation aboutit avec la cristallisation de la phase métastable Li₁₅Si₄ en dessous de 70-50 mV (vs. Li⁺/Li⁰)¹³, comme le montre l'apparition des pics de Bragg caractéristiques

de cette phase Figure I.8.b. Dans cette phase, 12 atomes de lithium entourent chaque atome de silicium, ce qui correspond à la stœchiométrie en lithium maximale atteignable à température ambiante²⁸. En délithiation, la transformation de $\text{Li}_{15}\text{Si}_4$ en la phase amorphe Li_2Si ($z \approx 2$)¹³ se produit aux alentours de 450 mV (vs. Li^+/Li^0) selon un mécanisme biphasé, comme le montre respectivement, la disparition des pics de Bragg et le quasi plateau (Figure I.8b). Enfin, la phase amorphe Li_2Si se délithie de manière homogène suivant une réaction de type solution solide¹³, pour aboutir au silicium amorphe (a-Si). Lors de la deuxième réduction, le a-Si se re-lithie de manière homogène avec un profil en tension différent (observable Figure I.8c), qui est typique d'une réaction de type solution solide¹³. La première et la seconde pente correspondent à la lithiation d'un environnement respectivement, dominé par des atomes de silicium et par des atomes de lithium¹³. Le $\text{Li}_{15}\text{Si}_4$ se forme aussi en fin de lithiation. Toutefois, cette phase ne se forme pas lorsque le silicium est de taille nanométrique ou que le *C-rate* est trop élevé, pour des raisons cinétiques¹³. La deuxième délithiation est identique à la première et la Figure I.8d résume l'évolution de la structure du silicium lors du cyclage. À noter que lors de la première lithiation d'un a-Si obtenu par mécano-synthèse par exemple, un front de réaction est observé⁵², mais toutefois atténué par rapport au c-Si⁵³. En effet, il y aurait moins de liaison pendante que pour du a-Si obtenu après délithiation et donc une quantité significative de Li serait toujours nécessaire pour affaiblir les liaisons Si-Si (mais réduite par rapport à c-Si)²⁸.

La lithiation du silicium s'accompagne de contraintes mécaniques, particulièrement au niveau du front de réaction¹³. Les prédictions sur la nature des contraintes indiquent qu'elles diffèrent selon la structure du silicium ou l'étape de cyclage²⁸. Ainsi, lors de la lithiation du c-Si la contrainte de cerclage est compressive dans le cœur (c-Si) et en traction dans la coquille (Li_xSi). Lors de la délithiation du Li_2Si amorphe la situation est similaire, cependant c'est l'inverse pour la lithiation du a-Si (après une première délithiation par exemple)²⁸. Ces situations sont illustrées Figure I.9c, I.9b et I.9a, respectivement.

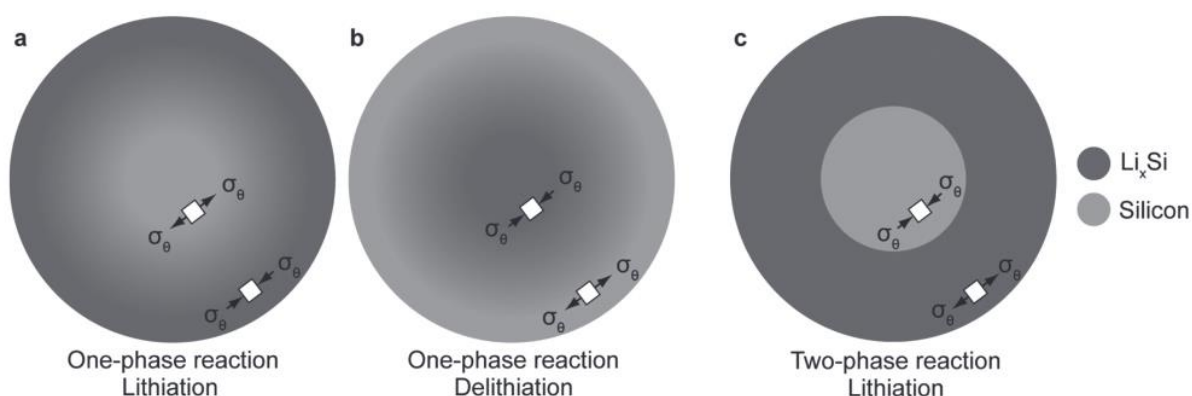


Figure I.9 Schémas représentant la nature de la contrainte de cerclage lors du cyclage, pour des particules de silicium sphériques²⁸: (a) Lithiation monophasée du a-Si; (b) Délithiation monophasée de la phase amorphe Li_2Si ; (c) Lithiation biphasée du c-Si (ou a-Si lors de la première lithiation).

La nature des contraintes et leur évolution lors du cyclage pour les différentes structures du silicium ont un impact direct sur les performances électrochimiques. Par exemple, un couplage chemo-mécanique pour la modélisation de lithiation du c-Si a montré que l'avancement du front de réaction vers le cœur de la particule sphérique intensifie la contrainte compressive, ce qui ralentit le front de lithiation⁵⁴. Cela va jusqu'à stopper la réaction avant la lithiation complète de la particule, ce qui a été observé expérimentalement *in situ* par microscopie électronique à transmission (TEM)⁵³. Toutefois, cela n'a pas été observé pour le a-Si⁵². De plus, il existe un couplage entre la contrainte et le potentiel de la réaction⁵⁵. La compression dans le cœur du c-Si abaisse son potentiel de lithiation et la contrainte en tension à la surface de la particule lors de la délithiation l'augmente²⁸, réduisant l'efficacité énergétique au premier cycle.

La lithiation du c-Si a lieu préférentiellement selon certaines directions²⁸. En effet, l'expansion dans la direction latérale $\langle 110 \rangle$ est approximativement 5 et 8 fois supérieure à celle des directions $\langle 100 \rangle$ et $\langle 111 \rangle$, respectivement²⁸. La différence de mobilité des plans cristallographiques est à l'origine de cette lithiation anisotrope du c-Si. À l'inverse la lithiation du a-Si se fait de manière isotrope²⁸.

Malgré l'augmentation de la densité d'énergie que promet l'emploi du silicium comme matériau d'électrode négative, il s'accompagne de nombreuses problématiques qui sont détaillées dans les prochains sous-chapitres. Elles sont intrinsèques au matériau ou sont dues à son expansion volumique qui peut atteindre 280 %¹³.

2.5.2. Problématiques intrinsèques au silicium

2.5.2.1. *Fracture des particules*

Les contraintes en tension engendrées par la lithiation et la délithiation des particules de silicium peuvent entraîner leur fracturation, après l'initiation d'une craquelure, comme l'illustre la Figure I.10. Alors, celles-ci s'isolent électriquement et ne contribuent plus à la capacité de la LIB, tout en augmentant la densité de courant supporté par le reste de l'électrode.

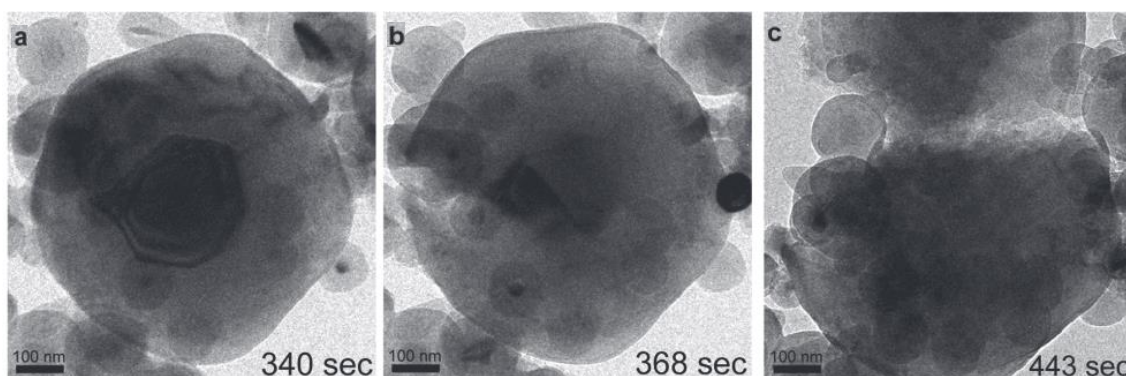


Figure I.10 Images TEM *in situ* de la lithiation d'une particule sphérique de c-Si: (a) Expansion de la particule; (b) Initiation d'une craquelure au milieu gauche de la particule; (c) Fracturation de la particule. Cette figure est adaptée de McDowell M. T. et al²⁸.

L'intensité des contraintes dépend de plusieurs facteurs dont la cinétique de lithiation et la taille des particules²⁸. Ainsi, réduire à la fois la vitesse de lithiation/délithiation et la taille des particules limite les fractures²⁸. En effet, réduire les dimensions des particules augmente leur résistance mécanique. Dans les faits, il existe un diamètre critique des particules sphériques au-dessus duquel les particules se fracturent systématiquement. Il a été estimé *in situ* par TEM à approximativement 150 et 870 nm pour le c-Si⁵³ et le a-Si⁵², respectivement. Cette différence peut s'expliquer par une meilleure distribution des contraintes lors de la lithiation isotrope du a-Si. La nanostructuration des particules de silicium par exemple avec l'ajout de porosité permet aussi d'augmenter le diamètre critique de celles-ci⁵⁶. Il existe donc plusieurs leviers efficaces pour empêcher la fracturation des particules.

2.5.2.2. Nanoporosification des particules

La seconde problématique est la formation d'une structure bi-phasique de silicium et de pores lors de la délithiation, tel qu'illustré Figure I.11. Cette évolution structurale est propre à tous les composés subissant un désalliage (oxydation) et a été étudié par exemple pour les alliages AgAu⁵⁷. L'épaisseur des filaments de matière et de pore semble être inversement proportionnel à la température de fusion (T_f) de l'élément noble⁵⁸. Ainsi, l'épaisseur des filaments de silicium est estimée à 7 nm⁵⁸, mais dépend aussi d'autres facteurs que T_f .

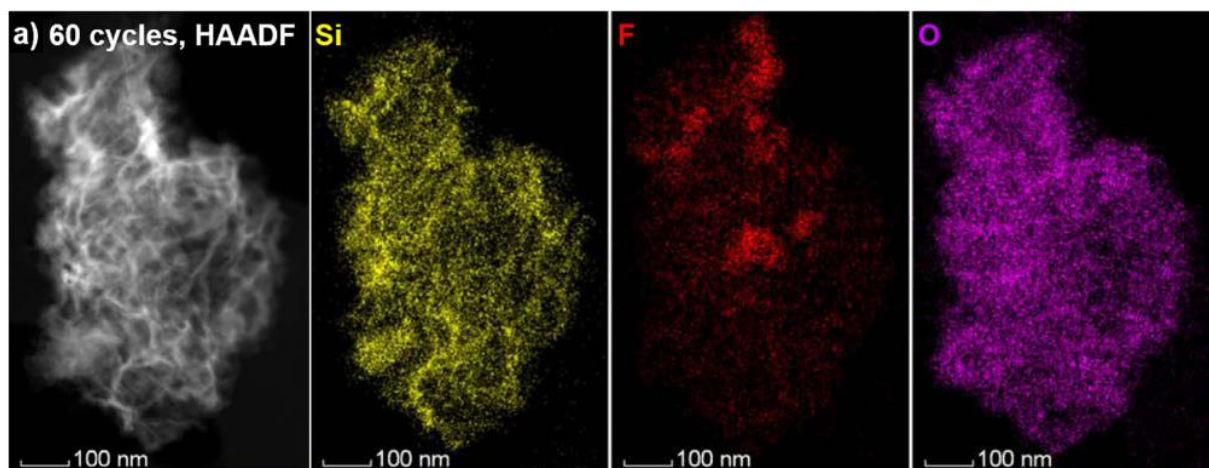


Figure I.11 Images et cartographies (silicium, fluor et oxygène de la SEI) STEM-EDX d'une particule de silicium devenue poreuse après 60 délithiation. Cette figure est adaptée de Wetjen M. et al⁵⁹.

Dans les conditions opérationnelles d'une LIB, ces facteurs sont la concentration en élément à désallier, le *C-rate* et la taille des particules. Plus ces trois paramètres sont bas, plus la tailles des

filaments est importante, au point qu'en deçà d'un seuil de concentration, de cinétique et de dimension, l'évolution vers la structure biphasique n'a pas lieu⁵⁸. En effet, lorsque la cinétique est trop lente la diffusion de surface de l'élément noble prend le dessus et une couche de cet élément se forme à la surface de la particule⁵⁸. La situation est identique lorsque la concentration en élément à désallier est trop faible, alors la diffusion de celui-ci à travers la couche de l'élément noble se fait par voie solide et la structure n'évolue pas⁵⁸.

Néanmoins, un faible *C-rate* et un bas taux de lithiation ne sont pas souhaitables pour une application en LIB, et dans des conditions de cyclage standard d'une électrode, la nanoporosification est la norme. Malheureusement, Cette structure offre plus de surface de silicium pour la dégradation de l'électrolyte et de volume de pore pour la formation de la SEI, tel que le montre la Figure I.11.

2.5.3. Problématiques extrinsèques au silicium

2.5.3.1. Craquelure et délamination

La lithiation/délithiation des particules de silicium engendre leur expansion/contraction et donc la déformation macroscopique de l'électrode. Ces déformations sont couplées à des contraintes qui vont se manifester dans le film d'électrode, à son interface avec le collecteur de courant et dans ce dernier. Lorsqu'elles dépassent les seuils de résistance à la fracture d'un de ces 3 éléments, des craquelures de différentes natures peuvent être initiées, comme l'illustre la Figure I.12. Ces craquelures se forment lorsque le film d'électrode est en tension, c'est-à-dire lors de la délithiation, mais il existe aussi des mécanismes de rupture en compression (lors de la lithiation). La mécanique de la rupture des couches minces sur un substrat a été étudié de manière approfondie par Hutchinson J.W. et Suo Z.⁶⁰, mais aussi par Thouless M. D.⁶¹. À noter que le collecteur de courant a une importance significative sur la mécanique de la rupture des électrodes, mais ses propriétés sont trop souvent omises dans la littérature.

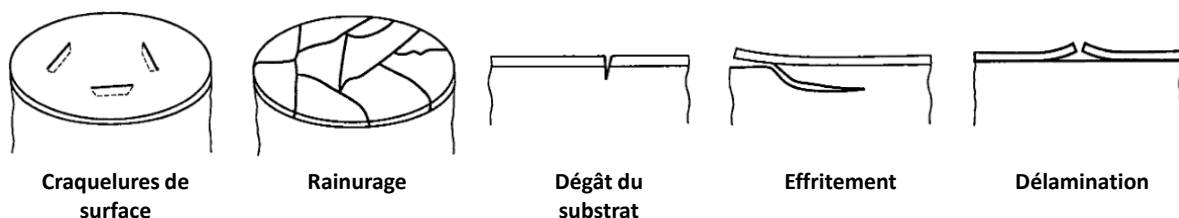


Figure I.12 Différents mécanismes de rupture possibles de l'électrode de silicium et/ou du collecteur de courant. Cette figure est adaptée de Hutchinson J. W. et Suo Z.⁶⁰.

Lors de la délithiation une portion de l'électrode peut s'isoler électriquement si elle se détache suite à une délamination ou à une craquelure se propageant parallèlement à l'interface avec le

collecteur de courant⁶⁰. Dans ce cas, le problème est identique à celui de la fracture d'une particule de silicium mais à une échelle nettement supérieure. Pour y remédier il faut augmenter les résistances à la fracture, ou diminuer les contraintes en limitant par exemple l'épaisseur du film d'électrode⁶² ou l'expansion volumique du silicium²⁹.

2.5.3.2. Déstabilisation de la SEI

Les contraintes de l'expansion/contraction des particules de silicium se font aussi ressentir sur la SEI. Lorsqu'elle rompt, la surface du silicium se retrouve exposée à l'électrolyte dont la dégradation se poursuit. L'étude du comportement mécanique de la SEI se fait généralement sur couche mince de silicium^{63–65} (l'électrolyte ne contient pas de FEC dans ces études), car l'analyse d'une particule sphérique est très complexe à mettre en œuvre expérimentalement. Malgré cette limitation, les mécanismes de la rupture sont identiques à ceux du film d'électrode, comme le montre la délamination et les craquelures de la SEI dans les Figures I.13a et I.13b, respectivement.

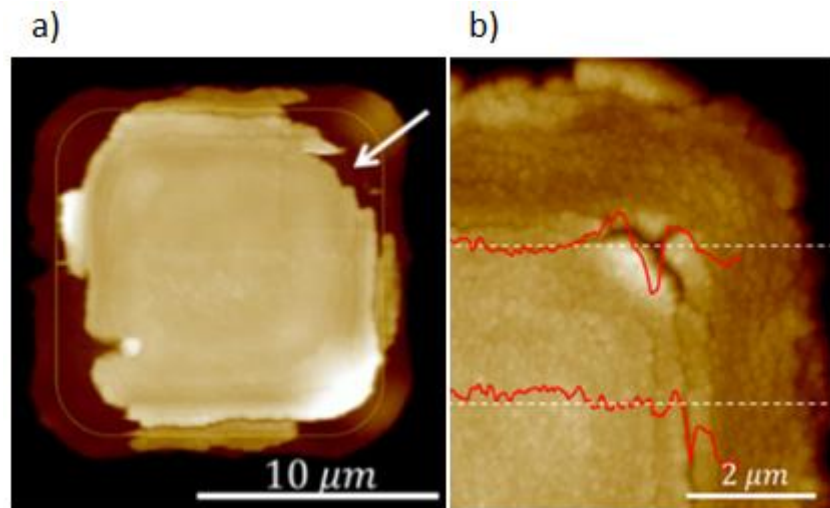


Figure I.13 Différents mécanismes de rupture de la SEI sur couche mince de silicium, analysés par microscopie à force atomique: (a) La flèche indique une zone de délamination; (b) Le profil en hauteur indique la présence de craquelures profondes. Ces figures sont respectivement adaptées de Guo K. et al⁶⁵ et de Kumar R. et al⁶⁴.

Il est donc très probable que les principes de mécanique de la rupture et les paramètres à maximiser pour y remédier s'appliquent autant à la SEI qu'au film d'électrode.

2.6. Formulation d'une électrode

2.6.1. Généralités

Une électrode de LIB n'est généralement pas constituée que de matière active (MA). En effet, pour assurer l'activité électrochimique de celle-ci, il faut la présence d'électrons et d'ions Li^+ à sa surface (simultanément en un point discret, comme le montre la Figure I.14). Cependant, la MA est rarement bonne conductrice électrique et ionique (de Li^+). Ces rôles vont donc revenir à d'autres éléments : l'additif conducteur électrique (ACE) et l'électrolyte dans la porosité, respectivement. Ainsi, l'ACE permet de faire passer le courant électrique de la MA au collecteur de courant et inversement, avec le moins de résistance possible, tandis que l'électrolyte dans la porosité permet la conduction ionique entre la MA des deux électrodes. Enfin, un liant est utilisé en outre pour assurer l'intégrité mécanique entre la MA, l'ACE et le collecteur de courant, qui ensemble forment une électrode composite, comme schématisé Figure I.14.

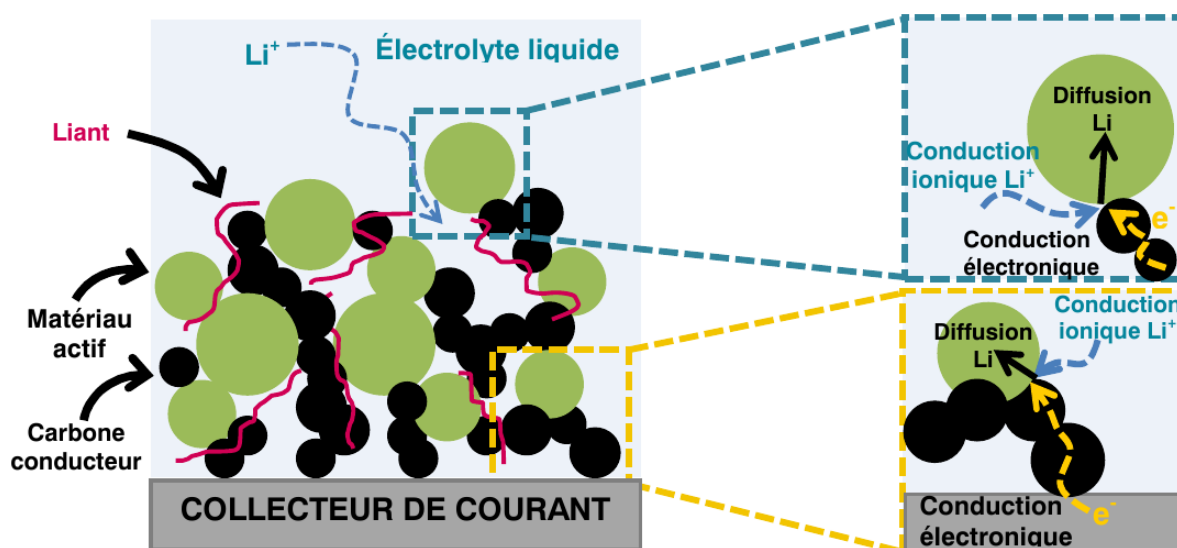


Figure I.14 Schéma simplifié d'une électrode composite⁶⁶.

Il existe en principe une multitude de combinaisons possible entre le liant (composition, poids moléculaire), l'ACE (composition (carbones, métaux de transition...), taille et forme des particules) et la MA. En pratique, il faut les meilleures interactions possibles entre les différents éléments de l'électrode composite lors de sa formulation, c'est-à-dire en présence de solvant, pour améliorer la fonctionnalité de l'électrode. Ce qui exclut en réalité un certain nombre de combinaisons. La méthode décrite par Easley A. D. et al⁶⁷ permet à priori de faire un tri en utilisant les paramètres de solubilité d'Hansen pour évaluer la compatibilité des éléments entre eux.

À noter que l'ACE le liant et la porosité sont considérés comme de la masse/volume « mort(e) » ou inactive, dans le sens où ils n'apportent habituellement pas de capacité en eux-mêmes. Ainsi, dans l'industrie leur proportion est minimisée afin de maximiser la densité d'énergie des LIB. La détermination des proportions optimales se fait le plus souvent de manière empirique (essais et erreurs), car la capacité obtenue dépend de nombreux paramètres et les interactions entre les éléments de la formulation sont complexes et difficilement caractérisables et modélisables⁶⁸. En conséquence, l'utilisation d'un plan d'expérience est souhaitable pour obtenir un bon compromis entre un nombre de formulation restreint et l'identification des facteurs d'impact, voire même l'observation de synergie entre éléments⁶⁹.

Le but des sous-chapitres suivants est d'expliquer plus précisément le fonctionnement des éléments structurant l'électrode composite et de faire un bref état de l'art sur les ACE et liants couramment utilisés pour le silicium et sur ceux utilisés pour nos formulations. Le détail de la composition de l'électrode composite de silicium se trouve au chapitre 2 : Matériaux et méthodes.

2.6.2. ACE

L'évolution de la conductivité électrique d'une électrode avec l'ajout d'ACE suit un mécanisme de percolation. C'est-à-dire qu'à partir d'une fraction volumique critique d'ACE, la conductivité électrique augmente de plusieurs ordres de grandeur⁷⁰, qui s'accompagne d'une nette augmentation de la capacité expérimentale de l'électrode⁷¹. Au-dessus de ce seuil, la conduction se fait par effet tunnel. Alors, la conductivité électrique réelle de l'ACE (σ_{ACE}^{eq}) dépend de la distance entre les particules (w) comme le décrit l'éq. (14) :

$$\log(\sigma_{ACE}^{eq}) \propto -w \quad (14)^{70,71}$$

Ainsi, lorsque la percolation est atteinte, pour augmenter la conductivité électrique des électrodes, il faut réduire la fraction volumique de liant, car c'est lui qui sépare physiquement les particules d'ACE en s'adsorbant sur elles^{70,71}. Il est aussi nécessaire de multiplier les points de contact entre la MA et l'ACE pour rendre la surface de la MA véritablement active⁷², comme l'illustre la Figure I.14. Enfin, la conductivité électrique effective de l'électrode dépend de la fraction volumique (φ) et de la tortuosité (τ) de la phase ACE selon l'éq. (15), si la conductivité électrique de la MA et du liant est strictement inférieure à celle de l'ACE (ce qui est le cas expérimentalement) :

$$\sigma_{e-} = \frac{\varphi_{ACE}}{\tau_{ACE}} \sigma_{ACE}^{eq} \quad (15)^{73}$$

Pour les électrodes à base de silicium plusieurs études montrent que les ACE avec un grand facteur de forme sont bénéfiques :

-L'enchevêtrement et la flexibilité des fibres de carbone permettent d'atténuer les déformations structurelles de l'électrode⁷². Leur grande taille permet aussi de préserver le contact électrique entre des morceaux détachés et le reste de l'électrode⁷⁴;

-Les plaquettes de graphite/graphène facilitent le glissement par friction des particules de silicium dans le plan des plaquettes⁷⁵, comme le ferait un lubrifiant^{74,76};

-Leur surface spécifique élevée maximise les points de contact avec le silicium pour le transfert électrique⁷⁶ et pour l'accroche avec le liant⁷⁴.

À noter qu'il existent des liants conducteur tel que le poly(3,4-éthylènedioxythiophène) poly(styrène sulfonate) (PEDOT PSS) utilisable en complément ou en substitue de l'ACE⁷⁷ (mais très coûteux). Mais aussi que le silicium devient un bon conducteur électrique lorsqu'il est lithié⁷⁸.

2.6.3. Liants

La résistance mécanique macroscopique de l'électrode est régie par celles des interfaces (σ_{int}) entre le liant et les éléments qu'il colle selon l'éq. (16) :

$$\sigma_{int} = f_b \times \rho_l \quad (16)^{71,79}$$

Avec f_b la force de la liaison entre le liant et la particule collée (par exemple) et ρ_l la densité surfacique de liant adhérent de part et d'autre de l'interface entre les deux particules. Lorsque les liaisons du liant sont les plus fragiles alors f_b prend la valeur de celles-ci. Il est donc nécessaire d'augmenter simultanément la force des liaisons dans la phase de liant et à l'interface, car la rupture se fera dans la zone la plus fragile. Si la résistance de l'interface est supérieure à la limite d'élasticité du liant, alors le mécanisme de déformation plastique du liant rentre en jeu lorsque cette contrainte est dépassée⁷⁹. Ainsi, une quantité d'énergie non négligeable supplémentaire se dissipe avec l'élongation du liant avant sa rupture⁷⁹.

Le liant se retrouve ab/adsorbé sur les nombreux éléments hétérogènes de l'électrode composite, par exemple sur les particules de silicium et d'ACE, entre-elles et entre celles-ci et le collecteur de courant en cuivre. Il y a donc potentiellement un large spectre de valeur pour σ_{int} . Néanmoins, il faut principalement différencier deux résistances à la fracture, celle à l'interface collecteur de courant/électrode, l'adhésion et celle dans la masse de l'électrode⁶⁰, la cohésion. Toutes deux influent sur la mécanique de rupture des électrodes et donc sur leur comportement mécanique en cyclage. Par exemple, un collecteur de courant rugueux permet d'augmenter ρ_l et ainsi d'améliorer la résistance à l'interface⁸⁰.

Les liaisons (physiques ou chimiques) envisageables dépendent de la chimie du liant et des groupements de surface des particules et du collecteur de courant. Une certaine compatibilité est donc nécessaire, comme celle qui existe entre le silicium, le graphène (et plus généralement les ACEs carbonés) et les liants poly(acide carboxylique) tels que la carboxyméthylcellulose (CMC), l'alginate (Alg) ou l'acide polyacrylique (PAA), illustrés respectivement Figure I.15b et I.15a.

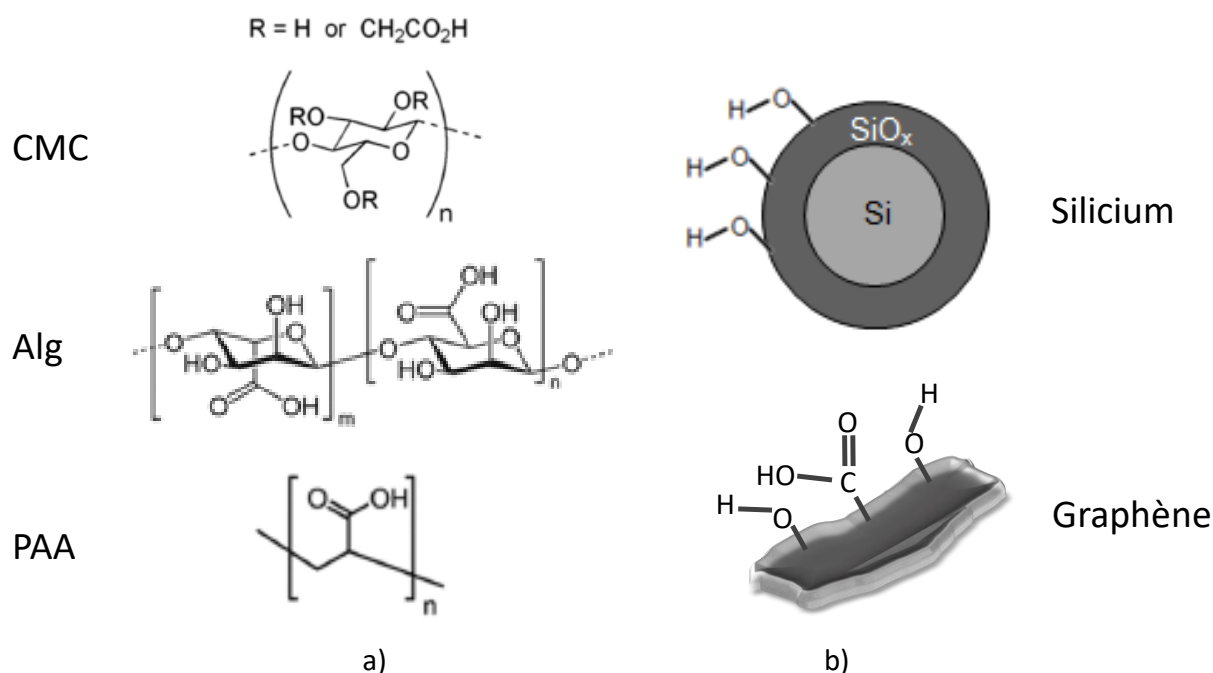


Figure I.15 (a) Exemples de liants poly(acide carboxylique); (b) Particules de silicium et de graphène et leurs groupements de surface. Représentations schématiques, pas à l'échelle.

Les fonctions acides carboxyliques peuvent former des liaisons hydrogènes avec les groupements hydroxyles du silicium et du graphène, mais aussi avec les acides carboxyliques de ce dernier. En effet, ces groupements sont présents à la surface du graphène, selon les données fournisseur de XGsciences⁸¹, et les silanols proviennent de la couche native de SiO_x. Les hydroxyles peuvent aussi former des esters avec les groupements acides, par réaction de condensation (avec de l'eau comme coproduit). La formation de des liaisons est favorisée à potentiel hydrogène (pH) acide, car les fonctions carboxyles doivent être sous cette forme pour la réaction d'estérification. Par exemple, la formation de silyl-ester s'observe à pH $\approx 3^{82-84}$ dans les électrodes de silicium avec de la CMC. Cependant, les liants CMC et Alg sont généralement sous forme de sel de sodium et une solution tampon est nécessaire pour atteindre un pH acide, proche de leur pKa₁. La présence de ces cations permet des interactions dipolaires, comme l'illustre la Figure I.16b sur le silicium, mais qui est aussi envisageable pour le graphène. À noter, qu'à pH acide, l'oxydation par voie humide du collecteur de courant en cuivre entraîne la formation de carboxylate de cuivre⁸⁵. Enfin, les chaînes celluloseuses

(A) CMC-Graphite

CMC

Graphite

Charged surface

Hydrophobic interaction

$R = H$ or $\text{CH}_2\text{CH}_2\text{COO}^-\text{Na}^+$

(B) CMC-Si

CMC

Si

Hydrogen bonding
Ion-dipole interaction

La CMC et l'Alg ont aussi d'autres avantages, car outre l'enchevêtrement physique des chaînes polymères et les liaisons hydrogènes inter-chaînes, la présence de groupements hydroxyles et acides carboxyliques permet la réticulation par estérification⁸⁷⁻⁸⁹. La réaction de condensation a lieu au-dessus des 120 °C⁸⁹ dans les conditions de formulation d'électrode et se fait généralement pendant l'étape de séchage (par exemple à 150 °C sous vide⁸⁸). Pour le PAA la formation d'anhydride par réaction de condensation (entre deux acides carboxyliques) est aussi envisageable^{88,90}, mais probablement à plus haute température.

L'amélioration des performances des électrodes de silicium grâce au liant poly(acide carboxylique) peut se rationaliser en considérant l'éq. (16) et la formation de liaisons aux interfaces avec les autres matériaux, et/ou dans la phase du liant. Pour le premier cas, que ce soit à travers des liaisons hydrogènes ou covalentes, f_b sera toujours plus élevée que pour une simple adsorption du liant (interactions de Van der Waals), comme le montre le Tableau I.2. Dans le deuxième cas, la réticulation du liant par des liaisons chimiques renforce le liant et permet de mieux atténuer les contraintes en les répartissant sur plus de chaînes polymères⁸⁷.

Table I.2 Ordre de grandeur de l'énergie des différentes liaisons ou interactions⁹¹.

	Van der Waals	Empilement π - π	Liaison hydrogène	Liaison halogène	Liaison métal-ligand (coordination)	Liaison ionique	Liaison covalente
Énergies de liaison ou d'interaction (Kj.mol ⁻¹)	< 5	2 à 50	4 à 120	10 à 180	100 à 300	100 à 350	200 à 400

Toutefois, les liaisons hydrogènes sont réversibles et peuvent apporter un caractère auto réparateur aux électrodes⁹². Donc, leur remplacement systématique par des liaisons covalentes n'est pas forcément bénéfique. D'autres paramètres comme le taux de réticulation du liant sont aussi à modérer, car même s'il permet d'augmenter la contrainte à la rupture et la dureté (qui est notamment relié à la limite d'élasticité⁹³), en excès il va finalement induire l'effet inverse sur l'élasticité et la résistance à la traction⁸⁹.

Dans l'environnement d'une LIB, le liant est au contact d'un électrolyte, généralement un/des solvant(s) organique(s) et un sel de lithium dissout. Hors, le liant peut absorber cet électrolyte^{94,95} ce qui dans le cas d'électrodes formulées avec de la NaCMC (mais aussi avec d'autre liant), réduit leurs propriétés mécaniques (module élastique et dureté)⁹⁶. Le liant peut aussi servir de SEI artificielle comme cela a été montré dans seulement quelques études sur des électrodes de graphite et de silicium. Dans le cas du graphite, le liant peut supprimer la co-intercalation du solvant avec le Li⁺ entre les feuillets de graphène et ainsi empêcher leur exfoliation^{94,97}. Pour le silicium, des études spectroscopiques (infrarouge et résonance magnétique nucléaire, IR et NMR) ont montré que les liants poly(acide carboxylique) subissent une lithiation irréversible lors du cyclage et que moins de SEI est formé par la dégradation de l'électrolyte. Enfin, un liant LiPAA agissant comme une SEI artificielle a été observé *in situ* dans des électrodes composites en silicium/graphite⁹⁸.

Le liant joue aussi un rôle prépondérant dans la répartition des éléments de l'électrode composite à l'état d'encre, et donc influe sur la morphologie finale des électrodes et tous les impacts que cela peut avoir sur la conductivité électrique, ionique et les propriétés mécaniques de celles-ci.

2.6.4. Interactions entre les éléments de l'électrode composite dans l'encre

Dans l'encre, le liant s'ad/absorbe à la surface des particules de silicium et d'ACE, mais avec une affinité qui dépend des liaisons/interactions possibles et de l'aire disponible (normalisé par quantité de matière *i.e.* la surface spécifique)⁹⁹. Il y a donc une compétition entre l'ab/adsorption du liant sur le silicium et sur l'ACE, qui influe sur la quantité de liant nécessaire pour le bon fonctionnement des électrodes^{99,100}.

Une fois absorbé, le liant intervient dans les mécanismes d'attraction/répulsion des particules. Trois de ces derniers sont particulièrement importants⁷¹ :

- L'interaction de Van der Waals (universel);
- L'interaction électrostatique de la double couche électrique (séparation des charges à l'interface solide/liquide);
- L'interaction stérique en présence de molécules ad/absorbées.

La première interaction est systématiquement attractive, tandis que les deux autres peuvent aussi être répulsive, si les charges entre particules sont de même signe, et selon la structure des molécules et leur concentration, respectivement⁷¹. Lorsque que l'encre est au repos si le bilan des forces est attractif alors la suspension flocule et les particules sédimentent. Pour empêcher cela, il faut que le potentiel zeta des particules en solution soit élevé (plusieurs dizaines de mV en valeur absolue¹⁰¹) et/ou que le liant crée de l'encombrement stérique⁷¹. Par exemple, la NaCMC se ionise en solution, et en s'ad/absorbant à la surface des particules elle fournit simultanément une répulsion stérique et électrostatique. Cependant, lorsque la force ionique en solution est élevée, à cause d'une forte concentration en sel ou de NaCMC, les interactions électrostatiques sont écrantées^{102,103}. L'écrantage engendre aussi le repliement des chaînes^{102,104} et un pH acide neutralise les charges de la CMC favorisant des associations inter-chaînes (liaisons hydrogènes)¹⁰⁵. Ces deux mécanismes affaiblissent probablement la répulsion stérique.

L'eau est utilisée comme solvant des poly(acide carboxylique) et les propriétés rhéologiques de l'encre caractérisent son comportement au repos et en écoulement. Une contrainte à l'écoulement élevée et un comportement de gel physique¹⁰¹ sont des bons indicateurs de la stabilité de l'encre (peu de risque de sédimentation et/ou de ségrégation du liant). La viscosité influe sur la processabilité de l'encre pendant son enduction et dépend au premier ordre de la quantité de solvant/de la fraction de solide. Une trop faible viscosité conduit souvent à une ségrégation du liant lors du séchage^{106,107}, particulièrement pour les petites molécules, comme l'illustre la pellicule de liant à la surface de l'électrode (Figure I.17a). À l'inverse, une forte viscosité gêne la désagglomération des particules lors du

broyage¹⁰⁷ (voir Figure I.17c). La Figure I.17b montre une électrode avec bonne dispersion des éléments. Le comportement de l'encre est rhéofluidifiant lors de l'application d'un gradient de cisaillement, par exemple pendant l'enduction. Cela signifie que sa viscosité diminue et que son application sur le collecteur de courant est facilitée.

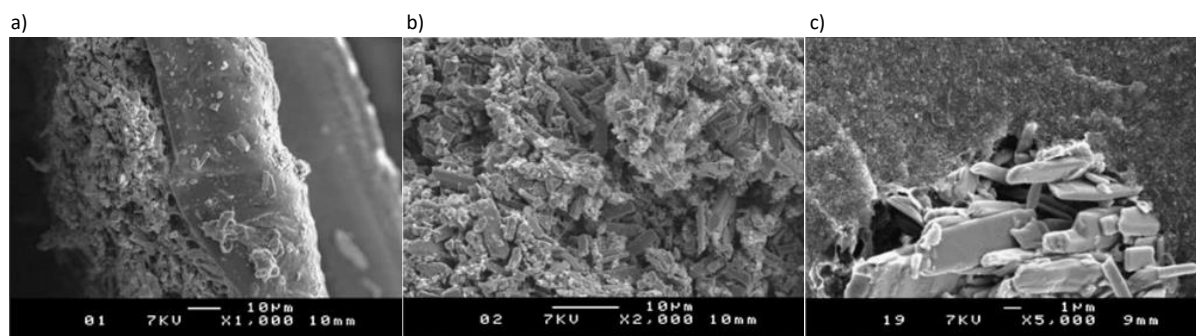
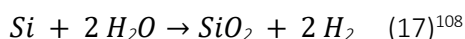


Figure I.17 Images SEM d'électrodes composites formulées avec différentes quantité de solvant¹⁰⁷: (a) Une quantité de solvant trop importante entraîne la ségrégation du liant; (b) Électrode avec un bonne dispersion des éléments; (c) Une quantité de solvant trop faible empêche la désagglomération des particules.

Lors de la formulation de l'encre, l'étape de broyage entraîne l'oxydation humide du silicium, qui est décrite par l'éq. (17) :



Le taux d'oxydation obtenu est nettement plus important que dans le cas d'une simple agitation magnétique¹⁰⁸, probablement à cause de l'élévation de la température et de la diminution de la taille des particules lors du broyage. Néanmoins, Roland A., et al¹⁰⁹ et Mazouzi D. et al⁸⁵ ont montré que moins l'encre est acide lors de la formulation, plus la surface du silicium est oxydée dans l'électrode.

Une fois enduite sur le collecteur de courant, l'encre sèche, avec dans un premier temps l'évaporation de la pellicule de solvant à la surface du film. La quantité d'eau à la surface devient rapidement insuffisante pour suivre le taux d'évaporation, alors l'eau du cœur de l'électrode remonte par capillarité pour alimenter la couche stagnante à la surface^{110,111}. Au fur et à mesure que le solvant continue de s'évaporer, les particules de l'électrode s'affaissent en partant du haut et forment une couche de consolidation¹¹¹. Lorsque l'eau ne remplit plus que le strict volume de pores de l'électrode entièrement consolidée et tandis que l'évaporation continue, l'interface gaz/liquide commence à pénétrer le volume de l'électrode à travers les pores les plus larges¹¹¹. Enfin, l'évaporation se termine par le solvant adsorbé dans les pores les plus petits, comme ceux situés dans les agglomérats de particules. L'évaporation par capillarité engendre un mouvement relatif entre les particules de la couche

de consolidation et le solvant, vers le bas et le haut, respectivement¹¹¹. Ce phénomène explique la possible accumulation du liant à la surface de l'électrode au dépend de l'interface avec le collecteur de courant. C'est particulièrement le cas lorsque les molécules de liant n'ont pas le temps de diffuser de la couche de consolidation plus concentrée vers le cœur de l'électrode qui l'est moins¹¹¹.

2.6.5. Pores

La porosité de l'électrode contient l'électrolyte qui permet le transport des ions Li^+ , et la conductivité ionique effective (σ_{Li^+}) s'exprime selon l'éq. (18) qui est semblable à l'équation (15) pour la conductivité électrique :

$$\sigma_{\text{Li}^+} = \frac{\tau_{\text{Pores}}}{\tau_{\text{Pores}}} \sigma_{\text{Electrolyte}} \quad (18)^{71,73}$$

La tortuosité des pores peut être déterminée sur des échantillons concrets grâce aux mesures structurales 3D (de type tomographie), suivies de méthodes assistées par ordinateur sur des phases segmentées¹¹² (cela peut aussi s'appliquer à l'ACE).

Le liant joue aussi un rôle ici, car il peut participer lui-même à la conduction des ions Li^+ grâce au mécanisme de saut d'ions par exemple⁷¹, à condition que sa conduction ionique soit du même ordre de grandeur que celle de l'électrolyte ($\sigma_{\text{Electrolyte}}$), mais aussi grâce à sa capacité à potentiellement absorber l'électrolyte.

Karkar et al.¹¹³ ont étudié l'influence de la réduction de la porosité sur des électrodes composites de silicium grâce au calandrage, tout en s'affranchissant de son effet délétère sur le liant. Il semblerait que jusqu'à 30 %_v de porosité, la perte équivalente de σ_{Li^+} n'influe pas sur les performances électrochimiques.

Pour conclure, il est intéressant de comparer les ordres de grandeur des conductivités électrique et ionique de nos électrodes. L'ACE et l'électrolyte utilisés sont respectivement, des plaquettes de graphène, $\sigma_{\text{ACE}} \approx 10^5 \text{ S.cm}^{-1}$ (GnPM15, donnée fournisseur) et du LP30, $\sigma_{\text{Electrolyte}} = 0,015 \text{ S.cm}^{-1}$ (à 20 °C)¹. Il est difficile d'évaluer la tortuosité des deux réseaux, par contre la fraction volumique de pores est 15 fois supérieure à celle du GnPM15, avec environ 60 et 4 %_v, respectivement. Pour que la polarisation due à σ_e soit significative par rapport à celle due à σ_{Li^+} , les conductivités doivent être du même ordre de grandeur. À partir de σ_e supérieure à 10 fois σ_{Li^+} , la résistance du réseau percolant électrique est négligeable¹¹⁴, ce qui est à priori le cas dans nos électrodes. Comme expliqué dans le sous-chapitre sur l'ACE, la conductivité réelle de celui-ci va dépendre de l'épaisseur de liant. L'éq. (19) permet de calculer l'épaisseur équivalente (w_{eq})⁷⁰ de liant correspondant à une conductivité donnée :

$$\log(\sigma_{\text{ACE}}^{\text{eq}}) = -0,04 \times w_{\text{eq}} + \log(\sigma_{\text{ACE}}) \quad (19)^{70}$$

Alors en première approximation, pour que la résistance du réseau percolant électrique soit négligeable il faut que $\sigma_{ACE}^{eq} \geq 2,3 \text{ S.cm}^{-1}$, ce qui impose que w_{eq} soit inférieur ou égale à environ 90 nm, ce qui est le cas dans nos électrodes.

2.7. Les liants de coordination pour électrode négative à base de silicium

La chimie de coordination se base sur des liaisons intermoléculaires entre un cation métallique multivalent et un ligand organique, qui peut être neutre (amine, pyridine, phosphine...) ou négativement chargé (carboxylate, phosphonate, sulfonate, phenolate...). L'énergie de liaison associée est plus élevée que celle des liaisons hydrogènes, mais plus faible que celles des liaisons covalentes (voir Tableau I.2). Ces liaisons sont également généralement réversibles. Comme l'illustre la Figure I.18., du fait de ces caractéristiques, exploiter cette chimie pour la réticulation des liants semble prometteur, en particulier parce qu'elle peut conduire à des propriétés d'autoréparation.

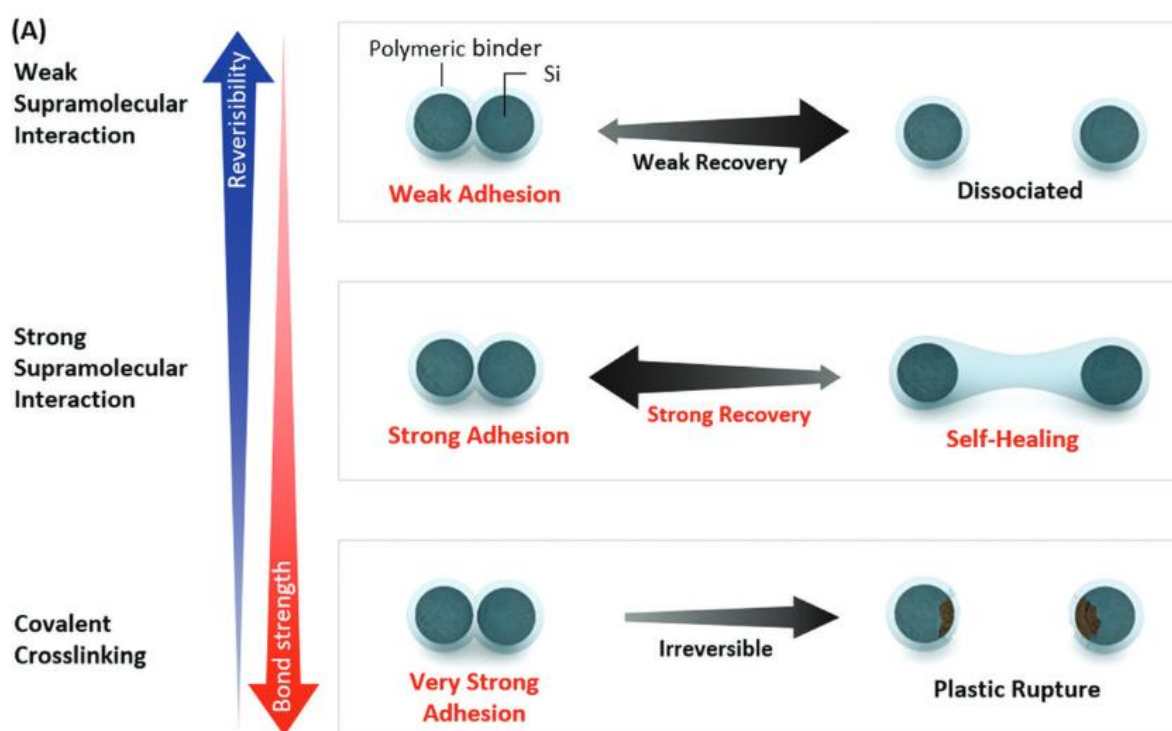


Figure I.18 Interactions et liaison covalente des liants pour électrodes de silicium classifiées selon leur force d'adhésion et leur réversibilité⁸⁷.

Un des intérêts de cette chimie est qu'il existe de nombreuses combinaisons cation métallique-ligands possibles, ce qui permet de moduler finement la force des liaisons. D'autre part, cette chimie est souvent facile à mettre en œuvre, notamment dans les conditions de formulation des

électrodes de silicium (milieu aqueux, température ambiante...), avec des liants classiques dès lors qu'ils sont porteurs de fonctions complexantes (PAA, CMC, Alg...).

En 2014, l'ajout de cations Ca^{2+} au liant Alg dans des électrodes négatives à base de silicium (ou composite silicium et graphite) a été proposé^{115–121}. Cette approche a ensuite été étendue à d'autres cations métalliques, tels que Al^{3+} , Ba^{2+} , Mn^{2+} et Zn^{2+} ¹¹⁸; ou Cu^{2+} , Fe^{2+} et Ni^{2+} ¹²⁰. Ce n'est que plus récemment que d'autres polymères organiques ont été utilisés : la CMC et Cu^{2+} ⁸⁵; un polymère fonctionnalisé par des groupements catéchol et Fe^{3+} ¹²²; le PEDOT PSS et Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , In^{3+} et Sn^{4+} ¹²³; et un polymère fonctionnalisé par des groupements imidazole et Zn^{2+} ¹²⁴.

Les performances électrochimiques obtenues avec ces électrodes sont détaillées dans le Tableau I.3. Il est difficile de comparer les liants de coordination entre eux sur la base des performances électrochimiques, car les compositions et grammages des électrodes varient trop selon les études. Néanmoins, toutes montrent que le liant de coordination augmente les performances électrochimiques par rapport au liant sans cation, avec notamment une meilleure CE au premier cycle et une meilleure rétention de capacité au cours du cyclage.

Table I.3 Synthèse des performances électrochimiques, des propriétés mécaniques et des propriétés de la SEI, pour des électrodes négatives à base de silicium formulées avec un liant de coordination. Les abréviations (calc.), (unk.) et (not vis.) signifient respectivement, calculé à partir des données de l'auteur, données non fournies et non calculable, et graphique non lisible.

Publi.	Active material	Binder (B)	Conductive additive	MA:B:ACE (w%)	MA loading (mg.cm ⁻²)	Theoretical MA specific capacity (mAh.g ⁻¹)	Theoretical electrode areal capacity (mAh.cm ⁻²)	1 st cycle capacities : (mAh.g ⁻¹) (mAh.cm ⁻²)	1 st cycle CE (%)
Liu J. et al (2014) ¹¹⁵	SINPs / C (composite)	Ca ²⁺ -Alginate	Carbon black	(42.4/10.6):29:18	unk.	2938 (calc.)	unk.	3790 ± 120 unk.	72.5 ± 0.7
Zhang L. et al (2014) ¹¹⁶	SiSMPs	Ca ²⁺ -Alginate (0.15 n/n)	Super P carbon black	70:15:15	1 - 1.1 4 ^(*)	3580	3.6 - 3.9 14.3 ^(*)	3595 ± 15 // 3450 ^(*) 3.8 - 4.2 // 13.8 ^(*)	80.1 // unk. ^(*)
Yoon J. et al (2014) ¹¹⁷	SINPs	Ca ²⁺ (Cl ₂)-Alginate (n/n unk.)	Super P carbon	60:20:20	0.4 - 0.5 0.8 - 0.9 ^(*)	3580	1.4 - 1.8 2.9 - 3.2 ^(*)	2823 ± 57 (calc.) // 2740 (calc.) ^(*) 1.1 - 1.4 // 2.2 - 2.5 ^(*)	80.8 ± 14.6 // 87.7 ^(*)
Wu Z.-Y. et al (2017) ¹¹⁸	SINPs	Ca ²⁺ -Alginate (0.02 n/n calc.)	Acetylene black	60:20:20	0.3 - 0.5 ^(a) 1 - 1.2 ^(b)	3580	1.1 - 1.8 ^(a) 3.6 - 4.3 ^(b)	3450 ^(a) // 3390 ^(a*) // 3250 ^(b) 1 - 1.7 ^(a) // 1 - 1.7 ^(a*) // 3.3 - 3.9 ^(b)	82.7 ^(a) // (not vis.) ^(a*) // 86.2 ^(b)
Wu Z.-Y. et al (2017) ¹¹⁸	SINPs	Al ³⁺ -Alginate (0.02 n/n calc.)	Acetylene black	60:20:20	0.3 - 0.5 ^(a) 1 - 1.2 ^(b)	3580	1.1 - 1.8 ^(a) 3.6 - 4.3 ^(b)	3460 ^(a) // 3200 ^(a*) // 3360 ^(b) 1 - 1.7 ^(a) // 1 - 1.6 ^(a*) // 3.4 - 4 ^(b)	86.3 ^(a) // (not vis.) ^(a*) // 85.9 ^(b)
Wu Z.-Y. et al (2017) ¹¹⁸	SINPs	Ba ²⁺ -Alginate (0.02 n/n calc.)	Acetylene black	60:20:20	0.3 - 0.5 ^(a) 1 - 1.2 ^(b)	3580	1.1 - 1.8 ^(a) 3.6 - 4.3 ^(b)	3510 ^(a) // 3340 ^(a*) // 3360 ^(b) 1.1 - 1.8 ^(a) // 1 - 1.7 ^(a*) // 3.4 - 4 ^(b)	85.5 ^(a) // 83.5 ^(a*) // 85.6 ^(b)
Wu Z.-Y. et al (2017) ¹¹⁸	SINPs	Mn ²⁺ -Alginate (0.02 n/n calc.)	Acetylene black	60:20:20	0.3 - 0.5	3580	1.1 - 1.8	3350 // 3410 ^(*) 1 - 1.7 // 1 - 1.7 ^(*)	82.1 // (not vis.) ^(*)
Wu Z.-Y. et al (2017) ¹¹⁸	SINPs	Zn ²⁺ -Alginate (0.02 n/n calc.)	Acetylene black	60:20:20	0.3 - 0.5	3580	1.1 - 1.8	2460 // 2640 ^(*) 0.7 - 1.2 // 0.8 - 1.3 ^(*)	72 // 81.5 ^(*)
Gendensuren B. and Oh E.-S. (2018) ¹¹⁹	SINPs / C (composite)	Ca ²⁺ (Cl ₂)-Alg-g-PAAm (n/n unk.)	Carbone nanotube	(19/57):15:9	1.2 - 1.4	1174 (calc.)	1.4 - 1.6	1170 1.4 - 1.6	72.8
Gu Y. et al (2018) ¹²⁰	SINPs	Cu ²⁺ -Alginate (0.09 n/n)	Acetylene black	70:15:15	0.45	3580	1.6	3500 1.6	83.1
Gu Y. et al (2018) ¹²⁰	SINPs	Ca ²⁺ -Alginate (0.09 n/n)	Acetylene black	70:15:15	0.45	3580	1.6	3410 1.5	79.2
Gu Y. et al (2018) ¹²⁰	SINPs	Fe ²⁺ -Alginate (0.09 n/n)	Acetylene black	70:15:15	0.45	3580	1.6	3380 1.5	82
Gu Y. et al (2018) ¹²⁰	SINPs	Ni ²⁺ -Alginate (0.09 n/n)	Acetylene black	70:15:15	0.45	3580	1.6	3600 1.6	81.8
Gu Y. et al (2018) ¹²⁰	SINPs	Ca ²⁺ -Alginate (0.1 n/n)	Super P carbon	70:15:15	unk.	3580	unk.	2250 unk.	unk.
Yang S. et al (2018) ¹²¹	SINPs / NG (composite)	Ca ²⁺ -Alginate (0.1 n/n)/CMC/SBR	Super P carbon	(26.9/66.5):(3.1/1.4/0.7):1.4 (calc.)	unk.	1236 (calc.)	unk.	916 unk.	86.2
Mazouzi D. et al (2019) ⁸⁵	SiSMPs	Cu ²⁺ -CMC (0.11 n _M /n _{COOH})/AC/(Na+K+SO ₄)	GnP15	71.4:(7.5/7.6/1.8):10.7	1.4 - 1.6	3580	5 - 5.7	3960 5.5 - 6.3	82 ± 1
Jeong Y. K. and Choi J. W. (2019) ¹²²	SINPs	Fe ³⁺ -PDBP PDBP : poly(DMA ₃₃ -co-BA ₆₆ -co-PEGdA ₁) (0.33 n _M /n _{DMA})	Super P	70:15:15	0.7 1.2 ^(*)	3580	2.5 4.3 ^(*)	1460 ± 80 // 1330 ^(*) 1 // 1.6 ^(*)	98.3 // 90.1 ^(*)
Liu X. et al (2020) ¹²³	SINPs	Mg ²⁺ (Cl ₂)-PEDOT:PSS (0.24 m _{MgCl2} /m _{PEDOT:PSS})	none	76.4:23.6:0 (calc.)	unk.	3580	unk.	3490	unk.
Liu X. et al (2020) ¹²³	SINPs	Ca ²⁺ (Cl ₂)-PEDOT:PSS (0.28 m _{CaCl2} /m _{PEDOT:PSS})	none	75.8:24.2:0 (calc.)	unk.	3580	unk.	3370	unk.
Liu X. et al (2020) ¹²³	SINPs	Sr ²⁺ (Cl ₂)-PEDOT:PSS (0.40 m _{SrCl2} /m _{PEDOT:PSS})	none	74.1:25.9:0 (calc.)	unk.	3580	unk.	3410 ± 10	unk.
Liu X. et al (2020) ¹²³	SINPs	Ba ²⁺ (Cl ₂)-PEDOT:PSS (0.52 m _{BaCl2} /m _{PEDOT:PSS})	none	72.5:27.5:0 (calc.)	unk.	3580	unk.	3430	unk.
Liu X. et al (2020) ¹²³	SINPs	In ³⁺ (Cl ₃)-PEDOT:PSS (0.55 m _{InCl3} /m _{PEDOT:PSS})	none	72:28:0 (calc.)	unk.	3580	unk.	3480	unk.
Liu X. et al (2020) ¹²³	SINPs	Sn ⁴⁺ (Cl ₄)-PEDOT:PSS (0.65 m _{SnCl4} /m _{PEDOT:PSS})	none	70.8:29.2:0 (calc.)	unk.	3580	unk.	3460	80.5
Kim J. et al (2021) ¹²⁴	SiMPs / C (composite)	Zn ²⁺ -Im-PEG-CMC/SBR (1:2:4 Zn ²⁺ -Im-PEG n/n 0.5:4.5:5 (PEG-Im-Zn ²⁺)):CMC:SBR w/w)	Super P	(6.9/73.1):(0.5/4.5/5):10 (calc.)	3.67	650	2.4	635 ± 8 (calc.) 2.33 ± 0.01 (calc.)	81.8

50 th cycle capacities : (mAh.g _{AM} ⁻¹) (mAh.cm ⁻²)	Electrolyte Salt Solvents Additives	Cycling conditions : Cell and temperature (°C) Cycle (c.); Current (mA.g ⁻¹) Voltage window (V)	Mechanical tests	SEI characterizations	Comments	Publi.
2060 // 1310 (*) unk.	1M LiPF ₆ EC:DMC:DEC 1:1:1 (v/v) 2 w% VC	2025 coin cell; unk. 1c. 100; rest 420 // 3c. 100; rest 1300 (*) 0.01 - 1.2	unk.	unk.	-Theoretical capacities : -Si = 3580 (mAh.g ⁻¹) / C = 372 (mAh.g ⁻¹) -Discharge capacity	Liu J. et al (2014) ¹¹⁵
3166 ± 6 // 2670 (*) 3.2 - 3.5 // 10.7 (*)	1M LiPF ₆ EC:DMC:EMC 1:1:1 (v/v)	CR2032 coin cell; unk. 420 // 210 (*) 0.01 - 1	-Peel test (180°) : 3M tape // 200 μm.s ⁻¹ // Electrode laminate 2x3 cm ² 30.6 N; unk. rupture point	-EIS : No fit	-Rate capability available -Cycling on solar cell silicon waste (SISMPs) available -Charge capacity	Zhang L. et al (2014) ¹¹⁶
2390 (calc.) // 1900 (calc.) (*) 1 - 1.2 // 1.5 - 1.7 (*)	1.3M LiPF ₆ EC:EMC 3:7 (v/v) 10 w% FEC	CR2032 coin cell; unk. 2c. 200; rest 1000 0.01 - 1	unk.	-EIS : No fit	-Rate capability available -Cross-linking after slurry enduction -Charge capacity	Yoon J. et al (2014) ¹¹⁷
2710 ^(a) // 2320 ^(a*) // 1350 ^(b) 0.8 - 1.4 ^(a) // 0.7 - 1.2 ^(a*) // 1.4 - 1.6 ^(b)	1M LiPF ₆ EC:DMC:DEC 1:1:1 (v/v) 2 w% VC and 10 w% FEC	2025 coin cell; unk. 1c. 100; rest 420 ^(a) // 1c. 100; rest 2100 ^(a*) // 840 ^(b) 0.01 - 1.2	-Peel test (180°) : unk. tape // 167 μm.s ⁻¹ // Electrode laminate 0.8x3 cm ² 1.6 N; Delamination -Vickers hardness : 25 gf // 15 s dwelt // Binder laminate on glass 23.1 HV (with glass contribution?)	unk.	-First cycle capacity at 100 mA.g ⁻¹ is not provided for 0.3-0.5 mgSi.cm ⁻² electrodes -Cycling with AM:B:CA 80:10:10 (w%) available -Charge capacity	Wu Z-Y. et al (2017) ¹¹⁸
2780 ^(a) // 2450 ^(a*) // 1750 ^(b) 0.8 - 1.4 ^(a) // 0.7 - 1.2 ^(a*) // 1.8 - 2.1 ^(b)	1M LiPF ₆ EC:DMC:DEC 1:1:1 (v/v) 2 w% VC and 10 w% FEC	2025 coin cell; unk. 1c. 100; rest 420 ^(a) // 1c. 100; rest 2100 ^(a*) // 840 ^(b) 0.01 - 1.2	-Peel test (180°) : unk. tape // 167 μm.s ⁻¹ // Electrode laminate 0.8x3 cm ² 1.9 N; Delamination -Vickers hardness : 25 gf // 15 s dwelt // Binder laminate on glass 35 HV (with glass contribution?)	unk.	-First cycle capacity at 100 mA.g ⁻¹ is not provided for 0.3-0.5 mgSi.cm ⁻² electrodes -Cycling with AM:B:CA 80:10:10 (w%) available -Charge capacity	Wu Z-Y. et al (2017) ¹¹⁸
2860 ^(a) // 2370 ^(a*) // 1860 ^(b) 0.9 - 1.4 ^(a) // 0.7 - 1.2 ^(a*) // 1.9 - 2.2 ^(b)	1M LiPF ₆ EC:DMC:DEC 1:1:1 (v/v) 2 w% VC and 10 w% FEC	2025 coin cell; unk. 1c. 100; rest 420 ^(a) // 1c. 100; rest 2100 ^(a*) // 840 ^(b) 0.01 - 1.2	-Peel test (180°) : unk. tape // 167 μm.s ⁻¹ // Electrode laminate 0.8x3 cm ² 2.7 N; Delamination -Vickers hardness : 25 gf // 15 s dwelt // Binder laminate on glass 32.1 HV (with glass contribution?)	unk.	-First cycle capacity at 100 mA.g ⁻¹ is not provided for 0.3-0.5 mgSi.cm ⁻² electrodes -Cycling with AM:B:CA 80:10:10 (w%) available -Charge capacity	Wu Z-Y. et al (2017) ¹¹⁸
1440 // 1890 (*) 0.4 - 0.7 // 0.6 - 0.9 (*)	1M LiPF ₆ EC:DMC:DEC 1:1:1 (v/v) 2 w% VC and 10 w% FEC	2025 coin cell; unk. 1c. 100; rest 420 // 1c. 100; rest 2100 (*) 0.01 - 1.2	-Peel test (180°) : unk. tape // 167 μm.s ⁻¹ // Electrode laminate 0.8x3 cm ² 1.0 N; Delamination -Vickers hardness : 25 gf // 15 s dwelt // Binder laminate on glass 18.9 HV (with glass contribution?)	unk.	-First cycle capacity at 100 mA.g ⁻¹ is not provided for 0.3-0.5 mgSi.cm ⁻² electrodes -Cycling with AM:B:CA 80:10:10 (w%) available -Charge capacity	Wu Z-Y. et al (2017) ¹¹⁸
2010 // 1670 (*) 0.6 - 1 // 0.5 - 0.8 (*)	1M LiPF ₆ EC:DMC:DEC 1:1:1 (v/v) 2 w% VC and 10 w% FEC	2025 coin cell; unk. 1c. 100; rest 420 // 1c. 100; rest 2100 (*) 0.01 - 1.2	-Peel test (180°) : unk. tape // 167 μm.s ⁻¹ // Electrode laminate 0.8x3 cm ² 1.0 N; Delamination -Vickers hardness : 25 gf // 15 s dwelt // Binder laminate on glass 25.2 HV (with glass contribution?)	unk.	-First cycle capacity at 100 mA.g ⁻¹ is not provided for 0.3-0.5 mgSi.cm ⁻² electrodes -Cycling with AM:B:CA 80:10:10 (w%) available -Charge capacity	Wu Z-Y. et al (2017) ¹¹⁸
830 1 - 1.2	1.15M LiPF ₆ EC:DEC:DMC 3:5:2 (v/v) 0.4 w% LiBF ₄ and 2 w% VC and 5 w% FEC	CR2032 coin cell; unk. 60 mA.g ⁻¹ (calc.) 0.005 - 2	-Peel test (180°) : unk. tape // 833 μm.s ⁻¹ // Electrode laminate unk. cm ² electrolyte soaked then dried 4.5 N; unk. rupture point	-EIS : No fit -FTIR : Li ₂ EDC No Y scale	-Theoretical capacities : -Si = 3580 (mAh.g ⁻¹) / C = 372 (mAh.g ⁻¹) -Cross-linking during slurry preparation -Rate capability available -Discharge capacity	Gendensuren B. and Oh E.-S. (2018) ¹¹⁹
3010 1.4	1M LiPF ₆ EC:DEC:FEC 7:7:2 (v/v)	CR2032 coin cell; Room temp. 3c. 210; 5c. 420; rest 840 0.01 - 1	unk.	-XPS : Li _x PF _y and LiF No count scale	-Other Cu-Alginate (n/n) ratios tested -Charge capacity	Gu Y. et al (2018) ¹²⁰
2410 1.1	1M LiPF ₆ EC:DEC:FEC 7:7:2 (v/v)	CR2032 coin cell; Room temp. 3c. 210; 5c. 420; rest 840 0.01 - 1	unk.	-XPS : Li _x PF _y and LiF No count scale	-Other Ca-Alginate (n/n) ratios tested -Charge capacity	Gu Y. et al (2018) ¹²⁰
2560 1.2	1M LiPF ₆ EC:DEC:FEC 7:7:2 (v/v)	CR2032 coin cell; Room temp. 3c. 210; 5c. 420; rest 840 0.01 - 1	unk.	-XPS : Li _x PF _y and LiF No count scale	-Other Fe-Alginate (n/n) ratios tested -Charge capacity	Gu Y. et al (2018) ¹²⁰
3650 1.6	1M LiPF ₆ EC:DEC:FEC 7:7:2 (v/v)	CR2032 coin cell; Room temp. 3c. 210; 5c. 420; rest 840 0.01 - 1	-Traction : Dummbell // 2 cm width // 20 μm.s ⁻¹ // Binder laminate E = 2.8 GPa Breaking point = 33.5 MPa	-EIS : No fit -XPS : Li _x PF _y and LiF No count scale	-Other Ni-Alginate (n/n) ratios tested -Rate capability available -Charge capacity	Gu Y. et al (2018) ¹²⁰
2260 unk.	1M LiPF ₆ EC:DMC:DEC 1:1:1 (v/v) 10 w% FEC	2032 coin cell; 30 3c. 210; rest 840 0.01 - 1	unk.	unk.	-Charge capacity	Gu Y. et al (2018) ¹²⁰
898 unk.	1M LiPF ₆ EC:DMC:DEC 1:1:1 (v/v) 10 w% FEC	2032 coin cell; 30 3c. 210; rest 840 0.01 - 1	unk.	-EIS : No fit	-Theoretical capacities : -Si = 3580 (mAh.g ⁻¹) / NG = 372 (mAh.g ⁻¹) -Other AM:B:CA ratios tested -Rate capability available -Charge capacity	Yang S. et al (2018) ¹²¹
2770 3.9 - 4.4 1330 // 1280 (*) 0.9 // 1.5 (*)	1M LiPF ₆ EC:DMC 1:1 (v/v) 10 w% FEC 1M LiPF ₆ EC:DMC 1:1 (v/v) 10 w% FEC	Swagelok cell; Room temp. 1c. 96; 3c. 193; rest 385 0.005 - 1 2032 coin cell; unk. 1500 // 300 (*) unk.	unk.	unk.	-Discharge capacity	Mazouzi D. et al (2019) ⁸⁵
1910 unk.	1M LiPF ₆ EC:DEC 1:1 (v/v) 10 w% FEC	CR2016 coin cell; unk. 1000 0 - 1.5	unk.	-EIS : 2 el. // 100 c. R _{SEI} = 47.0 ± 0.6 Ω	-Rate capability available -Discharge or charge capacity ? -Specific capacity per gram of elect. or Si ? -Rate capability available -Unwashed salt counter-ion -Discharge capacity	Jeong Y. K. and Choi J. W. (2019) ¹²²
1850 unk.	1M LiPF ₆ EC:DEC 1:1 (v/v) 10 w% FEC	CR2016 coin cell; unk. 1000 0 - 1.5	unk.	-EIS : 2 el. // 100 c. R _{SEI} = 37.1 ± 0.5 Ω	-Rate capability available -Unwashed salt counter-ion -Discharge capacity	Liu X. et al (2020) ¹²³
160 ± 230 unk.	1M LiPF ₆ EC:DEC 1:1 (v/v) 10 w% FEC	CR2016 coin cell; unk. 1000 0 - 1.5	unk.	-EIS : 2 el. // 100 c. R _{SEI} = 52.2 ± 9.3 Ω	-Rate capability available -Unwashed salt counter-ion -Discharge capacity	Liu X. et al (2020) ¹²³
0	1M LiPF ₆ EC:DEC 1:1 (v/v) 10 w% FEC	CR2016 coin cell; unk. 1000 0 - 1.5	unk.	-EIS : 2 el. // 100 c. R _{SEI} = 51.9 ± 0.1 Ω	-Rate capability available -Unwashed salt counter-ion -Discharge capacity	Liu X. et al (2020) ¹²³
1640 unk.	1M LiPF ₆ EC:DEC 1:1 (v/v) 10 w% FEC	CR2016 coin cell; unk. 1000 0 - 1.5	unk.	-EIS : 2 el. // 100 c. R _{SEI} = 42.8 ± 2.7 Ω	-Rate capability available -Unwashed salt counter-ion -Discharge capacity	Liu X. et al (2020) ¹²³
2060 unk.	1M LiPF ₆ EC:DEC 1:1 (v/v) 10 w% FEC	CR2016 coin cell; unk. 1000 0 - 1.5	-Nano-indentation : max 1 mN // Electrode laminate H _{red} = 8 ± 4 Mpa E _{red} = 150 ± 40 Mpa -Peel test (180°) : 3M tape // 417 μm.s ⁻¹ // Electrode laminate unk. cm ² 4.8 gf.mm ⁻¹ ; unk. rupture point -Nano-indentation : max 0.5 mN // max 1 mN (*) // Binder laminate Elastic recovery ratio = 0.46 // 0.38 (*) Plastic (P) and Elastic (E) work = 25.6 and 13.9 pJ // unk. (*) E/P = 0.54 // 0.41 (*)	-EIS : 2 el. // 100 c. R _{SEI} = 38.3 ± 1.5 Ω	-Rate capability available -Unwashed salt counter-ion -Discharge capacity	Liu X. et al (2020) ¹²³
unk. 2.1	1M LiPF ₆ EC:DEC 1:1 (v/v) 10 w% FEC	unk. 1c. 65; rest 325 0.01 - 1.5 CR2032 coin cell		-EIS 2 el. // 10 c. R _{SEI} = 8.9 Ω	-Theoretical capacities : -Si = 3580 (mAh.g ⁻¹) / C = 372 (mAh.g ⁻¹) -Rate capability available -Full cell performance available -Discharge or charge capacity not specified	Kim J. et al (2021) ¹²⁴

Les études sont aussi unanimes quant à l'origine de l'augmentation de ces performances : la réticulation du liant par des cations métalliques augmente les propriétés mécaniques des électrodes. Cela permet de limiter/accommoder les effets de l'expansion volumique du silicium^{117,121} et de préserver l'intégrité mécanique des électrodes. Par exemple, les tests de pelage sur des électrodes montrent que la résistance à l'interface est améliorée (moins de délamination)¹¹⁸ ou que les films d'électrode sont plus résistants^{116,119,124}, sans que soit toutefois spécifiée la zone de la rupture (à l'interface ou dans le film). Des mesures de nano-indentation ont montré que les électrodes coordonnées présentent un module élastique et une dureté plus élevée¹²³, comme le montrent aussi des tests de dureté Vickers¹¹⁸. Des analyses sur des échantillons de liant réticulés indiquent que ceux-ci sont plus élastiques¹²⁴, et ont une résistance à la rupture plus élevée¹²⁰ après coordination. Il est intéressant de noter que l'absorption de l'électrolyte par le liant est réduite après coordination, comme cela a été montré pour le liant Alg-Ca²⁺^{117,119} (il existe cependant un contre-exemple¹¹⁶), ce qui peut s'expliquer par l'immobilisation des segments polymères⁸⁹. Cela permet de préserver les propriétés du liant dans les conditions opérationnelles d'une LIB. Enfin, des preuves d'autoréparation ont été apportées par Gendensuren B. et Oh E-S¹¹⁹, ainsi que par Jeong Y. K. et Choi J. W.¹²².

Certaines études s'accordent aussi à dire que l'utilisation d'un liant de coordination a un effet bénéfique sur la SEI. Cette dernière serait plus stable en présence du liant de coordination^{85,117,124}. De plus, dans certains cas, l'accommodation de l'expansion volumique du silicium par le liant est décrit explicitement comme étant à l'origine de l'amélioration de la stabilité de la SEI^{116,120,121}. La SEI serait aussi plus fine¹¹⁹⁻¹²¹, compacte¹²⁰, homogène¹²¹ et déformable¹¹⁷, ou encore le liant de coordination permettrait de jouer le rôle de SEI artificielle¹²¹.

L'objectif de cette thèse est donc d'utiliser des liants de coordination Zn²⁺-poly(acide carboxylique) pour régler les problématiques dues à l'expansion volumique des particules de silicium dans des électrodes négatives de LIB. Dans l'équipe, la coordination du liant a été découverte historiquement grâce à la corrosion et la migration d'ions Cu²⁺ du collecteur de courant, lors d'une étape de maturation⁷⁹ des électrodes. Ici, le liant est directement réticulé en solution avec l'ajout d'un sel/oxyde de Zn(II). Ce dernier est un bon complexant au mode de coordination varié. Il est aussi différenciable du Cu²⁺ provenant de la corrosion du collecteur de courant, et analysable par NMR car diamagnétique. Cette thèse traite de la compréhension du rôle exact de ces liants de coordination dans l'amélioration des performances des électrodes de silicium et des mécanismes mis en jeu.

2.8. Références

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3. Chapitre 2 : Matériaux et méthodes

3.1. Préparation des matériaux

3.1.1. Les solutions de liant

Tout d'abord, une solution tampon de pH 3 est préparée en dissolvant de l'acide citrique ($0,171 \text{ mol.L}^{-1}$, 99 %; Sigma-Aldrich) et du KOH ou du NaOH ($0,084 \text{ mol.L}^{-1}$, > 98 %; Sigma-Aldrich) dans de l'eau ultrapure. Ensuite, 5 mL de tampon plus le volume d'eau ultrapure nécessaire pour atteindre 8,2 mL de solution sont utilisés pour dissoudre 160 mg de NaCMC ($M_w \approx 700000 \text{ g.mol}^{-1}$, D.S. 0,9; Sigma-Aldrich). La poudre de NaCMC est ajoutée avant les solutions pour en faciliter la dissolution. De plus, l'électricité statique est préalablement retirée de cette dernière et du flacon avec un Zerostat III (Milty), pour éviter d'en répandre sur les bords du flacon. La solution ainsi obtenue constitue le liant de référence (également nommé liant sans Zn). Enfin, après dissolution complète et homogène de la NaCMC, la source de coordination est ajoutée en une seule fois, et la solution est laissée sous agitation jusqu'à homogénéisation. Pour l'échantillon contenant du LiOH ($\text{LiOH} \cdot \text{H}_2\text{O}$, $\geq 98 \%$; Sigma-Aldrich), celui-ci est ajouté de la même manière qu'une source de Zn. À chaque étape, les solutions sont agitées magnétiquement à température ambiante. Cependant, pour la source de Zn(II), l'agitation est poussée fortement pour que celle-ci se répande rapidement et de manière plus homogène dans la solution.

L'eau de coordination des sels est comptée dans les 8,2 mL de solution de liant. En revanche, l'eau ad/absorbée par la NaCMC, soit environ 15 % de sa masse, n'est pas prise en compte.

Pour cette thèse, les différentes sources de zinc utilisées sont : $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (cristal pur; Alfa Aesar), ZnO (99,99 %; Alfa Aesar) et $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98 %; Alfa Aesar). Leur quantité est ajustée pour atteindre un ratio de coordination théorique, qui est prédéfini tel que :

$$\text{Ratio de coordination} = \frac{n_{\text{Zn}}}{n_{\text{COOH}(\text{acide citrique} + \text{CMC})}} \quad (20)$$

Une autre molécule, la piperazine-N,N'-bis(acide 3-propanesulfonique) ($\geq 97 \%$; Milipore) a aussi été utilisé pour la solution tampon, mais qui contrairement à l'acide citrique n'est pas complexante vis-à-vis des métaux.

Les solutions de liant sont stockées au réfrigérateur pendant un à deux mois maximum, pour éviter notamment l'hydrolyse des chaînes celluloses de la CMC (ce qui dégrade ses propriétés rhéologiques¹). Avant leur utilisation, les solutions sont réchauffées à température ambiante sous agitation magnétique.

3.1.2. Le silicium

La poudre de silicium utilisée comme matériau actif a été obtenue par broyage mécanique d'une poudre commerciale de silicium (325 mesh, 99,96 %; Materion) à l'aide d'un attriteuseur HD-01 (Union Process). Le broyage a été effectué sous atmosphère d'argon pendant 20 h à 600 tr.min⁻¹, avec un rapport de masse bille/poudre de 10:1. La poudre de silicium telle que broyée est composée d'agglomérats micrométriques comme particules primaires ($d_{50} \approx 10 \mu\text{m}$, $S_{spe} \approx 20 \text{ m}^2.\text{g}^{-1}$)² et les particules secondaires sont inférieures au micron. La teneur en oxygène déterminée par un analyseur LECO est d'environ 1 %_m.

3.1.3. Les électrodes

160 mg de poudre de silicium, 24 mg de plaquettes de graphène, utilisées comme additif conducteur (grade xGnP M15, $e_{moy} \approx 7 \text{ nm}$, $d_{moy} = 15 \mu\text{m}$, $S_{spe} \approx 120\text{-}150 \text{ m}^2.\text{g}^{-1}$, selon les données du fournisseur; XGSciences) et 0,8 mL de solution de liant (volume déterminé par pesée) sont placés dans une jarre contenant trois billes ($d = 9,5 \text{ mm}$), le tout étant en nitrure de silicium. L'ensemble est mélangé à l'aide d'un mélangeur planétaire Pulverisette 7 (Fritsch) pendant 1 h à 500 tr.min⁻¹. Ensuite, l'encre ainsi préparée est enduite à l'aide d'une raclette sur une feuille de Cu. Trois grades de collecteur de courant ont été utilisés, le premier est laminé à froid (99,9 %, $e \approx 20 \mu\text{m}$; PI-KEM) le second est recuit (99,8 %, $e \approx 25 \mu\text{m}$; Alfa Aesar) et le dernier est texturé ($e \approx 13,6 \mu\text{m}$). Trois grammages d'électrode sont visés :

-Pour les électrodes à faible grammage, soit $1,0 \pm 0,1 \text{ mg}_{\text{Si}}.\text{cm}^{-2}$: un volume d'encre de 0,8 ml est utilisé et la hauteur de raclette est de 100 μm (modèle 3540, $v = 5,6 \text{ mm}.\text{s}^{-1}$; Elcometer);

-Pour les électrodes à grammage standard, soit $1,75 \pm 0,1 \text{ mg}_{\text{Si}}.\text{cm}^{-2}$: un volume d'encre de 0,8 ml est utilisé et la hauteur de raclette est de 150 μm (modèle 3540, $v = 5,6 \text{ mm}.\text{s}^{-1}$; Elcometer);

Les films ainsi préparés sont séchés à température ambiante pendant 12 h. Enfin, les électrodes sont poinçonnées ($d = 1 \text{ cm}$) puis séchées 2 h à 100 °C sous vide ($P \approx 10 \text{ mbar}$), avant une mesure de masse ($\Delta m = \pm 0,01 \text{ mg}$; OHAUS) et d'épaisseur ($\Delta e = \pm 1 \mu\text{m}$; Mitutoyo). Puis, elles sont séchées à nouveau pendant 1 h dans les mêmes conditions avant l'assemblage des batteries.

La Figure II.1 montre l'architecture générale de nos électrodes observées par SEM. Sur la vue de dessus (Figure II.1a), la rugosité de surface est bien visible, avec une bonne dispersion des particules de silicium et des feuillets de graphène (particules plus sombres ressemblant à des voiles et avec des bords très marqués). Sur la vue en coupe transversale (Figure II.1b), obtenue par gravure par faisceau d'ions focalisés (FIB), les feuillets de graphène apparaissent aussi plus sombres et sont de forme longiligne. Ces derniers semblent avoir une légère orientation préférentielle, parallèle au collecteur de

courant. Ils sont bien dispersés dans l'épaisseur de l'électrode entre les particules de silicium. Pour ces dernières, on observe à la fois des particules de forme irrégulière d'environ 1 à 2 μm de diamètre et des particules beaucoup plus petites mais agglomérées entre elles. De nombreux points de contact entre les particules de silicium et les feuillets de graphène sont visibles, ainsi qu'avec le substrat de cuivre. La porosité semble répartie de manière homogène. Toutefois, les chemins créés sont tortueux, ce qui freine la diffusion du Li^+ à travers l'électrode. La porosité semble contribuer à une fraction significative du volume de l'électrode. Elle n'est cependant pas quantifiable à partir d'une image 2D et représentative que d'une fraction minimale de l'électrode. Le liant quant à lui est très difficilement discernable, sauf dans les amas de particules.

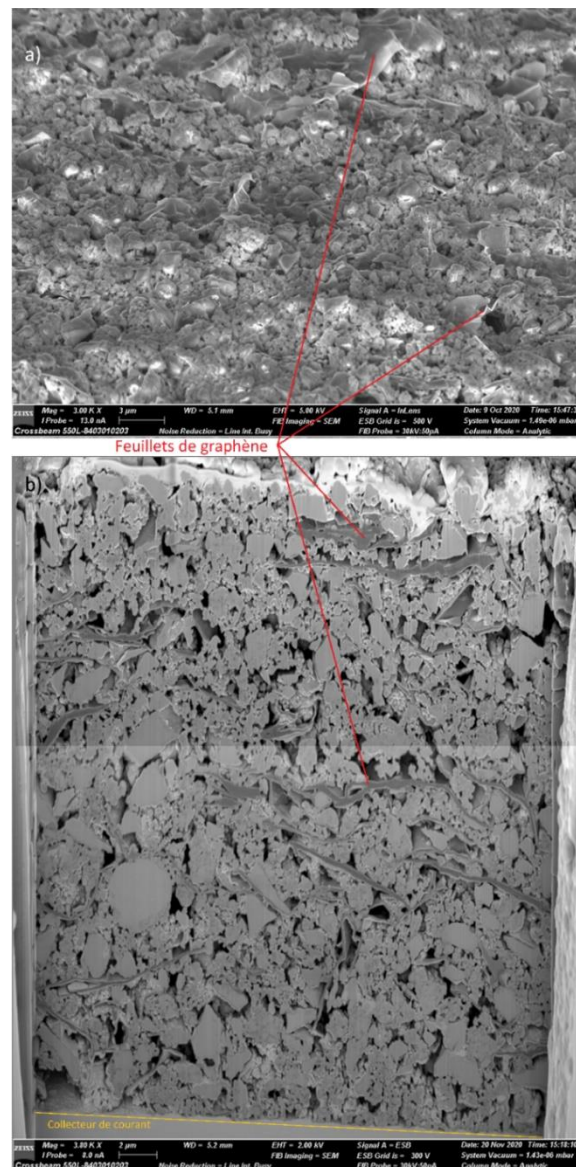


Figure II.1 Images SEM en électrons secondaires montrant l'architecture générale de nos électrodes: (a) Vue de la surface de l'électrode; (b) Vue d'une coupe d'électrode, depuis la surface (haut) jusqu'au collecteur de courant (bas).

3.1.4. La fraction de solide (SF)

Le pourcentage de matière sèche dans l'encre de l'électrode, tel que défini par l'éq. (21), correspond à la fraction de solide :

$$SF = \frac{m_{sec}}{m_{sec} + (V_l \times \rho_{H_2O})} \times 100 (\%_m) \quad (21)$$

Avec m_{sec} (mg) la masse des composants secs de l'électrode composite, c'est-à-dire la MA, l'ACE et le liant. La masse de solvant (*i.e.* l'eau), se calcule en multipliant V_l (ml) le volume de liant utilisé pour l'enduction, par ρ_{H_2O} la masse volumique de l'eau qui est égale à 997 mg.ml⁻¹. Par exemple, pour augmenter la fraction de solide il suffit de baisser le volume de liant pour l'enduction. Toutefois, pour préserver les mêmes proportions des éléments de l'électrode composite, la concentration de la solution de liant doit être augmentée. Ce qui est réalisé en diminuant la quantité d'eau ultrapure ajoutée au 5 mL de solution tampon.

3.2. Techniques de caractérisation

3.2.1. Électrochimie

Les électrodes sont assemblées en boîte à gants sous atmosphère d'Ar (O_2 et $H_2O < 1$ ppm), en configuration demi-cellule dans des cellules Swagelok 2 électrodes (Figure II.3b). La contre-électrode (qui est aussi l'électrode de référence) est un disque de lithium métallique ($d = 10$ mm, $e = 380$ μ m, 99.9 %; Aldrich) placé sur un collecteur de courant en Cu ($d = 12$ mm, $e = 250$ μ m). Deux couches de membranes en microfibres de verre (grade GF/D, $d = 13$ mm, $e = 670$ μ m; Whatman) sont utilisées comme séparateur. Les couches de séparateur sont imbibées de 300 μ L d'électrolyte composé de 1 mol.L⁻¹ de LiPF₆ dans un mélange EC:DMC en proportion 1:1 v:v, plus 10 %_m de FEC (99,9 %; Solvionic). Les électrodes avec un grammage de $1,75 \pm 0,1$ mg_{Si} cm⁻² sont cyclées à température ambiante à l'aide d'un potentiostat/galvanostat VMP multicanaux (Biologic) en mode galvanostatique entre 0,005 et 1 V (vs. Li⁺/Li⁰). Le *C-rate* est de C/40 pour le 1^{er} cycle, C/20 pour les 5 cycles suivants et C/10 pour les cycles restants (1C = 3820 mA.g_{Si}⁻¹). Avant le cyclage, les cellules sont laissées au repos pendant 2 h à la tension de circuit ouvert (OCV) et sont également laissées relaxer à l'OCV pendant 10 s et 1 min après chaque étape de décharge (lithiation) et de charge, respectivement. Pour les analyses post-mortem, une couche supplémentaire de séparateur est ajoutée au contact de l'électrode de silicium. Cette dernière est une monocouche de PP (grade 2500, $d = 13$ mm, $e = 25$ μ m; Celgard), qui empêche aux fibres du séparateur GF/D (partie blanche sur les électrodes du bas, Figure II.2a) de se prendre dans les aspérités et creux de l'électrode pendant le cyclage (des fibres sont pointées en vert, Figure II.2b). Dans ce cas, la période d'OCV avant le cyclage est allongée à 8 h, car le DMC imprègne très mal le PP.

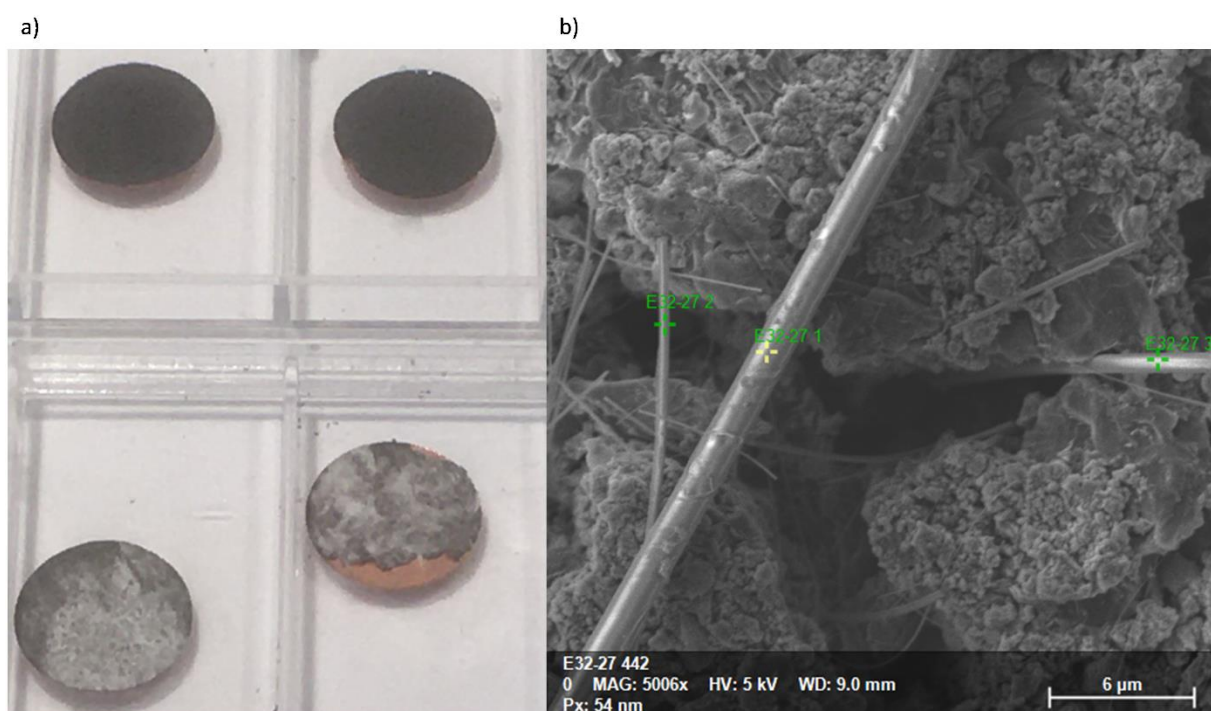


Figure II.2 (a) Image de la surface d'électrodes protégées par du Celgard en haut et en contact direct avec le séparateur GF/D en bas; (b) Image SEM des fibres à la surface et dans les fissures de l'électrode.

Les mesures de spectroscopie d'impédance électrochimique (EIS) sont effectuées dans des cellules Swagelok à trois électrodes (voir Figure II.3a). L'électrode de référence est constituée de trois morceaux de Li métallique disposés autour de l'empilement des électrodes plus séparateur. Ce dernier est composé d'une couche de PP et d'une couche de GF/D ($d = 25$ mm) et la quantité d'électrolyte est portée à 700 μL . Des électrodes de silicium avec un grammage de 1,0 et $1,75 \pm 0,1$ $\text{mg}_{\text{Si}}\cdot\text{cm}^{-2}$ sont utilisées pour les mesures EIS. Les cellules sont laissées au repos à l'OCV pendant au moins 4 h, puis trois étapes de EIS sont appliquées avec une amplitude sinusoïdale de 5, 15 et 25 mV entre 200 kHz et 10 mHz. Chaque étape est répétée une fois avant d'appliquer l'amplitude suivante (avec 15 min d'OCV avant chaque étape). Ceci est nécessaire pour vérifier la linéarité et la stationnarité du système. Après 1 h d'OCV, un cycle galvanostatique est réalisé entre 0,005 et 1 V (vs. Li^+/Li^0) à C/40. Après 2 h d'OCV, une autre série de mesures EIS est appliquée dans les mêmes conditions que la précédente. Les périodes d'OCV sont appliquées jusqu'à ce que $dE/dt < 1$ $\text{mV}\cdot\text{h}^{-1}$.

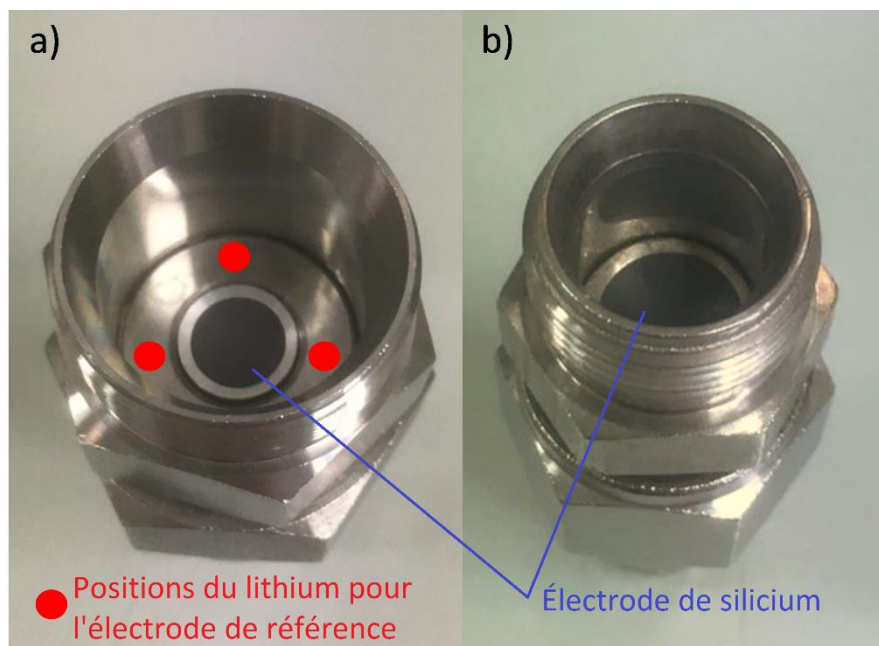


Figure 11.3 Comparaison des cellules Swagelok à demi assemblées: (a) Swagelok 3 électrodes; (b) Swagelok 2 électrodes.

3.2.2. Spectroscopies

3.2.2.1. Infrarouge à transformée de Fourier (FTIR)

Les liaisons de coordination des liants sont analysées à l'aide de spectres FTIR acquis avec un spectromètre ATR 7600 thermorégulé (Thermo Nicolet). Les solutions de liant sont préparées soit avec de l'eau ultrapure, soit avec de l'eau deutérée. Tout d'abord, une goutte de solution de liant est mise à sécher à 60 °C pendant 15 minutes sur le diamant du module ATR. Ensuite, la température est augmentée puis maintenue à 100 °C. Les spectres IR sont acquis en continu avec une résolution de 4 et 2 cm^{-1} et moyennés sur 30 et 100 acquisitions pour les solutions faites à l' H_2O et au D_2O , respectivement. Un spectre est acquis à 60 °C sans liant, pour corriger le fond continu. Aucune correction de la ligne de base n'est appliquée aux spectres de l'échantillon, mais une correction ATR est appliquée pour l'acquisition des spectres.

3.2.2.2. NMR

Pour l'étude des liaisons de coordination, des spectres de résonance magnétique nucléaire de rotation à angle magique (MAS) sont acquis pour des mélanges de silicium et de liant à l'état solide. Les échantillons sont préparés de la même manière que les électrodes (séchées 2 h à 100 °C sous vide, $P \approx 10$ mbar), mais sans graphène. De plus, l'encre est enduite sur du polyéthylène téréphtalate (Mylar) pour éviter le risque d'oxydation du collecteur de courant en Cu et la diffusion de Cu(II) paramagnétique dans l'électrode³. Des analyses supplémentaires sont aussi réalisées sur des composés de référence et

des liant secs (séchés à 60 °C). Un Bruker Avance III de 500 MHz est utilisé avec une sonde MAS Bruker de 4 et 2,5 mm, pour les analyses ^{13}C et ^{17}O , respectivement (le rotor est en zircone). Les spectres de polarisation croisée ^1H - ^{13}C ont été acquis avec un temps de contact de 2 ms, une fréquence MAS de 11 kHz (^{13}C) et un délai de recyclage allant de 2 à 5 s. Pour chaque acquisition, un schéma de découplage TPPM15 ^1H est utilisé, avec une intensité radiofréquence (RF) de 90 kHz. Les spectres MAS ^{17}O ont été acquis avec une excitation à une seule impulsion $\pi/12$ d'intensité RF de 71 kHz. La fréquence MAS a été réglée à 27 kHz et le délai de recyclage à 2 s. À noter qu'aucun découplage ^1H n'a été utilisé pour éviter le re-couplage dipolaire. De même, l'utilisation du double balayage en fréquence pour améliorer le signal a été écartée, car nous avons observé une distorsion spectrale pour certains échantillons. Les spectres ^{13}C et ^{17}O sont référencés par rapport au tétraméthylsilane et à l'eau, respectivement.

Des électrodes cyclées puis grattées de leur collecteur de courant sont analysées par NMR MAS ^7Li et ^{19}F , afin d'obtenir des informations sur la quantité de SEI formée selon les formulations d'électrode. Les mesures sont effectuées sur un Bruker Avance III de 500 MHz (fréquence de Larmor $\nu_0(^7\text{Li}) = 194 \text{ MHz}$, $\nu_0(^{19}\text{F}) = 470 \text{ MHz}$) avec un rotor en zircone ($d_{\text{ext.}} = 2,5 \text{ mm}$). Les spectres ^7Li et ^{19}F sont acquis avec une séquence contenant une impulsion unique et un écho de Hahn et un délai de recyclage de 30 et 15 s, respectivement. Des fréquences de rotation allant jusqu'à 25 kHz sont utilisées. De longs temps de recyclage sont utilisés pour assurer des mesures quantitatives, tous les spectres étant normalisés en prenant en considération le nombre de balayages, du gain du récepteur et de la masse de l'échantillon. Les intensités intégrées de ^7Li et ^{19}F sont déterminées en utilisant le logiciel de simulation spectrale Dmfit⁴. Les courbes d'étalonnage pour la quantification NMR sont réalisées en mélangeant du silicium avec différentes quantités de LiF ⁵. Ces courbes permettent la quantification absolue du lithium et du fluor dans les échantillons⁶. Les électrodes utilisées sont celles qui sont cyclées en EIS pendant 1 cycle, non rincées puis séchées à $T = 40 \text{ °C}$, $t = 20 \text{ h}$, $P \approx 1 \text{ mbar}$, sans exposition à l'air. Il est important de noter que même si les électrodes ne sont pas rincées, elles sont posées délicatement (pour ne pas perdre de matière) sur un papier absorbant. Cela a pour effet d'extraire la quasi-totalité de l'électrolyte liquide qui est contenu dans la porosité. En effet, des électrodes non cyclées ayant suivis la même procédure de démontage et de séchage que les électrodes pour la EIS présentent un gain de masse inférieur à 1 %.

3.2.2.3. Raman

La poudre de silicium est analysée avec un FT Raman MultiRam (Bruker) pour quantifier sa fraction amorphe. La taille du faisceau laser ($\lambda = 1064 \text{ nm}$) est d'environ 100 μm . Deux cents scans sont acquis de 50 à 1200 cm^{-1} . La puissance est de 60 mW pour éviter le rayonnement de corps noir, provenant de l'échauffement du matériau. Cela se manifeste par la présence d'une large bande à environ 3000 cm^{-1} , avec un épaulement autour de 3800 cm^{-1} .

3.2.2.4. Spectroscopie photoélectronique X (XPS)

La composition de surface des différents collecteurs de courant en Cu est analysée par XPS à l'aide d'un AXIS Ultra (Kratos) équipé d'une source monochromatique en Al ($E_{K\alpha} = 1486,6$ eV). Pour la mesure des régions d'intérêt, l'énergie de passage a été fixée à 20 eV permettant une résolution de 0,1 eV. Le signal C 1s de la contamination carbone est utilisé pour la calibration de l'énergie, en fixant sa position à 284,8 eV. Les spectres acquis sur une même gamme d'énergie sont sommés pour l'analyse de chaque échantillon.

3.2.3. Analyses des propriétés mécaniques

3.2.3.1. Rhéologie

Les propriétés d'écoulement des solutions de liant et des encres sont déterminées avec un rhéomètre MCR101 (Anton Paar). La géométrie utilisée est cône-plan ($d = 50$ mm, $h = 46$ μm , $\alpha \approx 0,984^\circ$) et plan-plan ($d = 50$ mm, $h = 300$ μm) pour les solutions et les encres respectivement. La géométrie cône-plan, contrairement à celle plan-plan, permet de mesurer la viscosité absolue. En effet, l'angle fait que la variation de hauteur induite contrebalance l'évolution de la vitesse de rotation le long du rayon de la géométrie, tel qu'illustré en Figure II.4. Pour les encres, la géométrie cône-plan ne peut être utilisée car la distance entre les deux surfaces ne peut pas être variée. Or, cette distance doit être supérieure à 10 fois la taille de la plus large particule, ce qui n'est pas le cas au vu des 15 μm de diamètre des feuillets de graphène.

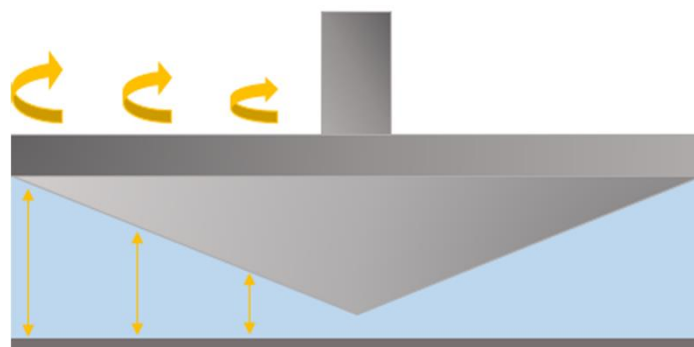


Figure II.4 Schéma de la géométrie cône-plan, pas à l'échelle.

La température est régulée à 20 °C à l'aide d'une sonde Peltier. Les solutions de liant sont sous agitation magnétique pendant 1 h à 300 tr.min⁻¹ puis sont laissées au repos au moins 30 minutes pour établir le même historique de travail. Par contre, les encres sont utilisées, juste après la fin de l'étape de broyage. Les modules de stockage (G') et de perte (G'') sont mesurées avec une déformation croissante de 0,01 à 100 % à une fréquence de 1 Hz. La contrainte de cisaillement et la viscosité sont mesurées en augmentant le taux de cisaillement de 0,01 à 1000 s⁻¹, puis en le ramenant à 0,01 s⁻¹. La

viscosité des liants est prise sur le balayage aller et le balayage retour sert à évaluer le thixotropie⁷. La viscosité de l'encre est prise sur le balayage retour, afin de reproduire les conditions de l'étape d'enduction de l'encre qui se fait après l'étape de mélange planétaire (un fort gradient de cisaillement qui désagglomère la structure de l'encre).

3.2.3.2. *Indentation*

Les propriétés mécaniques des films d'électrode séchés 2 h à 100 °C sous vide ($P \approx 10$ mbar) et des collecteurs de courant en Cu sont analysées grâce à un nano-indenteur NHT3 et d'un MicroCombi MCT3 (seulement pour les films d'électrode; Anton Paar). Le premier peut coupler une charge sinusoïdale à la charge standard pour rendre un profil en profondeur de la dureté et du module élastique. La tête (Berkovich) applique une force de 0,1 à 400 mN. L'amplitude de la contribution oscillante est de 5 % de la force maximale à tout moment et sa fréquence est de 5 Hz, avec un coefficient d'accélération (rampe de force RSC) de $0,1 \text{ s}^{-1}$. Pour le micro-indenteur (Vickers), le profil en profondeur est obtenu en appliquant des charges quasi-statiques. L'intensité de la charge est augmentée en 10 fois, de 30 mN à 1 N et est maintenue pendant 15 s à chaque fois. Le temps de chargement/déchargement est aussi de 15 s. La méthode d'Oliver et Pharr⁹ est utilisée pour déterminer la dureté et le module d'élasticité. Pour ces calculs, le coefficient de Poisson des films d'électrodes est postulé égal à 0,3. Enfin, les propriétés mécaniques sont évaluées dans des conditions similaires à celle d'une batterie. Pour ce faire, les électrodes sont trempées pendant 10 min dans du carbonate de propylène (PC) et le surplus est retiré avant les tests.

3.2.3.3. *Test de rayure*

Les propriétés d'adhésion et de cohésion des films d'électrodes sont déterminées à l'aide d'un scléromètre (BYK-Gardner). Tout d'abord, les revêtements sont découpés aux dimensions d'une lame de microscope ($26 \times 76 \text{ mm}^2$), puis séchés. Leur masse et leur épaisseur sont mesurées de la même manière que pour les électrodes. Les échantillons sont collés avec un ruban adhésif double-face sur les lames de façon à ce que les rayures soient normales à la direction de l'enduction du film de l'électrode. Ainsi, chaque rayure traverse le même profil d'épaisseur. Le stylet ($d = 1,9 \text{ mm}$, $\alpha = 60^\circ$, $d_{\text{pointe}} = 150 \text{ }\mu\text{m}$; BYK) est placé sur le revêtement puis chargé avec des poids de différentes masses, comme présenté Figure II.5. Ensuite, la plaque supportant la lame (collée dessus avec un ruban adhésif double-face) est déplacée ($v = 336 \text{ mm} \cdot \text{min}^{-1}$) pour réaliser la rayure.

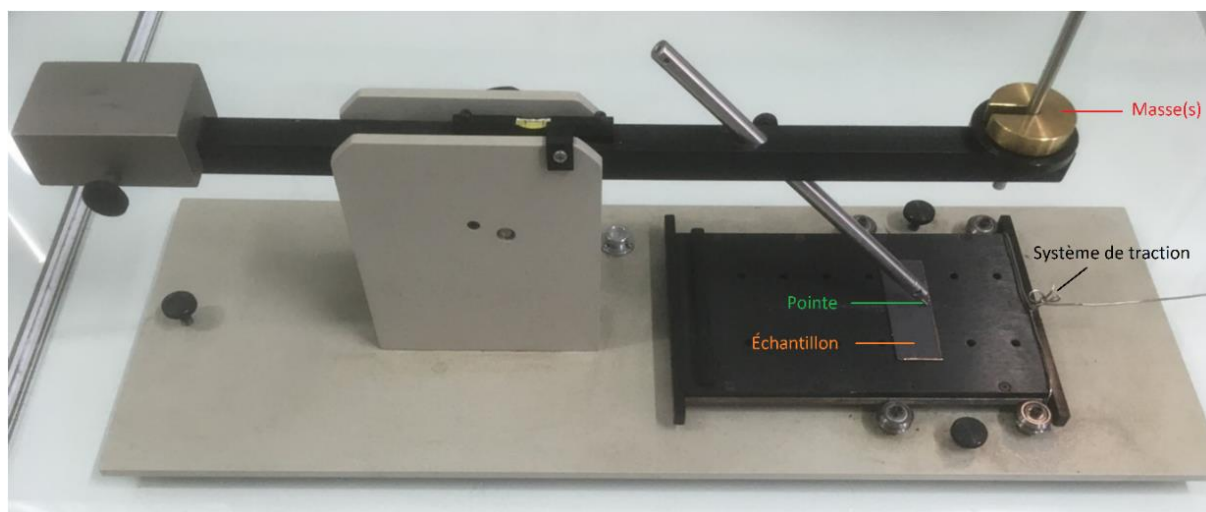


Figure II.5 Scléromètre, avec le stylet posé sur l'échantillon et chargé d'une masse, prêt à faire la rayure.

3.2.3.4. Dilatométrie *operando*

La variation de l'épaisseur des électrodes est mesurée *operando* grâce à une cellule électrochimique ECD-2 (EI-cell) intégrant un capteur de déplacement transformateur différentiel linéaire variable (LVDT). Ce capteur peut mesurer des variations de hauteur sur une plage de plus ou moins 500 μm avec une résolution de 0,05 μm . Une illustration en coupe des différents éléments de la cellule est présentée Figure II.6. La contre-électrode est constituée de Li métallique ($d = 16 \text{ mm}$, $e = 750 \mu\text{m}$, 99,9 %; Fisher). Un verre fritté mais poreux est utilisé comme séparateur ($e = 6 \text{ mm}$) et l'électrolyte est le même que celui pour le cyclage classique ($V \approx 2 \text{ mL}$). Ce fritté est fixe, de sorte que tous les déplacements mesurés sont ceux de l'électrode de travail. L'électrode de référence, composée de lithium, est en contact avec le séparateur, proche de l'électrode de travail. Une membrane métallique, placée au-dessus de l'électrode de travail, transmet les variations d'épaisseur de l'électrode au capteur.

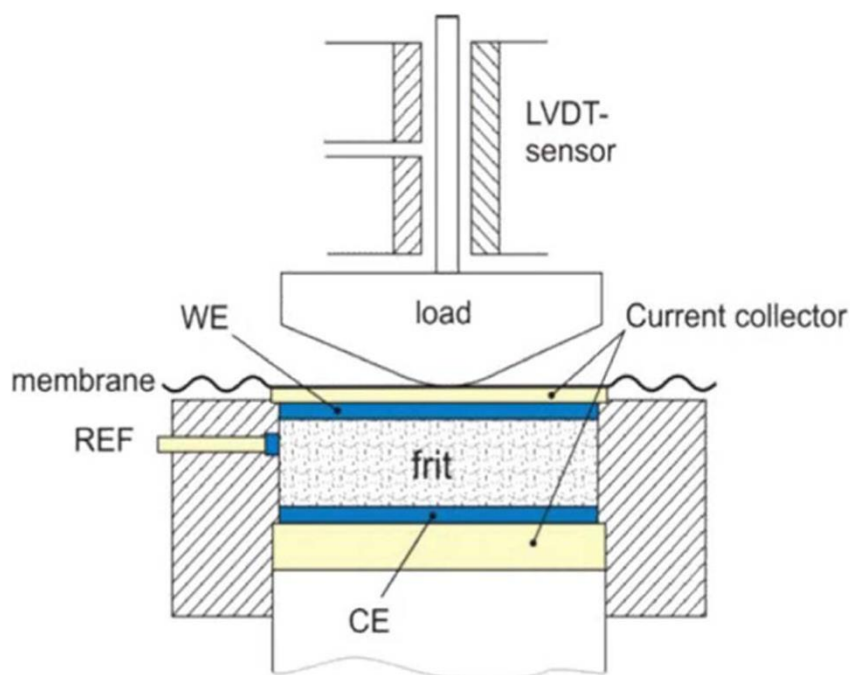


Figure II.6 Schéma de la cellule de dilatométrie couplée⁸, pas à l'échelle: électrode de travail, i.e. électrode de silicium et contre-électrode.

L'électrode de travail est la même que pour les cellules Swagelok. Toutefois, le collecteur de courant en Cu est plus épais ($e = 120 \mu\text{m}$, recuit, 99,9 %; Alfa Aesar), afin d'en limiter les risques de déformation plastique, qui pourrait biaiser la mesure dilatométrique. À noter que la compression exercée sur l'électrode de travail est plus faible (1,3 N, i.e. 17 kPa) que dans une cellule Swagelok (15,9 N, i.e. 202 kPa). Les conditions de cyclage sont identiques à celles des cellules Swagelok, à l'exception de la période OCV qui est fixée à 12 h. Cela permet la stabilisation de la dérive (linéaire) en épaisseur, qui est intrinsèque à l'équipement (typiquement de l'ordre de 10^{-2} à $10^{-1} \mu\text{m.h}^{-1}$) et sa correction. Certaines électrodes sont aussi limitées à une capacité de $1200 \text{ mAh.g}_{\text{Si}}^{-1}$.

3.2.3.5. Profilométrie

La rugosité de la surface des collecteurs de courant est mesurée à l'aide d'un profilomètre mécanique P-7 (KLA), utilisant un stylet à pointe de diamant avec un rayon de courbure de $2 \mu\text{m}$. Pour les collecteurs de courant laminé à froid et recuit, le stylet est passé orthogonalement à la direction des bandes de rugosité, en raison de leur orientation préférentielle. Pour ces deux collecteurs, le chargement du stylet est de 2 mg contre 0,5 mg pour le collecteur texturé. Enfin, quel que soit le collecteur, le stylet est passé à une vitesse de $100 \mu\text{m.s}^{-1}$ et la fréquence d'échantillonnage est de 1 kHz.

3.2.4. Microscopies

3.2.4.1. SEM

La surface et l'interface film/collecteur de courant des électrodes (après arrachement avec un ruban adhésif) sont métallisées au carbone, puis sont analysées avec une sonde EDX SDD (SAMx) dans un SEM 5800LV (Jeol) avec une tension et un courant de canon de 15 kV et 0,5 nA. Les rayures du test de rayure sont analysées de la même manière mais sans métallisation. Les images sont produites avec les électrons secondaires (SE).

Des images de la surface des collecteurs de courant sont obtenues à l'aide d'un SEM JSM 7600F (Jeol) avec une tension de canon de 5 kV et un détecteur SE dans la lentille.

3.2.4.2. FIB-SEM

Des coupes transversales des électrodes sont obtenues en utilisant un FIB-SEM 550 L (ZEISS) à faisceaux croisés entre la colonne SEM et une source de galium pour la colonne FIB. Cette dernière permet de générer un faisceau d'ion Ga^+ , servant dans notre cas à la gravure (elle peut aussi servir à observer les échantillons). Pour celle-ci, l'échantillon est penché afin d'être perpendiculaire à l'axe de la colonne FIB, elle-même inclinée par rapport à la colonne SEM, comme présenté figure II.7a. Ainsi, la gravure se fait normalement à la surface de l'électrode et la colonne SEM est bien orientée pour observer la coupe. La distance de travail entre la colonne SEM et l'échantillon doit être approximativement de 5,1 mm. La réalisation de la coupe transversale commence par le dépôt d'une couche de protection en platine, sur la surface de l'échantillon. Pour cela, un système d'injection de gaz émet du Pt sous forme gazeuse et qui interagissent avec les ions Ga^+ pour former un dépôt. Les dimensions de celui-ci sont $8 \times 20 \mu\text{m}^2$ ($l \times L$) et le courant du FIB est 700 pA. Le courant doit être compris entre $2 \times l \times L$ pA pour que le dépôt ne soit pas trop long et $5 \times l \times L$ pA pour qu'il ne soit pas trop attaqué par le faisceau d'ions. La tension du FIB est toujours fixée à 30 kV pour nos expériences.

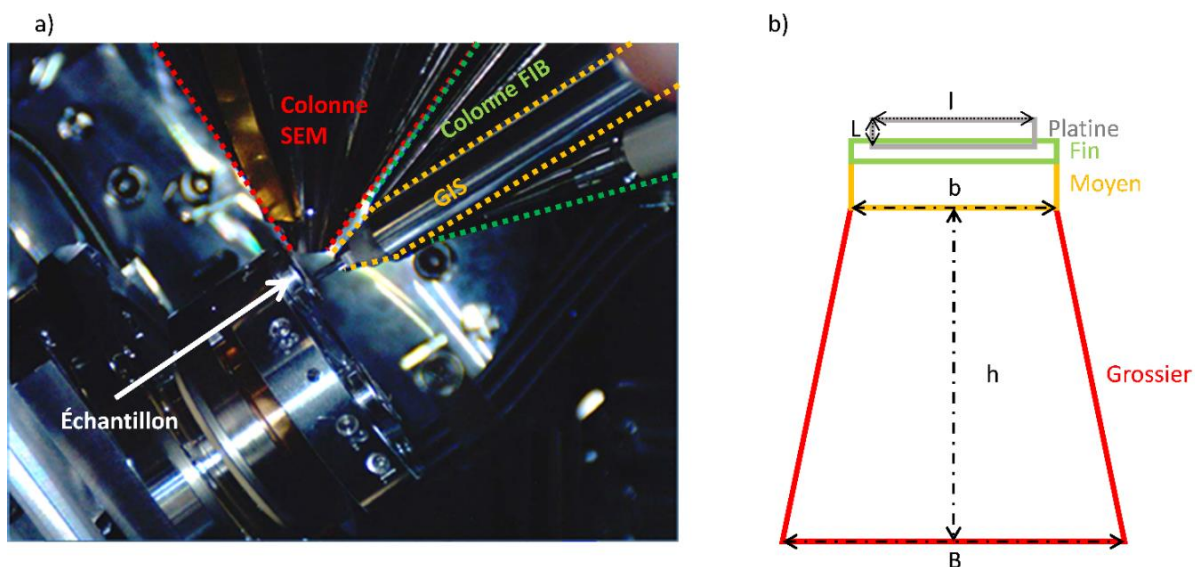


Figure 11.7 (a) Image de la chambre du FIB-SEM (contraste et luminosité modifiés); (b) Schéma représentant les différents éléments de la préparation de la coupe transversale, pas à l'échelle.

Ensuite, une première tranchée sous la forme d'un trapèze est creusée à quelque distance de la zone d'observation que l'on désire dégager (voire figure 11.7b). Ses dimensions : B , b et h sont égales à 30, 14 et 28 μm , respectivement et le courant du FIB est de 65 nA pour une gravure « grossière ». La dimension h doit être au moins 1,5 fois supérieure à l'épaisseur de l'échantillon pour découvrir la zone d'observation jusqu'au collecteur de courant. La deuxième tranchée dite « moyenne » mesure $14 \times 5 \mu\text{m}^2$ et un courant de 7 nA est utilisé pour la gravure. Enfin, la dernière tranchée « fine » de $14 \times 1,5 \mu\text{m}^2$ se fait en entamant légèrement la couche protectrice. Les images de la coupe transversale sont acquises avec un mélange de 40 et 60 % de SE (dans la lentille de la colonne SEM) et d'électrons rétrodiffusés (BSE), pour améliorer le contraste.

Toutefois, l'emploi du FIB entraîne généralement la contamination des échantillons. Le dépôt de platine (en blanc) reste visible à la surface des électrodes. De plus, du gallium et de cuivre (provenant de la gravure du collecteur de courant) sont parfois redéposés à la surface des particules localisées dans la porosité.

Des images de la surface des électrodes sont obtenues après un cycle, en utilisant uniquement la colonne SEM du FIB-SEM avec le détecteur SE dans la lentille. La tension et le courant du canon sont de 6 kV et 5 nA. Afin d'éviter l'exposition à l'air, une navette de transfert d'échantillons étanche (SEMILAB) est utilisée entre la boîte à gants et le FIB-SEM.

Certaines images sont post-traitées avec le logiciel ImageJ, pour modifier le contraste et la luminosité par exemple. Dans tous les cas, les modifications sont indiquées dans la légende de l'image.

3.2.4.3. TEM

Des expériences de STEM sont réalisées à l'aide du Nant'Themis, un microscope (S)TEM Themis Z G3 corrigé par sonde Cs (Thermo Fisher Scientific). Il fonctionne à 80 kV et est équipé d'un détecteur à champ sombre annulaire à grand angle (HAADF). Des cartographies élémentaires sont acquises en mode STEM à l'aide d'un spectromètre d'émission de rayons-X Super-X, composé de quatre détecteurs à dérive de silicium sans fenêtre. Ils fournissent un grand angle solide de collecte de 0,7 srad. Pour les électrodes à analyser, cette configuration assure une sensibilité limitée à l'orientation des agrégats par rapport aux détecteurs. Afin de limiter les effets de dégradation du faisceau d'électrons souvent observés sur les électrodes à base de silicium¹⁰, un petit angle de convergence d'environ 13 mrad et un courant limité à 100 pA sont utilisés. Ceci permet de réduire la dose d'électrons. Des tailles de pixel d'environ 5 nm sont choisies. Pour cette même raison, des acquisitions rapides de trames sont utilisées (quelques secondes par trame et 10 à 50 μ s de temps de pause). Ensuite, des centaines de trames sont additionnées pour chaque cartographie. Les quantifications effectuées sur les premières dizaines d'images donnent des résultats très semblables à celles effectuées sur les dernières dizaines d'images (non montré). Il y a donc peu de dégradation sous le faisceau, prouvant ainsi la fiabilité des rapports atomiques et des cartographies présentées. Les régions purement composées de LiF sont néanmoins légèrement dégradées dans ces conditions, sans implications majeures sur la pertinence des cartographies. Grâce à une valeur de 5 eV.canal⁻¹ pour la dispersion énergétique, les éléments légers sont mesurés de manière fiable, comme le confirme la quantification réalisée sur un échantillon de NaCMC. Les quantifications en pourcentage atomique sont réalisées à l'aide du logiciel Velox 2.14 et des sections transversales intégrées dans le logiciel (Brown-Powell). Les spectres sont moyennés sur plusieurs pixels est utilisé pour améliorer la fiabilité de la quantification. La résolution spatiale des cartographies peut être estimée à environ 15 nm. Une "méthode" est définie (fond, ajustement, correction d'absorption) et est systématiquement appliquée afin d'optimiser la comparaison relative des différentes cartographies et échantillons.

Des électrodes avant cyclage (sans additif conducteur xGnP15) sont analysées après avoir été grattées du collecteur de courant. La poudre ainsi récupérée est dispersée dans du cyclohexane, ce dernier ne réagissant pas avec nos matériaux. Une légère agitation du milieu permet de faire passer les plus petites particules en suspension. Puis, une goutte de cette suspension est déposée sur un film de carbone en dentelle supporté par une grille de cuivre. Les électrodes cyclées, puis grattées du collecteur de courant ($1,0 \pm 0,1 \text{ mg}_{\text{Si}}.\text{cm}^{-2}$ issues de tests EIS, après 1 cycle, non rincées puis séchées à $T = 40^\circ\text{C}$, $t = 20 \text{ h}$, $P \approx 1 \text{ mbar}$, sans exposition à l'air) sont déposées sur ces mêmes supports par simple contact avec la grille de cuivre. Un porte-échantillon sous vide (GATAN 648) permet de faire le transfert de la boîte à gant au TEM sans exposer les échantillons réactifs à l'air.

3.2.4.4. Microscopie optique *operando*

L'évolution de la surface d'électrodes lors du cyclage est évaluée *operando* grâce à une cellule ECC-Opto-Std-Aqu (El-cell). Les électrodes sont cyclées en suivant le même protocole que celui des cellules Swagelok, sauf qu'un régime de C/20 est appliqué. Le potentiostat/galvanostat est un SP-300 (Biologic). Les images sont acquises avec une caméra DFC320 (LEICA) installée sur un microscope MEF4 M (REICHERT). La cellule a une fenêtre d'observation de 2 mm de diamètre.

Cependant, des modifications de l'empilement d'électrodes plus séparateur sont nécessaires pour que la cellule fonctionne correctement. En particulier, certains éléments de l'empilement sont troués pour libérer le champ de vision jusqu'à la surface de l'électrode de silicium. Dans le détail et de bas en haut, il y a la fenêtre en quartz, puis vient la contre-électrode en Li ($d = 10$ mm) avec un trou en son centre ($d = 3,5$ mm). Deux couches de GF/D ($d = 10$ mm), aussi trouées en leur centre ($d = 2.5$ mm), sont utilisées comme séparateur. Le trou est plus petit dans le cas du séparateur afin de gêner la propagation des dendrites de Li, qui sont visible Figure II.8. Enfin, vient l'électrode de silicium avec une cale en Cu à son dos ($e = 250$ μ m), puis un ressort en acier inoxydable. Le ressort maintient l'empilement comprimé, tandis que la cale protège l'électrode trop fine pour supporter la pression du ressort sans se déformer. La cellule et l'empilement d'électrodes plus séparateur sont présentés Figure II.8, toutefois les dimensions de la fenêtre d'observation et des trous y sont supérieures. De plus, le collecteur de courant de la contre-électrode est une grille au lieu d'une feuille.

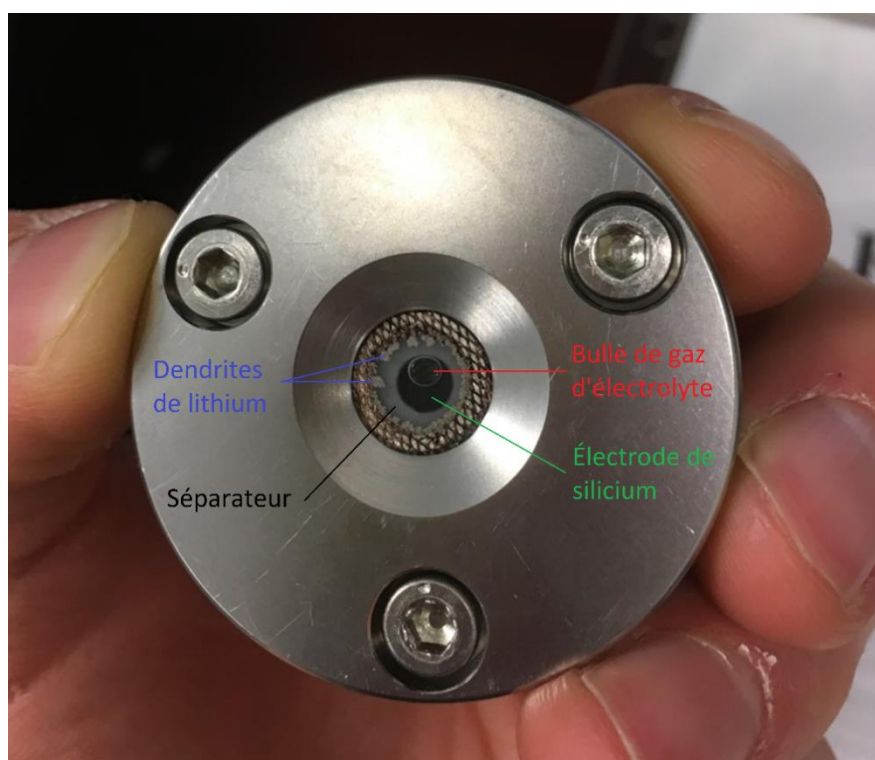


Figure II.8 Cellule de microscopie optique avec électrode de silicium après 1 cycle.

Lors de la première décharge, une bulle de gaz est générée par la formation de la SEI, comme observable Figure II.8. Malheureusement, elle bloque le champ de vision. Il n'est donc pas possible d'acquérir des images nettes sur cette période. Pour éliminer la bulle, le cyclage est arrêté après la première décharge (lithiation) et l'électrolyte de la cellule est renouvelé en boîte à gants. Seulement environ 200 images peuvent être ouvertes simultanément avec le logiciel Image-Pro Plus 5.1, en raison des performances limitées de l'ordinateur. Des étapes d'OCV sont ajoutées pour avoir le temps de les sauvegarder et de relancer l'acquisition. Une macro maison sur le logiciel Super macro est utilisée pour acquérir automatiquement les images toutes les 5 à 10 minutes. La surface des électrodes sont très régulières et manquent de contraste au grandissement x20 utilisé. Ainsi, la fonction CLAHE (amélioration de contraste local) (taille du bloc = 127, pente maximale = 2) d'ImageJ est utilisée pour améliorer ce dernier.

3.2.5. Autres

3.2.5.1. DRX

La poudre de silicium est analysée avec un diffractomètre de type D8 (Bruker) en géométrie Bragg-Brentano et équipé d'un monochromateur. La source RX est en Cu ($\lambda_{\text{K}\alpha 1} = 1,54056 \text{ \AA}$) et fonctionne à 40 kV et 40 mA. Pour l'analyse structurale du silicium, le diffractogramme est acquis entre $2\theta = 20$ et 102° avec un pas de $0,0169^\circ$ et 6 s par pas. Pour la quantification du silicium amorphe, le diffractogramme est acquis entre $2\theta = 20$ et 70° avec un pas de $0,0144^\circ$ et 4 s par pas. Dans ce cas, du MgO cristallin est ajouté comme standard (micro-absorption des rayons X similaire à celle du silicium). En détail, le MgO est déshydraté/déshydroxylé à 450°C pendant 12 h (avec une rampe de 2 h pour chauffer et refroidir), puis conservé dans un four à 100°C avant la mesure. Avant l'analyse DRX, le MgO et le silicium sont soigneusement mélangés pour assurer une homogénéité maximale. La fraction massique de silicium et de MgO est respectivement de 84,5 et 15,5 %, afin d'obtenir le même ordre de grandeur pour l'intensité des pic DRX des deux matériaux.

3.2.5.2. Analyse thermogravimétrique (TGA)

Pour mesurer évaluer la quantité de liant ab/adsorbé à la surface des particules de silicium, des encres contenant 80 mg de silicium plus 3,2 mL de liant ont été préparées de manière identique à celles utilisées pour les enductions. À l'exception du nombre de billes de nitrure de silicium placé dans la jarre pour le mélangeage planétaire (qui est porté à 6 au lieu de 3). D'autres échantillons ont été réalisés avec 2,36 mL de liant plus concentré, pour augmenter la SF. Ensuite, les encres ont été placées dans des flacons en verre pour 5 min de centrifugation à 5000 tr.min^{-1} . Le surnageant a été éliminé et la poudre restante mise à sécher, d'abord pendant 12 h à température ambiante puis pendant 12 h à 60°C . Enfin,

les échantillons ont été analysés par thermogravimétrie avec un appareil STA 449F3 Jupiter (NETZSCH), entre 30 et 540 °C à 5 °C.min⁻¹ sous air.

3.2.5.3. *Mesure de conductivité*

La résistivité des films d'électrode a été mesurée avec une tête de mesure 4 points 280SI (Four Dimensions Inc.). Les films ont été enduits sur du Mylar, qui est un polymère particulièrement isolant, pour s'affranchir de la contribution du collecteur de courant lors de la mesure. Le reste du protocole est identique à celui de l'enduction des électrodes classiques. La distance entre les sondes est d'environ 1 mm et la masse appliquée sur la tête de mesure est de 60 g. La résistance est mesurée à 100 emplacements différents, sur un carré d'enduction de dimension 3x3 cm². Enfin, la résistivité (r) se détermine selon l'éq. (22) :

$$r = \frac{R \times S}{e} (\Omega \cdot \text{cm}) \quad (22)$$

Avec R (Ω) la résistance mesurée, S la surface de contact entre la sonde et le film d'électrode, qui est égale à 0,283 cm², et e (cm) l'épaisseur du film.

3.2.5.4. *Mesure de pH*

Le pH des solutions de liants est obtenu grâce à une sonde connectée à un pH mètre PC 2700 (Eutech Instruments). Les mesures se font à 25 °C, après étalonnage à pH 10, 7 et 4 du pH mètre.

3.3. Références

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4. Chapitre 3 : Résultats expérimentaux

4.1. Résumé des résultats

4.1.1. Caractérisation morphologique à l'échelle nanométrique d'un liant de coordination et de l'interface d'électrolyte solide dans les électrodes à base de silicium pour les batteries Li-ion

La réticulation physique des liants polymères par la chimie de coordination améliore considérablement les performances électrochimiques des électrodes négatives à base de silicium. Pour comprendre l'origine de ces améliorations, le STEM-EDX est utilisé, car il est alors possible de sonder la morphologie des électrodes à l'échelle nanométrique. Avant le cyclage des électrodes, cette technique révèle que le liant forme une couche couvrante sur les particules de silicium. De plus, la coordination entre le Zn(II) et les carboxylates est homogène dans toute la phase du liant. Ensuite, après le premier cycle, la SEI formée est plus dense et aussi située de préférence sur les zones les plus pauvres en liant, particulièrement pour les électrodes avec le liant réticulé. La supériorité de celui-ci peut donc être attribuée à sa capacité à stabiliser l'électrode et la couche SEI grâce à de meilleures propriétés mécaniques. Il en résulte une impédance de SEI plus faible, une CE plus élevée au premier cycle, et une amélioration de 40 % de la rétention de capacité après 50 cycles, pour des électrodes fortement chargées délivrant plus de 6 mAh.cm⁻².

Contribution des auteurs :

L.H. : conceptualisation, investigation et écriture – ébauche originale. P.M. : conceptualisation, visualisation et investigation – imagerie TEM et cartographie STEM-EDX – et écriture – révision et édition. N.D. : conceptualisation et investigation – NMR du ⁷Li et ¹⁹F et écriture – révision et édition. T.D. : conceptualisation, supervision et écriture – révision et édition. L.R. : conceptualisation, supervision et écriture – révision et édition. B.L. : conceptualisation, supervision et écriture – révision et édition.

4.1.2. Liants de coordination réticulés pour les électrodes à base de silicium pour les batteries Li-ion : Impact bénéfiques sur les propriétés mécaniques et les performances électrochimiques

La préparation simple et versatile de liants réticulés Zn(II)-poly(carboxylates), réalisée par l'addition d'un précurseur de Zn(II) (ZnSO₄, Zn(NO₃)₂ ou ZnO) dans une solution de liant poly(acides carboxyliques) pré-optimisée est proposée. Ces liants conduisent à une amélioration

systématique et significative des performances électrochimiques, lorsqu'ils sont utilisés pour des électrodes négatives à base de silicium. La formation des liaisons de coordination est étudiée par rhéologie, spectroscopie FTIR et NMR. Les caractérisations mécaniques révèlent que le liant de coordination offre une meilleure cohésion du revêtement de l'électrode et une meilleure adhérence au collecteur de courant, ainsi qu'une dureté et un module élastique plus élevés, qui sont même préservés en présence d'un solvant organique (c'est-à-dire dans les conditions de fonctionnement de la batterie). Au final, l'expansion de l'électrode pendant la lithiation est réduite, ce qui réduit les défaillances mécaniques de l'électrode. Ces électrodes contenant un liant réticulé par des liaisons de coordination sont plus performantes que leurs homologues avec un liant non coordonnées, leur rétention de capacité est améliorée de plus de 30 % après 60 cycles.

Contribution des auteurs :

L.H. : conceptualisation, investigation et écriture – ébauche originale. P.M. : conceptualisation et investigation – cartographie STEM-EDX. N.D. : conceptualisation et investigation – NMR du ^7Li et ^{19}F . M.P. : investigation – NMR du ^{13}C et ^{17}O – et écriture – ébauche originale. S.M. : investigation – synthèse de l'acide citrique enrichi – et écriture – ébauche originale. D.L. : investigation – synthèse de l'acide citrique enrichi – et écriture – ébauche originale. T.D. : conceptualisation, supervision et écriture – révision et édition. L.R. : conceptualisation, supervision et écriture – révision et édition. B.L. : conceptualisation, supervision et écriture – révision et édition.

4.1.3. Impact du grade du collecteur de courant en cuivre, et de la fraction solide de l'encre sur les performances électrochimiques des électrodes à base de silicium pour les batteries Li-ion

Les électrodes à base de silicium sont bien connues pour subir des dégradations mécaniques importantes pendant le cyclage, ce qui rend leur utilisation pour des applications pratiques en LIB extrêmement difficile. De multiples stratégies, liées principalement à l'optimisation du matériau actif et du liant ont été proposées pour contourner ces inconvénients. Nous avons exploré ici les effets de deux paramètres expérimentaux supplémentaires, à savoir la fraction solide et le collecteur de courant, qui sont à notre connaissance négligés dans la littérature relative aux électrodes de silicium. La fraction de solide, qui est la quantité relative de matière sèche dans l'encre utilisée pour préparer les électrodes, est connue pour influencer la distribution des composants dans le revêtement composite final de l'électrode, et a donc un impact sur les caractéristiques mécaniques et de transport de l'électrode. Le collecteur de courant, par exemple par sa texturation, a également un impact significatif sur les propriétés mécaniques de l'électrode. Ici, de par la variation systématique de la fraction de solide de l'encre et du grade du collecteur de courant en cuivre, nous avons obtenus respectivement, des impacts

notables sur la structure de l'électrode et la mécanique de rupture. Au final, faisant varier ces paramètres, la rétention de capacité après 60 cycles a pu être améliorée jusqu'à environ 40 % pour une formulation de liant non coordonné. Les mécanismes concernés doivent cependant être encore mieux compris, mais à la lumière des améliorations possibles des performances électrochimiques, nous pensons que le SF et le CC de cuivre devraient être plus systématiquement abordés dans la littérature sur les batteries.

Contribution des auteurs :

L.H. : conceptualisation, investigation et écriture – ébauche originale. H.H. : conceptualisation et investigation – rhéologie des formulations ZnSO_4 et de sa référence, TGA et conductivité. N.H. : investigation – observation FIB-SEM – et écriture – révision et édition. T.D. : conceptualisation, supervision et écriture – révision et édition. L.R. : conceptualisation, supervision et écriture – révision et édition. B.L. : conceptualisation, supervision et écriture – révision et édition.

4.2. Articles

4.2.1. Publication N°1 : “Nanoscale Morphological Characterization of Coordinated Binder and Solid Electrolyte Interphase in Silicon-Based Electrodes for Li-ion Batteries”

Nanoscale Morphological Characterization of Coordinated Binder and Solid Electrolyte Interphase in Silicon-Based Electrodes for Li-ion Batteries

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Keywords

Silicon anode, Carboxymethyl cellulose binder, Coordination, Physical cross-linking, SEI, Li-ion batteries

Abstract

The physical cross-linking of polymeric binders through coordination chemistry significantly improves the electrochemical performance of silicon-based negative electrodes. Scanning electron microscopy coupled with energy dispersive X-ray spectroscopy is used to probe the nanoscale morphology of such electrodes. This technique reveals the homogeneous coordination of carboxylated binder with Zn cations and its layering on the silicon surface. The SEI formed after the first cycle is denser with Zn-coordinated binder and preferentially observed on binder-depleted zones. The superiority of coordinated binders can be attributed to their capacity to better stabilize the electrode and the SEI layer due to improved mechanical properties. This resulted in a lower SEI impedance, a higher first cycle coulombic efficiency, and a 40% improvement of capacity retention after 50 cycles for highly loaded electrodes of over 6 mAh.cm⁻².

Introduction

Silicon is envisioned to replace graphite as negative electrode active material for Li-ion batteries due to its approximately ten and three times higher specific and volumetric capacities, respectively. This comes from the significant increase in the amount of lithium alloyed with silicon (up to $\text{Li}_{3.75}\text{Si}$) compared to lithium intercalated in graphite (up to LiC_6). However, the silicon volume expansion induced by its lithiation is much higher, up to 280% vs. 10% for graphite¹. This translates to electrode morphology instability during cycling at different scales: (i) at the micrometer scale, upon binder bridge breakage, either between particles or between particles and the current collector, which lead to the appearance of cracks and delamination, respectively; and (ii) at the nanometric scale with the destabilization of the solid electrolyte interphase (SEI), which must reform, causing excess accumulation². Together with the intrinsic silicon material limitations (particle fracture^{3,4} and nano-porosification⁵), these constitute the main electrode failure mechanisms. To increase the SEI stability, improvements have been made on the electrolyte formulation. This has led to enhanced silicon electrode cycle life, also recently in full-cell configuration^{6,7}. In parallel, it is relevant to push the research on binders, especially to improve their mechanical properties as it appears to be a straightforward way to tackle the electrode cracking and delamination issues.

Studies have shown that binder reticulation through covalent or coordination bonds increases silicon electrode performance by helping to mitigate stress during cycling as long as the silicon/binder interface is not the breaking point⁸. However, these types of bonds are not of the same value because of differences in their strength and reversibility⁹. Specifically, coordination bonds offer significant strength, flexibility, and reversibility. They may also have self-healing properties, providing a stronger electrode resiliency to silicon volume variation¹⁰. Coordination binders are also advantageous in other ways. They are easy to process with simple addition of metallic salts to conventional formulation (no advanced polymer chemistry required). Moreover, they are easy to probe at the bulk scale with standard spectroscopic techniques (e.g. infrared spectroscopy). Such a strategy has been applied mainly to cross-linked alginate binders^{11–16}, though also to some other binder systems^{17–21}. The reticulation by coordination leads to clear improvement of the electrochemical performances, particularly of the capacity retention. This is attributed to better adhesion and cohesion of the electrodes upon cycling as assessed by various mechanical measurements (scratch test, peeling test, tensile test, and hardness measurement). It has also been proposed that the coordinated polymers may act as an artificial passivation layer and/or would lead to a more stable SEI. Binders with chemical and electrochemical stabilities are selected in order to resist the harsh environment of an operating Li-ion battery. When combined with electrical insulating properties (with only scarce exceptions, for example PEDOT and PEDOT:PSS^{20,22}), a conformal and electrolyte-impermeable binder-based layer would closely replicate a

SEI. In fact, this layer acts as a barrier to a direct contact between the electrolyte and the active electrode material in a similar way to the SEI layer. Additionally, binder reticulation through coordination bonds would improve the stability of such a preformed SEI layer. However, evidence at the proper scale (tens of nm) of such coordination bonding and of artificial SEI properties is currently lacking.

With respect to electrodes made with coordination binders, proof of coordination is often found by spectroscopic characterizations on bulk binder samples but seldom found on realistic electrode configuration with binder on silicon particles (except in the study of Mazouzi et al¹⁸). Some such evidence has also been provided by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX)^{15,17} for coordinated alginate binders, but these analyses lack in spatial resolution. This is most likely due to the difficulty in probing this kind of sample since there is a low volumetric/massic fraction of binder and the presence of highly absorbing carbonaceous components (which are added as electrode conductive additive). In addition, the structural similarity of the binder in the two mentioned configurations (bulk film and a composite electrode) is not guaranteed as intensive mixing and drying steps are required for the electrode manufacturing. In the case of composite electrodes, specific interfacial interactions are likely to affect the component distribution and result in different coordination patterns from those found in a bulk binder film. Moreover, the visualization of the binder conformation on the active material particles has rarely been achieved^{7,23}.

In this context, scanning transmission electron microscopy with energy-dispersive X-ray spectroscopy (STEM-EDX) can be invaluable in the characterization of pristine and cycled electrode samples. This allows for direct imaging of the binder and SEI distribution on the nanometric scale. A STEM-valence electron-energy-loss spectroscopy (VEELS) analysis could potentially be applied to retrieve those phases as it was done in the study of Xiong J., et al⁷. However, the EDX allows the discretization of their constitutive elements along with their relative quantification. This specificity is necessary to analyze the coordination through particular cations. Thus, as shown in the present study, coupling STEM and EDX delivers insight into the binder conformation and its evolution after cycling, as well as on the SEI formation. A method to improve the representativeness of EDX atomic elements quantification at the nanoscale of composite electrodes is also presented. A complementary and detailed study about the effectiveness of ZnSO₄ as a metallic precursor, with a comparison between ZnSO₄ and ZnO and the study of the mechanical and electrical properties of the corresponding electrodes will be reported elsewhere²⁴.

Results

We focused our attention on electrodes containing silicon as active material, graphene as a conducting additive, and carboxymethyl cellulose (CMC) together with citric acid (CA) as a binder. Like

other carboxylated polymers (such as polyacrylates), CMC has already been shown to be superior to less polar binders (such as polyvinylidene fluoride, PVDF) as carboxylate functions favor the formation of strong supramolecular and covalent binder-binder and binder-silicon interactions^{9,25}. Moreover, citric acid buffers the electrode ink at pH 3 which is essential to strengthen the interfacial interactions between CMC and silicon^{26,27}. It also mitigates the silicon oxidation during the processing of the electrode in aqueous ink^{28,29} and plays the role of a stabilizing surface agent²⁵.

It was demonstrated in previous works that the introduction of Cu(II) cations into the electrode leads to the formation of carboxylate-copper(II) bonds, enhancing its mechanical properties and electrochemical performance. This was done either through the controlled oxidation of the copper current collector⁸ or the deliberate addition of copper(II) sulfate in the ink¹⁸. Here we used a similar approach using zinc sulfate (ZnSO₄) as a coordination precursor. The formation of zinc carboxylate bonds at the bulk scale is evidenced by an upshift of both $v_{\text{asym}}(\text{COO}^-)$ and $v_{\text{sym}}(\text{COO}^-)$ peaks between the Zn-containing and Zn-free reference binder on the IR spectra Figure S1. To evaluate the influence of the coordination binder, electrodes (loading 1.75 mg_{Si}.cm⁻²) were formulated with and without ZnSO₄. Their composition, silicon:graphene:binder is approximately 70:10:20 w% (Table 1). They were cycled under galvanostatic conditions in half cells vs. lithium with LP30+10%FEC electrolyte (1 M LiPF₆ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v:v) plus 10 w% fluoroethylene carbonate) over a range of 0.005 to 1 V vs. Li⁺/Li⁰ (see experimental section in Supporting Information).

Table 1. Composition of the electrodes. The Zn-free formulation was optimized in a previous work³⁰.

Formulation	Electrode composition (w%)					
	Silicon	Graphene	NaCMC	Citric acid	KOH	ZnSO ₄
Zn-free	73.4	11	7.2	7.4	1.0	0
Zn-containing	69.9	10.5	6.8	7.0	1.0	4.8

The mean specific discharge capacity (based on 3-4 experiments for each formulation) as a function of number of cycles for both formulation is shown in Figure 1a. Their first cycle capacities are similar and exceed the theoretical value of silicon (3580 mAh.g_{Si}⁻¹) by an amount of approximately 450 mAh.g_{Si}⁻¹. The graphene additive contribution can be roughly estimated to 50 mAh.g_{Si}⁻¹³⁰, hence the extra capacity mainly arises from the electrolyte degradation (electroreduction) with the SEI formation (see below). Regarding the capacity retention, the gap between the two formulations appreciably widens starting from the second cycle to the 50th. The binder containing zinc sulfate

maintains the best performance with approximately $2500 \text{ mAh.g}_{\text{Si}}^{-1}$ at the 50th cycle vs. $1750 \text{ mAh.g}_{\text{Si}}^{-1}$ for the Zn-free electrode, *i.e.* an increase in capacity retention of more than 40%. A linear fit between the 15th and the 50th cycle also indicates that the capacity decay is approximately three times higher for the Zn-free electrode (3 vs. $9 \text{ mAh.g}_{\text{Si}}^{-1}.\text{cycle}^{-1}$). These results are similar to our previous findings on electrodes containing Cu(II)¹⁸, although with a higher active mass loading here. Potential vs. capacity curves for the 1st and 50th cycles are shown in Figures 1c and 1d, respectively. Figure 1b shows the coulombic efficiency (CE) as a function of cycle number. Notably, there is a distinct difference between the two formulations right from the first cycle. In the presence of Zn, the CE is 3.5% higher. Upon cycling, the CE fluctuates for both formulations before stabilizing above 99% from approximately the 20th cycle. This coincides with the onset of the steady decay in discharge capacity. Therefore, our results confirm the enhanced performance with coordination binders as was observed in previous works. However, as mentioned in the introduction, none have been able to precisely localize the cations in the silicon electrode binder phase. We subsequently investigated the electrode by STEM-EDX both before and after the first cycle. For the latter, the SEI layer is expected to remain thin enough to allow distinguishing of the morphological differences between formulations if any exist.

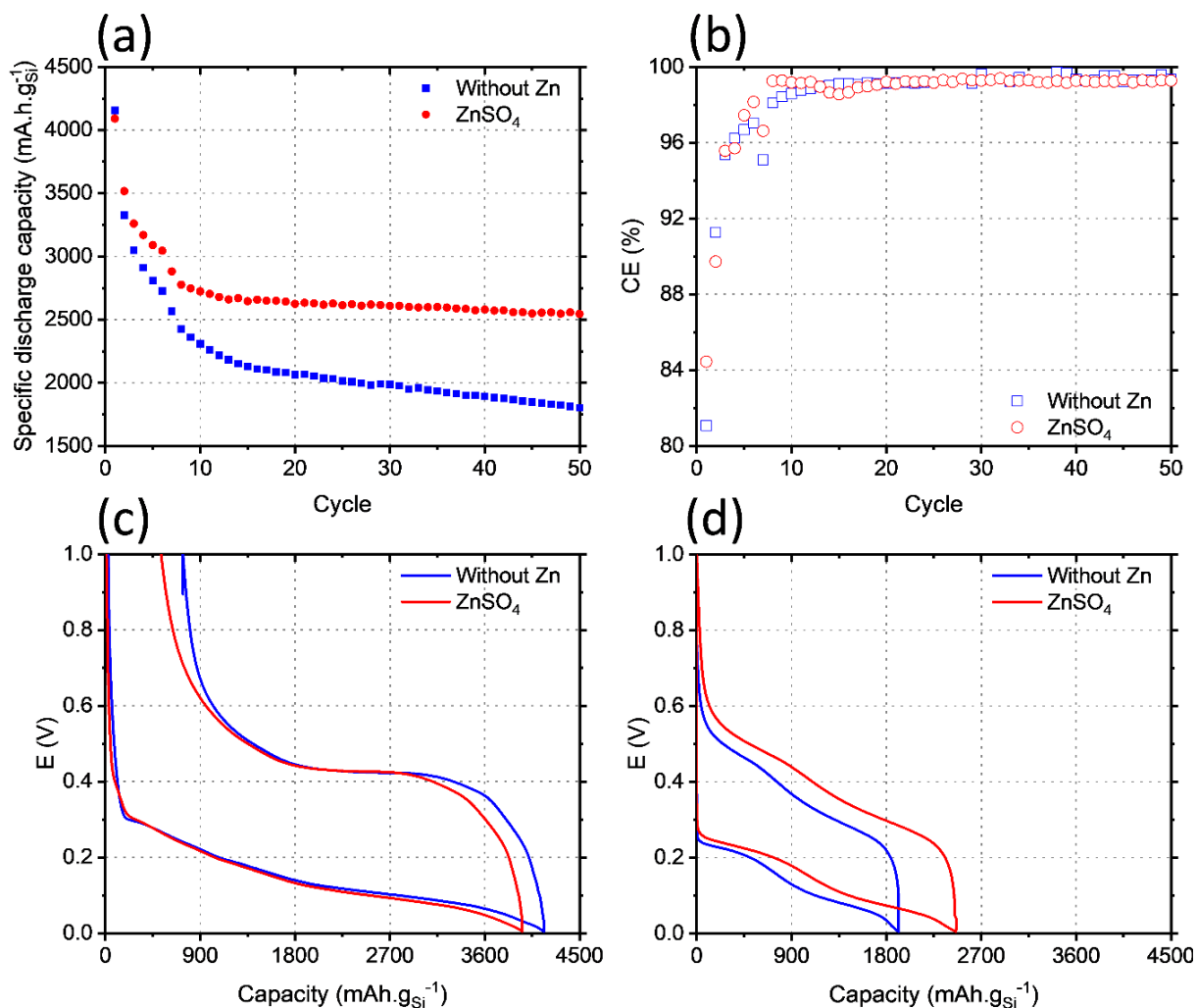


Figure 1 Electrochemical performance of the electrodes ($1.75 \pm 0.10 \text{ mg}_{\text{Si}}.\text{cm}^{-2}$) without and with ZnSO_4 cycled in half-cells: (a) Average specific discharge capacity over 4 (Zn-free) and 3 (with Zn) electrodes as a function of cycle number; (b) Corresponding average coulombic efficiency as a function of cycle number; (c) Typical cell voltage as a function of the delivered specific capacity for the first cycle; (d) Typical cell voltage as a function of the delivered specific capacity for the 50th cycle. The electrodes were cycled at $C/40$ for the 1st cycle, then $C/20$ for 5 cycles, and $C/10$ for the remaining cycles.

Pristine (graphene-free) electrodes, with and without zinc(II), were first analyzed. Simple TEM imaging was not a good option as samples lacked the contrast associated with crystalline structures (see Figure S4). In both cases, the binder as well as approximately 60_w% of the silicon is amorphous (see Figures S2, and S3 and Table S1 for XRD and Raman a-Si quantification, respectively). Therefore, it is very difficult to distinguish between the silicon and binder components and an EDX contrast is required for adequate distinction.

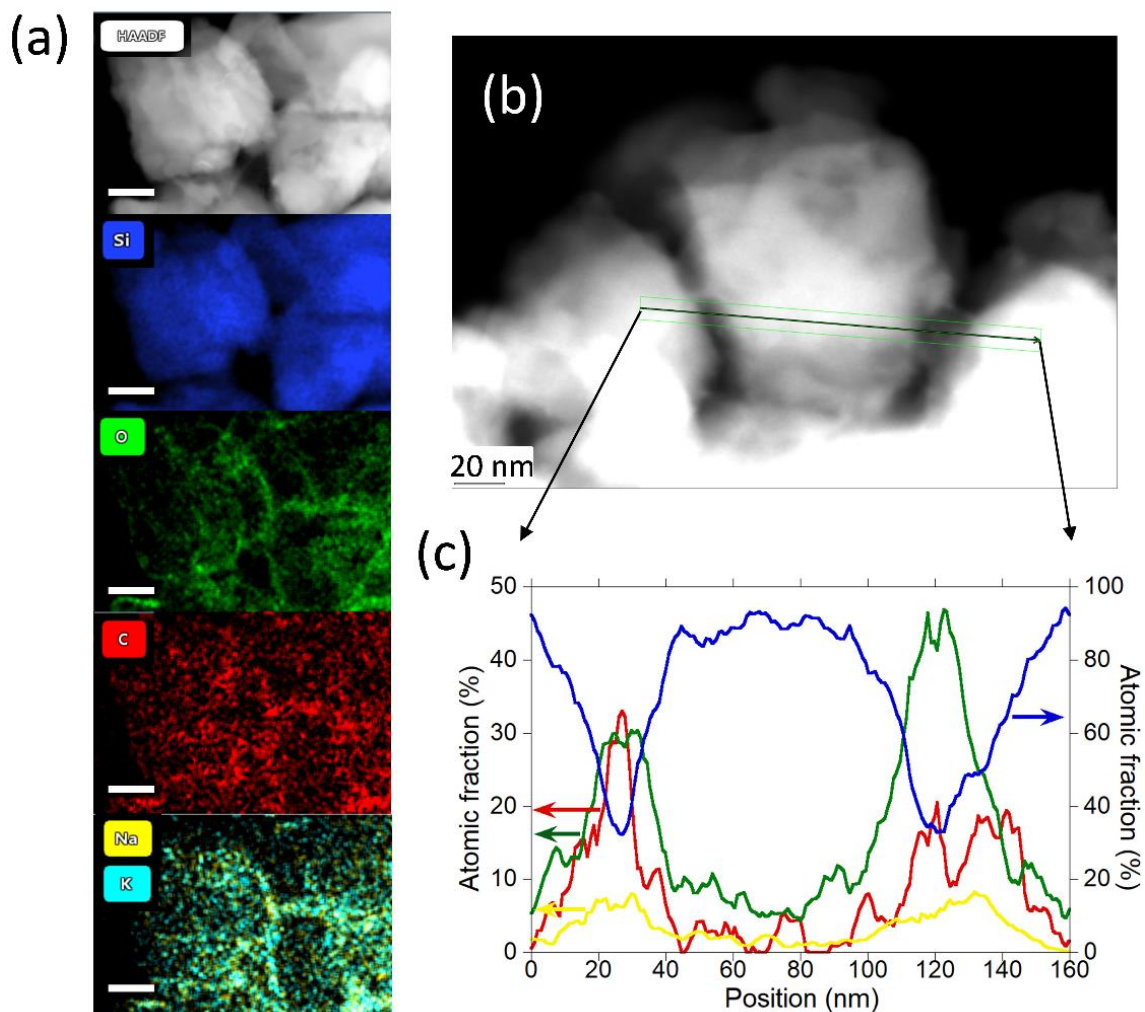


Figure 2 Pristine sample containing silicon and Zn-free binder; (a) STEM-HAADF image and corresponding net count elemental maps for silicon (blue), oxygen (dark green), carbon (red), and sodium (yellow) and potassium (cyan). Scale bar is 50 nm; (b) STEM-HAADF image containing another region of interest, where an EDX line scan was extracted. Scale bar is 20 nm; (c) Atomic percentages along the line scan shown in (b) are given for C (red), O (dark green) and Na plus K (yellow) on the left-hand side scale and on the right-hand side scale for Si (blue).

Figure 2a shows a high-angle annular dark-field (HAADF) image and elemental maps of a pristine electrode made with the reference binder (Zn-free). These images are representative of most of the region of interests (ROIs) selected for STEM-EDX analysis (see Figure S7a). They are focused on nanometric silicon particles located on the edge of agglomerates which are otherwise too thick for the electron transmission. Since carbon, sodium, and potassium are exclusively present in the binder (see Table 1), they can be considered as markers of this phase. Oxygen is also present in the binder. However, it is also particularly concentrated at the surface of the silicon particles due to the native SiO_x layer contribution. Oxygen was thus ruled out from the binder markers. The binder markers (C, Na, K) are

detected across the analyzed areas (Figure 2a). Since net counts are used here to generate the maps, elevated intensities for these markers between particles (especially for Na, K) constitute a confirmation of the binding role of the polymer. Higher intensities are found between silicon particles as is expected if the polymer covers most of the sample surface. A second ROI of the same sample is shown in Figure 2b, with the corresponding EDX line scan quantification in Figure 2c. It should be understood that, as the polymer covered the entirety of the Si particles, its atomic percentage contribution in the maps would still be lower than 5-10% at the center of these Si particles due the transmission configuration. Considering for example a 100 nm diameter particle, the polymer would need to be at least 5 nm thick to represent 10% in the quantification. Atomic percentages for the markers range mainly from 5 to 30%. The highest percentages are measured in between Si particles, in line with the mappings results. However, the percentages seem very low in some areas. The corresponding holes in the binder layer could result from bonded particles separated during the preparation of the sample for the TEM analysis. Since TEM experiments are necessarily performed on particles having detached from the bulk electrode material, the missing layer of binder could be still attached to previously neighboring particles.

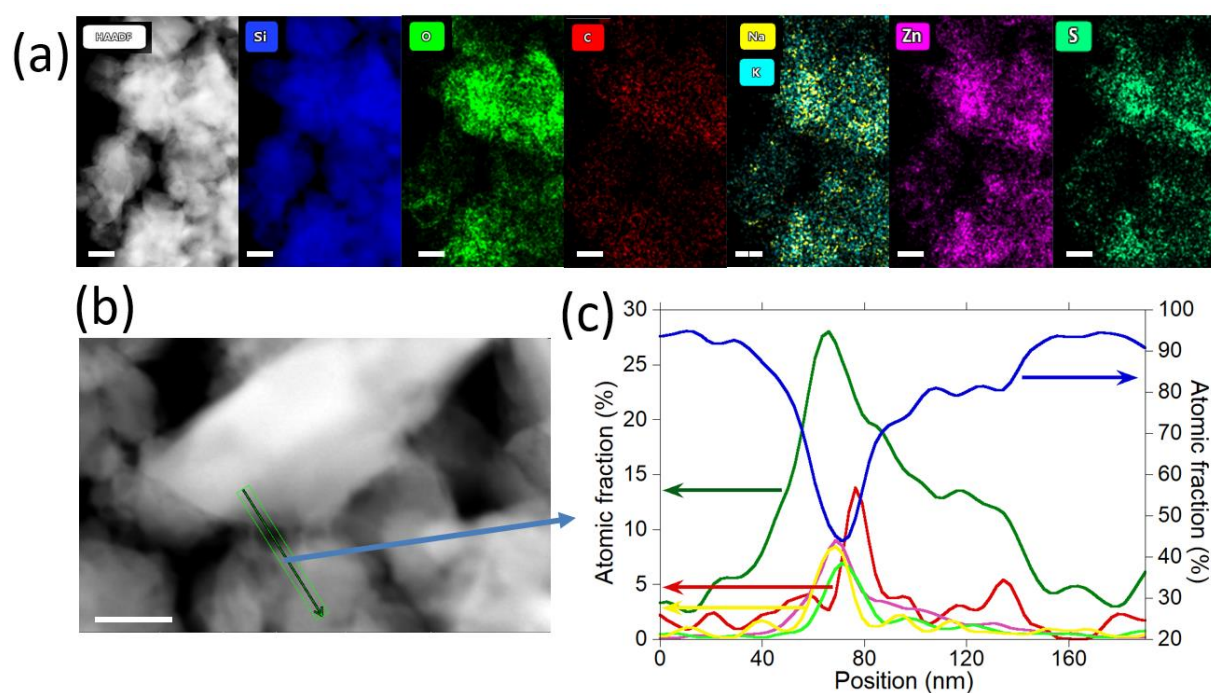


Figure 3 Pristine sample containing silicon and binder with ZnSO_4 ; (a) STEM-HAADF image and corresponding net count elemental maps for silicon (blue), oxygen (dark green), carbon (red), sodium (yellow) and potassium (cyan), zinc (pink), and sulfur (light green). Scale bar is 100 nm; (b) STEM-HAADF image containing the region where an EDX line scan was extracted. Scale bar is 100 nm; (c) Atomic percentages along the line scan shown in (b) are given for C (red), O (dark green), Na and K (yellow), zinc (pink), and sulfur (light green) on the left-hand side scale and on the right-hand side scale for Si (blue).

The same analysis was carried out on the Zn-containing electrode (Figure 3, other ROIs are presented figure S7b). When considering once again C, Na, and K as binder markers, the organic components (CMC and citrate) are still found to cover most of the silicon particles' surface. The distribution of zinc and sulfur was also considered. First, neither Zn-rich particles nor agglomerates (such as Zn(0) or ZnO) were observed. Second, the concordance between alkali ions and carbon with zinc and sulfur in Figure 3a is evident. This indicates that the Zn(II) ions are well distributed throughout the binder, and the coordination network is very homogenous at the tens of nm scale. A line scan quantification illustrating this finding is shown in Figure 3b and 3c. As for the Zn-free electrode, the binder's markers appear more concentrated at the particle junctions, highlighting its binding role. Interestingly, we observe a shift in the position of the maximum of the peaks relating to C and to Zn at the level of the interface with the silicon particle, the Zn being closer to the silicon than the C. This suggests that the Zn promotes the attachment of the binder to the silicon surface, thanks to possible ion-dipole interactions⁹.

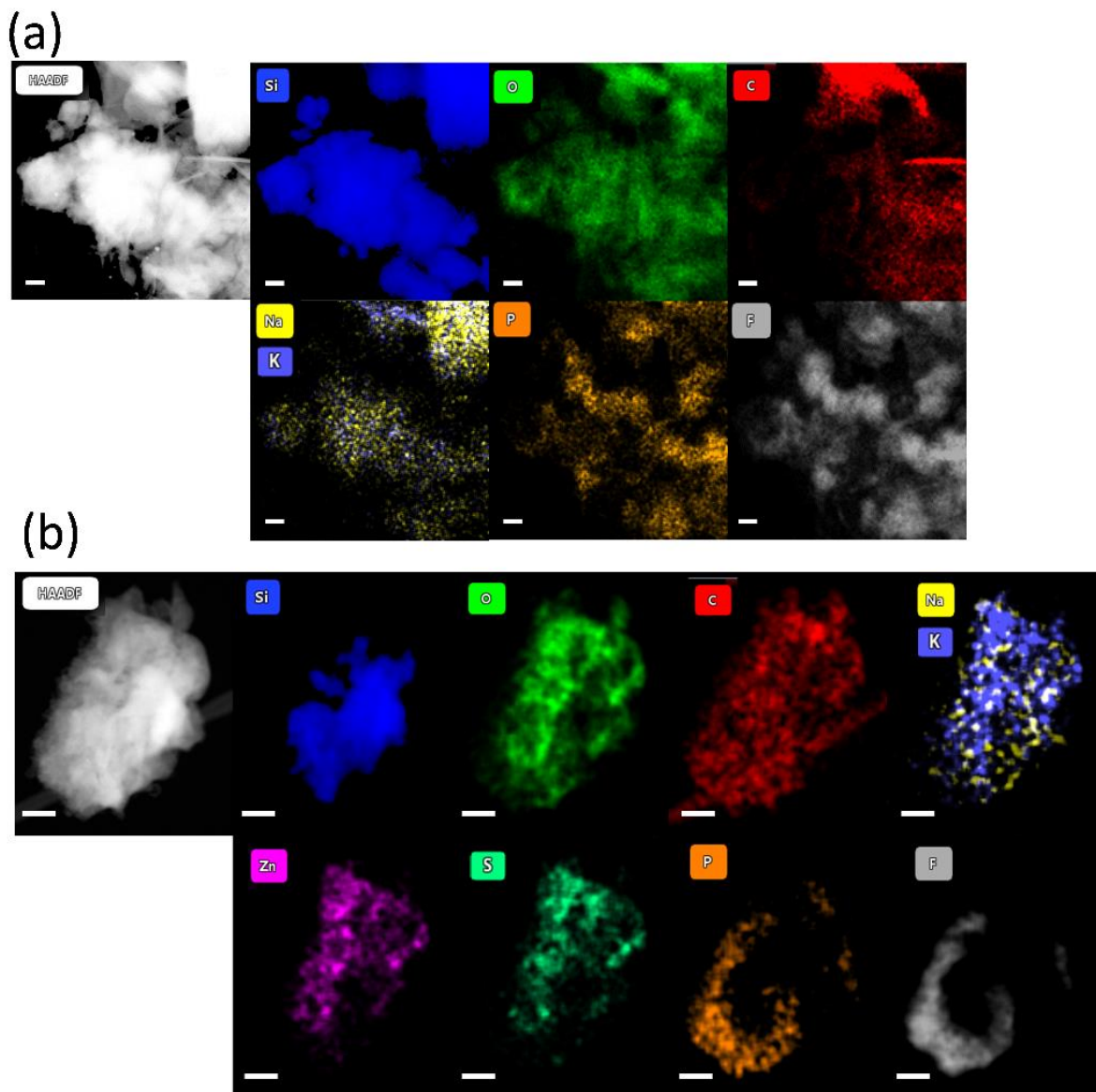


Figure 4 Cycled electrode containing silicon, graphene, and binder with and without ZnSO_4 ; STEM-HAADF image and corresponding net count elemental maps for silicon (blue), oxygen (dark green), carbon (red), sodium (yellow) and potassium (blue), zinc (pink), sulfur (light green), phosphorus (orange), and fluorine (grey); (a) Without zinc sulfate; (b) With zinc sulfate. Scale bars are 100 nm.

STEM-EDX HAADF image and elemental maps of both electrodes after one cycle are presented in Figure 4 (with other ROIs also shown in Figure S8). First, for the Zn-containing formulation, no metallic zinc particles were detected, indicating that the binder is electrochemically stable, at least during the first cycle. Indeed, the reduction of Zn(II) to Zn(0) could be expected based on its redox potential (2.28 V vs. Li^+/Li^0). The coordination of Zn(II) with the carboxylate moieties and the dissemination of the Zn(II) -carboxylate complexes within the electrically insulating binder phase likely prevent its reduction. Second, focusing on the binder, the carbon can no longer be considered as one of its markers as it is

also present in the SEI (arising from the degradation of the carbonate solvent) as well as in the graphene additive. Examining both Figure 4a (Zn-free electrode), especially the corresponding sodium and potassium map, and Figure 4b (electrode with Zn) including zinc and sulfur maps as well, it appears that the binder repartition has been modified after one cycle. Even if most Si particles are covered by the binder in both formulations, some particles look bare (for example the small silicon particle in the upper left corner that is Na and K free in Figure 4a). Additionally, the binder no longer appears to be particularly concentrated between the Si particles. Although some SEI could decrease the likelihood of identifying the binder in between particles, it is also possible that this evolution is a consequence of the binder deformation and/or partial rupture under the stress arising with silicon particle expansion and contraction⁷. Phosphorus and fluorine (arising from LiF, Li_xPO_yF_z, ...) are used as inorganic SEI markers and their respective positions are identified as highly correlated in both formulations. Their spatial distribution however seems to be strongly dependant on the formulation of the electrode. In Figures 4a and S8a (Zn-free), the SEI appears woolly and sparse with some big pieces located between distant silicon particles. In opposition, Figures 4b and S8b (with Zn) show the SEI appears denser and more conformal to the silicon particle. This suggests a stronger SEI adhesion to the silicon particle surface or a less strained SEI layer. In the latter case, this would be in agreement with the idea that Zn(II) reticulation inside the binder phase helps mitigate the strain within the electrode, which plays on the relative displacement between the particles, thus relieving deformation and stabilizing the SEI. Though previously theorized, only scarce evidence of binder behaving as artificial SEI has been gathered on graphite or silicon electrodes. In graphite, it has been shown that the binder can suppress the co-intercalation of solvent with Li⁺ and thus prevent the graphite layers exfoliation^{31,32}. In silicon, spectroscopic characterizations (IR, XPS) showed that binders such as citric acid, polyacrylic acid (PAA), and carboxymethyl cellulose sodium salt (NaCMC) go through an irreversible lithiation upon cycling and that less SEI is formed^{25,33,34}. Only very recently has visual evidence of binder (LiPAA) acting as artificial SEI been observed in silicon/graphite composite electrodes⁷. Here, the spatial distribution of the binder markers (Na, K, Zn, and S) does not match the inorganic SEI ones. Specifically, Zn and S (as well as Na and K to some extent) seem to be localized in the regions containing low concentrations of F and P (see the bottom part of figure 4b, as well as figure S8b). This strongly suggests that, as postulated, the coordinated binder is working to some extent as an artificial SEI while the Zn-free binder might be less efficient in doing so. Noteworthy, Han B. et al.³⁵ found that by adding 0.1 M M^x(TFSI)_x (M = Mg, Zn, Al and Ca) as a second salt into the electrolyte (1.2 M LiPF₆ in 30 w% EC + 70 w% EMC, plus 10 w% FEC or not), resulted in the in situ formation of Li–M–Si ternary Zintl phases during the lithiation process of Si-based electrodes (formulated with Li-polyacrylate binder), and in an appreciable improvement of cyclability. We believe the formation of a Zintl phase (Zn–Si–Li) in situ is unlikely in our system, as the Zn is trapped inside the electronically insulating binder phase. We attempted through ⁷Li MAS NMR

measurements to detect if a Li-Zn-Si phase had formed after 50 cycles, but we could not find any trace of it (not shown). Furthermore, in our working conditions, the addition of 0.01 M ZnTFSI in our electrolyte did not result in any electrochemical performance improvement for the Zn-free electrode. Upon increasing the amount of ZnTFSI up to 0.1 M, a quick capacity fading was even observed. This behavior was also reported in the study of Han B. et al.³⁵ with the Zn(TFSI)₂ containing electrolyte.

Table 2. Atomic ratios of elements quantified by EDX for electrodes with and without ZnSO₄ at the pristine state and after one cycle, averaged over 10 (Zn-free, pristine), 21 (with Zn, pristine), 15 (Zn-free, 1 cycle) and 10 (with Zn, 1 cycle) ROIs. Theoretical ratios determined for the formulation of the pristine electrodes are also presented.

	Pristine theoretical		Pristine experimental		One cycle experimental	
	No Zn	ZnSO ₄	No Zn	ZnSO ₄	No Zn	ZnSO ₄
C/Si	0.18	0.18	0.04	0.02	0.25	0.27
O/Si	unknown ^a		0.17	0.09	0.35	0.52
(Na+K)/Si	0.02	0.02	0.01	0.01	0.01	0.02
Zn/Si	/	0.01	/	0.01	/	0.02
(Na+K)/C	0.10	0.10	0.20	0.54	0.03	0.06
(Na+K)/Zn	/	1.48	/	1.10	/	0.98
Zn/S	/	1.00	/	2.08	/	1.12
F/Si	/	/	/	/	0.29	0.17
P/Si	/	/	/	/	0.023	0.006
F/P	/	/	/	/	12.7	27.3

^a The theoretical O/Si ratio is unknown as the oxygen content at the surface of silicon particles has not been precisely determined.

Table 2 presents atomic ratios of elements quantified by EDX for both electrode formulations, at the pristine state and after one cycle. An example of raw quantification results and associated errors is presented in Table S2. Ratios can vary significantly from one ROI to another as they may vary as a function of the sizes of particles (hence their surface proportion) or aggregates. To obtain a more statistically representative profile of the electrodes, we weighted each ROI by its number of total counts (Tables S3). In doing so, larger ROIs were favored over smaller ones since larger volumes produce more X-rays under the same conditions. Consequently, the standard deviation associated with an element quantification is greatly reduced, as is compared in Tables S3a and S3b. The weight coefficient associated to a specific ROI is the following:

$$w = \frac{N}{t \times S} \quad (1)$$

N corresponds to the total number of counts gathered on all 4 detectors. The spectra of one or several detectors were excluded in some cases since unfavourable localized sample orientation would have lowered the quantification accuracy in these (especially for light elements). The time frame, in seconds, corresponds to t , and S is the equivalent scanned surface area in micrometers square. For an EDX acquisition, the frame is larger than the ROI size so as to contain it. Indeed, ROIs were chosen as containing only sample material. However, the obtained counts were gathered only from the ROIs, which were of various sizes and thus various equivalent scanning times. Consequently, the time and surface are shortened to the effective ROI time span and surface area. The as-obtained quantification of each element is subsequently multiplied by w . Then, the obtained value is summed with the other ROIs results for each element. Finally, the sum for each element is normalized by the total value of all quantified elements to obtain the corresponding element quantification. An example of the balancing procedure can be found in Table S3b. However, this method contains a flaw stemming from the fact that the sample thickness also influences the number of counts in a complex way (absorption, fluorescence...). As such, aggregates of similar thicknesses were chosen (from STEM-HAADF imaging), therefore we are confident this does not change the trends discussed below. In Table 2 are also gathered theoretical ratios as expected from the formulation of the pristine sample (Table S4). Silicon percentages are measured as over 80 at% and around 50 at% in the pristine and cycled samples, respectively. This could be a consequence of the presence of the SEI after one cycle, though these measurements are not considered adequate for extracting quantification. Nevertheless, the fact that these values are rather stable from one ROI to the other (Table S3a) in each case make them a good normalizing factor for the other elements. Consequently, carbon, oxygen, and sodium and potassium over silicon atomic percentage ratios are first discussed as they should quantify the relative amount of binder adsorbed on Si particles.

First, considering pristine electrodes, we can notice that the experimental C/Si ratio is 5 to 10 times lower than the theoretical ratio for the Zn-free and with Zn samples, respectively. Theoretical C/Si ratios were not expected to be attained exactly. Indeed, the polymeric binder (processed in a liquid state) will not distribute itself homogeneously on the electrode material surface. A fraction of the binder is ad/absorbed on the electrode materials during the preparation of the ink under the effect of interfacial interactions³⁶. This fraction is expected to distribute evenly and homogeneously on the electrode materials. However, under the effect of capillary pressure, the remaining part of the binder recedes with the solvent during the drying process from larger pores towards smaller ones. Therefore, the binder concentrates in the smallest pores, which are situated inside the particle agglomerates³⁷.

This results in a heterogeneous distribution of the binder with some areas more abundant than others. It is likely that, in the pristine electrodes, the zones with the lowest binder content are observed as they are more friable and therefore more easily fragmented into small-sized objects deposited on the TEM grid. The higher value of the C/Si ratio for the Zn-free electrode suggests that the organic part of the binder (CMC and CA) is preferentially absorbed during the preparation of this ink. Although, this hypothesis will have to be confirmed because, as previously mentioned, the most friable zones of the electrode are observed. However, with an equal binder content, higher cohesion is expected in the electrode containing the Zn(II) crosslinked binder. As such, the observable areas of the electrode with Zn would contain less binder due to the difference in cohesion. Experimental (Na+K)/Si ratio are about 2 times lower than the theoretical ratio for both formulations. Conversely, the experimental (Na+K)/C ratio is 2 and 5 times higher than the theoretical ones, for the Zn-free and with Zn samples, respectively. This can be explained by the organic and cationic binder parts interacting specifically at the particle interface. Thus, their respective ad/absorbed fraction during the ink preparation could be different. An alternative interpretation would be that the organic part of the binder degrades under the electron beam. However, as explained in the experimental section and shown in S.I. (see Figure S5a, S5b and S5c), this second hypothesis can be ruled out. On another hand, the Zn/Si experimental ratio is close to the theoretical one (only 1.4 times lower) for Zn containing electrodes. Continuing the discussion above, this suggests that Zn adsorbs more readily than organic binder and Na and K cations. This is coherent with electrostatic interaction between the silicon surface and Zn^{2+} being twice as strong as it is with monovalent cations. The Zn/S ratio of 2.1 (vs. $\text{Zn/S} = 1$ in the ink) confirms the significant adsorption of Zn at the surface of silicon together with its complexation with carboxylate moieties of the binder. The experimental O/Si ratio is affected by the presence of the oxidized silicon layer. This ratio is about 2 times higher for the Zn-free sample despite the sulfate presence for the ZnSO_4 samples. This could be the result of the less acidic pH of the corresponding ink, *i.e.* 3.5 vs. 2.9 with ZnSO_4 . Indeed, the silicon oxidation during aqueous ink preparation is reduced at more acidic pH^{18,38}. It could also indicate a larger amount of organic binder ad/absorption at the silicon surface in the absence of Zn for the analyzed particles and aggregates. This result is in line with the experimental C/Si ratio, which also has a value twice as high for the Zn-free compared to the ZnSO_4 -containing formulation. This EDX elementary quantification raises some questions, especially regarding the interactions within the electrode ink and the subsequent partition of these constituents over the silicon surface. Nevertheless, it should be kept in mind that the analyzed samples are very small (in the one to ten micrometer square range). They might not be fully representative of the entire electrode in which heterogeneities can be observed at larger scales³⁹.

The interpretation of the elemental ratios for cycled electrodes is more complicated since the C/Si ratio now contains both the SEI and graphene contributions. In addition, the C/Si and O/Si ratios increase, whereas the ratio (Na+K)/C decreases significantly. These evolutions account for the presence of the organic degradation products of the electrolyte solvents on the silicon and graphene particles surface. Comparatively, the (Na+K)/Si and (Na+K)/Zn ratios are less affected since no electrolyte degradations products would contain those elements. Table 2 also presents ratios of SEI elements pertaining to LiPF_6 and FEC degradation products (LiF , $\text{Li}_x\text{PO}_y\text{F}_z$, SiOF_x) quantified by EDX for both electrode formulations after one cycle. Both F/Si and P/Si ratios are higher for the Zn-free electrode, which suggests a larger degradation of the lithium salt and FEC additive. Moreover, the F/P ratio is approximately twice as high as in the case of the Zn-containing formulation. As the phosphorus solely comes from the LiPF_6 , it could mean that more salt is decomposed or confined in the Zn-free electrode. To obtain information on the organic part of the SEI, C/Si and O/Si ratios can be used. However, this is under the assumption that there is the same relative quantity of graphene in the ROIs of both formulations. As a result, one can see that for the electrode with Zn, the C/Si and O/Si ratios evolved from being lower to the higher than the Zn-free electrode after one cycle. This suggests that the organic SEI has developed more on the Si particles in the coordination binder formulation. This observation must be put into perspective by recalling once again that it is the most friable zones of the electrodes which are observed, and therefore the lowest in binder content. To have a more global and complete vision of the SEI formation at the first cycle, ^{19}F and ^7Li NMR measurements were undertaken.

Table 3. Normalized quantity of SEI elements determined by solid state ^{19}F and ^7Li NMR. Each analysis was carried out on 2 to 3 electrodes per analysis and 3 analysis per formulation.

	Without Zn	ZnSO ₄
Diamagnetic ^{19}F ($\mu\text{mol.mg}_{\text{el}}^{-1}$)	4.08	4.05
Electrolyte ^{19}F ($\mu\text{mol.mg}_{\text{el}}^{-1}$)	0.66	0.25
<i>LiPF_{6(s)}</i> ($\mu\text{mol.mg}_{\text{el}}^{-1}$)	0.09	0.04
<i>LiPF_{6(l)}</i> ($\mu\text{mol.mg}_{\text{el}}^{-1}$)	0.02	0
SEI ^{19}F ($\mu\text{mol.mg}_{\text{el}}^{-1}$)	3.42	3.8
<i>LiF</i> ($\mu\text{mol.mg}_{\text{el}}^{-1}$)	3.16	3.56
<i>Li_xPO_yF_z</i> ($\mu\text{mol.mg}_{\text{el}}^{-1}$)	0.26/z	0.25/z
Diamagnetic ^7Li ($\mu\text{mol.mg}_{\text{el}}^{-1}$)	8.84	9.02
Electrolyte ^7Li ($\mu\text{mol.mg}_{\text{el}}^{-1}$)	0.11	0.04
<i>LiPF_{6(s)}</i> ($\mu\text{mol.mg}_{\text{el}}^{-1}$)	0.09	0.04
<i>LiPF_{6(l)}</i> ($\mu\text{mol.mg}_{\text{el}}^{-1}$)	0.02	0
SEI ^7Li ($\mu\text{mol.mg}_{\text{el}}^{-1}$)	8.73	8.98
<i>LiF</i> ($\mu\text{mol.mg}_{\text{el}}^{-1}$)	3.16	3.56
<i>Li_xPO_yF_z</i> ($\mu\text{mol.mg}_{\text{el}}^{-1}$)	0.26/z	0.25/z
<i>Li in others</i> ($\mu\text{mol.mg}_{\text{el}}^{-1}$)	5.57-0.26x/z	5.42-0.25x/z

The NMR quantification of ^{19}F and ^7Li in Table 3 for the cycled electrodes compare quantitative results for the SEI. An absolute quantification could be reached using ^7Li and ^{19}F MAS NMR calibration curves obtained from the NMR spectra of reference samples made of silicon mixed with various amounts of LiF⁴⁰. This method allows calculation of Li and F contents in micromoles per mg of electrode. In the experimental spectra of cycled electrodes, resonances of the fluorinated species (such as LiF, Li_xPO_yF_z and LiPF₆ at -205, -75/-80 ppm and -72 ppm, respectively) can be deconvoluted relatively easily as they span over a broad chemical shift range in the ^{19}F NMR spectra (see Figure S9a). Unfortunately, the same is not possible for the ^7Li NMR spectra as all the resonances corresponding to lithiated species belonging to the SEI (organic, inorganic, and lithiated binder molecules) typically emerge between -2 and 2 ppm (see Figure S9b). Consequently, the determination of the absolute amounts of LiF and LiPF₆ with known formula have been performed from the ^{19}F MAS NMR results. Although the quantity of fluorine involved in Li_xPO_yF_z can be determined precisely, the amount of Li_xPO_yF_z depends on

the exact chemical formula. Considering the very low intensity of the corresponding ^{19}F MAS NMR resonances, such quantity can be considered as negligible. In a second step, by subtracting the amount of μmol s of identified lithiated fluorinated species (e.g. LiF , LiPF_6 and $\text{Li}_x\text{PO}_y\text{F}_z$, the latter depending on the value of “z”) from the total amount of ^7Li NMR obtained from ^7Li MAS NMR spectrum fit/quantification, a determination of the quantity of μmol s of Li in other lithiated species, including lithiated carbonates, alkyl-carbonates and semi-carbonates is obtained. This value corresponds to the organic part of the SEI (labeled as “others” in Table 3). These products typically stem from the electrolyte solvent degradation, but also from the FEC additive degradation, as most of its decomposition reactions include a defluorination path⁴¹. Concerning the ^{19}F quantification, fluorine appears to be present almost exclusively as LiF , which was expected from the EDX data. However, a larger quantity of LiF is formed per milligram of electrode for the Zn-containing formulation (approximately +11%) whereas it was measured in smaller quantity by EDX (Table 2). We believe that the NMR is more accurate in terms of quantification because it probes the whole electrode and over 10 milligrams of both formulations were analyzed. In the case of surfaces analyzed by STEM-EDX, analyzed quantities are indeed incommensurably lower as they amount to typically a few square micrometers in area as can be seen in Table S3b. The greater quantity of LiPF_6 in the Zn-free electrode could suggest a more porous SEI in accordance with STEM-EDX observations (Figure 4). Concerning the F/P ratios, the same trend is found between both characterization techniques. On one hand, the ratios are measured as approximately 17 and 23 by NMR, assuming a LiPO_2F_2 stoichiometry, for electrodes without Zn and with Zn, respectively (assuming a $\text{Li}_2\text{PO}_2\text{F}_3$ stoichiometry, these ratios become 21 and 32). On the other hand, the ratios are found to be 13 and 27 for the EDX experiments for the Zn-free and the Zn-containing electrodes, respectively. It should first be stressed that the values are remarkably close between both techniques and, in any case, are well within the error usually admitted for EDX quantification. The discrepancies could be linked to the high sensitivity of this ratio when the P quantity is small (higher absolute error), which is in fact the case. Moreover, certain hypotheses on the $\text{Li}_x\text{PO}_y\text{F}_z$ stoichiometry must be made and may be inappropriate if this stoichiometry change slightly from one formulation to another. The SEI organic part is labelled as “others” in the ^7Li quantification, Table 3. In the case of hypothetical but plausible (i) LiPO_2F_2 or (ii) $\text{Li}_2\text{PO}_2\text{F}_3$, the remaining lithium involved in organic species would account for minimum values of (i) 5.5 and 5.3 $\mu\text{mol.mg}_{\text{el}}^{-1}$ or (ii) 5.4 and 5.2 $\mu\text{mol.mg}_{\text{el}}^{-1}$, in the Zn-free and the Zn-containing formulation, respectively. This result therefore supports the presence of same amount of lithium involved in organic SEI species after 1 cycle in both electrodes. For the identification of the organic SEI species, other techniques such as XPS could be used^{23,33,34}.

Electrochemical impedance spectroscopy (EIS) measurements were carried out to relate the SEI morphology, nature, and quantity (evaluated by STEM-EDX and MAS NMR) to its impedance, R_{SEI} . The

latter was extracted from the EIS spectra with a $R1_{SEI}/C_{pe1}/R_{CT}/C_{pe2}/W_{open1}$ model (see Figure S10c) using the Zfit software. $R1$, R_{SEI} and R_{CT} are resistances, C_{pe1} and C_{pe2} are constant phase elements, and W_{open1} is an open Warburg element. Typical spectra for the Zn-free and Zn-containing electrodes are presented in Figure S10a and S10b, respectively. The R_{SEI} impedance of the Zn-containing formulation is $12 \pm 5 \Omega$, which is less than that measured for the Zn-free one with $18 \pm 5 \Omega$. This impedance evolution can be understood considering previous analyses. Figure 1b shows that Zn-containing electrodes have higher first cycle CE, which can have two origins: (i) a better mechanical stability of the electrode at the origin of a deeper lithiation and/or delithiation and/or (ii) less degradation of the electrolyte. However, NMR quantification indicates there is more inorganic SEI for $ZnSO_4$ electrodes, with +11 w% of LiF. The better CE of Zn-containing electrodes is therefore attributable to their improved mechanical stability. It is however interesting to note that the impedance of the SEI is lower for the Zn-containing electrodes. In fact, this result is in good agreement with the STEM-EDX morphological observations. Figures 4a and 4b show that inorganic SEI is denser, therefore logically forms thinner or fewer deposits on the surface of the electrode material. Furthermore, the presence of liquid $LiPF_6$ was only detected for Zn-free electrode by NMR and can hardly be envisioned other than by confinement in the SEI porosity (because of the sample preparation). Thus, the thicker and less continuous SEI layer for the Zn-free electrode hinders the diffusion of lithium ions more than the thinner, more continuous SEI layer in the Zn-containing electrodes. We hypothesize that the Zn-reticulated binder also is more efficient in limiting the expansion and contraction of the electrode. As such, it minimizes the mechanical stresses imposed on the SEI due to less relative displacement and friction of the silicon particles. The preserved SEI would consequently keep its thin and dense morphology^{15,17,18}. Finally, the fact that more LiF forms in the first cycle with the Zn reticulated binder is in itself not detrimental. This can be understood by taking into consideration results using electrolyte with and without FEC additive. Very recently, Zhang X., et al⁴² showed that in case of electrolyte with FEC (and silicon nanoparticles), the SEI's Li^+ content by mass of electrode was higher than without this additive. In fact, it was almost twice as much in the first cycle and this trend pursued for over 10 cycles. A thinner SEI layer was also observed by cryogenic TEM (ensuring minimum damage to the SEI) when FEC was used, demonstrating its higher density. The capacity retention was also greatly improved with the electrolyte containing the FEC additives, which was attributed to a more stable SEI. The observations deduced from Figures 4b and S8b illustrate that the inorganic part of the SEI rarely piles up on top of the coordinated binder layer. Therefore, this layer seems to act efficiently as an artificial SEI. CMC should also barely be wetted by carbonate-based electrolyte⁴³. For the latter with $LiPF_6$ salt, the electrolyte uptake of NaCMC was measured to vary between 8-20 w%^{32,44}. As the reticulation reduces the polymer segments mobility (demonstrated for covalently cross-linked polymer), this should reduce its swelling⁴⁵. Therefore, the same behavior should be expected for our coordinated binder.

Conclusion

In this work, we used STEM-EDX to analyze binder and SEI characteristics in electrodes with and without Zn(II) as a reticulating agent. It was revealed to be a powerful tool in providing visual proof of phenomena previously only hypothesized. It showed that the binder was homogeneously reticulated by the zinc and that this combination acts efficiently as both binder and protective coating (although not fully conformal). In cycled electrode, the inorganic part of the SEI was only present in regions where the Zn coordinated binder was not (or was barely). Therefore, we conclude that it is acting as an efficient artificial SEI. Moreover, this inorganic part of the SEI is denser in the Zn-containing electrode, which could be due to a stabilizing effect of the Zn-crosslinked binder, and likely explains its lower impedance observed in EIS experiments. However, when it comes to quantification, STEM-EDX is less conclusive. First, since it is unable to determine the local thickness of aggregates, adding to the uncertainty of absolute quantifications. Second, even when multiple ROIs are analyzed and gathered to provide more accurate results, they only represent a tiny fraction of the electrode. For more representative SEI quantifications, solid state NMR was thus necessary. It showed that a slightly more SEI was formed for the Zn-containing formulation (mostly LiF). Nevertheless, both techniques, STEM-EDX and MAS-NMR agreed in respect to the F/P ratio within this inorganic SEI. Therefore, the formation of a more stable and efficient SEI layer, together with the mechanically improved binder network significantly enhances the capacity retention of electrodes containing Zn cation as a coordination agent of carboxylate bearing binder. Metal ion-ligand coordination chemistries are a new way to explore for designing new binders with improved performance for Li-ion batteries in general, and more particularly to improve the cycle life of Si and alloying-based negative electrodes.

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Nanoscale Morphological Characterization of Coordinated Binder and Solid Electrolyte Interphase in Silicon-Based Electrodes for Li-ion Batteries

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1. Material preparation

1.1. Silicon powder

The Si powder used as active material was obtained by ball-milling Si powder (325 mesh, 99.96%; Materion) using a HD-01 attritor (Union Process) for 20 hours. The milling was performed under argon atmosphere at 600 rpm with a ball-to-powder mass ratio of 10:1. The as-milled Si powder was composed of micrometric agglomerates as primary particles ($d_{50} \approx 10 \mu\text{m}$, $S_{\text{BET}} \approx 20 \text{ m}^2\cdot\text{g}^{-1}$) and secondary particles of under one micron. The oxygen content determined by a LECO analyzer was approximately 1 w%.

1.2. Binder solution

First, a pH 3 buffer solution (0.171 M citric acid + 0.084 M KOH) was prepared by dissolving citric acid (99%; Sigma-Aldrich) and KOH salt (> 98%; Sigma-Aldrich) in ultrapure water. Next, 5 mL of buffer solution diluted to a total volume of 8.2 mL with ultrapure water was used to dissolve 160 mg of NaCMC ($M_w \approx 700\,000 \text{ g}\cdot\text{mol}^{-1}$, D.S. 0.9; Sigma-Aldrich). The as-obtained solution is the reference binder (also named Zn-free binder). For the coordinated binder (also named ZnSO_4 binder), 202 mg of $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$ (Pure cryst.; Alfa Aesar) was added once the NaCMC was completely dissolved and the solution was left to homogenize. During each step, solutions were magnetically stirred at room temperature. The Zn-binder coordination ratio, defined as the number of moles of Zn over carboxylic acid moieties (from citric acid and CMC), was equal to 0.22. The salt' coordination water was counted in the 8.2 mL of binder solution. The approximately 15 w% of ad/absorbed water in NaCMC was however not taken into account.

1.3. Electrodes fabrication

160 mg of Si powder, 24 mg of graphene platelet conductive additive (xGnP M15 grade from XGSciences, average thickness ≈ 7 nm, average diameter = 15 μm , and surface area $\approx 120\text{-}150\text{ m}^2\cdot\text{g}^{-1}$ according to supplier data) and 0.8 mg of binder solution were added to a silicon nitride vial with 3 balls ($d = 9.5$ mm) of the same material. The ink was mixed using a Pulverisette 7 (Fritsch) planetary mixer for 1 h at 500 rpm. The ink solid loadings were 21.5 and 22.3 w% for the reference and Zn binders, respectively. The as-prepared ink was tape casted with a doctor blade on a Cu foil (99.9 %, thickness $\approx 20\text{ }\mu\text{m}$, cold rolled; PI-KEM) using an Elcometer film applicator (model 3540, $s = 56\text{ mm}\cdot\text{s}^{-1}$). The blade gap was fixed at 100 μm for an electrode loading of $1.0 \pm 0.1\text{ mg}_{\text{Si}}\cdot\text{cm}^{-2}$ and at 150 μm for an electrode loading of $1.75 \pm 0.1\text{ mg}_{\text{Si}}\cdot\text{cm}^{-2}$. As-prepared films were dried at room temperature for 12 h. Finally, electrodes were cut (diam. = 1 cm), dried 2 h at 100 $^{\circ}\text{C}$ under vacuum ($P \approx 10\text{ mbar}$) prior to mass measurement ($\Delta m = \pm 0.01\text{ mg}$), and dried again for 1 h under the same conditions prior to cell assembly.

2. Material characterization

2.1. IR spectroscopy characterization of the binder coordination

Binder coordination bonds were identified using spectra acquired with a thermoregulated ATR 7600 spectrometer (Thermo Nicolet). First, a drop of binder solution was allowed to dry for 15 minutes on the ATR diamond at 60 $^{\circ}\text{C}$. Then, the temperature was increased to 100 $^{\circ}\text{C}$ and held for spectrum acquisition (averaged over 30 scans). An ATR correction was applied and the resolution was fixed to 4 cm^{-1} . The background spectrum was acquired at 60 $^{\circ}\text{C}$ without binder, and no baseline correction was applied to the sample spectra.

Figure S1 shows the IR spectra in transmittance for the dried ZnSO_4 and Zn-free binder solution. The $\nu_s(\text{C}=\text{O})$ and $\nu_{\text{asym}}(\text{COO}^-)$ peaks are broad, most likely because they include several contributions. In particular, there is the ν_{2b} peak from H_2O , which is located around 1645 cm^{-1} . The $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$ peaks are also most likely broadened by the presence of different carboxylates since there are multiple cations (Na, K and Zn) and carboxylate/carboxylic acid bearing molecules (CMC and citric acid). There are 25 and 13 cm^{-1} upshifts for the $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$ peaks for the reference and ZnSO_4 binders, respectively. This shift is evidence of zinc carboxylate formation upon Zn^{2+} salt addition to the reference binder.

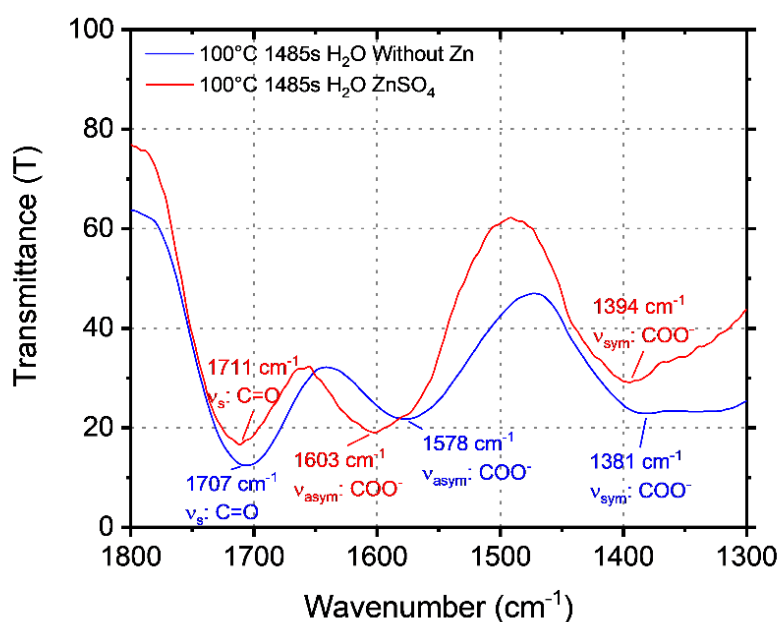


Figure S1 IR spectra of reference and ZnSO_4 binder solution after evaporation.

2.2. XRD and Raman spectroscopy characterization of the silicon powder

The silicon powder was analyzed with a D8 type diffractometer (Bruker) that was in a Bragg-Brentano geometry and equipped with a monochromator. The source was Cu ($\lambda_{\text{K}\alpha 1} = 1.54056 \text{ \AA}$) and it was operated at 40 kV and 40 mA. For the silicon structural analysis, the diffractogram was acquired between $2\theta = 20$ and 102° with a step of 0.0169° and 6 s per step. For silicon amorphous quantification, the diffractogram was acquired between $2\theta = 20$ and 70° with a step of 0.0144° and 4 s per step. In this case, crystalline MgO was added as a standard (chosen for its similar X-ray micro-absorption to silicon). The MgO was dehydrated/dehydroxylated at 450°C for 12 h (with a 2 h ramp to heat up and cool down) and then kept in an oven at 100°C until measurement. Before XRD analysis, MgO and Si were thoroughly mixed to ensure the maximum homogeneity. The Si and MgO weight fractions were chosen to be 84.5 and 15.5 %, respectively, to obtain the same order of magnitude for both material XRD peak intensity. The silicon powder was also analyzed with a FT Raman MultiRam (Bruker) to quantify its amorphous fraction. The laser ($\lambda = 1064 \text{ nm}$) beam size was approximately $100 \text{ }\mu\text{m}$. Two hundred scans were acquired from 50 to 1200 cm^{-1} . The power was set to 60 mW to avoid black body radiation (large band at approximately 3000 cm^{-1} with a shoulder around 3800 cm^{-1}) from the material heating. Six measurements were performed on different spots of the sample for statistical reasons. The results of these characterizations are presented Figures S2 and S3.

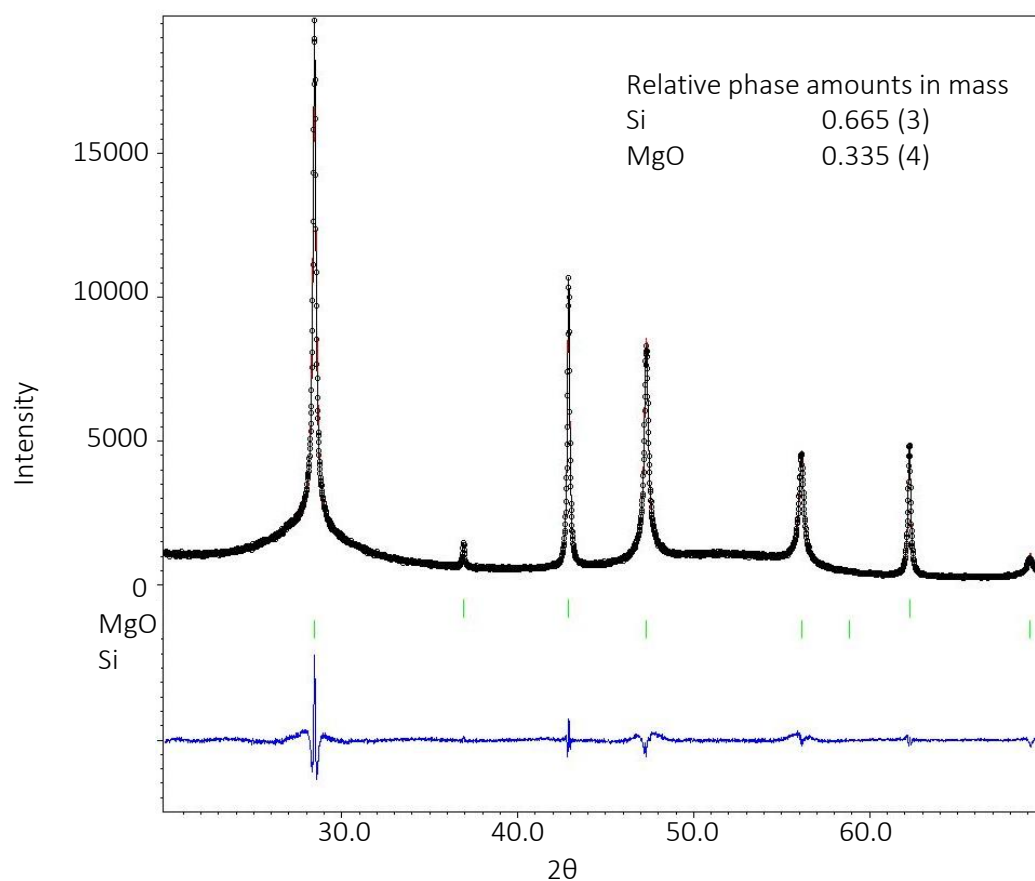


Figure S2. Rietveld refinement of the MgO and silicon powder XRD pattern using fundamental approach with residual in blue.

It is possible quantify the amorphous Si phase by following the procedure outlined by Deniard P.². A Rietveld refinement was performed on the diffractogram of the silicon powder and MgO standard as can be seen Figure S2. For this, the Jana2020^[<http://jana.fzu.cz/>] software was used following the fundamental approach. The silicon phase was fitted first with the atomic positions fixed at $U_{iso} = 0.005$, then the following parameters were refined:

1. Scale factor and sycos
2. Cell parameters
3. Lorentzian crystallites size
4. Gaussian strain.

Next, after unlocking the atomic position, the U_{iso} was refined. The MgO phase was subsequently refined following the same procedures. Finally, relative phase amounts in mass analyzed by XRD were retrieved.

The XRD samples c-Si fraction (with the MgO standard) is calculated following eq. (S1):

$$(W\varphi)_{real} = (W\varphi)_x \frac{(Ws)_{real}}{(Ws)_x} \quad (S1)$$

With $(W\varphi)_{real}$ being the c-Si $w\%$ when the MgO standard is also counted; $(W\varphi)_x$ being the c-Si $w\%$ measured by Rietveld refinement on the diffractogram, which is 66.5 $w\%$; $(Ws)_{real}$ being the $w\%$ of the MgO standard, which is 15.5 $w\%$; $(Ws)_x$ being the standard $w\%$ measured by Rietveld refinement on the diffractogram, which is 33.5 $w\%$. The calculated $(W\varphi)_{real}$ is 30.8 $w\%$. Next, we calculated the c-Si fraction of the silicon powder following eq. (S2):

$$(W\varphi)_{raw} = \frac{(W\varphi)_{real}}{1 - (Ws)_{real}} \quad (S2)$$

We obtained $(W\varphi)_{real}$ equal to 36.4 $w\%$. Thus, the quantity of a-Si in our powder is 63.6 $w\%$ as determined by XRD. The sensitivity of the technique is around 3 $w\%^2$. Crystallites inferior to 5 nm are counted as a-Si.

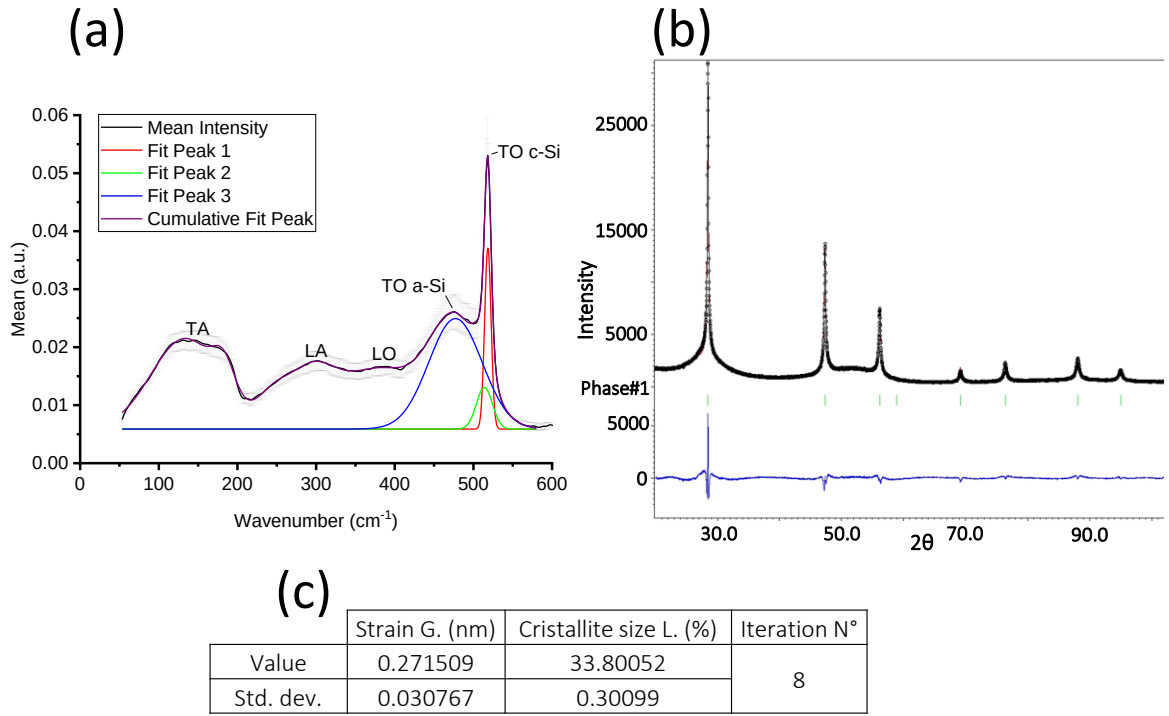


Figure S3 Structural characterizations of the silicon powder; (a) Eight-peak fit (not all peaks are shown) of the averaged Raman spectrum with its standard deviation; (b) Rietveld refinement of silicon powder XRD pattern using the fundamental approach, with its residual in blue; (c) Silicon crystallites size and micro-strain as a result of the Rietveld refinement.

The Raman spectrum of the silicon powder, Figure S3a, contains the peaks from the different phonons of crystalline and amorphous silicon. In a-Si, the selection rule which allow only phonons with zero momentum is relaxed³. Thus, many phonon modes with different energies become possible. The c-Si unique phonon mode is located at 520 cm⁻¹³. For a-Si, there are four modes⁴:

1. TO: transverse optical at 480 cm⁻¹
2. LO: longitudinal optical at 380 cm⁻¹
3. LA: longitudinal acoustic at 300 cm⁻¹
4. TA: transverse acoustic at 140 cm⁻¹.

The whole pattern was fitted with eight Gaussians (to match the whole pattern, not shown), specifically with one for the c-Si peak and one for the a-Si TO peak. The c-Si peak is very asymmetric, which either comes from a broad range of crystallites size or from surface modes of the hexagonal c-Si since the peak width depends on crystallites size and shape (and possibly strain)³. Thus, a third Gaussian was used to fit the transition between those two peaks. This extra peak is also attributed to c-Si.

The peaks area of c-Si and a-Si TO is related to their respective volumetric fraction such that⁴:

$$Xc = \frac{Ic}{Ic+Ia} \quad (S3)$$

With Xc being the c-Si %; Ic and Ia being the peaks area of the c-Si peaks and a-Si TO peak, respectively. However, both a-Si TO and c-Si phonon excitation cross sections are different. Thus, Ia must be corrected such that Xc becomes⁵:

$$Xc = \frac{Ic}{Ic+y \times Ia} \quad (S4)$$

With y being the c-Si over a-Si excitation cross sections ratio. It is corrective term which depends on the crystallites size L . Bustarret E., et al⁶ proposed the following expression for y :

$$y = 0.1 + e^{\left(-\frac{L}{250}\right)} \quad (S5)$$

A Rietveld refinement using the fundamental approach was performed on the silicon powder XRD pattern (figure S3b). The same procedure was followed as for the Si plus MgO pattern using only the silicon phase. A crystallite size of 33.8 nm and a micro-strain of 0.28 % were retrieved (see Figure S3c). Such value of micro-strain could explain the necessity of a second peak (its area is denoted Igb) to fit the whole c-Si contribution to the Raman spectrum.

Finally, the a-Si in our silicon powder is 53.4 % as presented Table S1. With the densities of a-Si and c-Si being 2.285 and 2.33, respectively, the quantification obtained by XRD or Raman should be comparable. Unfortunately, there is a difference of approximately 10 percentage points. We expect the Raman quantification to be less accurate for several reasons. First, the amount of matter analyzed is rather small (the beam size is in the order of 100 μm) compared to XRD and the standard deviation was rather large (over 6 measurements) as can be seen figure S3a. Second, it relies on two techniques (Raman plus XRD, which increases the risk for and propagation of error) and the relation between

the c-Si over a-Si excitation cross sections ratio is not yet fully understood. In fact, other expressions for y were proposed, and are purportedly more accurate⁵.

Table S1 Parameters obtained from Raman fit and XRD pattern refinement and the value obtained for X_c (and X_a) following eq. (S4) for the silicon powder.

I_c	I_{gb}	I_a	$y(L)$	X_c (%)	X_a (%)	Crystallite size (Å)
0.322	0.184	1.618	0.359	46.57	53.43	338

2.3. STEM-EDX observations

Scanning transmission electron microscopy (STEM) experiments were carried out using the Nant'Themis, a (S)TEM Themis Z G3 Cs-probe corrected microscope (Thermo Fisher Scientific) operated at 80 kV and equipped with a high-angle annular dark field (HAADF) detector. Pristine electrodes (without xGnP15) powder was dispersed in cyclohexane after being scratched from the current collector. Then, a drop of this dispersion was deposited onto a lacey carbon film supported by a copper grid. Cycled electrodes (from EIS tests, after 1 cycle, not rinsed, dried at 40 °C for 20 h under vacuum without air exposure, then scratched) were deposited onto a lacey carbon film by simple contact of the powder with the copper grid. A vacuum transfer sample holder (GATAN 648) was used to prevent any air from contacting the reactive sample before its introduction into the Nant'Themis.

Figure S4 shows TEM images of the silicon powder mixed with the reference binder (Zn-free). It reveals the mainly amorphous character of the silicon powder. However, crystalline planes can be spotted, for example in the bottom image left-hand bottom corner.

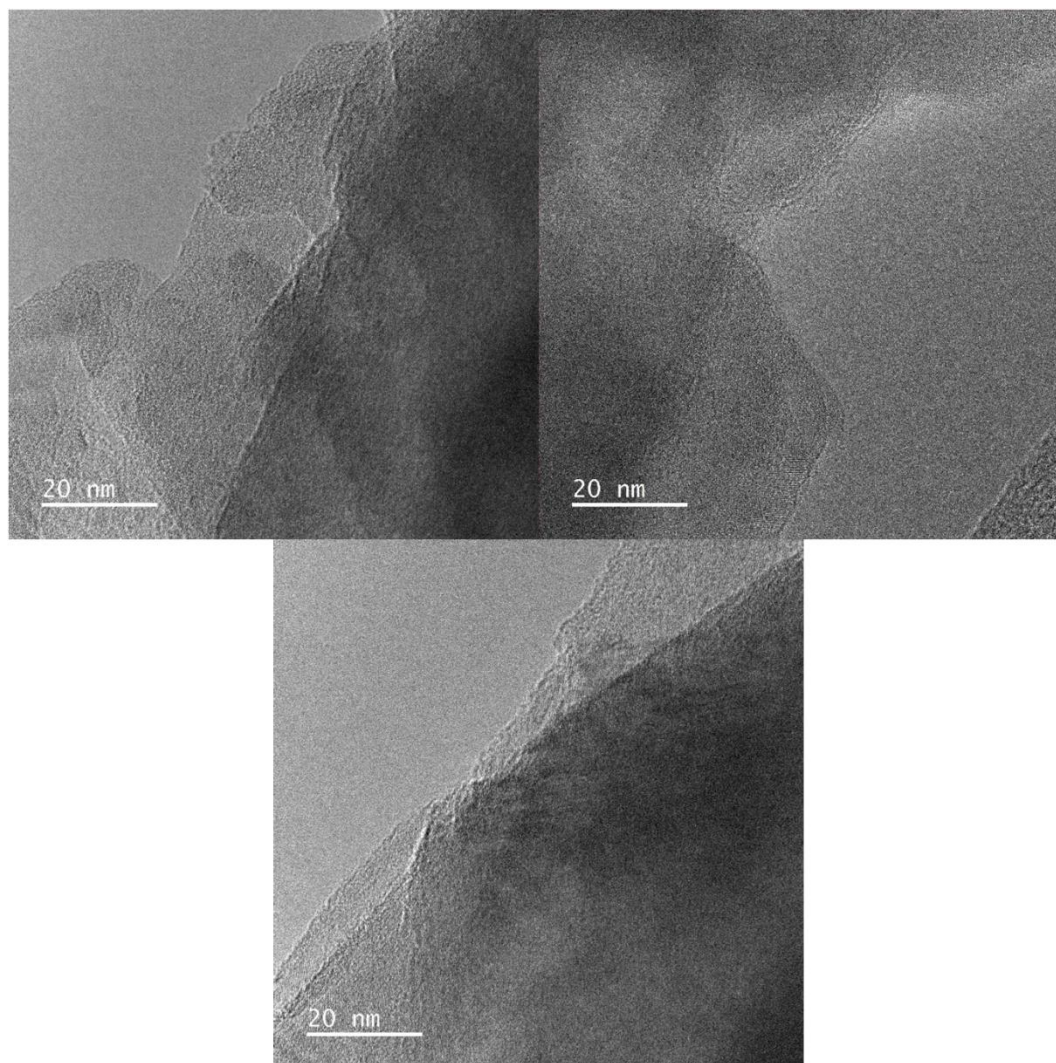


Figure S4. TEM images of a pristine sample containing silicon and binder without zinc.

Elemental maps were acquired in STEM mode using a Super-X X-ray emission spectrometer consisting of four windowless silicon-drift detectors (SDDs) providing a large collection solid angle of 0.7 sr. This configuration ensured a limited sensitivity to the aggregates' orientation with respect to the detectors. In order to limit electron beam degradation, an effect often observed with Si-based electrodes⁷, a small convergence angle of approximately 13 mrad and limited current of 100 pA were used, thus reducing the electron dose. For this same reason, fast frame acquisitions were used (a couple of seconds per frame and 10-50 μ s dwell time) and hundreds of frames were summed for each map. Pixel sizes of approximately 5 nm were chosen. Quantifications performed on the first tens of frames gave very similar results to those performed on the last tens of frames, thus proving the reliability of given atomic ratios and maps. Figure S8a shows for example two different areas that were identified and used for EDX elemental quantification. Area #1 is focused on the middle of a particle where the silicon percentage is at its highest. Area #2 is focused between two particles, where the binder markers' percentages are at their highest. There is no major difference in the quantification for both areas

between the first and the second batch of fifty spectrums, as can be seen in figure S8b and S8c, respectively. Thus, no significant degradation is expected for long EDX spectrums acquisitions, whether it be for silicon particles or the binder.

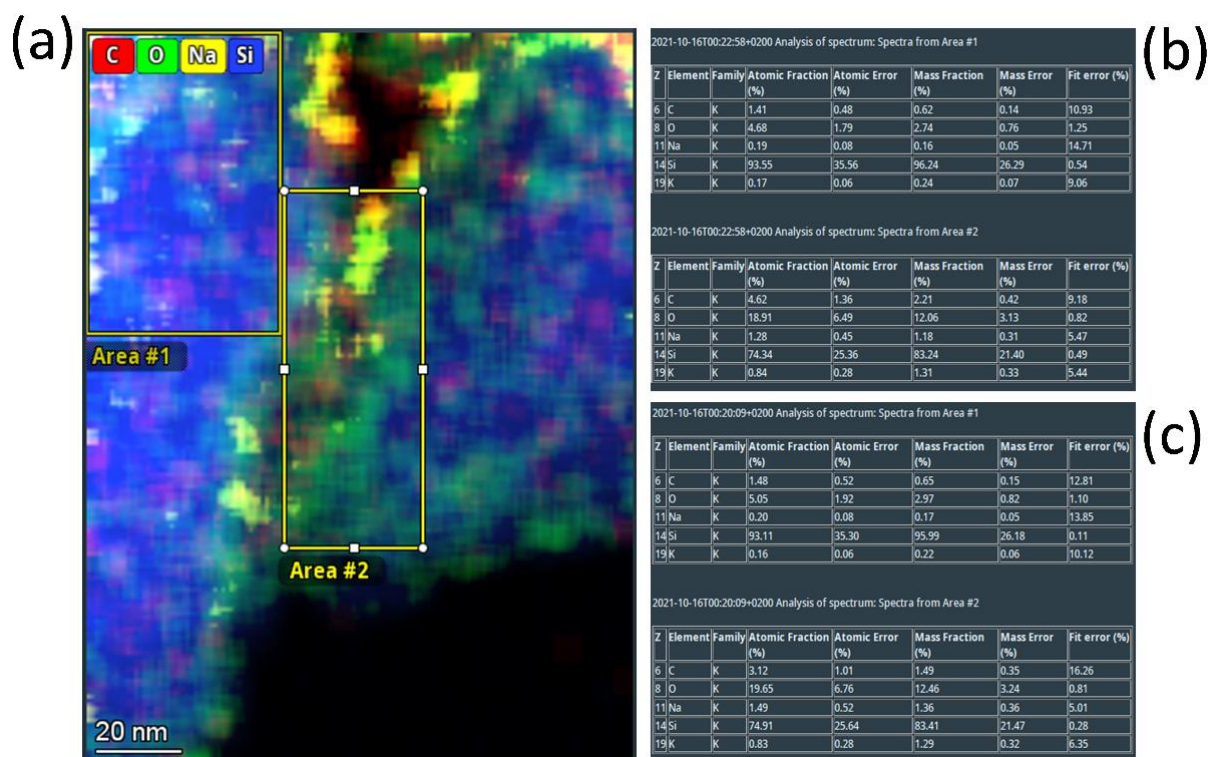
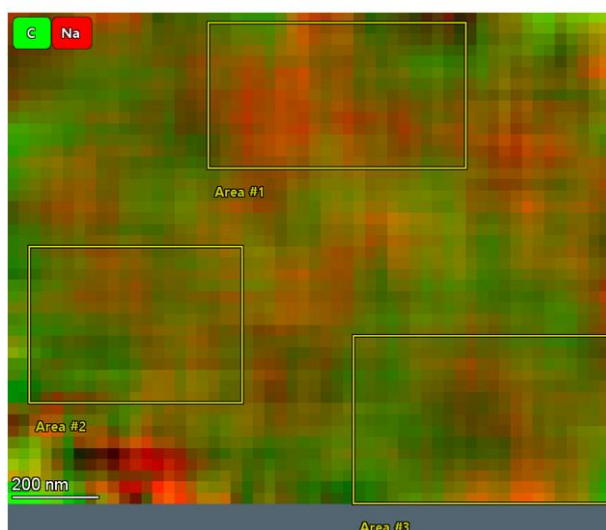


Figure S5. Pristine sample containing silicon and Zn-free binder; (a) Stacked counts elemental maps for carbon (red), oxygen (dark green), silicon (blue), and sodium (yellow); (b) EDX elemental quantification results from the first fifty acquired spectrums in area #1 and #2 of the ROI denoted in (a); (c) EDX elemental quantification results from the next fifty acquired spectrums in area #1 and #2 of the ROI denoted in (a).

To complement these results, Figure S9 presents the results of a quantification done on a pure NaCMC sample. With a 5 eV/channel value for energy dispersion, light elements could be reliably measured, as was confirmed by quantification performed on a NaCMC sample. A very good accordance between the experimental ratios of light elements on NaCMC and the theoretical ratios was obtained, which highlights the EDX reliability on light elements quantification. Regions purely composed of LiF were nevertheless slightly degraded under these conditions, though this has no major implications on the relevance of the maps presented here.

(a)



(b)

2020-07-29 21:27:24 Analysis of spectrum: Spectra from Area #2

Z	Element	Family	Atomic Fraction (%)	Atomic Error (%)	Mass Fract (%)
6	C	K	51.46	8.38	43.01
8	O	K	42.47	10.95	47.29
11	Na	K	6.07	1.57	9.70

2020-07-29 21:27:24 Analysis of spectrum: Spectra from Area #1

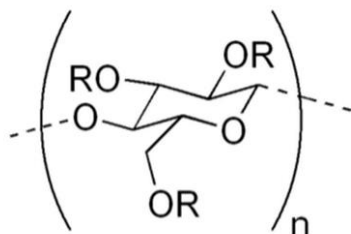
Z	Element	Family	Atomic Fraction (%)	Atomic Error (%)	Mass Fract (%)
6	C	K	51.00	8.25	42.44
8	O	K	42.32	10.89	46.92
11	Na	K	6.68	1.72	10.64

2020-07-29 21:27:24 Analysis of spectrum: Spectra from Area #3

Z	Element	Family	Atomic Fraction (%)	Atomic Error (%)	Mass Fract (%)
6	C	K	52.94	8.41	44.56
8	O	K	41.59	10.62	46.62
11	Na	K	5.47	1.39	8.82

Carboxymethyl cellulose sodium salt

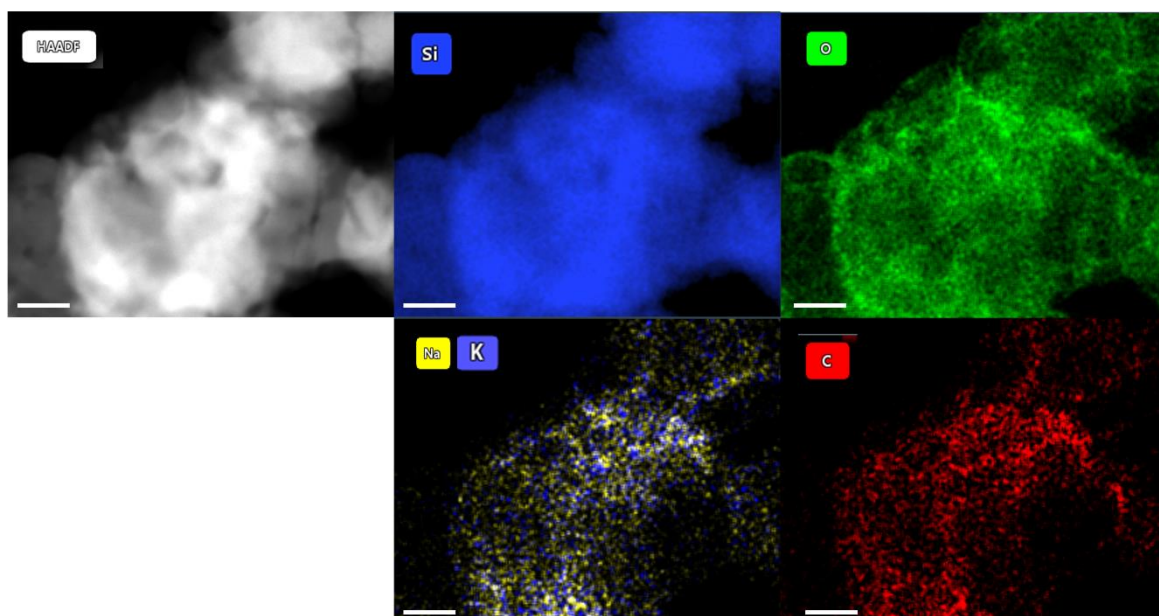
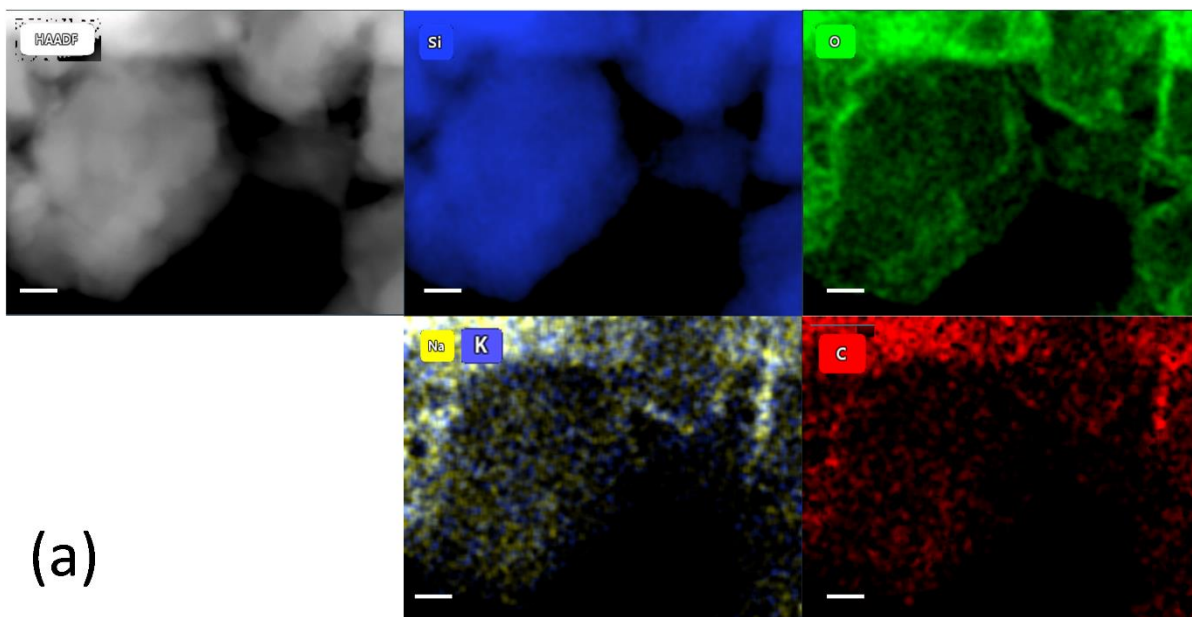
(c)

R = H or CH₂CO₂Na (D.S. = 0.9)

Area	O/C	Na/C
#1	0.83	0.13
#2	0.83	0.12
#3	0.79	0.10
Average	0.81	0.12
std. dev.	0.02	0.01
Theoretical ratios	0.87	0.12

Figure S6. NaCMC sample analyzed by STEM-EDX; (a) Stacked counts elemental maps for carbon (green) and sodium (red); (b) EDX elemental quantification results from the acquired spectrums in area #1, #2, and #3 of the ROI presented in (a); (c) NaCMC structure with its theoretical O/C and Na/C ratios compared to the averages obtained from the quantifications in (b).

Figure S7 shows regions of interest (ROI) on pristine electrodes different from those presented in Figure 2 and 3 while Figure S8 shows regions of interest (ROI) on cycled electrodes different from those in Figure 4. In these, the large carbon fibrils can easily be discerned and attributed to the TEM grid. In Figure S8a, Zn-free electrode's SEI appears more disseminated and less dense while in Figure S8b, the ZnSO₄ electrode's SEI looks dense, thin, and anchored to the particles.



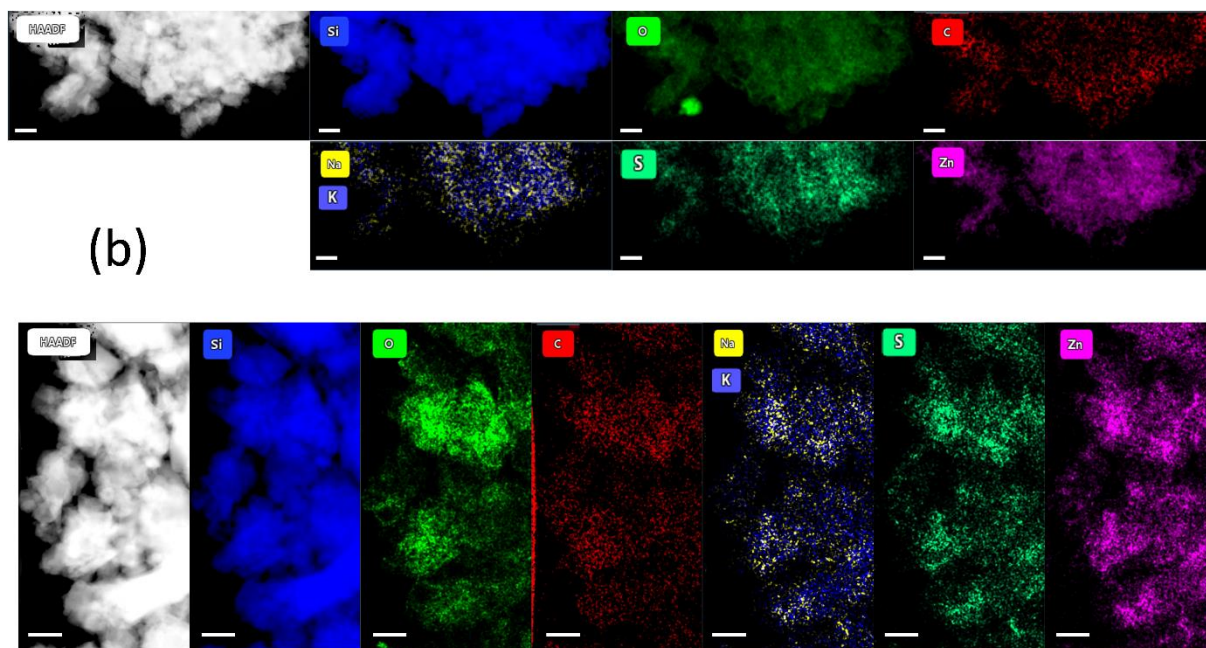
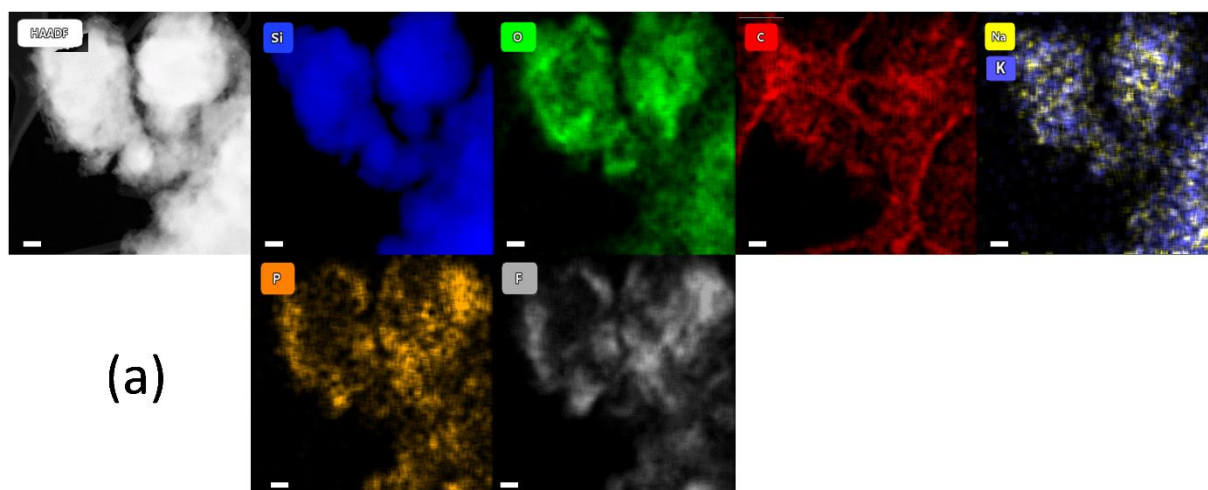
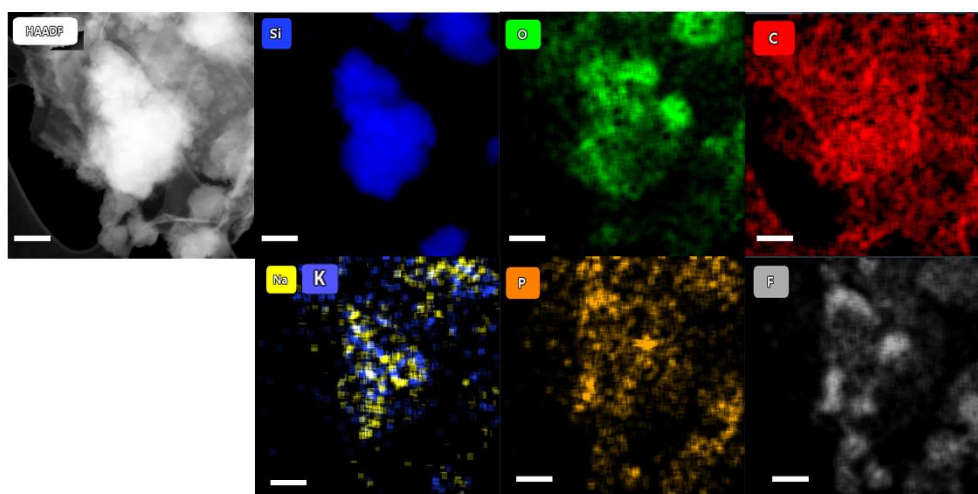
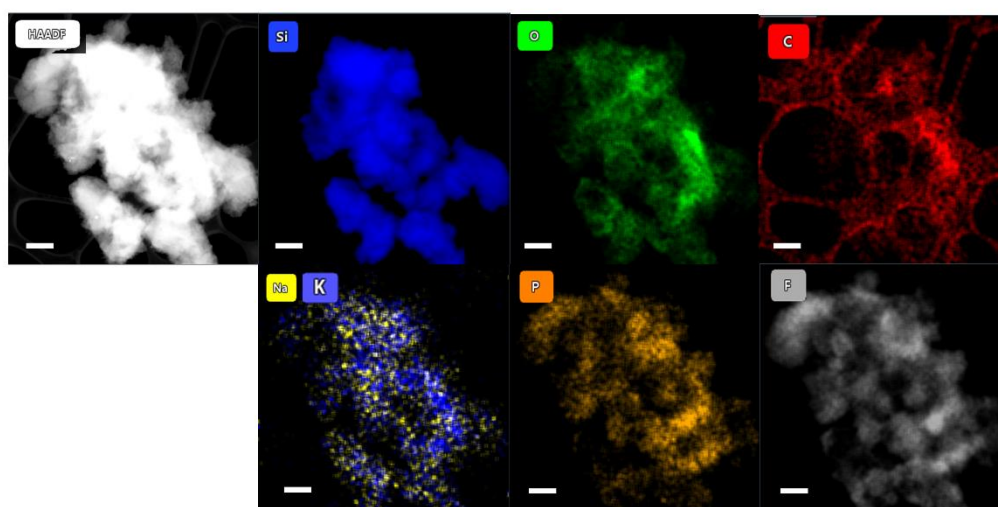


Figure S7 (a) STEM-HAADF image of pristine samples containing silicon and Zn-free binder and corresponding net count elemental maps for silicon (blue), oxygen (dark green), sodium (yellow) and potassium (blue), and carbon (red). Scale bar is 20 and 50 nm for the top and bottom ROIs, respectively; (b) STEM-HAADF image of pristine samples containing silicon and binder with ZnSO₄ and corresponding net count elemental maps for silicon (blue), oxygen (dark green), carbon (red), sodium (yellow) and potassium (blue), zinc (pink), and sulfur (light green). Scale bars are 200 nm.



(a)



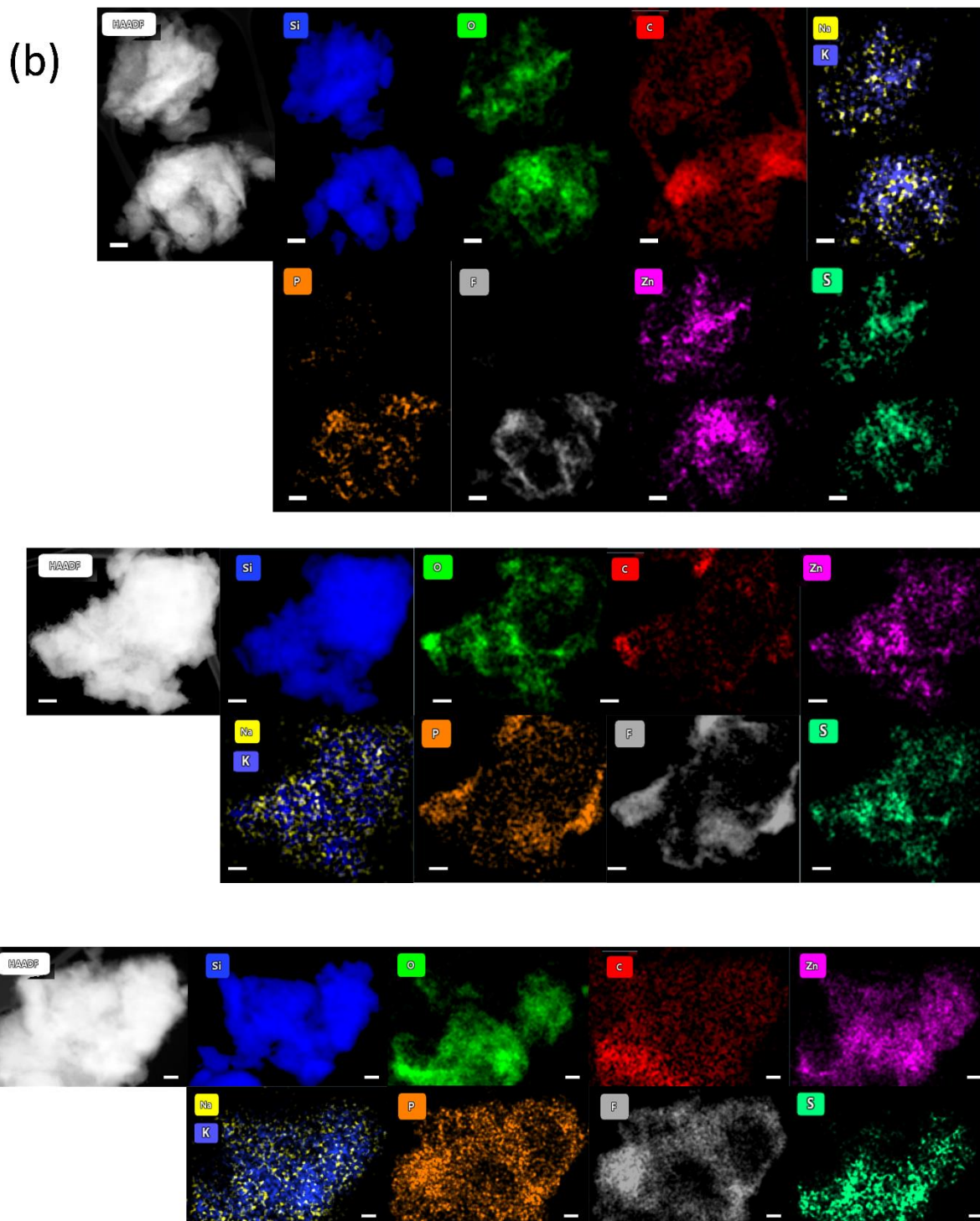


Figure S8 (a) STEM-HAADF image of cycled electrode samples containing a Zn-free binder and corresponding net counts elemental maps for silicon (blue), oxygen (dark green), carbon (red), sodium (yellow) and potassium (blue), phosphorus (orange), and fluorine (grey). Scale bars are 100, 200 and 200 nm, for the top, middle and bottom ROIs, respectively; (b) STEM-HAADF image of cycled electrode samples containing a ZnSO₄ binder and corresponding net counts elemental maps for silicon (blue), oxygen (dark green), carbon (red), sodium (yellow) and potassium (blue), zinc (pink), sulfur (light green), phosphorus (orange), and fluorine (grey). Scale bars are 100 nm for all ROIs.

2.4. STEM-EDX quantifications

Atomic percentage quantifications were performed using the Velox 2.14 software and built-in cross sections (Brown-Powell). Pixel averaging was used to improve reliability of quantification. The spatial resolution can be estimated to be around 15 nm. A methodology was defined and systematically used in order to optimize the relative comparison of the various maps and samples. Tables S2, S3 and S4 illustrate the different steps of the elemental quantifications of the samples.

First, Table S2 gives elements raw quantification for one ROI (atomic and mass fractions with the errors associated).

Table S2 Quantification results of the ROI 1658, for a pristine sample containing the Zn-free binder.

Element	Atomic Fraction (%)	Atomic Error (%)	Mass Fraction (%)	Mass Error (%)	Fit error (%)
C	1.24	0.37	0.56	0.10	1.52
O	12.00	4.33	7.26	1.94	0.04
Na	0.49	0.18	0.43	0.11	0.31
Si	86.01	30.69	91.36	23.85	0.03
K	0.26	0.09	0.39	0.10	0.82

Next, table S3a presents the results of an elemental quantification based on simple averaging of all ROIs with equal weight given to each. The large standard deviation obtained for some elements or ratios are not related to the quantification errors from the EDX quantification. They solely come from differences in the ROI compositions. Table S3b presents the balancing method followed as explained in the main text (see equation 1). First, the proper detectors are selected. The blanks in table S3b come from the detectors whose contribution were not considered in the overall ROI EDX spectrum. Thus, their counts contribution was discarded in the w factor calculation as well. Some ROIs were discarded in the process of establishing the ratios such as those with less than 25 at% of silicon, which for the cycled ZnSO_4 formulation represents 3/13 zones, and those with no sodium quantified, which for the cycled without Zn formulation represents 2/17 zones. Then, a background is defined by adding so called background boxes in the regions where no peaks are present. Special care is taken in the low energy region where background is ill defined and peaks are overlapping. In the EDX quantification software window, Brown-Powell is selected as the ionization cross-section model. The spectrum fit is optimized, and the sample thickness and density are fixed to 50 nm and 1.5 g/cm³, respectively. These values were systematically chosen and will be more or less accurate for different ROIs. However, as they are not determinable, fixing these parameters made the procedure standardized. In the image browser window, pre-filtering with pixel averaging is selected. The post filtering is also selected if better quality mapping pictures are required. Then, ROIs are defined with the polygon tool to fit the particles complex geometry. Areas where the grid was clearly visible were avoided as much as possible to minimize error. Finally, all frame spectra are selected for the quantification of the ROIs.

Table S3. Examples of the different procedures to obtain the atomic percentage ratios, for a pristine sample containing the Zn-free binder; (a) Atomic percentage and non-weighted ratio of elements; (b) Acquisition parameters necessary to compute w (see equation 1 in the main text) and the calculated atomic percentage with balancing.

(a)

Without Zn ROIs	C	O	Na	Si	K	C/Si	O/Si	(Na+K)/Si	(Na+K)/C
1644	3.2	8.4	0.78	86.3	0.43	0.037	0.10	0.014	0.38
1648	2.3	9.7	0.67	87.0	0.35	0.026	0.11	0.012	0.45
1658	1.2	12.0	0.49	86.0	0.26	0.014	0.14	0.009	0.60
1710	0.9	12.9	0.22	85.8	0.13	0.011	0.15	0.004	0.37
1717	2.1	9.9	0.55	87.3	0.26	0.023	0.11	0.009	0.40
1722	4.8	15.9	0.64	78.4	0.31	0.061	0.20	0.012	0.20
1729	5.4	12.7	1.05	80.3	0.53	0.068	0.16	0.020	0.29
1737	2.8	10.0	0.84	85.9	0.42	0.033	0.12	0.015	0.45
1752	4.2	10.9	0.71	83.9	0.41	0.049	0.13	0.013	0.27
1801	3.1	14.9	0.22	81.6	0.24	0.038	0.18	0.006	0.15
Mean ($_{ar}\%$)	3.0	11.7	0.62	84.2	0.33	0.036	0.14	0.011	0.36
Std. dev. ($_{ar}\%$)	1.5	2.4	0.26	3.1	0.12	0.019	0.03	0.005	0.13

(b)

Without Zn ROIs	D1 (cps)	D2 (cps)	D3 (cps)	D4 (cps)	t (s)	S (μm²)	l (px)	L(px)	px size (nm)	Scan dim. (μm²)	w (cps/(s μm²))	C	O	Na	Si	K	
1644	1372	1204		1234	14	0.232	512	512	1.31	0.45	605	1.90E+03	5.10E+03	4.70E+02	5.20E+04	2.60E+02	
1648	1986	1730		1823	3.81	0.099	312	219	1.31	0.118	12342	2.80E+04	1.20E+05	8.30E+03	1.10E+06	4.30E+03	
1658	896	837		900	2.45	0.031	235	181	0.93	0.037	29307	3.60E+04	3.50E+05	1.40E+04	2.50E+06	7.60E+03	
1710		731		794	9.23	0.03	470	362	0.46	0.037	4507	4.20E+03	5.80E+04	9.90E+02	3.90E+05	5.90E+02	
1717	1182	1095			1.6	0.019	138	184	0.93	0.022	65010	1.30E+05	6.40E+05	3.60E+04	5.70E+06	1.70E+04	
1722	932	834			1.98	0.022	147	216	0.93	0.027	32583	1.50E+05	5.20E+05	2.10E+04	2.60E+06	1.00E+04	
1729	1041	929			3.99	0.043	367	198	0.93	0.063	7881	4.30E+04	1.00E+05	8.30E+03	6.30E+05	4.20E+03	
1737	1487	1306		1211	3.99	0.048	367	198	0.93	0.063	16019	4.50E+04	1.60E+05	1.30E+04	1.40E+06	6.70E+03	
1752	2015	1889		1721	4.33	0.061	342	229	0.93	0.068	19240	8.00E+04	2.10E+05	1.40E+04	1.60E+06	7.90E+03	
1801	1026	977		702	869	1.55	0.004	195	134	0.47	0.006	405664	1.30E+06	6.00E+06	8.90E+04	3.30E+07	9.70E+04
											593158	1.80E+06	8.20E+06	2.10E+05	4.90E+07	1.60E+05	Sum
												3.0	13.8	0.35	82.6	0.27	(%)
												0.77	2	0.20	2.4	0.06	Std. dev. (%)

In complement, Table S4 gives the theoretical and experimental elemental composition of pristine samples (without GnPM15) as determined from the formulation components and by STEM-EDX, respectively. The fraction of hydrogen in the theoretical quantification must be disregarded (and the values normalized once again) for a proper comparison with the experimental quantifications since hydrogen is not quantified by EDX. The theoretical quantification of elements (to compute the ratios) presented table S4a and S4b are derived from the electrode composition in Table 1.

Table S4. Theoretical and experimental elemental composition of pristine samples (without GnPM15) as determined from the formulation components and by STEM-EDX, respectively; (a) Zn-free binder sample; (b) ZnSO₄ binder sample.

(a)

Without Zn						
Composition	C	O	Na	Si	K	H
Theo. (w%)	6.34	8.59	0.71	82.78	0.82	0.76
Exp. (w%)	1.39	8.51	0.31	89.39	0.40	0.00
Theo. (at%)	10.95	11.14	0.64	61.21	0.44	15.62
Theo. (at%)	12.98	13.21	0.76	72.54	0.52	0.00
Exp. (at%)	3.01	13.81	0.35	82.57	0.26	0.00

(b)

ZnSO ₄								
Composition	C	O	Na	Si	S	K	Zn	H
Theo. (w%)	5.99	10.27	0.68	78.29	1.08	0.78	2.19	0.72
Exp. (w%)	0.69	4.56	0.52	91.71	0.42	0.33	1.78	0.00
Theo. (at%)	10.49	13.49	0.62	58.61	0.71	0.42	0.70	14.96
Theo. (at%)	12.34	15.87	0.73	68.92	0.83	0.49	0.83	0.00
Exp. (at%)	1.56	7.75	0.61	88.76	0.36	0.23	0.74	0.00

Absorption from particle morphology (side scattering) and roughness can reduce the characteristic (peak: P) and bremsstrahlung (background: B) intensities (which is especially true for nanoparticles)⁸, which may lead to elemental quantification errors. To counter this experimental bias, it is possible to calculate the P/B ratio of the elements. This corrects the absorptions and electrons incidence angle effects, as well as the instrumental parameters imprecisions⁸. It is based on the assumption that both characteristic and bremsstrahlung intensities are generated at similar depth (which is an approximation⁹). It does not provide a direct quantification, but it is possible to compute elemental ratios like $C_{(P/B)}/Si_{(P/B)}$ for example. This ratio approximation is valid because the mass thickness of the generated X-rays is of the same order of magnitude for our elements when the analysis is performed at 80 kV¹⁰. Finally, the obtained values are comparable for both formulations, like the at% ratios. This analysis was however not pursued because of the analysis time required and the fact that the NMR quantification provided more representative results.

2.5. NMR spectroscopy

⁷Li and ¹⁹F solid state magic angle spinning nuclear magnetic resonance (MAS NMR) experiments of cycled then scratched electrode coating were performed on a 500 MHz Bruker Avance III (Larmor

Frequency $\nu_0(^7\text{Li}) = 194 \text{ MHz}$, $\nu_0(^{19}\text{F}) = 470 \text{ MHz}$) with zirconia rotor ($d_{\text{ext}} = 2.5 \text{ mm}$). ^7Li and ^{19}F spectra were acquired using a single pulse and Hahn echo sequence with 30 and 15 s recycle delays, respectively. Spinning frequencies up to 25 kHz were used. Long recycle times were also used to ensure quantitative measurements. All spectra were normalized according to the number of scans, the receiver gain, and the sample mass. ^7Li and ^{19}F integrated intensities were determined by using spectral simulation dmfit software¹¹. Quantitative NMR was also performed by mixing Si with various amounts of LiF to obtain calibration curves which allowed for absolute quantification lithium and fluorine content in the samples¹². The electrodes were retrieved following EIS tests. After one 1 cycle, they were placed on absorbent paper to remove the majority of the electrolyte contained within its porosities and further dried at 40 °C for 20 h under vacuum, without exposing the reactive sample to air. Pristine electrodes had a mass gain of less than 1 % after mimicking battery conditions for a night and following this same dismantling and drying procedure. As such, no electrolyte is expected to remain in the electrodes.

Figure S9 gives the normalized ^{19}F and ^7Li NMR spectra for both electrodes. The ^{19}F NMR spectra of the Zn-free and ZnSO_4 electrodes, presented figure S6a, contain different contributions. They span over a broad chemical shift range and can thus be deconvoluted. There is mainly LiF, with four spinning side bands, then the LiPF_6 in a pseudo-liquid/confined (with two isotropic resonances) or solid form and its side band, and finally the $\text{Li}_x\text{PO}_y\text{F}_z$. Conversely, it is not possible to deconvolute the different contributions of the ^7Li spectrum shown in Figure S9b.

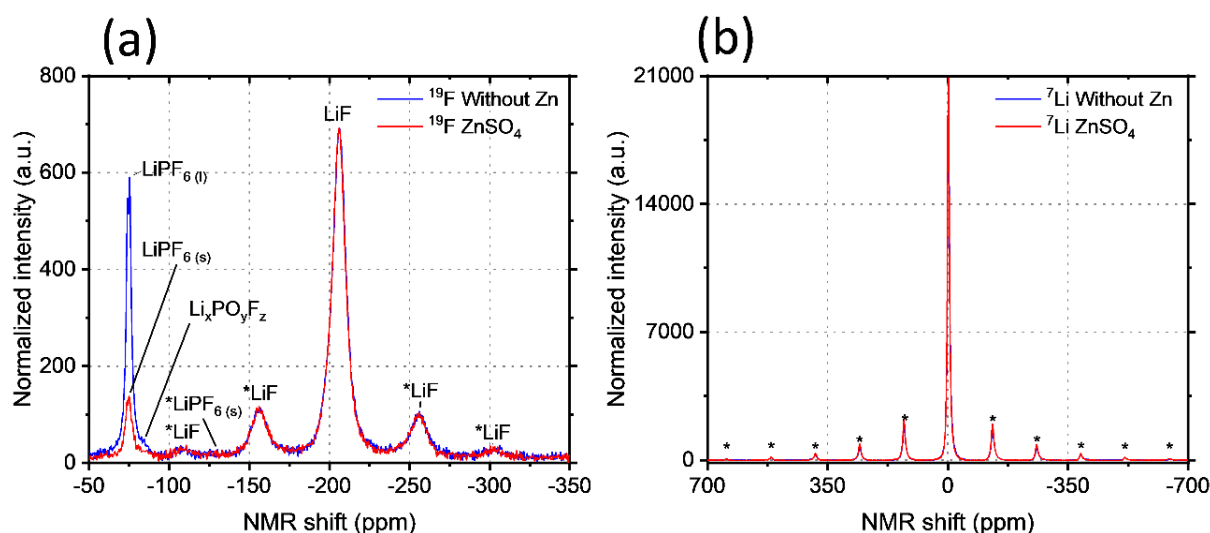


Figure S9. Normalized NMR spectra of cycled samples containing silicon, graphene, and the reference or ZnSO_4 binder; (a) ^{19}F spectra; (b) ^7Li spectra. The isotropic resonance as well as the spinning side bands (marked with an asterisk) from the different molecular contributions are shown.

2.6. Electrochemical measurements

Electrodes were assembled in Swagelok cells in an Ar filled glove box (O_2 and $H_2O < 1$ ppm) in half-cell configuration. The counter and reference electrode was a metallic Li disc (diam. = 10 mm, thickness = 380 μm , 99.9%; Aldrich) placed on a Cu current collector (diam. = 12 mm, thickness = 250 μm). Two layers of glass microfiber membranes (GF/D grade, diam. = 13 mm, thickness = 670 μm ; Whatman) were used as separator. The separator layers were soaked with 300 μL of electrolyte made from 1 M LiPF_6 in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v:v) plus 10 wt. % fluoroethylene carbonate (99.9%; Solvionic). Si electrodes with a loading of $1.75 \pm 0.1 \text{ mg}_{\text{Si}}.\text{cm}^{-2}$ were used for the cycling tests performed at room temperature using a multichannel VMP system (Biologic) in galvanostatic mode between 0.005 and 1 V (vs. Li^+/Li^0). The C-rate was C/40 for the 1st cycle, C/20 for the next 5 cycles, and C/10 for the subsequent cycles ($1\text{C} = 3820 \text{ mA.g}_{\text{Si}}^{-1}$). Prior to cycling, cells were left for 2 h at the open circuit voltage (OCV). They were also allowed to relax at OCV for 10 s after each discharge (lithiation) and 1 min after each charge (delithiation) step. For reproducibility, 3 to 4 cells were tested for each Si electrode formulation.

Electrochemical impedance spectroscopy (EIS) measurements were carried out in three-electrode Swagelok cells. The reference electrode was made of three Li-metal chunks disposed around the electrode and separator stack, in which the separator is composed of 1 layer of polypropylene (PP) (2500 grade, diam. = 13 mm, thickness 25 μm ; Celgard) and one of GF/D (diam. = 25 mm). The amount of electrolyte was increased to 700 μL . Si electrodes with a loading of both 1.0 and $1.75 \pm 0.1 \text{ mg}_{\text{Si}}.\text{cm}^{-2}$ were used in the EIS measurements. Cells were left to rest at OCV for at least 4 h to mitigate wetting issue with the DMC in the electrolyte blend and the PP separator layer. Then, three EIS steps were applied with single sines of 5, 15 and 25 mV in amplitude between 200 kHz and 10 mHz. Each step was repeated once before applying the next amplitude (with 15 min of OCV before each step) to verify the system linear and stationary response. After 1 h at OCV, galvanostatic cycling was performed between 0.005 and 1 V (vs. Li^+/Li^0) for 1 cycle at C/40. Then, after 2 h of OCV, another series of EIS steps was applied under the same conditions. OCV periods were applied until $dE/dt < 1 \text{ mV.h}^{-1}$. For reproducibility, three cells were tested for each Si electrode formulation.

The EIS spectra of the different electrodes are presented Figure S10a and S10b for the Zn-free and ZnSO_4 formulations, respectively. They were fitted with the model proposed Figure S10c with the Zview software. The fitting procedure was the following:

1. All parameters are locked;
2. The resistors are freed and set to 1 ohm, then the spectrum is fitted;
3. The CPE-T are freed and set to 1e^{-6} and 1e^{-4} , respectively, then the spectrum is fitted;

4. The W_o -R and W_o -T are freed and set to the value of 1, then the spectrum is fitted;
5. The CPE-P are freed, then the spectrum is fitted, verifying that their value does not go below 0.5 or above 1. Otherwise, they are locked to the closest value (0.5 or 1).
6. The W_o -P value remain locked to 0.5.

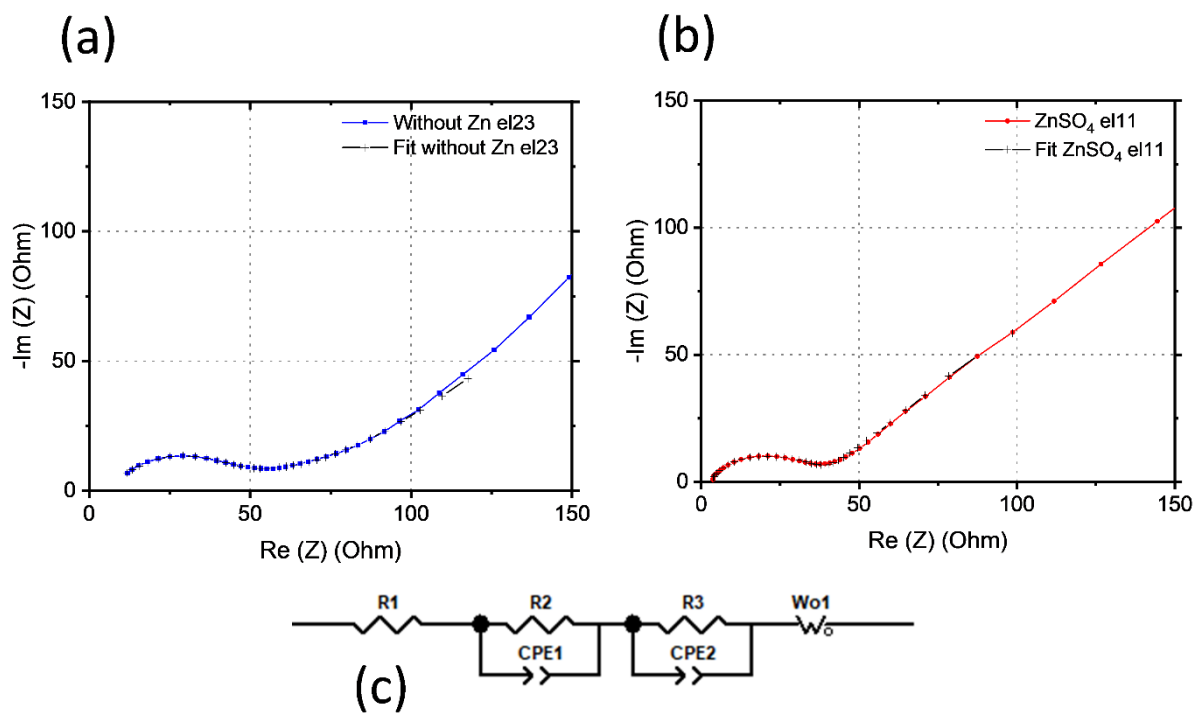


Figure S10. EIS spectrum example of both formulation electrodes with their respective fit; (a) Zn-free formulation; (b) ZnSO_4 formulation; (c) Model used to fit the spectra.

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4.2.2. Publication N°2 : “Coordinatively Crosslinked Binders for Silicon-Based Electrodes for Li-ion Batteries: Beneficial Impact on Mechanical Properties and Electrochemical Performance”

Coordinatively Cross-linked Binders for Silicon-Based Electrodes for Li-ion Batteries: Beneficial Impact on Mechanical Properties and Electrochemical Performance

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ABSTRACT

A simple and versatile preparation of Zn(II)-poly(carboxylates) reticulated binders by the addition of Zn(II) precursors (ZnSO₄, ZnO or Zn(NO₃)₂) into a pre-optimized poly(carboxylic acids) binder solution is proposed. These binders lead systematically to a significantly improved electrochemical performance when used for the formulation of silicon-based negative electrodes. The formation of carboxylate-Zn(II) coordination bonds formation is investigated by rheology, FTIR and NMR spectroscopies. Mechanical characterizations reveal that the coordinated binder offers a better electrode coating cohesion and adhesion to the current collector, as well as higher hardness and elastic modulus, which are even preserved in presence of a carbonate solvent (*i.e.* in battery operation conditions). Ultimately, as shown from *operando* dilatometry experiments, the electrode expansion during lithiation is reduced, mitigating electrode mechanical failure. Such coordinatively reticulated electrodes outperform their uncoordinated counterparts with an improved capacity retention of over 30% after 60 cycles.

KEYWORDS

Li-ion batteries, silicon-based negative electrode, ionic cross-linked binder, Zn-carboxylate bonds.

INTRODUCTION

The benefits and limitations of silicon as negative electrode material for lithium-ion batteries have already been clearly identified. The full lithiation of Si up to $\text{Li}_{15}\text{Si}_4$ leads to high gravimetric and volumetric theoretical capacities (approximately 3600 mAh.g^{-1} and 2200 mAh.cm^{-3} , respectively), but it is associated with a substantial volume variation upon cycling (up to $\sim 300\%$), giving rise to various failure mechanisms including silicon particles pulverization, loss of adhesion to the current collector, and solid electrolyte interphase (SEI) instability. Various strategies are explored to circumvent these issues. These are related to the active material optimization (*e.g.* Si nanostructuration, surface coating) and to the management of the electrode mechanical properties, especially through the binder optimization (which was thoroughly reviewed recently¹⁻⁴).

Polar oxygenated polymers, such as polyacrylic acid (PAA), guar gum, alginate (Alg), carboxymethylcellulose (CMC), which can strongly interact with the Si particles surface, have been shown to outperform traditional binders such as polyvinylidene fluoride (PVDF). Strengthening the electrode through binder reticulation or cross-linking is another promising strategy.⁵ Covalent organic cross-linking,⁶ and more recently supramolecular cross-linking⁷ (through ionic or hydrogen bonding, or even mechanical interlocking), are promising avenues, but they usually require specific tailor-made organic components. An alternative strategy relies on the formation of cation-ligand coordination bonds between the organic chains, also sometimes referred to as (metal) ionic cross-linking. Initially developed with Alg binders,⁸⁻¹³ this strategy was recently extended to CMC,^{14,15} to a catechol functionalized polymer,¹⁶ and to an imidazole functionalized binder.¹⁷ This method is easy to implement, as it simply requires the addition of a metallic salt to an already established binder formulation with a polymer bearing complexing groups. We previously demonstrated this with CMC and copper sulfate.¹⁵ Coordination bonds are also highly dynamic, hence potentially prone to sustain strong mechanical stresses and to induce self-healing properties in the electrodes.¹⁸

In the present study, attention is focused on a pre-optimized formulation comprised of CMC and citric acid, which already lead to respectable electrochemical performance. Nevertheless, addition of Zn(II) precursors leads to a significant improvement in electrochemical performance, notably to the capacity retention. Spectroscopic investigations (infrared and solid-state NMR) point to the formation of Zn-carboxylate bonds. We recently demonstrated that such a coordinated binder act, at least partially, as an artificial SEI.¹⁹ We here show that such bonds have also a beneficial impact on the electrode's mechanical properties in both the dry and carbonate solvent-soaked states as evidenced by scratch tests and nano-indentation experiments. Additionally, *operando* dilatometry experiments

confirm that this mechanical strengthening leads to a reduction of the electrode expansion upon cycling, reducing the risk of failure.

RESULTS AND DISCUSSION

Electrode composition and electrochemical performance.

Inks for electrode fabrication were prepared by mixing an aqueous binder solution with a given amount of silicon and conducting additive (graphene), to reach a final silicon/graphene/binder composition close to 70:10:20 _w% (see **Table 1**). The reference binder solution was already thoroughly studied by our research group in the last years (see ¹⁵ and the references therein). It consists of sodium carboxymethylcellulose (NaCMC) dissolved in a buffer solution of citric acid (CA) and sodium or potassium hydroxide, which is required to reach the desired pH of 3-3.5. The effect of the addition of Zn(II) ions was evaluated together with the coordination ratio, *i.e.* the amount of Zn(II) vs. the total number of carboxylic groups (coming both from CMC and CA), and the nature of the metallic precursor (ZnSO₄, Zn(NO₃)₂ and ZnO). ZnO is particularly appealing as it considerably reduces the dead mass in the electrode, but its basic nature in acidic solutions leads to a significant pH increase (pH > 4). Therefore, another reference ink containing additional LiOH was prepared to reach a similar pH value as the ZnO solution (4.4 and 4.3, respectively). In regards to the coordination ratio, Zn/RCO₂H = 0.22 and 0.66 were used since our previous study on Cu-CMC-CA coordination binder suggested that a ratio above 0.1 leads to optimal electrochemical performance.¹⁵ **Table 1** summarizes the binder formulations used in this study, the corresponding ink solid fractions and pH, and the electrode compositions.

Table 1. Binder formulations, corresponding electrode compositions, and ink properties.

Formulation name		Electrode composition (w%)						Ink property	
Salt	Coord. ratio	Silicon	Graphene	NaCMC	Citric acid	KOH ^o /NaOH [■] (+LiOH) ^o	Zn precursor	Solid fraction (w%)	pH
w/o	0	73.4	11.0	7.2	7.4	1 ^o	0	21.5	3.5
ZnSO ₄	0.66	63.7	9.6	6.2	6.4	0.9 ^o	13.2	24.0	2.6
ZnSO ₄	0.22	69.9	10.5	6.8	7.0	1 ^o	4.8	22.3	2.9
Zn(NO ₃) ₂	0.22	69.3	10.4	6.8	6.9	1 ^o	5.6	22.5	2.7
ZnO	0.22	71.8	10.8	7.0	7.2	0.7 [■]	2.5	21.8	4.3

w/o + LiOH	0	73.1	11.0	7.2	7.3	1.4 [■]	0	21.5	4.4
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For the electrochemical evaluations, electrodes with a Si mass loading equal to $1.75 \text{ mg}_{\text{Si}}.\text{cm}^{-2}$ were used. The specific discharge capacity per cycle (mean and standard deviation results from multiple cell tests, see **Table S1**) is shown in **Figure 1a** for electrodes containing 0.22 and 0.66 equivalents of ZnSO_4 per carboxylic group (RCO_2H) (labeled ZnSO_4 (0.22) and ZnSO_4 (0.66), respectively) and the related zinc-free reference. Regardless of the formulation, the initial discharge capacities are higher than the theoretical capacity ($3580 \text{ mAh.g}_{\text{Si}}^{-1}$ considering the formation of $\text{Li}_{15}\text{Si}_4$). This excess capacity is of approximately 580, 520, and $330 \text{ mAh.g}_{\text{Si}}^{-1}$ for the reference, ZnSO_4 (0.22) and ZnSO_4 (0.66) electrodes, respectively. The graphene contribution is of approximately $50 \text{ mAh.g}_{\text{Si}}^{-1}$. This value is obtained by taking 350 mAh.g^{-1} as the capacity of xGnP15^{20,21} and considering only its faradic contribution. Based on a previous study,²¹ the contribution of the binder organic components is likely to be negligible. Specifically, no reduction peak at 1.6-1.7 V (vs. Li^+/Li^0), characteristic of the reduction of carboxylic acidic protons,^{22,23} is detected on the dQ/dV curves (**Figure S1**). Furthermore, the addition of ZnSO_4 does not lead to additional reduction peaks on these curves, indicating that the reduction of Zn(II) to Zn(0) does not occur, or only to a negligible extent. This is in full agreement with previous findings on Ni-Alg binder²⁴ and our own STEM-EDX analysis on Zn-CMC-CA binder,¹⁹ where no significant formation of metallic particles upon electroreduction was detected. As such, the contribution of the whole binder to the extra capacity can be neglected. On the other hand, from our recent ^7Li NMR quantifications,¹⁹ the amount of Li in the SEI (in the form of LiF , $\text{Li}_x\text{PO}_y\text{Fz}$ and other species) corresponds to an extra 345 and $373 \text{ mAh.g}_{\text{Si}}^{-1}$, for the ZnSO_4 (0.22) and its reference formulation, respectively (see equation (1) in the SI).¹⁹ Therefore, both in the presence and absence of Zn(II) , the electrolyte degradation is the major source of extra capacity. Interestingly, the latter is decreased for Zn-containing electrodes, in agreement with previous work which indicates that coordinated binder act, at least partially, as an artificial SEI.¹⁹

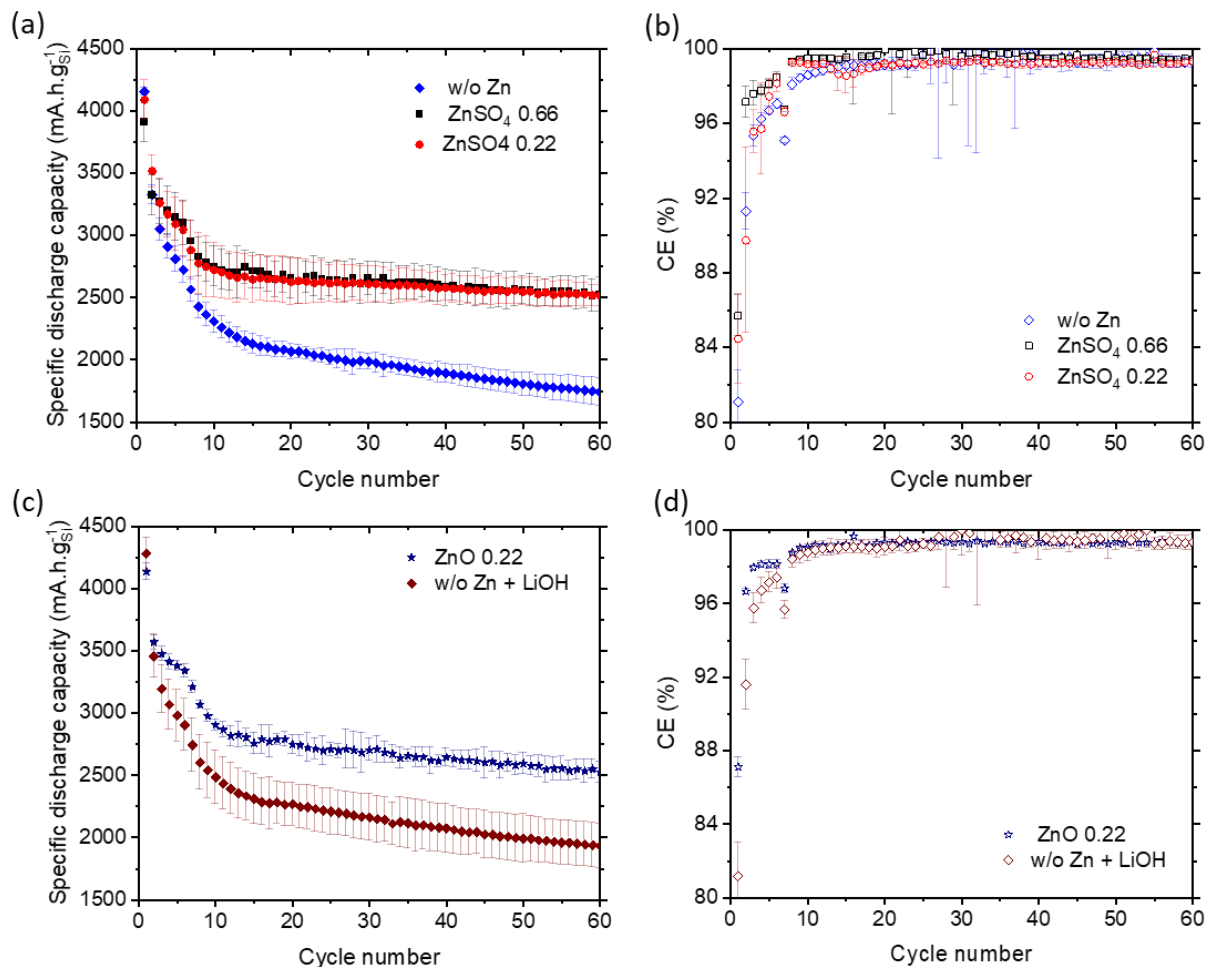


Figure 1. Evolution with cycling of the specific discharge capacities and CE for $1.75 \text{ mg}_{\text{Si}} \cdot \text{cm}^{-2}$ electrodes: (a, b) Formulations based on ZnSO_4 ; (c, d) Formulations based on ZnO . The C-rate was C/40 for the 1st cycle, C/20 for the next 5 cycles and C/10 for the subsequent cycles.

Both formulations containing ZnSO_4 perform similarly and are clearly superior to the reference with a discharge capacity of about 2520 vs. 1740 $\text{mAh} \cdot \text{g}_{\text{Si}}^{-1}$ at the 60th cycle. Moreover, the capacity loss rate is much more pronounced for the latter, which reaches approximately 9 vs. only 3 $\text{mAh} \cdot \text{g}_{\text{Si}}^{-1}$ per cycle for electrodes containing ZnSO_4 .

Figure 1b shows the coulombic efficiency (CE) of the three formulations at each cycle. For the first cycle, the CE are around 86, 85 and 81%, for the formulations corresponding to ZnSO_4 (0.66), ZnSO_4 (0.22) and no Zn, respectively. For the next 5 cycles (C/20 cycling), the ZnSO_4 (0.66) formulation presents a significantly better CE. Both reference and ZnSO_4 (0.22) formulation CE fluctuate and overlap. Finally, from about the 20th cycle on (cycling at C/10), the CE stabilizes at around 99.6, 99.2 and 99.4% for ZnSO_4 (0.66), ZnSO_4 (0.22) and no Zn, respectively. This corresponds to the period where the electrode capacity declines linearly with each cycle. Interestingly, the CE does not reflect the capacity

loss per cycle. Overall, the Zn(II)-rich ($\text{Zn}/\text{RCO}_2\text{H} = 0.66$) electrodes have a higher CE at each cycle. Unfortunately, that does not translate into a better discharge capacity retention. In the end, the electrochemical performance stagnates (or even decreases) after a certain level of cross-linking is reached. This is in agreement with our previous findings on Cu-CMC-CA binder¹⁵ as well as with the literature on covalently cross-linked binders.⁶

Figure 1c shows the specific discharge capacity per cycle (mean and standard deviation results from multiple cell tests, see **Table S1**), for the formulation containing ZnO (0.22) and the corresponding reference (prepared at a similar pH through the addition of LiOH). These electrodes have the same silicon loading as those in **Figure 1a**. Their initial capacity also exceeds the theoretical capacity by about 560 and 720 $\text{mAh.g}_{\text{Si}}^{-1}$ for the formulation containing ZnO and corresponding reference, respectively. Again, by examining the dQ/dV curves (**Figures S1**), the capacity associated with the reduction of the binder components are shown to be negligible in line with the absence of significant reduction peaks associated with protons from carboxylic acids and Zn(II). Using again ^7Li NMR, the amount of Li in the SEI was evaluated (see **Table S2**); it reaches 363 $\text{mAh.g}_{\text{Si}}^{-1}$ for the electrode containing ZnO (0.22), supporting the fact that the formation of the SEI is at the origin of this extra capacity. In fact, the main reduction peak(s) on the dQ/dV curves at 0.9-1.1 V (vs. Li^+/Li^0) seen for both formulations is associated with the reduction of FEC.^{22,25,26} Interestingly, this phenomenon is more intense for formulations without Zn, which confirms that the coordination with Zn increases the ability of the binder to act as an artificial passivation (SEI) layer.¹⁹

Like with ZnSO_4 , the ZnO formulation capacity retention is higher than its reference formulation with a discharge capacity of about 2530 vs. 1930 $\text{mAh.g}_{\text{Si}}^{-1}$ at the 60th cycle. The capacity loss by cycle is also higher for the latter, which reaches approximately 8 vs. 5.6 $\text{mAh.g}_{\text{Si}}^{-1}$ for ZnO-containing electrodes. The CE for the formulation containing ZnO and its reference are shown in **Figure 1d**. For the first cycle, the CE are about 87 and 81%, respectively. The latter formulation's CE remains lower until the 20th cycle, at which time it stabilizes at approximately 99.5 vs. 99.3% for ZnO-containing electrodes.

In sum, we confirmed that the straightforward addition of a Zn(II) precursor (whatever its nature, see also **Figure S2b** for the electrochemical performance with addition of $\text{Zn}(\text{NO}_3)_2$) to an aqueous CMC-CA formulation leads to a significant improvement of the electrochemical performance, notably to an improved CE and a better capacity retention. Consequently, Zn containing binders, inks, and electrodes were further studied with the aim of establishing relationships between their microscopic structures, macroscopic mechanical properties, and electrochemical performance.

Characterization in solution of binders and inks.

Figures 2a and **2b** show the viscosities as a function of the shear rate for the binder solutions ZnSO_4 (0.66), ZnSO_4 (0.22), and their reference, as well as the respective inks (*i.e.* containing also Si and graphene). The extensive rheological studies of NaCMC aqueous solutions by Lopez et al.^{27–33} is at the basis of our results analysis. The degree of substitution (D.S.), which represents the average number of sodium carboxylate groups per monomer, is an important parameter that dictates the solubility of NaCMC in water. In fact, the cellulose backbone is hydrophobic, whereas the carboxylate/ic groups are hydrophilic. In our case, the D.S. is equal to 0.9 (from supplier data), which is enough to solubilize the polymer. However, because it is inferior to 1, a significant monomer fraction is unsubstituted,²⁷ which might recur in large polymer segments without interruption, as the substitution is not homogenous. With increasing polymer concentration, inter-chain polymer interactions develop and result in hydrophobic behavior, leading to increased viscosity and eventually gelation.²⁸ This is particularly true for our formulations, as the NaCMC concentration is 83 mM (*i.e.* 19.5 g/L, approximately 2 w%) and the degree of polymerization reaches approximately 3000, such that our binder can be considered as a concentrated entangled NaCMC solution.²⁹ The addition of inorganic bases (here LiOH, NaOH or KOH) may help to solubilize the unsubstituted polymer blocks, reducing the hydrophobic behavior,^{28,34} but it typically requires higher concentrations than the ones used in the present study. For example, 7–10 w% of NaOH is required to dissolve cellulose³⁴ and 0.5 M NaOH was found to be insufficient to totally remove hydrophobic interactions for NaCMC with a D.S. around 0.8.³⁰

In a more general manner, the presence of salt has the effect of charge screening along the polymer chains. However, the distance up to which the polymer chain behave like a rigid rod,²⁷ *i.e.* the intrinsic persistence length, depends on the electrostatic contribution (among others).²⁹ While the electrostatic interactions are screened by salts,²⁸ the chain dimension evolves from rod-like to worm-like.^{28,29} As such, the solution viscosity decreases as the chain flexibility increases. It is also reported to reduce the solvent quality exponent³⁵ without influencing its entanglement properties.^{29,35} Even if divalent salts (here Zn(II) precursors) display increased ionic strength over monovalent ones, inducing a greater screening,³¹ the electrostatic interaction are most likely already screened for our formulations. In fact, at our NaCMC concentration the chains should be highly screened even in a salt free solution (*i.e.* not buffered), simply from the Na^+ concentration associated with NaCMC.³²

As shown in **Figure 2a**, the viscosity at 0.01 s^{-1} is significantly higher for the ZnSO_4 (0.22) formulation than for the Zn-free binder solution with around 300 vs. 60 Pa.s, respectively, both of which are higher than the 30 Pa.s of the Zn-rich binder (ZnSO_4 (0.66)). The increase in viscosity at low shear rate upon addition of Zn(II) could be due to electrostatic interaction (*i.e.* coordinative bridging) between the carboxylates groups and Zn(II) ions. At our given CMC concentration, the viscosity increase could reach up to an order of magnitude thanks to the interchain cross-linking.³³ Here, the value is lower,

probably because a significant part of Zn(II) ions are solely coordinated to CA, rather than to CMC. The viscosity decrease upon further addition of Zn(II) (*i.e.* for ZnSO₄ (0.66)) relates to a different phenomenon. Sharratt et al.³¹ showed that upon addition of a higher amount of a metallic salt to a solution of NaCMC, a transition from a monophasic to a biphasic solution occurs. In the case of Zn(II), CMC forms aggregates with an estimated diameter of 26 nm. Interestingly, this behavior was only found for divalent cations specifically interacting with CMC, such as Ca(II), Zn(II) and Ba(II), but not Mg(II).³¹ Based on the previously published data, at our given CMC concentration, slightly more than 40 mM of Zn(II) salt would be required for this transition (for a D.S. of approximately 1.3). In our study, we used a 2 to 6 times (Zn/RCO₂H = 0.22 and 0.66, respectively) higher concentration. For the latter, the binder solution is most likely in the biphasic state, with the polymer chain folding into aggregates with intra-chain Zn(II)-carboxylate interactions, leading to a lower viscosity. For the Zn-poor formulation (ZnSO₄ (0.22)), it is possible that the monophasic to biphasic boundary is not crossed, because a fraction of Zn(II) is interacting with CA instead of CMC. With increasing shear rate, the viscosity decreases due to chain alignment in the flow direction as well as disruption of inter-chain short contacts (due to hydrophobic interactions, coordination, and steric/entanglements). The higher ionic strength in the Zn-containing inks might then increase the CMC chains folding, which increases the attractive intra-chain interactions. This process might explain the fact that the Zn-free inks are more viscous than Zn-containing ones at high shear rate.

Figure 2b present the viscosity as a function of the shear rate for the binder containing ZnO (0.22) and its reference. In contrast to our finding with ZnSO₄, the viscosities of both formulations are almost identical. This is at a first sight surprising, but could be related to the pH of the solutions: at least from a thermodynamic viewpoint, cation-carboxylate complexes are stable in a given pH range but they can dissociate at pH higher than the pK_a of the carboxylic/carboxylate couple.³⁶ For the given formulations, the pH of the binder solution containing ZnSO₄ (*i.e.* 2.9) and ZnO (*i.e.* 4.3) are respectively, lower and higher than the pK_a of NaCMC ($\approx$ 3.4). Zn(II) might then interact to a lesser extent with the CMC carboxylate groups upon addition of ZnO than ZnSO₄, reducing the interchain cross-linking and therefore the viscosity. In these experimental conditions, *i.e.* with ZnO, most of the Zn(II) ions might then be more likely complexed by CA (in the form of molecular complexes), which presents higher second and third pK_as (4.76 and 6.40). We further attempted to investigate the carboxylates in solution for the ZnSO₄ and ZnO (0.22) binders by Raman spectroscopy (λ = 514.53 nm, dispersive Raman spectrometer coupled to a confocal microscope; Renishaw Invia). Unfortunately, almost no signal was recovered most likely due to the light diffusion in the viscous and slightly opaque/turbid binder solutions. Therefore, no information was retrieved.

The different rheological behaviors of the binder observed here show a complex interplay between pH, the presence of both salts/molecules, and divalent cations. These parameters also govern

the binder states at rest, as can be seen from the storage and loss modulus curves shown in **Figures S4a** and **S4b**. In fact, only the ZnSO_4 (0.22) binder behaves like a physical gel ($G' > G''$) and exhibits a small G'' overshoot above 20% strain, proving that the binder is cross-linked, which is also in line with the viscosity results.

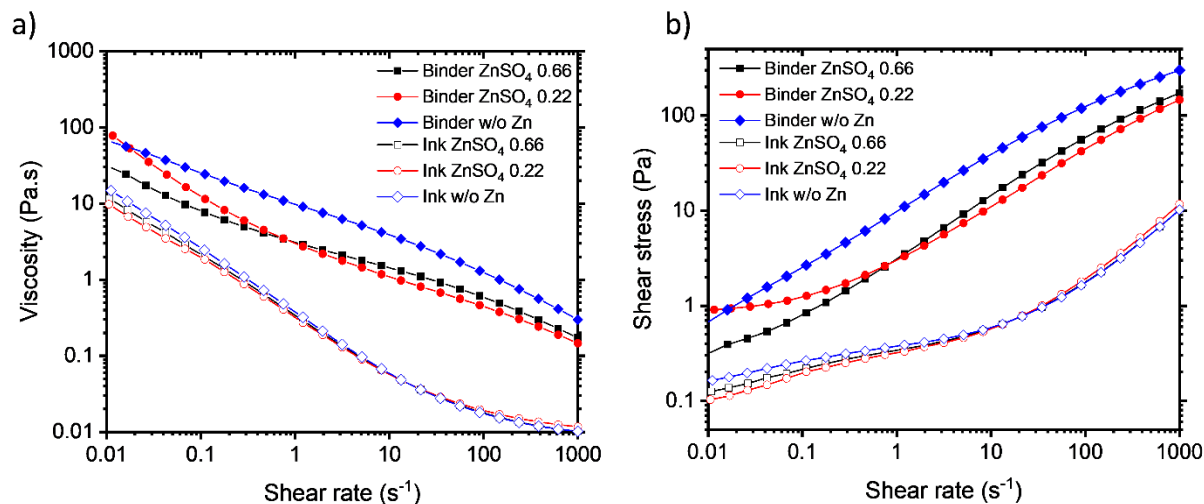


Figure 2. Viscosity as a function of shear rate of binder solutions and respective inks: (a) Solutions based on ZnSO_4 ; (b) Solutions based on ZnO .

The ink (binder solution with Si and graphene) viscosity was also studied (**Figures 2a** and **2b** for the inks containing ZnSO_4 and ZnO , respectively). All inks behave similarly, indicating that their viscosity seems insensitive to the binder composition. Hence, the solid fraction (especially of silicon and graphene) in the ink, which is the same for all formulations, seems to determine their rheology. During tape casting, the shear rate applied by the blade is equal to the tape casting speed divided by the blade gap. It is approximately 37 s^{-1} , for a $150 \mu\text{m}$ blade gap. The respective ink viscosity is 28 mPa.s^{-1} , which represents very little flow resistance. Nonetheless, at rest (equivalent to a low shear rate) the viscosity is enhanced, which is interesting for slurry stability during drying. For this latter step, the yield stress is a better indicator, as it is the necessary force to induce flow and hence represents the percolating network strength. It is usually extracted from the shear stress curves (**Figures S3**) by using for example a Herschel-Bulkley model fit. However, this method did not seem appropriate in our case, and the reader is referred to the SI and **Figure S3** for explanations. Therefore, the shear stress value at 0.01 s^{-1} was selected as the yield stress. Among the ZnSO_4 -based inks, it is approximately equal to 0.16, 0.10 and 0.13 Pa for Zn-free, ZnSO_4 (0.22) and ZnSO_4 (0.66), respectively. For the ZnO -based inks, it is equal to 0.19 and 0.17 Pa for Zn-free and ZnO (0.22), respectively. Overall, the yield stress is of the same order of magnitude for all formulations and remains fairly low (but consistent with the solid fraction used

here²⁰). These values are such that segregation or settling could occur over time if the ink drying is too fast or too slow, respectively.³⁷

Localized characterization in the solid state of binders and electrodes.

Figures 3 show the IR transmittance spectra of solid products obtained after drying the binder solutions at 100 °C (see the experimental section for details). For the ZnSO₄-containing binder (ZnSO₄ (0.22) and ZnSO₄ (0.66), **Figure 3a**), in order to prevent any overlap between the bands arising from the water (ν_{2b} bending mode of H₂O at approximately 1645 cm⁻¹³⁸) and carboxylic/carboxylate groups, solutions were formulated with D₂O instead of H₂O. For every composition, three bands are visible in the range 1300-1800 cm⁻¹: a first one at 1700-1715 cm⁻¹ associated to C=O vibrations of protonated carboxylic groups, and two other ones at 1570-1610 and 1370-1400 cm⁻¹ attributed to asymmetric and symmetric carboxylate vibrations, respectively. They clearly indicate that each binder contains both non-bonded carboxylic groups and carboxylate groups likely in interaction with the cations. The ν_{asym} and ν_{sym} peaks of the carboxylates are particularly broad, likely because they contain multiple contributions. This is clearly visible for Zn/RCO₂H = 0.22 and 0.66 and for Zn(NO₃)₂ (0.22) in **Figure S2a**. This is expected considering that the binders contain several cations (Na⁺, K⁺, Zn²⁺) and several types of carboxylic/ate groups arising both from CMC and CA. Their convolution causes this broadening and prevents any deep analysis for lack of resolution. Indeed, for simple compounds (*e.g.* model metal-carboxylates complexes), the difference $\Delta\nu_{asym}-\nu_{sym}$ can be used as a mean to propose a possible M-carboxylate coordination motif,^{39,40} but such an approach cannot be applied here. However, when compared to the reference formulation (Zn/RCO₂H = 0), the addition of ZnSO₄ induces a significant shift towards higher wavenumber of both the ν_{asym} (23 and 29 cm⁻¹ for ZnSO₄ (0.22) and ZnSO₄ (0.66), respectively) and ν_{sym} vibration bands (17 and 23 cm⁻¹ for ZnSO₄ (0.22) and ZnSO₄ (0.66), respectively). These shifts are indicative of the different environments for the carboxylate groups, in agreement with the formation of Zn(II)-carboxylate coordination bonds.

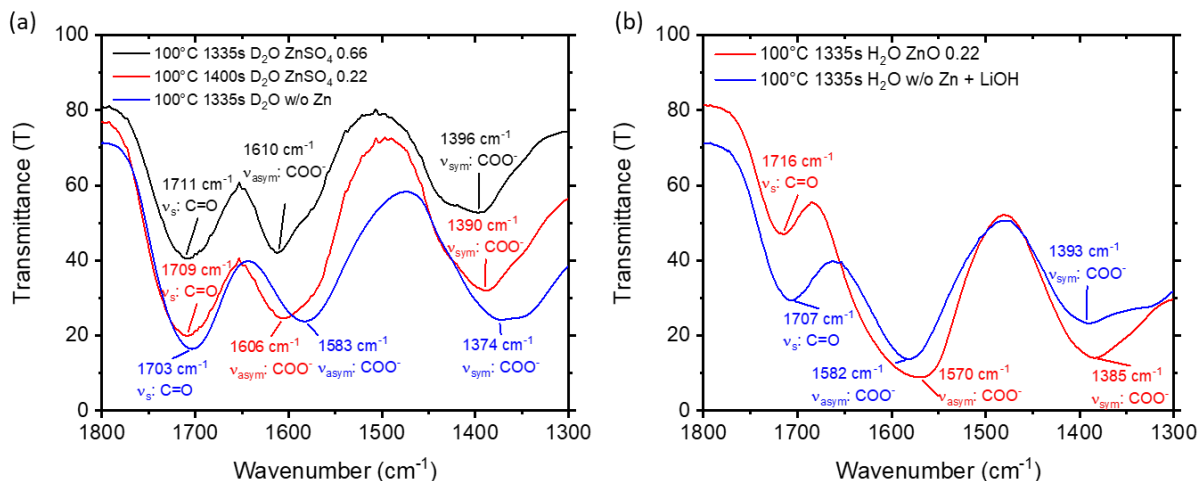


Figure 3. IR spectra of dried binders: (a) Solutions based on ZnSO_4 , which were prepared with deuterated water; (b) Solutions based on ZnO , which were prepared with ultra-pure water. The time stamp in each legend refers to the time at which the spectra was acquired, while the sample was still heated.

The same experiment was conducted for binders prepared with ZnO (0.22) and their reference, this time using H_2O (see **Figure 3b**). No H_2O ν_{2b} vibration band was clearly resolved, but the presence of the $2\nu_{2b}$ and ν_1 large bands above 3000 cm^{-1} (not shown) clearly indicates the presence of water in the samples.³⁸ Both the ν_{asym} and ν_{sym} were shifted upon addition of ZnO when compared to the Zn -free reference (-12 and -7 cm^{-1} , respectively), again in agreement with the presence of different local environments for the carboxylates and likely the formation of Zn(II) -carboxylate bonds. Nevertheless, whereas these bands were upshifted with ZnSO_4 , they are downshifted with ZnO . Furthermore, the values of $\Delta\nu_{\text{asym}}-\nu_{\text{sym}}$ are also different (191 and 186 cm^{-1} for Zn -free and ZnO (0.22), respectively). This suggests that the coordination modes might be different between both ZnSO_4 (0.22) and ZnO (0.22) formulations. This could arise either because different coordination motifs are favored depending on the pH, as suggested by rheological measurements (more Zn(II) -CA complexes and less Zn(II) -CMC ones with ZnO), or because the counter ion is different (SO_4^{2-} might still be interacting with Zn(II)). Alternatively, this difference could come from the variation of the number of protons surrounding the carboxylates with the pH.

It was not possible to carry out the same experiment for the binders in solution as only the signal of the solvent would be visible. Nonetheless, similar features were observed for the partially dried solutions (heated at 60°C , **Figure S5**), suggesting that the Zn -carboxylate coordination bonds already exist in the hydrated binder, hence supporting our interpretations of the rheological results.

In sum, these IR analyses suggest the presence of carboxylate- Zn(II) bonds in the solid, but no definitive information on the nature of the coordination motif and the origin of the carboxylate groups

(CMC and/or CA) was obtained. In an attempt to gain additional information, ^{17}O solid state NMR experiments were carried out. ^{17}O is a spin-5/2 quadrupolar nucleus having a low natural abundance (0.04%).⁴¹ ^{17}O NMR signals of carboxyl and carboxylate groups can spread over a wide chemical shift range and present large quadrupolar coupling constants. The ZnSO_4 (0.22), its reference and the ZnO (0.22) binders were prepared using $\approx 40\%$ ^{17}O enriched CA (enriched on carboxylic functions by adapting a previously published procedure).⁴² Thus, only the signal of carboxylic/ate groups from the CA molecules is expected to be visible on the ^{17}O NMR spectra (and not the CMC ones). The corresponding spectra are shown in **Figure S6** together with the ones of the ^{17}O -enriched CA and the Zn-citrate coordination polymer $\text{Zn}_3(\text{CA})_2(\text{H}_2\text{O})_2$ (prepared following a procedure published elsewhere⁴³). For pristine CA, signals with sharp and well-defined features are visible in the region characteristic of carboxylic acid groups, as is expected for a crystalline starting material. The line shapes reflect the effects of the second-order quadrupolar interaction, as ^{17}O is a spin 5/2 isotope. For the reference Zn-free electrode, a ^{17}O NMR signal is also seen, indicating the presence of labeled CA, as expected. However, in contrast to crystallized CA, this signal exhibits a clear asymmetry due to an electric field gradient distribution (which is associated with the quadrupolar interaction). This suggests that CA is present only in a disordered form in the binder, which may be indicative of its homogenous mixing with CMC. Upon addition of Zn(II) (whatever the precursor), again a signal characteristic of disordered carboxylate environments is detected. Nevertheless, while significant differences in ^{17}O signatures of CA could have been expected upon complexation of Zn(II) (as shown in **Figure S6a**, when comparing the ^{17}O NMR data of crystalline CA and $\text{Zn}_3(\text{CA})_2(\text{H}_2\text{O})_2$), the variations between the ^{17}O signatures of the binders (whether containing Zn(II) or not) were actually less pronounced, showing in all cases broad asymmetric line shapes with a maximum peak position at approximately 180 ppm at 11.7 T. Further analyses in another magnetic field would be needed to pinpoint the changes in chemical shift and quadrupolar parameters upon complexation and try to extract information regarding the nature of the CA cation-carboxylate interactions. Nevertheless, and importantly, these preliminary ^{17}O NMR experiments tend to suggest a homogeneous distribution of the CA inside the binder (with or without addition of Zn(II)), leading to a distribution in local carboxylic/carboxylate environments.

Electrode preparation requires intensive mixing and drying steps which could have an impact on the materials distribution. Therefore, binder coordination was also evaluated in the electrode conditions by ^1H - ^{13}C CP-MAS-NMR. The analysis was performed on binders mixed with silicon (in the same quantities as for electrodes), but without graphene to avoid signal masking. Four formulations were considered: the formulations containing ZnSO_4 (0.22) and ZnO (0.22), and their respective references. The corresponding spectra are presented in **Figure S7a**. For each composition, all the signals characteristic of the CA and CMC were detected as expected. The signals centered

at approximately 170-180 ppm are of particular interest as they correspond to the carboxylic/ate groups and thus are a priori sensitive to the formation of coordination bonds.⁴⁴ As a matter of fact, for all electrodes, a broad and unresolved signal centered at 180 ppm was detected which showed variations in peak maximum position and line width depending on the binder composition. This suggests changes in protonation state and/or cations bonded to the carboxylic/carboxylate functions between the different electrodes. Indeed, the ¹³C NMR analysis of reference molecular compounds (NaCMC, CA, Na₃CA and Zn₃(CA)₂, **Figure S7d**) indicates that the signal shift related to the carboxylates can reach 3-8 ppm upon complexation of metal cations. Here, the ¹³C peak maxima of the more acidic electrode formulations were on average at lower chemical shifts compared to those of the more basic formulations (see discussion related to **Figure S7** in the SI). A more systematic investigations on the Zn(II) quantity influence and the degree of protonation of carboxylic/carboxylate groups in these systems would be needed to go further in the interpretation of these ¹³C NMR results, though this is beyond the scope of the present work.

None of the spectroscopic techniques described above lead to a clear conclusion regarding the relative involvement of CA and CMC in the coordination network. One could argue that CA, having 3 carboxylic/ate groups, should interact more strongly with Zn(II) than CMC, and hence CA-Zn bonds are more favorably formed than CMC-Zn bonds. The relative amount of CA-Zn and CMC-Zn bonds might also vary between the different formulations, as it seems to be multifactorial (pH, Zn(II) precursor, concentration). Rheological studies showed that Zn(II) cations, which are preferentially interacting with carboxylate groups,^{31,33} do not always lead to CMC inter-chains crosslinking in solution (through coordination bonds). Therefore, this raises questions on the possible predominance of one type of coordination bond vs. the other and its relationship with the electrochemical performance enhancements. We attempted to answer these questions by replacing CA in the binder solution by piperazine-N,N'-bis(3-propanesulfonic acid) (PIPPS), which has a similar first pK_{a1} (≈ 3.7 vs. 3.1 for CA) but is less complexing (it is indeed commonly used to prepare non-complexing buffer in biochemistry). Electrodes were prepared both with and without ZnSO₄. The correspondings specific discharge capacity and coulombic efficiency are shown in **Figures S8a** and **S8b**, respectively. In the absence of Zn(II), the specific capacity dropped down within very few cycles ($< 500 \text{ mAh g}^{-1}$ after 10 cycles). In the presence of Zn(II), the capacity retention is far better, with a specific capacity still above 1000 mAh g^{-1} after 50 cycles. As Zn(II) should predominantly interact with CMC in the latter formulation, this experiment is evidence of the direct relationship between the formation of Zn-CMC bonds (and therefore probably of extended coordination network) and the capacity retention improvement. However, the capacity is still lower than the one observed for the formulation containing CA instead of CMC (see **Figures 1a** and **1b**). This indicates that CA also has a pivotal role, for example acting as a co-

ligand in the coordination network and/or as an artificial passivation layer on Si, as was already reported by Lucht et al.^{45,46}

Characterization of the mechanical properties of the electrodes at the macro and microscopic scales.

The electrode mechanical properties were studied in order to evaluate the benefit associated with the presence of coordinated binder. First, scratch tests allow the evaluation of both cohesion and adhesion strengths (see SI and **Figure S9** for details). The critical scratch load as a function of the electrode silicon loading for every formulation is shown in **Figure 4**. It corresponds to the load upon which the current collector is visible at the bottom of the scratch (see an example in **Figure S9**). As expected, whatever the formulation, the critical load increases with the silicon loading, hence the quantity of matter plowed.⁴⁷

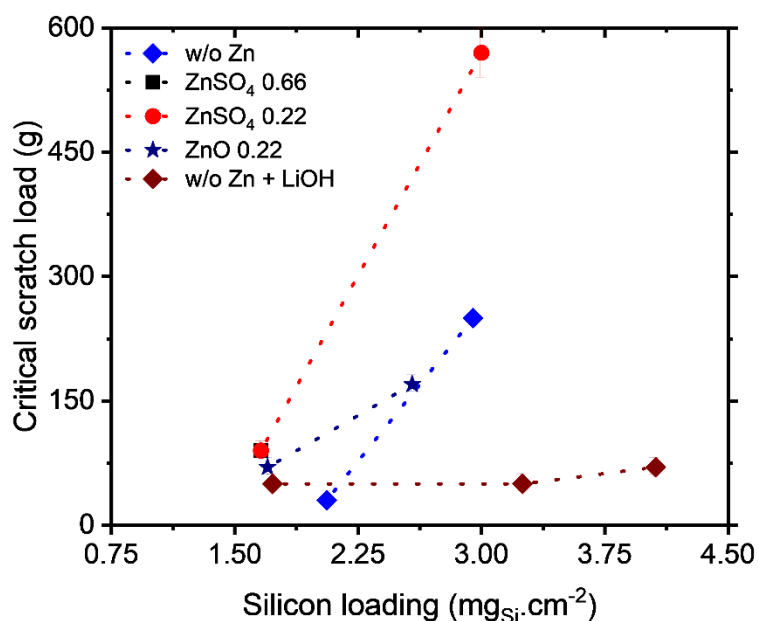


Figure 4. Critical scratch load as a function of the silicon loading of the different binder electrode coatings.

The trend between coordinated binders and their respective references is clear. Whatever the Zn(II) precursor, all coordinated binders have higher critical scratch load than their non-reticulated reference over the whole loading range tested. For example, at approximately 1.7 mg_{Si}·cm⁻² (corresponding to the electrodes used for the electrochemical studies), the critical load is 40% higher for the ZnO (0.22) containing coating than for its reference. Thus, binder Zn-carboxylate coordination enhances both adhesion and cohesion strengths.

The effect of the amount of cation was also evaluated with ZnSO_4 . Again, for a loading corresponding to the electrodes used in the present study, both the Zn(II)-poor (ZnSO_4 (0.22)) and Zn(II)-rich (ZnSO_4 (0.66)) electrodes present an identical critical load. This is in agreement with the absence of major differences in their electrochemical behavior (see **Figure 1**). In fact, for binders cross-linked through covalent bonds, an excess of the reticulation degree can produce an opposite effect on the mechanical properties, decreasing tensile strength as well as elasticity.⁶

If one compares the Zn precursors (at $\text{Zn}/\text{RCO}_2\text{H} = 0.22$) at a given silicon loading, the electrodes formulated with ZnO present lower critical loads than the ones formulated with ZnSO_4 . Three phenomena can explain this lower adhesion/cohesion, and all rely on the pH of the ink (2.9 and 4.3 for ZnSO_4 and ZnO, respectively). First, a lower level of coordination cross-linking of the CMC chains can be expected (see the discussion above). Second, the binder is bonded to the silicon surface through either weak hydrogen bonds, or strong silyl-ester covalent bonds (formed upon drying). The former happens between carboxylic acid and silanol and the latter comes from their condensation reaction which occurs upon drying the electrode.^{15,48,49} The formation of silyl-ester bonds is favored at acidic pH.⁵⁰ Hence, a lower ratio of strong silyl-ester bonds to weak hydrogen bonds (if any) is expected in the formulation based of ZnO than ZnSO_4 . Third, the copper current collector corrosion is also favored at $\text{pH} \approx 3$.^{15,21} This induces the formation of strong Cu(II)-carboxylates bonds between the binder and the current collector and throughout the whole electrode.¹⁴ At $\text{pH} \approx 5$, Roland et al⁵¹ did not found any dent in the copper. There is only a scarce presence of copper (as Cu-carboxylate) through the electrode thickness, which anyway, reveal a slight current collector corrosion. Overall, the three mechanisms explain the lower adhesion and cohesion of the formulation containing ZnO than the one containing ZnSO_4 .

Nano-indentation experiments were further used to determine the electrode hardness and elastic modulus, both in the dry state and wetted with propylene carbonate solvent (the latter is easier to handle than the LP30 + 10_w% FEC electrolyte). Studies were also conducted by micro-indentation, which gave similar results, although impacted by the current collector mechanical properties and the reduced porosity (see SI and **Table S4** for details). **Table 3** presents the hardness and elastic modulus obtained for the electrodes containing ZnSO_4 (0.22) and the corresponding reference. Typical hardness and elastic modulus depth profile are available in **Figure S10**. Again, both electrodes have similar active mass loadings, which are also relevant compared to the $1.75 \pm 0.1 \text{ mg}_{\text{Si}}.\text{cm}^{-2}$ electrodes selected for electrochemistry. However, their porosities are quite different, with 56.6 vs. 66.2% for the electrode with and without ZnSO_4 , respectively. Specifically, these values are slightly lower (for the former) and higher (for the latter) than their cycled counter parts (see **Table S1**), though in the same range as the ones found for the other electrodes. It is difficult to quantify the impact of the porosity on the mechanical properties. Qualitatively, both the compressive elastic modulus and the hardness are expected to decrease with porosity. However, the relationship is not linear, and two stages are

succeeding. In the first, the porosity is high, and the indenter will densify the electrode by deforming the matrix. In the second, the porosity is low, and the electrode is already compact, thus the indenter will deform the silicon and graphene particles (because they represent a higher volume fraction than the binder). At this stage, hardness and elastic modulus dependence on porosity is at its highest.⁵² In our case, the electrodes are mostly porous, so the impact of their porosity difference should be minimal. Looking at the results, in the dry state, the hardness and elastic modulus of the electrode containing ZnSO₄ are about 2 and 1.5 times higher than the reference electrode ones, respectively. This confirms that the binder Zn-carboxylate reticulation significantly enhances the coating cohesion strength. It is interesting to see that Cuauhtémoc et al.¹⁴ found a similar magnitude of improvement with a formulation equivalent to Cu-CMC-CA, although using micro-indentation, whose differences with nano-indentation are explained in the discussion associated to **Table S4**.

Table 2. Mechanical properties assessed by nano-indentation of a ZnSO₄ (0.22) and its reference electrodes, in both the dry state and soaked in propylene carbonate.

<i>Salt</i>	<i>Coord. Ratio</i>	<i>Film condition</i>	<i>Active mass loading (mg_{Si}.cm⁻²)</i>	<i>Porosity (v%)</i>	<i>Hardness (Mpa)</i>	<i>Elastic modulus (Gpa)</i>
w/o Zn	0	dry	1.93	66.2	25 – 45	1.5 – 2.5
w/o Zn	0	electrolyte	1.93	66.2	15 – 20	1 – 1.5
ZnSO ₄	0.22	dry	1.86	56.6	50 – 60	3 – 4.5
ZnSO ₄	0.22	electrolyte	1.86	56.6	50 – 65	3 – 4.5

When soaked in propylene carbonate (to mimic the electrolyte), only the reference electrode showed reduced mechanical performance. Wang et al. already reported this behavior for silicon electrodes formulated with NaCMC (and other binders).⁵² It is known that NaCMC can uptake around 10 to 20_w% of carbonate based electrolyte.^{53,54} Such an uptake should induce a rather small swelling,⁵⁵ but it appears sufficient to reduce the electrode mechanical properties. Remarkably, for the electrode containing ZnSO₄, the hardness and elastic modulus remain nearly unchanged after electrolyte soaking. They are approximately 3 times higher than the standard electrode in this state. The fact that the mechanical properties are nearly insensitive to the electrolyte means that, upon binder reticulation, its electrolyte uptake and successive swelling decrease. This effect could arise from the immobilization of polymer segments, which is expected for chemically cross-linked binders.⁶ Such a reduced uptake was already reported by few groups for Ca(II)-Alg reticulated binders,^{9,13} although opposite behaviors were

also measured.¹⁰ Eventually, the binder reticulation through coordination bonds not only improves the mechanical property of the pristine electrode in the dry state, but also preserves them in presence of a carbonate solvent. Then, the question arises: how is this improvement going to impact the electrodes mechanical properties during lithiation/delithiation? To answer this question, *operando* dilatometry experiments were carried out.

Characterization of the electrode mechanical properties from operando dilatometry

Figures 5a and **5b** show the thickness variation of a ZnSO₄ (0.22) electrode and its Zn-free reference, respectively. Both electrodes were cycled under galvanostatic conditions at a C/40 rate. The first one was duplicated in order to evaluate the experiment reproducibility (see **Figure S11b**). Their silicon loading is around 2 mg_{Si}.cm⁻², *i.e.* similar to the one used for electrochemical cycling. A 120 µm thick current collector was used to avoid any bending of the electrodes upon the dilatometry measurements, as was observed with the standard 20 µm thick one (not shown). This bending likely comes from the lower pressure applied on the working electrode inside the dilatometry electrochemical cell compared to the standard Swagelok cells (1.3⁵⁶ vs. 15.9 N, *i.e.* approximately 17 vs. 202 kPa). This lower pressure is also known to reduce the overall electrochemical performance obtained with the dilatometry cell.^{56,57} The discharge capacity was limited to 1200 mAh.g_{Si}⁻¹ since it was not possible to cycle the Zn-free reference electrode at full capacity. It was only possible to do so for the electrode containing ZnSO₄ (see **Figure S11a**). Nonetheless, at full or limited capacity, the cycling performance of both formulations was rather poor compared to standard Swagelok cells (see **Table S1**). Therefore, only the first cycle is discussed.

The results are clear: while for the reference electrode the expansion reaches 224% at the end of the first 1200 mAh g⁻¹ discharge, it is limited to 67% for the electrode containing ZnSO₄. This confirms the great ability of the Zn cross-linked CMC/CA binder to limit the lithiation-induced volume expansion of the composite electrode.

Considering that the volume increase arises exclusively from the expansion of Si upon lithiation, it is possible to compare the theoretical and experimental volume expansion using the following equation:

$$\Delta V_{el} = \omega_{Si} \frac{\rho_{app}}{\rho_{Si}} \frac{\Delta V_{Si}}{(1-\varepsilon_0)} = \varepsilon_{Si} \frac{\Delta V_{Si}}{(1-\varepsilon_0)} \quad (1)^{56}$$

where ΔV_{el} stands for the electrode volume expansion (%); ω_{Si} is the silicon mass fraction in the electrode; ρ_{exp} is the apparent electrode density at the pristine state; ρ_{Si} is the true silicon density (2.33 g.cm⁻³); ΔV_{Si} is the intrinsic volume expansion of the Li_{3.75}Si phase and is equal to 280%,⁵⁸ and ε_0 is the pristine electrode porosity; ε_0 and ε_{Si} are the pores and silicon volume fraction, respectively. The reader is referred to **Table S5** for the parameter values of the different electrodes. By taking the

term $(1-\varepsilon_0)$, we consider that the volume expansion of Si is not buffered by the electrode porosity (*i.e.* the pores volume expand by the same factor that the Si particles).⁵⁹

Equation (1) was modified to make it discharge (lithiation) time-dependent:

$$\Delta V_{el} = \omega_{Si} \frac{\rho_{app}}{\rho_{Si}} \frac{\Delta V_{Si}}{(1-\varepsilon_0)} \frac{\Delta t}{t} \quad (2)$$

where Δt stands for the experimental discharge time (h); t is the corresponding C-rate time for a complete discharge and is equal to 40 h in the present case as the C-rate is C/40.

The thickness is a 1D parameter whereas volume is a 3D parameter. However, the electrode expansion/contraction only occurs in the out-of-plane direction since the in-plane expansion is prevented by the fixed dimensions of the Cu substrate. It can thus be assumed that the measured variation of the electrode thickness is equivalent to its volume variation.

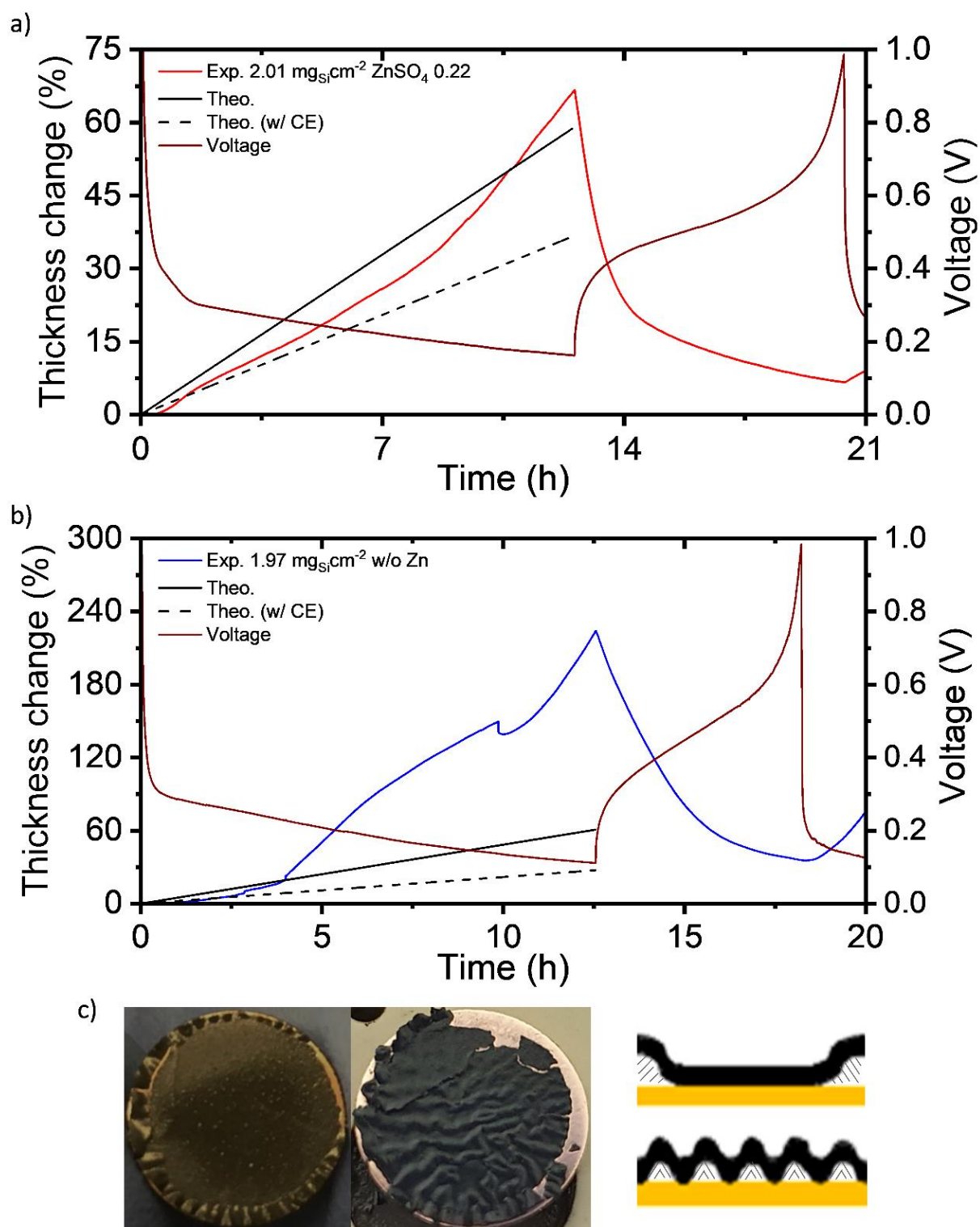


Figure 5. Experimental and theoretical thickness variation and voltage as a function of time (with a discharge capacity limited at $1200 \text{ mAh.g}_{\text{Si}}^{-1}$): (a) Electrode containing ZnSO_4 (0.22); (b) Zn-free reference electrode; (c) Postmortem electrode pictures (left: containing ZnSO_4 , right: without Zn(II)) and schematic representation of their buckling (top: containing ZnSO_4 , bottom: Zn-free), not to scale.

For the electrode containing ZnSO_4 , the theoretical thickness expansion (red dashed line in **Figure 5a**) is in accordance with the experimental one, at least regarding the maximum expansion (63% vs. 67%) measured at a discharge capacity of $1200 \text{ mAh g}^{-1}_{\text{Si}}$. This is also true for its duplicate shown in **Figure S11b**. On the other hand, when the electrode is cycled at full capacity (**Figure S11a**), its maximum expansion is higher than expected from the theoretical curve (268% vs. 188% at the end of the full discharge). This suggests that some changes occur in the electrode architecture, which are not considered in the theoretical calculation. Moreover, the thickness does not increase linearly with the discharge time. This point will be discussed later. Another dead angle is the lithium lost in SEI etc..., which do not participate in silicon lithiation and reduce the overall electrode expansion. To evaluate its incidence the theoretical thickness expansion multiplied by the CE (as a fraction) was computed (see dashed line, **Figure 5 and S11**). Unfortunately, the electrode mechanical degradation (among others) will also be reflected in the CE. As such, the theoretical thickness expansion taking into account the CE can be seen as a lower limit. Only the experimental thickness variation of the ZnSO_4 (0.22) electrode duplicate (**Figure S11b**) was bounded by the theoretical expansions, likely thanks to both lowest silicon loading and limited cycling.

For the Zn-free reference electrode (**Figure 5b**), the thickness variation is far higher than expected from its theoretical curve and compared to the Zn(II) formulation. This is probably due to the electrode buckling, as shown on the postmortem picture of the electrode (see right image in **Figure 5c**). Note that in the ZnSO_4 electrode case, the buckling is also observed but only on the electrode circumference (see left image in **Figure 5c**). Thus, its impact on the dilatometric response must be much less important. The thickness drop observed at around 10 h (equivalent to $\sim 960 \text{ mAh g}^{-1}_{\text{Si}}$) most likely comes from the electrode structure collapse. Since the electrode without Zn(II) failed massively, it is difficult to compare the thickness variation for both formulations. However, this is additional proof that reference electrodes are mechanically weak compared to the reticulated ones. Nevertheless, it is interesting to investigate the failure mechanism.

Buckling of a coating is caused by a high compressive growth stress in combination with insufficient coating adhesion.^{60,61} Therefore, the mechanical degradation (buckling) occurred during lithiation in dilatometric cell. This is at the opposite of crack formation which happen upon delithiation.^{60,61} Interestingly, electrodes used in dilatometry suffered of buckling and most likely of cracking, whereas only the latter happened for electrodes cycled in Swagelok cells. This means that the pressure applied on the Si electrode upon cycling (12 times lower in dilatometric cell than in Swagelok cell as previously stated) has a major impact on its mechanical behavior and thus on its electrochemical performance. Buckling will not be discussed extensively as it is not the standard mechanical failure mechanism of electrodes, but details can be found in ref. ⁶⁰. Nonetheless, applying the one dimensional

blister theory, the critical stress σ_c required for the film to buckle can be calculated.^{60,61} Namely, the following proportional relationship holds:

$$\sigma_c \propto E(h/b)^2 \quad (3)$$

where E is the film elastic modulus (GPa); h is the electrode coating thickness (μm), and b is the half of the blister delaminated width (μm). The blister dimension b was measured on **Figure 5c** and is equal to 278 ± 22 and 271 ± 22 μm (on an average of 6 measurements), for the Zn-free and ZnSO_4 (0.22) electrode, respectively. Wet E values presented in **Table 2** were used together with the film thickness of 27.75 and 36.5 μm for the Zn-free and ZnSO_4 (0.22) electrode, respectively. The critical stress is approximately 6 times higher for the Zn(II) containing electrode, confirming again its superior mechanical properties. Equation (3) holds if $h \ll b$, which is reasonable in our case. Fully applying the critical stress formula^{60,61} yields a value of 11 and 62 MPa for the Zn-free and ZnSO_4 (0.22) electrode, respectively. Thus, tens of MPa should be a lower limit estimation of the developed stress in our electrodes.

Silicon volume expansion follows the Vegard's law⁶² such that it increases linearly with the alloying lithium content. Thus, one can expect the volume expansion of electrode to be linear with the discharge time as shown from the theoretical expansion curves (red dashed lines on **Figures 5 and S11**). However, none of the electrodes follows this trend. Several factors might explain this behavior:

- Although the main part of the lithium incorporated in the electrode part alloys with silicon, a significant fraction is involved in the SEI formation and in the graphene lithiation. This affects the kinetics of the electrode expansion, which depends on the amount of lithium reacting with silicon/graphene/SEI, all of them having different expansion coefficients. It also means that the electrode expansion kinetics might evolve with time (with periods of either acceleration or deceleration). For instance, as seen in **Figure 5a-b**, no thickness change is observed during the first ~40 min of discharge, *i.e.* at a potential higher than ~0.4 V, where SEI formation mainly occurs and not Si lithiation.
- Deformation (elastic or plastic, rupture) of the electrode constitutive elements (silicon, graphene, binder and SEI) is also expected.
- The electrode porosity and its evolution with cycling can impact on the electrode thickness variation.⁵⁶ Actually, the volumetric expansion of the SiLi_x particles can be partially buffered by the electrode porosity, especially at low discharge capacities, which is not considered for the theoretical thickness expansion curve. On the other hand, as seen in **Figure 5a**, from about 8.5 h of discharge (equivalent to ~820 $\text{mAh g}^{-1}_{\text{Si}}$), a significant increase of the expansion rate (curve slope) is observed, which may indicate that the electrode porosity becomes ineffective in accommodating the volume expansion of the SiLi_x particles. This can be due to their larger size in comparison with the electrode pore size so they impinge on each other.⁶³ This could then induce a rearrangement of the position of the SiLi_x particles in the

vertical direction, accentuating the electrode thickness expansion.⁵⁶ This rearrangement is larger when the electrode is cycled at full capacity, resulting in an expansion higher than expected from the theoretical curve (**Figure S11a**).

Upon delithiation, every electrodes contract, but the behavior is also non-linear. The factors mentioned for the lithiation hold true for the delithiation (including the SEI, which is also electrochemically evolving during delithiation⁶⁴).

Focusing exclusively on the electrodes containing ZnSO₄, an irreversible thickness variation can be observed at the end of the delithiation. This behavior has been systematically observed in *operando* dilatometry^{56,57,63,65–68} and is usually attributed to an incomplete silicon delithiation because of the electrical disconnection of some Si particles and/or an irreversible plastic deformation of the electrode.^{56,57,65} However, it is very difficult to evaluate the relative significance of both mechanisms. It can also be noted that for the full-capacity cycled electrode, a higher irreversible expansion is observed at the end of the first charge compared to the electrode cycled at 1200 mAh g⁻¹ (67% vs. 7%), which means that the Si particles do not come back to their initial position and that irreversible changes in the electrode architecture have occurred.

In sum, the electrodes containing Zn(II) present improved mechanical properties compared to their reference counterparts. This translates into enhanced adhesion and cohesion of the electrode coating, higher hardness and elastic modulus both in the dry state and when soaked in carbonates, and reduced expansion upon electrochemical cycling. This is very likely related to the formation of a reticulated coordination network. However, these coordination compounds also affect the SEI formation. Through a deep STEM-EDX study on similar electrodes prepared with ZnSO₄, we recently showed that the coordination compounds (comprising Zn, alkaline ions and the organic carboxylates) cover a significant Si particles fraction in the pristine state. After one electrochemical cycle and degradation of the LP30 + 10 w% FEC electrolyte, elements participating to the SEI (particularly the inorganic F and P elements) are not found in these regions, suggesting that the coordination binder also act as an artificial SEI.¹⁹ Similar STEM-EDX analyses were carried out on the electrode prepared with ZnO and lead to the same conclusion. As shown **Figure S12** in the pristine electrode, all elements involved in the coordination binder phase (Zn, Na, O, C) are well dispersed. After one cycle (**Figure S13**), the coordination binder elements constitutive are still present on all Si particles, but the richer area contain very little SEI characteristic elements, while the poorer area contain a larger amount of them (*e.g.* see the central part of the Si particle located in the image bottom part).

CONCLUSION

The straightforward addition of Zn(II) precursors to a well-established formulation of Si electrodes leads to a significant improvement of their electrochemical performance, notably the capacity retention. Spectroscopic investigations are in line with the formation of Zn-carboxylate coordination bonds, although the complexity of the formulations (comprising different cations: Zn, Na, K and complexing molecules: CMC, CA) prevents a precise description of the coordination motifs at play. Nevertheless, a controlled electrochemical study showed that each component (CA, CMC, Zn) is essential to reach a decent cyclability, suggesting the formation of complex, likely reticulated coordination compounds. Such coordination bonds profoundly affect the electrode mechanical properties in terms of adhesion to the current collector, cohesion, hardness, and elasticity, and ultimately lead to a reduced expansion of the electrodes during electrochemical cycling and improved toughness. Eventually, the beneficial effect of the coordination compounds on the electrochemical performance likely arises from both the electrodes mechanical strengthening and the formation of an artificial SEI at the surface of the Si particles. Considering the versatility offered by coordination chemistry, there is likely plenty of room to modulate the formulations composition and optimize the electrochemical performance. One issue will probably be to achieve a proper description of the resulting coordination network, both in the pristine state and upon cycling. The identification of simpler model formulations will help to address this issue.

EXPERIMENTAL SECTION

Material preparation

Binder solutions

First, a pH 3 buffer solution (0.171 M of citric acid + 0.084 M of KOH/NaOH) was prepared by dissolving citric acid (99%; Sigma-Aldrich) and KOH or NaOH salt (> 98%; Sigma-Aldrich) in ultra-pure water. Then, 5 mL of buffer plus the volume of ultra-pure water needed to reach 8.2 mL of solution was used to dissolve 160 mg of NaCMC ($M_w \approx 700\,000\text{ g}\cdot\text{mol}^{-1}$, D.S. 0.9; Sigma-Aldrich). The as-obtained solution was the reference binder ($\text{Zn}/\text{RCO}_2\text{H} = 0$). Finally, upon NaCMC complete and homogeneous dissolution, the Zn(II) precursor was added all at once, and left until homogenization. For the reference containing LiOH, LiOH•H₂O ($\geq 98\%$; Sigma-Aldrich) was also added all at once. For every step, solutions were magnetically stirred at room temperature. The water coming from the Zn(II) salts was taken into account to reach the final volume of binder solution (8.2 mL), whereas the approximately 15 % ad/absorbed water in NaCMC was not taken into account.

For this study, different precursors of Zn(II) were used: ZnSO₄•7H₂O (Pure cryst.; Alfa Aesar), (99.99%; Alfa Aesar), ZnO (99.99%; Alfa Aesar) and Zn(NO₃)₂•6H₂O (98%; Alfa Aesar). Their quantity was adjusted to reach a predefined theoretical molar coordination ratio:

$$\text{Coordination ratio} = \frac{n_{\text{Zn}}}{n_{\text{COOH(citric acid+CMC)}}} \quad (4)$$

Note that 0.9 and 3 COOH are considered per CMC monomer and CA molecule, respectively (the molecules scheme is available in **Figure S7e**). Another buffer molecule which is not complexing towards metals was also used instead of citric acid, namely piperazine-N,N'-bis(3-propanesulfonic acid) (≥ 97%; Millipore).

Electrodes

The Si powder used as active material was obtained by ball-milling commercial Si powder (325 mesh, 99.96%; Materion) using a HD-01 attritor (Union Process). The milling was performed under argon atmosphere for 20 h at 600 rpm with a ball-to-powder mass ratio of 10:1. The as-milled Si powder was composed of micrometric agglomerates as primary particles ($d_{50} \approx 10 \mu\text{m}$, $S_{\text{BET}} \approx 20 \text{ m}^2.\text{g}^{-1}$) and secondary particles were under 1 micron. The oxygen content determined by a LECO analyzer was approximately 1 w%.

160 mg of Si powder, 24 mg of graphene platelets used as conductive additive (xGnP M15 grade from XGSciences, average thickness $\approx 7 \text{ nm}$, average diameter = $15 \mu\text{m}$, surface area $\approx 120\text{-}150 \text{ m}^2.\text{g}^{-1}$, according to supplier data) and 0.8 mL of binder solution (by weight) were set in a vial with three balls ($d = 9.5 \text{ mm}$), both made of silicon nitride. The whole was mixed using a Pulverisette 7 (Fritsch) planetary mixer for 1 h at 500 rpm. Then, the as-prepared ink was tape casted with a doctor blade on a Cu foil (99.9%, thickness $\approx 20 \mu\text{m}$, cold rolled; PI-KEM). The blade gap was $h = 150 \mu\text{m}$ (model 3540, $s = 5.6 \text{ mm.s}^{-1}$; Elcometer). As-prepared films were dried at room temperature for 12 h. Finally, electrodes were punched (diam. = 1 cm) and dried 2 h at 100°C under vacuum ($P \approx 10 \text{ mbar}$), prior to mass ($\Delta m = \pm 0.01 \text{ mg}$; OHAUS), and their thicknesses ($\Delta e = \pm 1 \mu\text{m}$; Mitutoyo) were measured. Then, they were dried again for 1 h under the same conditions prior to assembly. Electrodes were selected if their active mass loading reached $1.75 \pm 0.1 \text{ mg}_{\text{Si}}.\text{cm}^{-2}$. Other silicon loadings were also targeted for specific characterization such as scratch tests and STEM-EDX analysis. For the latter, electrodes with a silicon loading equal to $1.0 \pm 0.1 \text{ mg}_{\text{Si}}.\text{cm}^{-2}$ were prepared following the same protocol (blade gap was $h = 100 \mu\text{m}$ model 3540, $s = 5.6 \text{ mm.s}^{-1}$; Elcometer).

Material characterization

Electrochemistry

Electrodes were assembled in Swagelok cells in Ar filled glove box (O_2 and $H_2O < 1$ ppm) in half-cell configuration. A metallic Li disc (diam. = 10 mm, thickness = 380 μm , 99.9%; Aldrich) placed on a Cu current collector (diam. = 12 mm, thickness = 250 μm) served as both counter and reference electrodes. Two layers of glass microfiber membranes were used as separator (grade GF/D, diam. = 13 mm, thickness = 670 μm ; Whatman). An extra monolayer of polypropylene (PP) separator in contact with the Si electrode (grade 2500, d = 13 mm; Celgard) was used for every electrode subjected to post-mortem analysis. As such, electrodes were protected from fiber inclusion coming from GF/D separators. The separator layers were soaked with 300 μL of electrolyte made of 1 M $LiPF_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v:v) plus 10 w% of fluoroethylene carbonate (FEC) (99.9%; Solvionic). Si electrodes were used for the cycling tests performed at room temperature using a multichannel VMP system (Biologic) in galvanostatic mode between 0.005 to 1 V (vs. Li^+/Li^0). The C-rate was C/40 for the 1st cycle, C/20 for the next 5 cycles and C/10 for the subsequent cycles ($1C = 3820 \text{ mA.g}_{Si}^{-1}$). Prior to cycling, cells were rested 2 h at open circuit voltage (OCV). This period was set to 8 h for cells containing the extra PP layer in the separator (because of wetting issue with the DMC of the electrolyte blend). Cells were also relaxed at OCV for 10 s and 1 min after each discharge (lithiation) and charge step, respectively. For the sake of reproducibility, three to four cells were tested for each Si electrode formulation and the results were averaged.

The cycling procedure of the ZnO (0.22) containing electrode used for the STEM-EDX and ^7Li and ^{19}F NMR quantifications, can be found in our previous publication.¹⁹

IR spectroscopy

Binder IR spectra were acquired with a thermoregulated ATR 7600 spectrometer (Thermo Nicolet). Typical binder solutions were prepared either with ultra-pure water or with deuterated water when indicated. First, a drop of binder solution was set to dry for 15 minutes on the ATR diamond at 60 °C. Then, the temperature was increased to 100 °C and held. IR spectra were continuously acquired with a resolution of 4 and 2 cm^{-1} and averaged over 30 and 100 scans for the H_2O and D_2O solutions respectively. A background was acquired at 60 °C without binder and no baseline correction was applied to the sample spectra. ATR correction was applied for spectrum acquisition.

Rheology

Binder solutions and ink flow properties were determined with a MCR101 (Anton Paar) rheometer. The geometry used was cone-plane (d = 50 mm, h = 46 μm , angle $\approx 0.984^\circ$) and plane-plane

($d = 50$ mm, $h = 300$ μm) for solutions and inks, respectively. Temperature was regulated to 20 $^{\circ}\text{C}$ with a Peltier probe. Binder solutions were magnetically stirred for 1 h at 300 rpm and then rested at least 30 minutes to set the same work history whereas inks were used as prepared. Storage (G') and loss (G'') modulus were measured with increasing strain from 0.01 to 100% at a frequency of 1 Hz. Shear stress and viscosity were measured with increasing shear rate from 0.01 to 1000 s^{-1} and then down again to 0.01 s^{-1} . Binder viscosities are taken on the forward scan and the back scan was used to evaluate any thixotropic behavior.²⁸ However, back scan ink viscosities are presented as tape casting occurs after the high-shear planetary mixing step.

STEM-EDX

Scanning transmission electron microscopy (STEM) experiments were carried out using the Nant'Themis, a (S)TEM Themis Z G3 Cs-probe corrected microscope (Thermo Fisher Scientific) operated at 80 kV and equipped with a high-angle annular dark field (HAADF) detector. Elemental maps were acquired in STEM mode using a Super-X emission X-ray spectrometer consisting of four windowless silicon-drift detectors (SDDs) providing a large collection solid angle of 0.7 srad. For the electrodes to be measured, this configuration ensured a limited sensitivity to the aggregate orientations with respect to the detectors. In order to limit electron beam degradation effects often observed on Si-based electrodes,⁶⁹ a small convergence angle of around 13 mrad and limited current of 100 pA were used, thus reducing the electron dose. For this same reason, fast frame acquisitions were used (couple of seconds per frame and 10 - 50 μs dwell time) and hundreds of frames summed for each map. Pixel sizes of approximately 5 nm were chosen. Quantifications performed on the first dozens of frames gave very similar results to those performed on the last dozens of frames, thus proving the reliability of given atomic ratios and maps. Regions purely composed of LiF were nevertheless slightly degraded in these conditions, without major implications on the relevance of the maps presented here. Thanks to a 5 eV/channel value for energy dispersion, light elements could be reliably measured.

Pristine electrodes (without xGnP15) powder was dispersed in cyclohexane after being scratched from the current collector. Then, a drop was deposited onto a lacey carbon film supported by a copper grid. ZnO (0.22) containing electrode powder with a silicon loading of 1.0 ± 0.1 $\text{mg}_{\text{Si}}.\text{cm}^{-2}$ was deposited onto a lacey carbon film by simple contact of the powder with the copper grid. After one cycle, the electrodes were not rinsed and further dried at $T = 40$ $^{\circ}\text{C}$, $t = 20$ h, $P \approx 1$ mbar without air exposure, then scratched from the current collector. A vacuum transfer sample holder (GATAN 648) was used to prevent any air contact of the reactive sample before its introduction into the Nant'Themis.

Scratch test

Electrodes coating adhesion and cohesion properties were determined using a sclerometer (BYK-Gardner). First, coatings were cut in the dimension of microscope slides (26 x 76 mm). Then, they were dried, weighted and measured (for the thickness) in the same way as the electrodes. Samples were taped on the slides such that the scratches were normal to the electrode tape casting direction. Thus, each scratch passed through an approximately equivalent thickness. The stylus ($d = 1.9$ mm, angle = 60° , $d_{\text{tip}} = 150$ μm ; BYK) was set on the coating and loaded with masses. Then, the plate was moved ($s = 336$ mm.min⁻¹) to make the scratch. Finally, scratches were analyzed with an SDD (SAMx) EDX probe in a 5800LV (Jeol) SEM with a gun voltage and current of 15 kV and 0.5 nA, respectively.

Indentation

Electrode coating mechanical properties were analyzed using a nano-indenter NHT³ and a MicroCombi MCT³ (Anton Paar). The former can couple a sinusoidal load to the standard one to render a hardness and elastic modulus depth profile. Electrodes were dried at 100 °C and 10 mbar for 1 h, to mimic battery conditions. The head (Berkovich) applied a maximum force of 0.1 to 400 mN. The oscillating contribution amplitude was 5% of the force at any moment and a frequency of 5 Hz and an acceleration coefficient (CSR strength ramp) of 0.1 s⁻¹ were used. For the micro-indenter (Vickers), the depth profile was obtained by applying quasi-static loads. The load intensity was increased 10 times, from 30 mN to 1 N, and was maintained for 15 s every time. The loading/unloading time was 15 s. The Oliver and Pharr⁷⁰ method was used to determine the hardness and elastic modulus. For the latter calculus, the Poisson coefficient was postulated to be 0.3. Finally, the mechanical properties were evaluated under battery operation conditions. To do so, the electrodes were soaked for 10 min in propylene carbonate (PC) and the surplus was removed before testing.

Operando dilatometry

Electrode thickness variation was monitored *operando* using an ECD-2 (El-cell) coupled dilatometric and a three electrode cycling cell whose scheme has been published elsewhere.⁶³ The thickness variation was measured with a LVDT sensor with a resolution of 0.05 μm . The counter electrode was metallic Li ($d = 16$ mm, thickness = 750 μm , 99.9%; Fisher). A lithium reference electrode was set in contact with porous sintered glass which was used as separator (thickness = 6 mm). The electrolyte ($V \approx 2$ mL) and working electrode were the same as for the Swagelok cells. The only exception was the Cu current collector (thickness = 120 μm , annealed, 99.9%; Alfa Aesar). Cycling

conditions were also identical except for the OCV period, which was set to 12 h for the cell linear drift calculus and correction. Some electrodes were also limited with a $1200 \text{ mAh.g}_{\text{Si}}^{-1}$ cutoff.

NMR spectroscopy

Solid state magic angle spinning nuclear magnetic resonance (MAS NMR) spectra were acquired for Si and binder blends prepared the same way as the electrodes but without graphite and tape casted on Mylar (dried at 100°C and 10 mbar for 1 h, to mimic battery conditions.). This was necessary to avoid any diffusion of paramagnetic Cu(II) in the electrode that would originate from the Cu current collector oxidation.¹⁵ Additional analyses were also performed on reference compounds and starting binder materials (dried at 60°C). ^{13}C and ^{17}O NMR spectra were acquired on a 500 MHz Bruker Avance III spectrometer using 4mm and 2.5 mm Bruker MAS probes, respectively. ^1H - ^{13}C Cross-Polarization NMR spectra were acquired with a 2 ms contact time, a MAS frequency of 11 kHz, and a recycle delay ranging from 2 to 5 s. For each acquisition, a ^1H TPPM15 decoupling scheme was used with a 90 kHz radiofrequency (RF) strength. ^{17}O MAS spectra were acquired with a single $\pi/12$ pulse excitation of 71 kHz RF strength. The MAS frequency was set to 27 kHz and the recycle delay to 2 s. ^{17}O signal enhancement using a Double Frequency Sweep pulse was discarded here, as we observed spectral distortion for some samples. ^{13}C and ^{17}O NMR spectra are referenced relative to TMS and H_2O , respectively.

^7Li and ^{19}F MAS NMR experiments were performed on a 500 MHz Bruker Avance III (Larmor Frequency $\nu_0(^7\text{Li}) = 194 \text{ MHz}$, $\nu_0(^{19}\text{F}) = 470 \text{ MHz}$) with zirconia rotor ($d_{\text{ext}} = 2.5 \text{ mm}$). ^7Li and ^{19}F spectra were acquired using a single pulse and Hahn echo sequence and a 30, 15 s recycle delay respectively. Spinning frequencies up to 25 kHz were used. Also, long recycle times were used to ensure quantitative measurements, with all spectra normalized taking into account the number of scans, the receiver gain and the mass of the sample. ^7Li and ^{19}F integrated intensities were determined by using spectral simulation Dmfit software.⁷¹ Quantitative NMR was also performed by mixing Si with various amounts of LiF to obtain calibration curves. It allowed lithium and fluorine absolute quantification in the samples.⁷² The electrodes (1.00 and $1.75 \pm 0.1 \text{ mg}_{\text{Si}}.\text{cm}^{-2}$) were cycled for 1 cycle, then not rinsed and further dried, $T = 40^\circ\text{C}$, $t = 20 \text{ h}$, $P \approx 1 \text{ mbar}$, without air exposure. It is important to note that even if the electrodes were not rinsed, they were gently placed on an absorbent paper. It had the effect of extracting almost all the liquid electrolyte contained in the porosity. Indeed, pristine electrodes had a mass gain of less than 1%, after mimicking battery conditions for a night and following the same dismantling plus drying procedure as cycled electrodes.

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SUPPORTING INFORMATION

Coordinatively Cross-linked Binders for Silicon-Based Electrodes for Li-ion Batteries: Beneficial Impact on Mechanical Properties and Electrochemical Performance

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Table S1 lists the electrode dimensions and 1st cycle electrochemical performance for every formulation tested in this study.

Table S1. Dimensions and 1st cycle electrochemical performance of all the tested formulations. Average values from electrodes assembled for cycling correspond to those of Figures 1 and S8. Values from electrodes assembled for dilatometry correspond to those of Figures 5 and S11.

	Formulation		Electrode dimension			1 st cycle electrochemical performance			
	Salt	Coord. Ratio	Active mass loading ($\text{mg}_{\text{Si}}.\text{cm}^{-2}$)	Silicon ($\text{v}\%$)	Pores ($\text{v}\%$)	Discharge capacity ($\text{mAh.g}_{\text{Si}}^{-1}$)	Charge capacity ($\text{mAh.g}_{\text{Si}}^{-1}$)	CE (%)	Nbr. of electrodes
Cycling	w/o Zn	0	1.75	27.0 ± 0.2	61.0 ± 0.3	4160 ± 30	3400 ± 80	81.1 ± 1.7	4
	ZnSO ₄	0.66	1.75	26 ± 4	60 ± 6	3910 ± 160	3350 ± 170	86 ± 1	4
	ZnSO ₄	0.22	1.75	26 ± 1	61 ± 2	4100 ± 200	3500 ± 200	84 ± 2	3
	Zn(NO ₃) ₂	0.22	1.75	27.8 ± 0.7	57 ± 1	4320 ± 20	3480 ± 10	80.5 ± 0.5	3
	ZnO	0.22	1.75	25.8 ± 0.7	62.2 ± 0.8	4140 ± 70	3610 ± 60	87.3 ± 0.5	3
	w/o Zn + LiOH	0	1.75	24.2 ± 0.6	64.6 ± 0.7	4300 ± 100	3500 ± 200	81.9 ± 2.1	4
	w/o Zn (PIPPS)	0	1.75	27.0 ± 0.8	61 ± 1	3930 ± 70	2800 ± 200	71.6 ± 0.7	3
	ZnSO ₄ (PIPPS)	1.14	1.75	26 ± 2	60 ± 3	3990 ± 80	3160 ± 440	78 ± 6	4
Dilatometry	w/o Zn	0	1.97	30.5	55.8	1200	542	45.2	1
	ZnSO ₄	0.22	2.01	23.6	64.8	1200	747	62.3	1
	ZnSO ₄	0.22	1.71	24.8	63.1	3769	2585	68.6	1
	ZnSO ₄	0.22	1.61	21.9	67.4	1200	751	62.6	1

Table S2 presents the NMR quantification of ¹⁹F and ⁷Li for ZnO (0.22) electrodes after the first cycle. The detailed quantification procedure can be found in our recent work.¹ Molecules labelled “Others” represent lithiated species, gathering lithiated carbonates, alkyl-carbonates and semi-carbonates. These products come from the electrolyte degradation, either the solvent molecules, or the FEC additive as most of its decomposition reactions include a defluorination path.² Interestingly the same trend is found for the ZnO (0.22) as for the ZnSO₄ (0.22), compared to the without Zn formulation. That is, a lower quantity of “Others” and a higher quantity of LiF at the first cycle. Also, the Li quantity in the SEI corresponds to an extra capacity which is:

$$C_{\text{Li}}\text{SEI} = \frac{{}^7\text{Li}_{\text{SEI}} \times F}{3.6 \times w_{\text{Si}} \times N A_{7\text{Li}}} \times 100 \text{ (mAh.g}_{\text{Si}}^{-1}) \text{ (S1)}$$

where ⁷Li_{SEI} is the amount of Li in the SEI, that is the sum of LiF, Li_xPO_yF_z and the “others” ($\text{mol.g}_{\text{el}}^{-1}$); *F* is the Faraday constant and is equal to 96 485.33 C.mol⁻¹; *w_{Si}* is the silicon weight fraction of the

considered formulation (see Table 1 in the main text), and NA_{7Li} is the natural abundance of ^7Li and is equal to 92.41%.

Table S2. Normalized quantity of SEI elements determined by solid state ^{19}F and ^7Li NMR, for a ZnO (0.22) electrode after the 1st cycle.

Formulation		NMR quantification ($\mu\text{mol.mg}_{el}^{-1}$)				
<i>Salt</i>	<i>Coord. Ratio</i>	$LiPF_6(s)$	$LiPF_6(l)$	$Li_xPO_yF_z$	LiF	Others
ZnO	0.22	0.03	0.00	$0.14/z$	3.56	$4.59-0.14x/z$

The 1st cycle dQ/dV curves for the formulations presented in Table 1 are presented in Figure S1. The curves are centered between 0.7 and 1.8 V (vs. Li^+/Li^0) where the degradation of FEC is expected.²⁻⁴ One or two peaks can be seen around 1 V (vs. Li^+/Li^0) for each formulation, which could be related to the one or two electrons reduction pathway of FEC.[5] However, in the case of the Zn-free formulations (Figures S1a and S1f), the peak areas are much more significant than for the Zn-containing formulation (Figures S1b to S1e). This means that the capacities associated with those peaks are higher and therefore correspond to the degradation of a larger quantity of FEC. In addition, no reduction peak at 1.6-1.7 V (vs. Li^+/Li^0) is visible in each formulation, which would be associated to the reduction of carboxylic acidic protons.^{2,6}

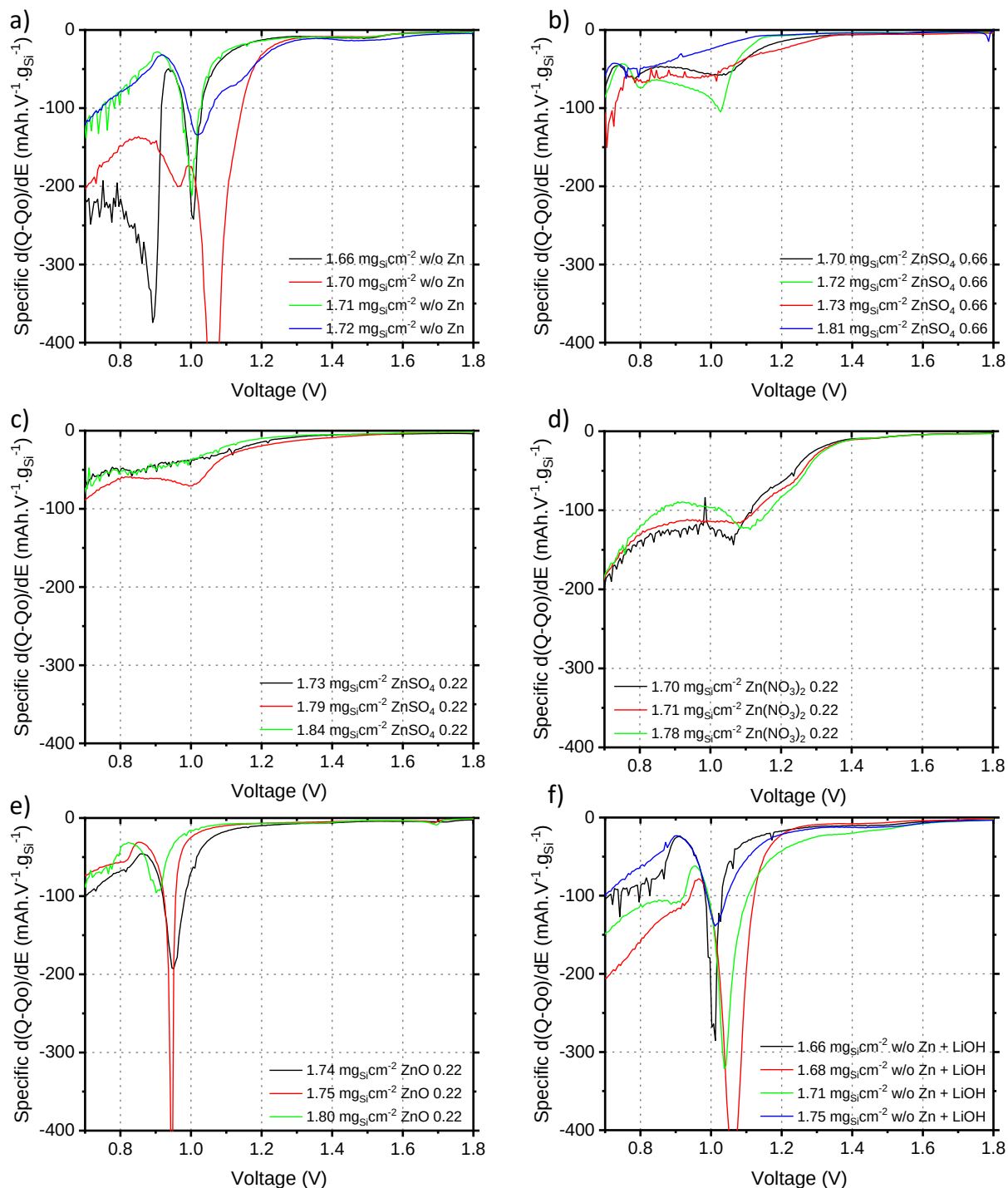


Figure S1. First cycle $d(Q-Q_0)/dV$ as a function of voltage for the formulations presented in Table 1: (a) W/o Zn; (b) ZnSO₄ (0.66); (c) ZnSO₄ (0.22); (d) Zn(NO₃)₂ (0.22); (e) ZnO (0.22); (f) w/o Zn + LiOH.

The IR spectra and electrochemical performance of the Zn(NO₃)₂ (0.22) binder and electrodes are presented in Figures S2a and S2b, respectively. For the Zn(NO₃)₂ formulation, ν_{asym} and ν_{sym} peaks of the carboxylates are upshifted compared to the reference (by 25 and 11 cm⁻¹, respectively), which was

also observed with the ZnSO_4 binders. Referring to the discussion accompanying Figure 3 in the main text, those shift are an indication that Zn(II) carboxylate are formed in the binder in presence of $\text{Zn(NO}_3)_2$. Figure S2b shows that the extra capacity at the first cycle is $737 \text{ mAh.g}_{\text{Si}}^{-1}$, which is the highest of all formulation, and the CE is only around 80.5%, which is even lower than for the Zn-free formulation. Therefore, we think that the nitrate's counter-ion reduction is responsible for this amount of extra-capacity and consequently much lower CE (because the reversible capacity, available Table S1, is in the average for the other formulations). Nonetheless, the capacity loss per cycle between the 16 and 64 cycle is $5.2 \text{ mAh.g}_{\text{Si}}^{-1}$, which is in between the respective ZnSO_4 and ZnO formulations. Further, the capacity retention is $2660 \text{ mAh.g}_{\text{Si}}^{-1}$ after 60 cycles, which is more than for the other two Zn(II) containing formulations. Finally, the CE is stabilized at approximately 99.1%, which is less than the other two coordinated formulations. It clearly appears that except for slight variations in the electrochemical signatures, every Zn(II) reticulated binder formulations deliver a better performance than the uncoordinated binder.

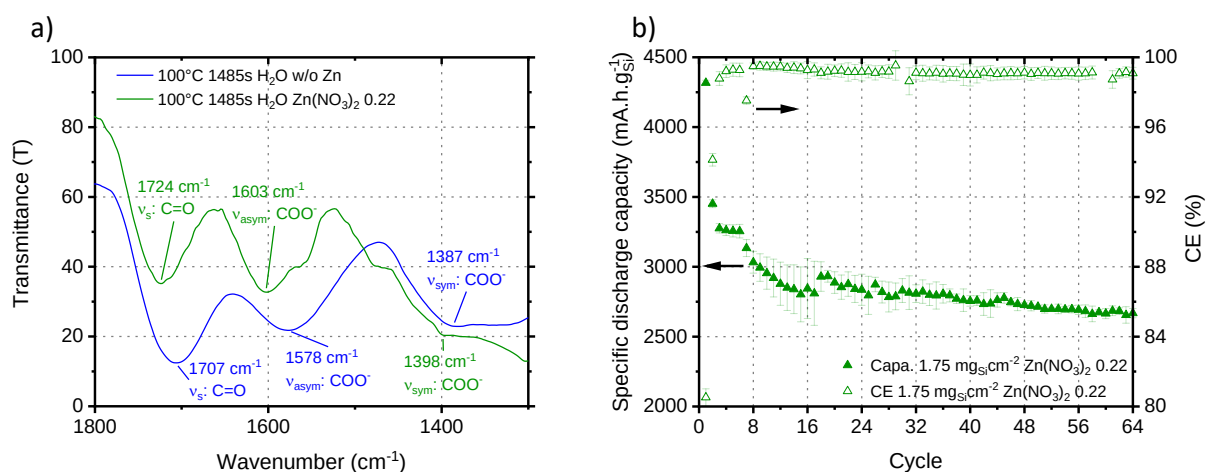


Figure S2. (a) IR spectra of $\text{Zn(NO}_3)_2$ (0.22) dried binder, which was prepared with ultra-pure water (the reference binder spectra is also shown for comparison). The time stamp in the legends refers to the time at which the spectra was acquired, while the sample was still heated; (b) Specific discharge capacity and CE per cycle of $1.75 \text{ mg}_{\text{Si}}\text{cm}^{-2}$ $\text{Zn(NO}_3)_2$ (0.22) binder electrodes (in full and shallow symbols, respectively).

Figure S3 presents the shear stress values related to the viscosity data of Figure 2. Herschel-Bulkley or other models fit were not exploited to obtain the inks yield stress value, because no shear-stress plateau was present in our data. Also, the curves inflexion towards lower shear stress value (at low shear rate) will likely induce overestimated yield stress values. This might originate from the polydispersity of the silicon and graphene particle size and of the NaCMC chains length.⁷

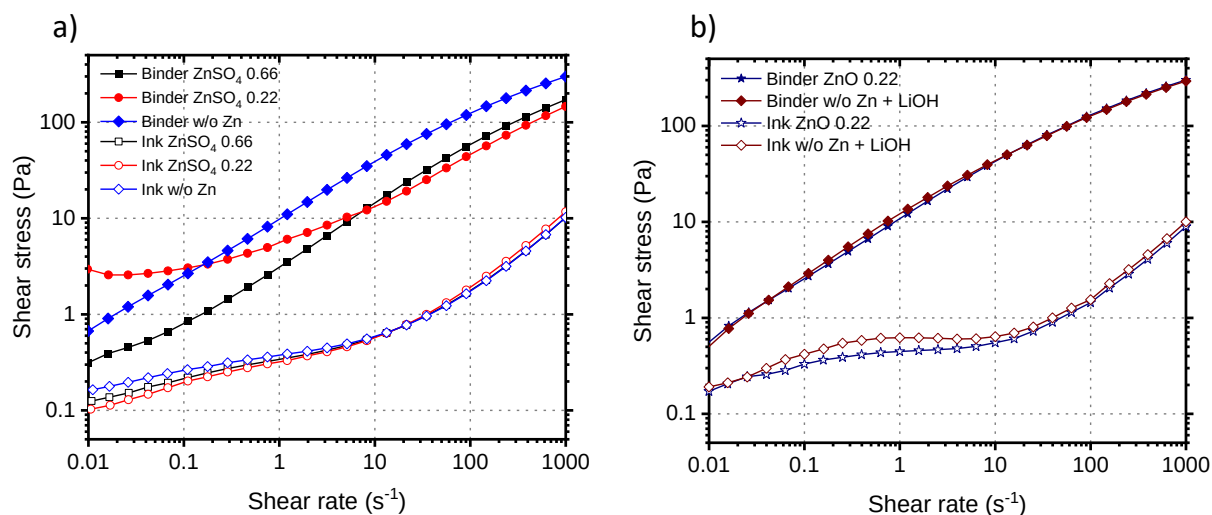


Figure S3. Shear stress as a function of shear rate of binder solutions and respective inks: (a) Solutions based on ZnSO₄; (b) Solutions based on ZnO.

The storage (G') and loss modulus (G'') measured as a function of strain are presented in Figures S4a and S4b for the binders based on ZnSO₄ ($Zn/RCO_2H = 0, 0.22$ and 0.66) and ZnO ($Zn/RCO_2H = 0$ and 0.22 , respectively). All the formulations behave like liquids ($G' < G''$) and exhibit a strain thinning behavior, indicating a lack of strong inter-chain association.⁸ The only exception is the binder containing ZnSO₄ with $Zn/RCO_2H = 0.22$, which behaves like a physical gel ($G' > G''$). It exhibits a small loss modulus overshoot, proving that the binder is highly reticulated.⁸ Overall, these results are in agreement with the binders' viscosity order of Figures 2a and 2b at $1 s^{-1}$, which is equivalent to the 1 Hz solicitation frequency used for those measurements.

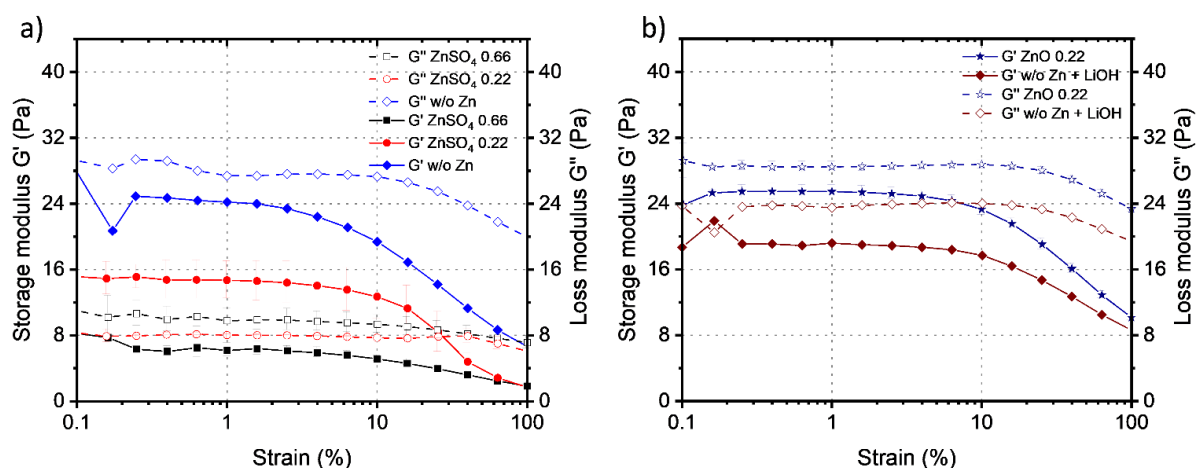


Figure S4. Storage and loss modulus of binders as a function of the strain of binder solutions: (a) Solutions based on ZnSO₄; (b) Solutions based on ZnO.

Figure S5 shows the transmittance IR spectra of the binder containing ZnSO_4 and the corresponding reference ($\text{Zn}/\text{RCO}_2\text{H} = 0, 0.22$ and 0.66), formulated in D_2O . It corresponds to the first spectra acquired after deposition of the binder drop on the ATR diamond. The binder is not yet dry, as can be seen from the presence of a peak at 1453 cm^{-1} characteristic of HDO.⁹ In fact, water is present in low amounts from both the Zn(II) salt coordination water and NaCMC ab/adsorbed water. The H/D ratio is 1, 2.1 and 4.4% for $\text{Zn}/\text{RCO}_2\text{H} = 0, 0.22$ and 0.66 , respectively. It is consistent with the relative HDO peak intensity in the three formulations. Interestingly, the $\nu_{\text{asym}}(\text{COO}^-)$ peak splitting is strongly marked for the samples containing ZnSO_4 , confirming the existence of at least two chemical environments for the carboxylate groups. Toda et al.¹⁰ studied the IR spectrum of a zinc-sodium stearate complex which contains two different carboxylate groups. However, they observed three ν_{asym} peaks since the alternation of two sodium carboxylates for one zinc carboxylate induces two non-equivalent Na-Zn(COO)₂ motif. Also, note that $\text{ZnNa}_2(\text{COO})_4$ and $\text{ZnK}_2(\text{COO})_4$ complexes exist¹¹ and their presence cannot be excluded in our case.

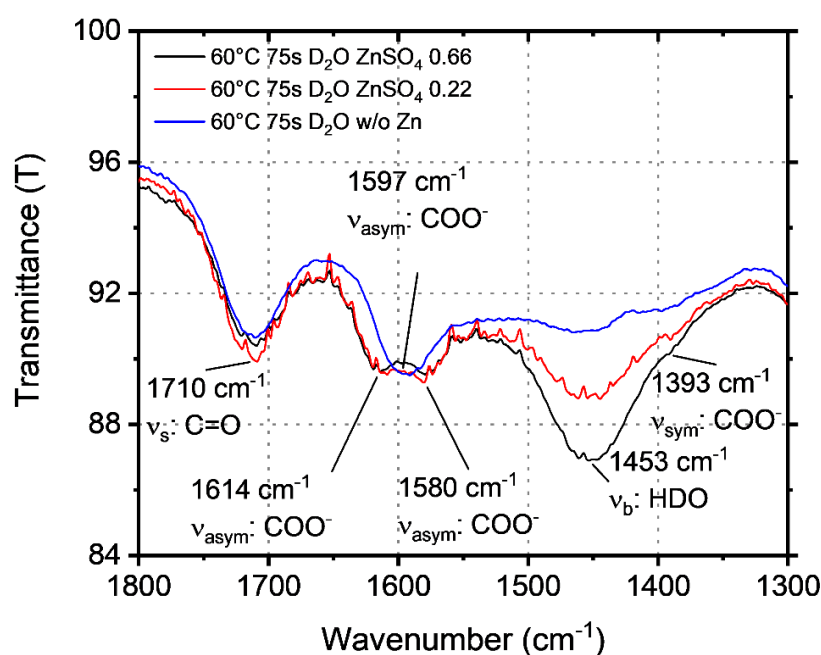


Figure S5. IR spectra of slightly dried binders with different coordination ratios. Solutions were prepared with deuterated water and were barely evaporated. The time stamp in each legend refers to the time at which the spectra was acquired, while the sample was still heated.

¹⁷O NMR spectra of $\text{Zn}_3(\text{CA})_2(\text{H}_2\text{O})_2$ and ZnSO_4 ($\text{Zn}/\text{RCO}_2\text{H} = 0, 0.22$ and 0.66) binder samples prepared with ¹⁷O enriched CA (on carboxylic functions only) are presented in Figure S6 and the reader is referred to the main text for the corresponding discussion.

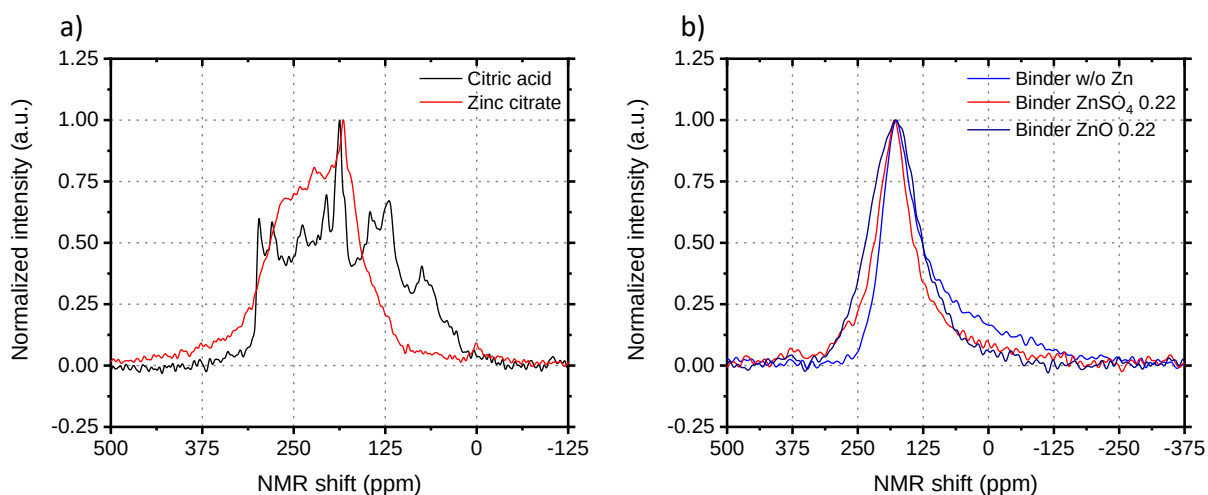


Figure S6. ^{17}O MAS NMR spectra (normalized to the highest-intensity signal): (a) Reference compounds; (b) Different binder samples.

Figure S7a shows the ^1H - ^{13}C cross-polarization normalized NMR spectra of electrodes made with ZnSO_4 and ZnO (both with $\text{Zn}/\text{RCO}_2\text{H} = 0.22$) and silicon. The main resonances spotted on the NMR spectra (Figure S7a) are attributed to both CMC and CA (see Figure S7c for comparison). Regarding the main signals, there are two distinct $-\text{CH}_2$ resonances, C_4 at around 44 ppm coming from CA and C_3 at 62 ppm coming from CMC. The signal at 103 ppm is attributed to the CMC C_2 carbon atom. The CA C_6 carbon atom, which is expected at about 75 ppm, overlaps with the signal of the other carbon atoms from the ring of CMC located between 65 and 90 ppm (but it can be seen in Figure S7c). Finally, the $\text{C}_1/\text{C}_5/\text{C}_7$ peak around 178 ppm is attributed to the carboxylate/carboxylic acid carbon atom of both CMC and CA. For the latter, both C_5 carboxylic acid carbon atoms and the C_7 one are chemically non-equivalent. Interestingly, there is a shift in the carboxylic/carboxylate peak maximum between the samples prepared at more acidic (ZnSO_4 with $\text{Zn}/\text{RCO}_2\text{H} = 0$ and 0.22) and more basic pH (ZnO with $\text{Zn}/\text{RCO}_2\text{H} = 0$ and 0.22). The $\text{C}_1/\text{C}_5/\text{C}_7$ peak is at approximately 176 ppm for the formers vs. 179 ppm for the latters. Looking at Figure S7b, it is clear the $\text{C}_1/\text{C}_5/\text{C}_7$ peak contains many contributions as the chemical shift spans from 168 to 184 ppm for the most acidic formulations, and from 171 to 187 ppm for the most basic ones. Unfortunately, the peak is broad and featureless, and it also covers the shift range expected when passing from citric acid to sodium or zinc citrate, for example. In detail, these shifts are within approximately 3-8 ppm, as can be seen in Figure S7d, whereas the $\text{C}_1/\text{C}_5/\text{C}_7$ peak's FWHM is around 8-10 ppm, such that it covers any possible shift. Therefore, no definitive information on binder coordination can be gathered with NMR analysis at this stage. Nonetheless, the $\text{C}_1/\text{C}_5/\text{C}_7$ peak at lower chemical shift for the most acidic binder solutions is interesting. Bridel et al¹² showed with solid ^{13}C MAS NMR that the chemical shift of silyl ester covalent bond is lower

than the one of carboxylic acid hydrogen bonded to SiOH (at approximately 170 vs. 175 ppm). Thus, the shift we observed could also originate from the formation of silyl-ester bonds at more acidic pH. This would be in agreement with the superior mechanical performance found for the electrodes prepared at more acidic pH, as is shown for example in Figure 4. A weak signal at 18 ppm is present, but only in the spectra reference electrodes, which could correspond to a methyl group of a yet unidentified impurity. ^1H - ^{13}C CP-MAS NMR is a non quantitative method, which particularly exacerbates the resonance intensity of carbon atoms surrounded by a large number of protons. So, if any impurity is present, it must be in very low quantity.

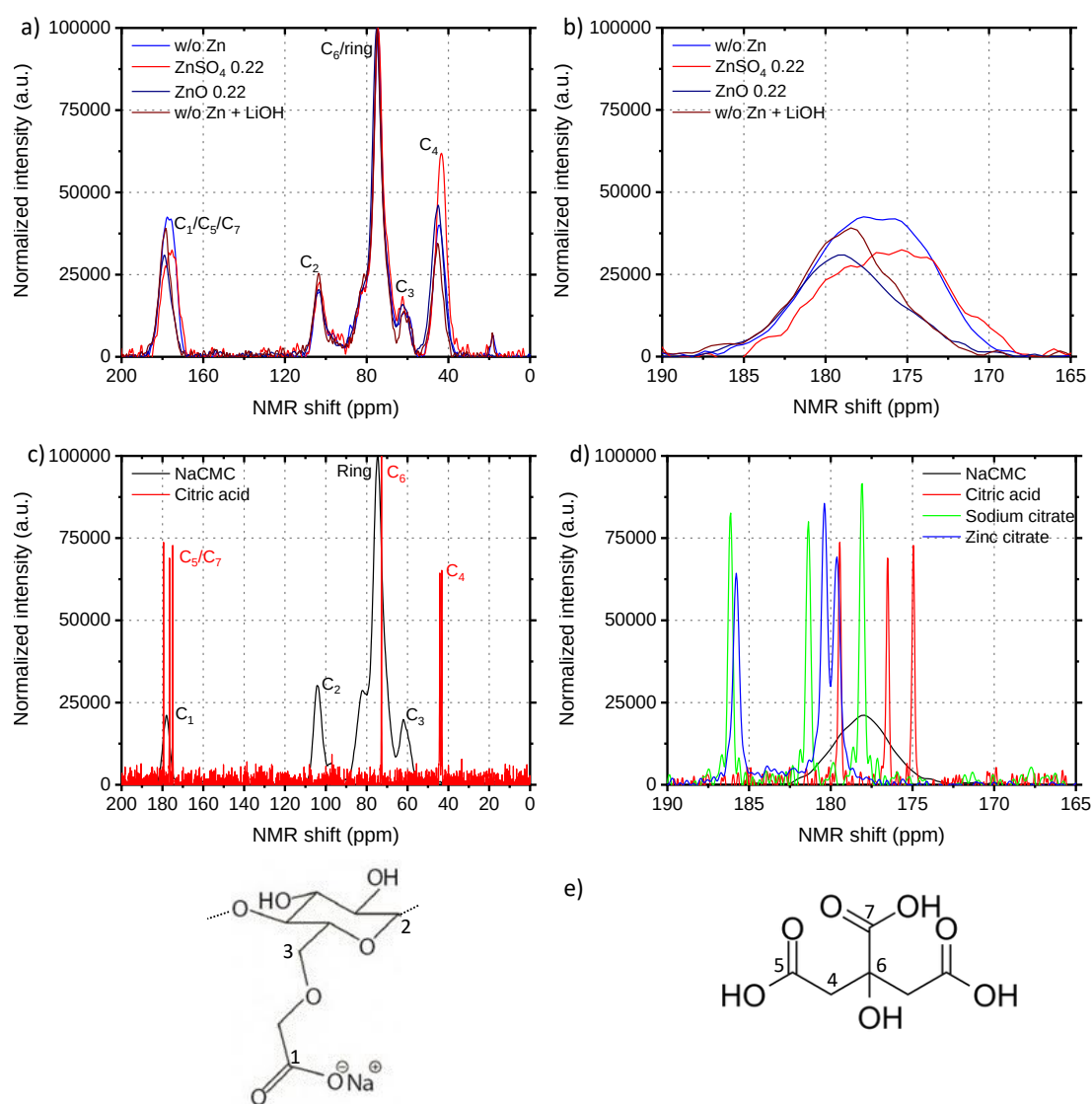


Figure S7. ^1H - ^{13}C CP MAS-NMR spectra of pristine electrode powders (Si plus binder): (a) W/o Zn, ZnSO_4 (0.22), ZnO (0.22) and w/o Zn + LiOH (spectra normalized to the highest intensity resonance); (b) Same spectra as in (a) but focused on the carboxylic/carboxylates signals; (c) ^1H - ^{13}C CP MAS-NMR spectra of NaCMC and citric acid powders (spectra normalized to the highest intensity resonance); (d) Same spectra as in (c) plus other reference compounds, but focused on the carboxylic/carboxylates signals; (e) Respective carbons marked on both NaCMC and citric acid.

The specific discharge capacities of the electrodes formulated with piperazine-N,N'-bis(3-propanesulfonic acid) (PIPPS), both with ($\text{Zn}/\text{RCO}_2\text{H} = 0.22$) and without ZnSO_4 , are shown in Figure S8a. The particularity of these formulations is that CA was replaced for PIPPS in the buffer. It is a poorly metal-complexing molecule. Its first $\text{pK}_{\text{a}1}$ is equal to 3.73 vs. 3.13 for the citric acid such that the formulated binders pH are 4.1 and 4.3 for the ZnSO_4 and its reference, respectively, as mentioned in Table S3. Also, the molecular weight of PIPPS is higher. Therefore, its concentration was lowered in the binder to keep the Si:graphene:binder $\text{w}\%$ constant between PIPPS and CA formulations. This modification induced a pH shift between binders (PIPPS vs. CA ones) which is higher than that between the buffer molecules. Nonetheless, binder pH with PIPPS are similar to those of ZnO (0.22) with citric acid such that there should not be any unexpected pH influence on the electrochemical performance. The amount of ZnSO_4 was also kept constant between the PIPPS and CA formulation for the aforementioned reasons. Therefore, the corresponding coordination ratio becomes 1.14 as CMC is now the only molecule bearing carboxylic acid.

Table S3. Formulations with PIPPS, corresponding electrode composition and ink property.

Formulation name		Electrode composition (w%)						Ink property	
Salt	Coord. ratio	Silicon	Graphene	NaCMC	PIPPS	NaOH	Zn precursor	Solid fraction (w%)	Binder pH
w/o	0	73.9	11.1	7.2	7.4	0.4	0	26.9	4.3
ZnSO_4	1.14	70.3	10.5	6.9	7	0.4	4.9	27.9	4.1

The capacity retention is approximately 1150 and 110 $\text{mAh.g}_{\text{Si}}^{-1}$ at 50 cycles, for $\text{Zn}/\text{RCO}_2\text{H} = 0.22$ and 0, respectively. It is much lower than for their respective citric acid formulations. The latter has been previously reported to serve as an artificial SEI (and to form Li-citrate after the first lithiation).^{13,14} It significantly mitigates the electrolyte degradation on silicon (thanks to uniform silicon particle coverage¹³), thus improving its electrochemical performance. Interestingly, the formulation containing ZnSO_4 has a better capacity retention. That means that even if CMC counts as approximately a fourth of the COO^-/COOH groups in the binder (the rest comes from citric acid), its coordination plays a determinant role. However, the capacity retention is still much lower than that of the citric acid formulation. Therefore, the coordination with CA is required to close the gap. This highlights the

necessity of combining both molecules to achieve compelling mechanical properties through coordination.

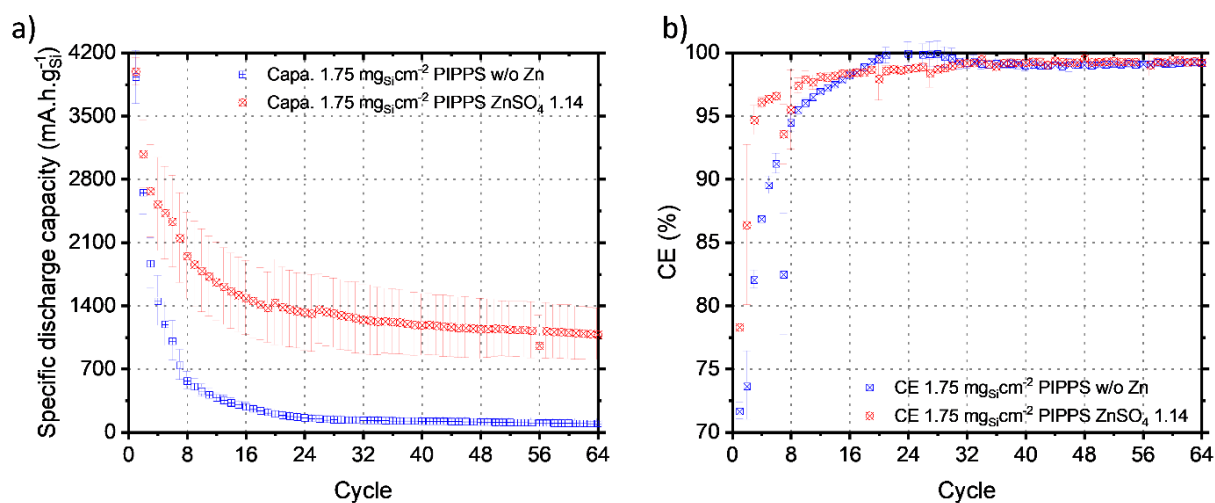


Figure S8. (a) Specific discharge capacity and (b) CE by cycle of electrodes with Piperazine-*N,N'*-bis(3-propanesulfonic Acid) as acidic buffer molecule: ZnSO₄ (1.14) and its reference.

A typical example of electrode coating mechanical failure from a scratch test is presented in Figure S9a. The current collector is visible at the scratch tip, with electrode matter being plowed on the side (as confirmed by silicon and carbon EDX mapping, see Figures S9b and S9c, respectively). The presence of Cu is confirmed by its EDX mapping in Figure S9b. This mapping is necessary, as the current collector is sometimes not so visually apparent. To obtain the local silicon loading, the thickness was mapped with 8 points on the tab. The mean thickness value corresponds to the whole tab silicon loading. The failure position on the tab is subsequently deduced by SEM observation coupled with the thickness mapping, which enables the local thickness to be retrieved. Finally, a cross product provides the local silicon loading of the failure zone.

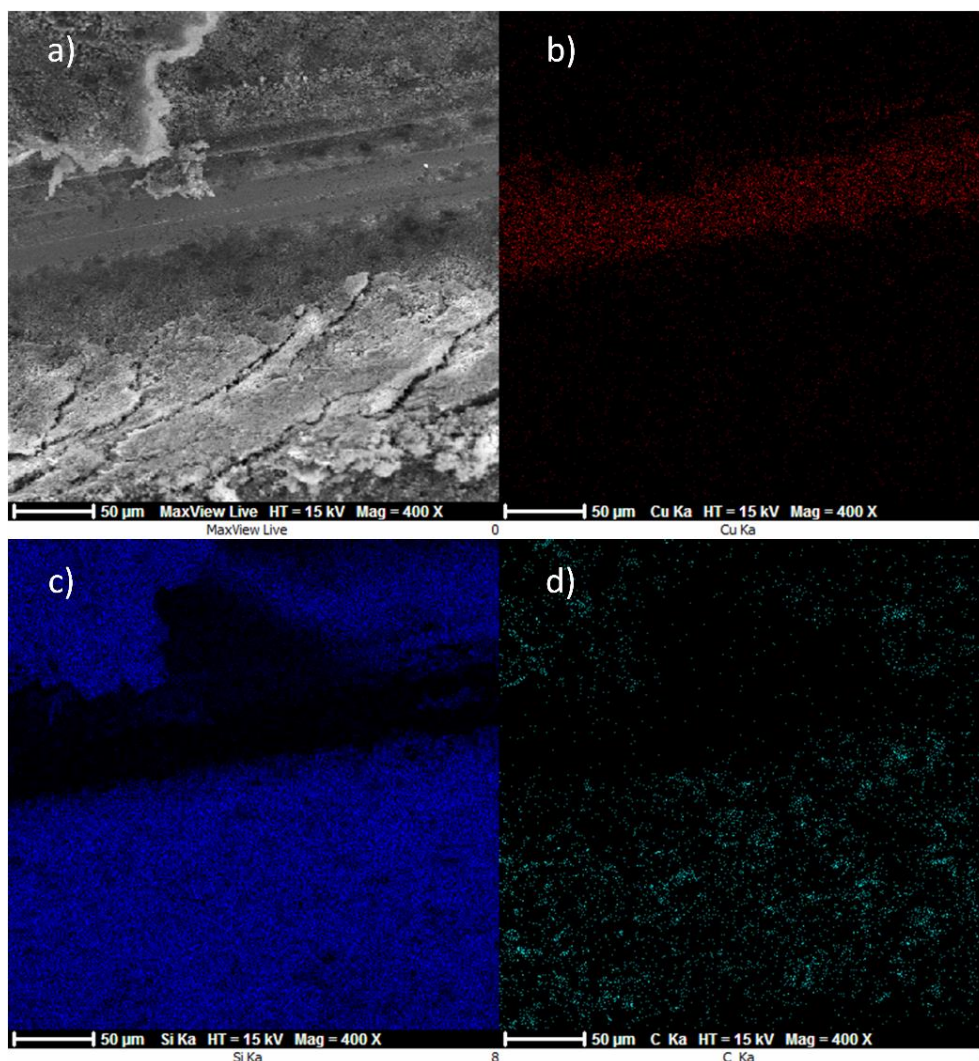


Figure S9. EDX images (x400) of a 260 g scratch from a Zn-free electrode coating: (a) Secondary electrons; (b) Silicon mapping; (c) Copper mapping; (d) Carbon mapping.

Figure S10 presents the elastic modulus and hardness indentation depth profiles where an initial drop, followed by a plateau, then an increase in these magnitudes can be observed. The initial drop (low indentation depth), the intensity of which is the most variable when repeating the measurement, is attributable to the crushing of the surface roughness. Then, accurate values for the coating, presented in Table 2, are extracted from the plateau, where neither the influence of rugosity nor current collector are present. For the latter, its influence is observed at high indentation depth, with a continuous hardness and modulus increase (because of its growing contribution). The so-called wet samples were saturated with propylene carbonate for 10 minutes then the excess solvent was absorbed before measurement.

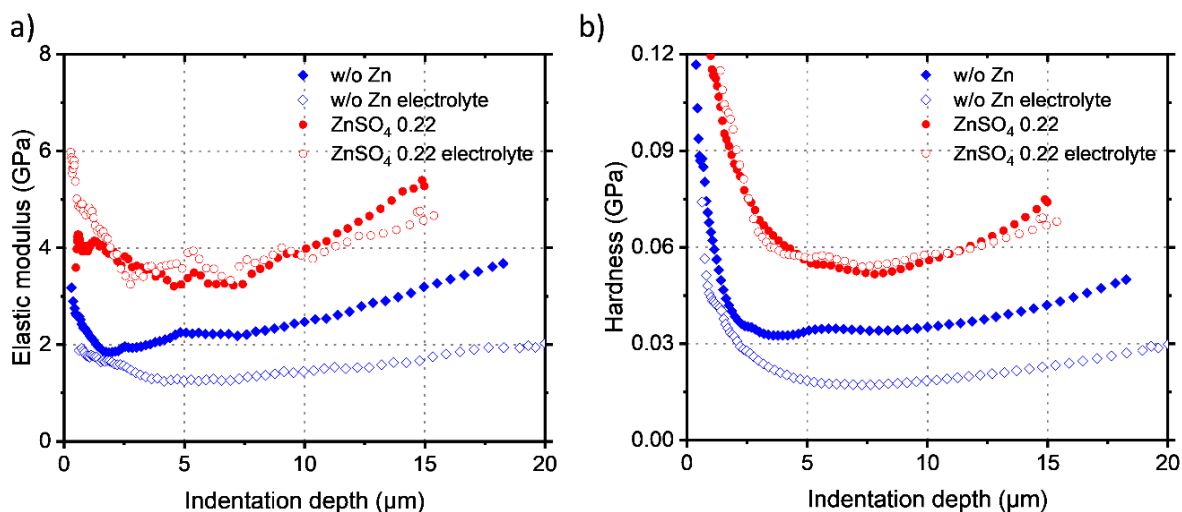


Figure S10. Averaged nano-indentation curves: (a) Elastic modulus and (b) hardness vs. indentation depth.

As explained in the discussion accompanying Table 2 in the main text, Cuauhtémoc et al¹⁵ used micro-indentation instead of nano-indentation. For the former, values are extracted at high indentation depth (more than 20 μm). As such, the influence of both current collector and reduced porosity is significant because the electrode is compacted by the indenter. This also explains the superior values found with micro-indentation in Table S4, as it applies a much greater maximal force of 1 vs. 0.4 N for the nano-indenter. Thus, the former sinks deeper in the electrode and the current collector impact on the measured properties is amplified.

Table S4. Dimensions and mechanical properties assessed by micro-indentation, of a ZnSO_4 (0.22) and its reference electrodes, both in the dry and soaked in propylene carbonate state.

Formulation			Electrode dimension		Micro-indentation	
Salt	Coord. Ratio	Film condition	Active mass loading ($\text{mg}_{\text{Si}} \cdot \text{cm}^{-2}$)	Porosity ($\text{v}\%$)	Hardness _{it} (MPa)	Elastic modulus _{it} (GPa)
w/o Zn	0	dry	1.93	66.2	40 - 50	3 - 4.0
w/o Zn	0	electrolyte	1.93	66.2	25 - 30	2 - 3.0
ZnSO_4	0.22	dry	1.86	56.6	55 - 75	5.5 - 6.5
ZnSO_4	0.22	electrolyte	1.86	56.6	65 - 110	3 - 5.5

Thickness variation during cycling is shown in Figure S11 for two ZnSO_4 (0.22) electrodes, both at full capacity (Figure S11a) and at limited capacity (1200 $\text{mAh.g}_{\text{Si}}^{-1}$, Figure S11b). For the figure description and results interpretation, the reader is referred to the discussion accompanying Figure 5 in the main text.

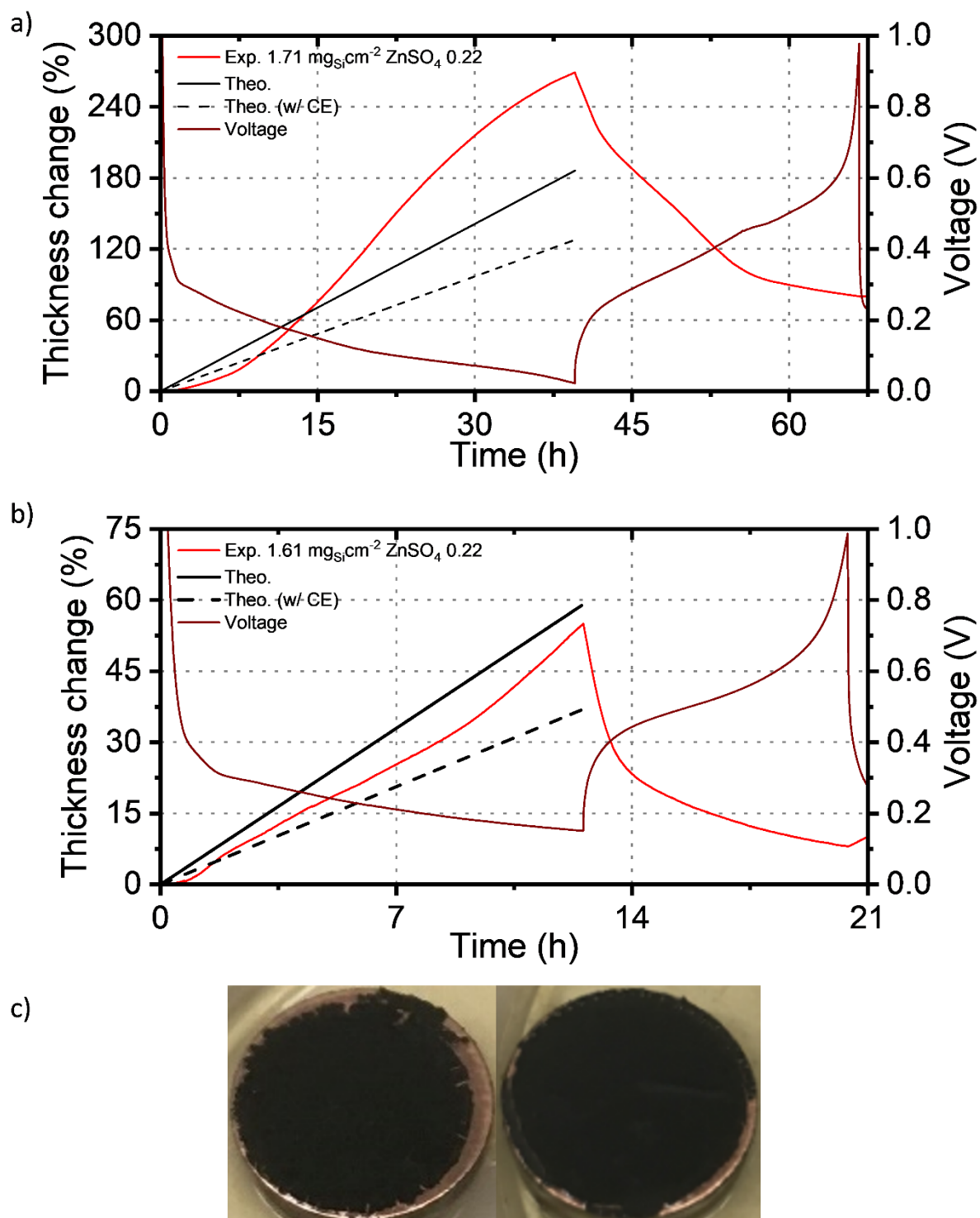


Figure S11. Experimental and theoretical thickness variation and voltage as a function of time of ZnSO_4 (0.22) electrodes: (a) Without cutoff; (b) With cutoff; (c) Respective postmortem electrode pictures.

Table S5 compiles the dimensions of all the electrodes used for the *operando* dilatometry experiments. These are the parameters required to determine the theoretical volume expansion of the electrodes with eq. (1) and (2).

Table S5. Dimensions of ZnSO₄ (0.22) and its references electrodes used for dilatometry experiments.

Electrode	ω_{Si} (w%)	ϵ_0 (v%)	ρ_{app} (g.cm ⁻³)	m_{EI} (mg)	e_{EI} (μm)	Area _{EI} (cm ²)
w/o Zn 1.97 mg _{Si} .cm ⁻²	73.4	55.8	0.971	2.12	27.8	0.785
ZnSO ₄ (0.22) 2.01 mg _{Si} .cm ⁻²	69.9	64.8	0.788	2.26	36.5	0.785
ZnSO ₄ (0.22) 1.71 mg _{Si} .cm ⁻²	69.9	63.1	0.828	1.92	29.6	0.785
ZnSO ₄ (0.22) 1.61 mg _{Si} .cm ⁻²	69.9	67.4	0.732	1.81	31.5	0.785

Figure S12 shows a high-angle annular dark-field (HAADF) image and elemental mappings of a pristine electrode containing ZnO (0.22) formulated without graphene. The STEM-EDX characterization couples element discretization with high-resolution imaging at the nanometer scale, which is perfect to study coordination binder at the electrode level conditions. The region of interest (ROI) is representative of most of the ROIs gathered in the STEM-EDX analysis (not shown). They are focused on nanometric silicon particles located on the edge of agglomerates because inner particles are too thick for the electron transmission. Focusing on the binder, the carbon and sodium should exclusively be present in this phase (see Table 1). Oxygen is also present in the binder. However, it is also particularly concentrated at the silicon particles surface due to the native SiO_x layer contribution, such that the oxygen was ruled out of the binder markers. Focusing on the particles, one can see that the binder properly covers the silicon particles. In addition, there is a clear match in position between alkali ions and carbon with zinc. As such, Zn(II) ions are well distributed throughout the binder and no Zn rich particles or agglomerates (such as Zn(0) or ZnO) are observed. We deduce that the coordination network is very homogeneous at the tens of nm scale. This is consistent with the ¹⁷O and ¹³C solid state NMR signatures of carboxylic acid/carboxylate groups presented here. These conclusions were also drawn for the ZnSO₄ (0.22) binder in our previous study,¹ thanks to a similar STEM-EDX analysis.

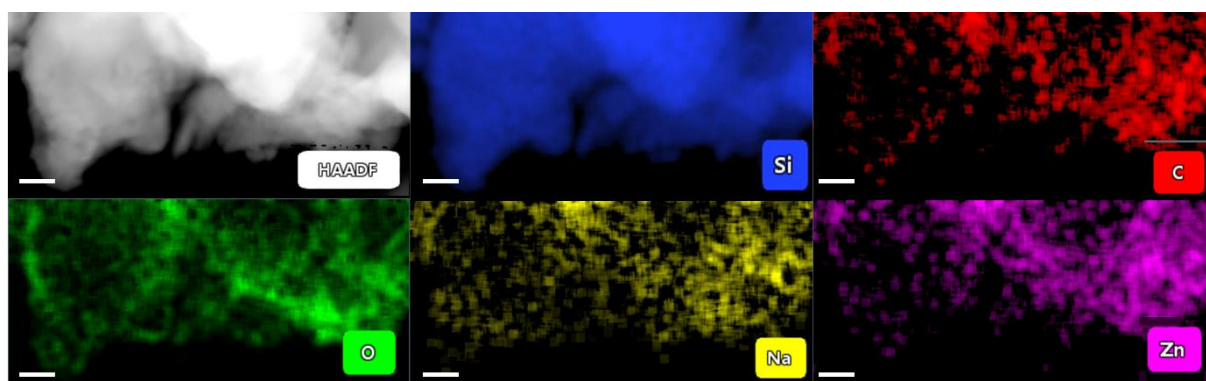


Figure S12. STEM/EDX elemental mapping of a ZnO (0.22) pristine sample. Scale bar is 50 nm.

A STEM-EDX HAADF image of a similar electrode after one cycle is presented in Figure S13. First, no metallic zinc particles are spotted, indicating that the binder is electrochemically stable at least during the first cycle. In fact, the reduction of Zn(II) in Zn(0) could be expected based on its redox potential (2.25 V vs. Li^+/Li^0), but the coordination of Zn(II) with the carboxylate moieties and the dissemination of the Zn(II)-carboxylate within the electrically insulating binder phase likely prevent its reduction. Nonetheless, a first cycle analysis is most likely insufficient to assess of the Zn reactivity in the binder phase. For example, Lou et al¹⁶ studied the cycling behavior of a Cu-citrate MOF vs. lithium metal in half-cell and estimates that Cu^{2+} is reduced to Cu(0) (its reduction potential is 3.35 V vs. Li^+/Li^0) during the first discharge. Then, it remains inactive for a couple of discharge/charge before regaining activity over subsequent cycling.

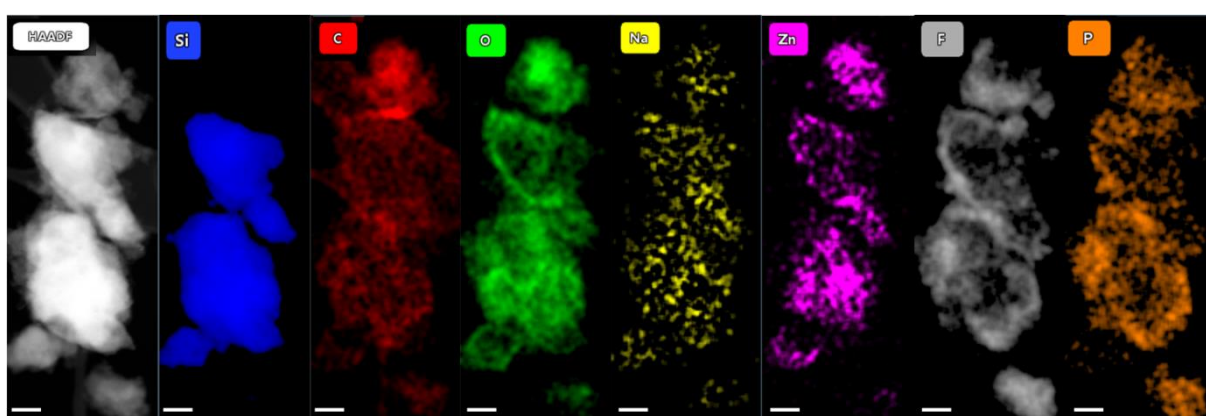


Figure S13. STEM/EDX elemental mapping of a ZnO (0.22) electrode after the 1st cycle. Scale bar is 100 nm.

With the SEI formation, the carbon can no longer be counted as a binder marker because the electrolyte solvents will decompose in carbonate type species (lithiated carbonates, alkyl-carbonates and semi-carbonates). The FEC will also decompose into organic species (and LiF) with the formation of polycarbonates and reticulated polyethylene oxide type polymers.² Nonetheless, the binder evolution can be followed through its remaining markers, Na and Zn, and seems barely changed after one cycle. Even more interestingly, the spatial distribution of the binder markers does not match those of the inorganic SEI (P and F). This strongly suggests that ZnO (0.22) binder is also working as an artificial SEI (to some extent). These conclusions were also drawn for the ZnSO₄ (0.22) binder in our previous study¹ in contrast to the observations on the electrode containing no Zn(II). For the latter, the inorganic SEI also appeared wooly and with large heaps connecting particles whereas it is more conformal in presence of Zn(II) coordinated binders.

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4.2.3. Publication N°3 : “Impact of the Cu Current Collector Grade and Ink Solid Fraction on Electrochemical Performance for Silicon-Based Electrodes for Li-Ion Batteries”

Impact of the Cu Current Collector Grade and Ink Solid Fraction on the Electrochemical Performance of Silicon-Based Electrodes for Li-Ion Batteries

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Keywords

Silicon anode, Carboxymethyl cellulose binder, Current collector, Solid fraction, Solid loading, Coordination, Li-ion batteries

Abstract

Silicon-based electrodes are well-known to suffer dramatic mechanical degradations during cycling, rendering their use for practical battery applications extremely challenging. Multiple strategies, related mostly to the optimization of the active material and the binder have been proposed to circumvent these drawbacks. We here explored the effects of two other elements, namely the solid fraction (SF), and the current collector (CC), which are to our knowledge largely overlooked in the literature related to Si electrodes. SF, which is the relative amount of dry matter (active material, conductive additive and binder) in the ink used to prepare electrodes, is known to influence the electrode's components distribution in the final composite electrode coating, and thus impacts on electrode's mechanical and transport properties. While CC modification, for example through texturation also has a significant impact on the mechanical behavior of the electrode. Here, different ink SF and copper CC grade were investigated to study their impacts on the electrode structure and cracks formation. Ultimately, the capacity retention after 60 cycles could be improved by up to approximately 40 % for an already optimized binder formulation. The underlying mechanisms still need to be better understood, but in

light of the possible electrochemical performance improvements, we believe that both SF and copper CC should be more systematically addressed in battery literature.

Introduction

Silicon is a promising negative electrode material for next generation Li-ion batteries due to its high theoretical gravimetric and volumetric capacities. At the highest lithiation stoichiometry, *i.e.* $\text{Li}_{15}\text{Si}_4$ they reach 3600 mAh.g^{-1} and 2200 mAh.cm^{-3} , respectively. However, its well-known limitations, which are mainly related to its high volume variation (up to 280 % at full lithiation), are not yet fully resolved.¹ One of them is the electrode cracking and delamination, which is known to be detrimental to electrochemical performance. To circumvent these mechanical issues, various electrode formulations have been investigated, especially regarding the binder nature as it plays a key role on the electrode mechanical behavior.^{2,3} Other electrode components, such as the Cu current collector, but also some electrode processing parameters, such as the ink solid fraction, are also likely to impact on the mechanical and electrochemical properties of Si-based electrodes.

There are many grades of copper foil with different mechanical properties depending on their manufacturing process. Their mechanical properties, such as elastic modulus and yield strength, can be determining in the fracture mechanics of a thin film covering them,⁴⁻⁶ and in the case which interests us an electrode film. However, and to our knowledge, the influence of the copper current collector grade has never been investigated for electrodes containing high volume variation alloying materials such as silicon.

Second, the influence of the solid fraction, which is the dry matter fraction in the ink formulation, has already been studied but only for positive electrode formulations.⁷⁻⁹ Even if the number of studies available is small, they all give very interesting results. In fact, there is an optimal solid fraction for which the composite electrode elements (active material, conductive additive, and binder) are more homogeneously dispersed. Below this optimum value, the amount of solvent in the ink is too high and during drying, particles sedimentation and/or binder migration occur, which results in phase segregation across the electrode film.^{7,8} Above this optimum value, the ink viscosity is too high, which hinders the de-agglomeration of the electrode components and their efficient dispersion in the ink, and again it results in phase segregation.⁷ In both cases, the electrochemical performance is reduced. Eventually, SF tuning improves electrode characteristics such as adhesion and conductivity (among others) as Das et al.⁹ have shown for LiFePO_4 electrodes.

Therefore, in the present study, the influence of the Cu current collector (Cu CC) mechanical properties and the ink solid fraction (SF) on the performance of Si-based electrodes is investigated. Additionally, standard binder formulations and coordinatively cross-linked formulations¹⁰⁻¹² are

compared, and their respective influence is also highlighted. The results show that the Cu CC grade and the SF significantly influence the cyclability of silicon-based electrodes. They also underline the robustness of the electrode formulation based on cross-linked polymer by coordination chemistry, which electrochemical behavior appears much less sensitive to the Cu CC grade and SF.

Results and discussion

Inks for electrode fabrication were prepared by mixing a fixed amount of silicon and conducting additive (graphene) with a varying amount of binder solution, whose concentration was tuned to systematically reach a final Si/graphene/binder composition close to 70:10:20 _w%. The reference binder solution consists of sodium carboxymethylcellulose (NaCMC) dissolved in a buffer solution made of citric acid (CA) and sodium or potassium hydroxide. Then, Zn(II) ion can be introduced, for example in the form of a salt (ZnSO₄, Zn(NO₃)₂) or an oxide (ZnO). The effect of the nature of the metallic precursor,¹² and coordination ratio,¹¹ which is the molar ratio of Zn over COOH moieties, have been previously evaluated. Interestingly, whatever the Zn(II) ion source, the electrochemical performance are significantly improved thanks to the formation of a cross-linked network made of Zn-carboxylate coordination bonds, as compared to the reference (Zn-free) binder electrodes. The Zn cross-linked binder significantly improves the electrode mechanical properties,¹² solid electrolyte interphase (SEI) stability,¹⁰ and thus the overall electrochemical performance. Table 1 summarizes the ZnSO₄ and Zn-free formulations which are used in this study. Their areal mass loading was fixed at $1.75 \pm 0.1 \text{ mg}_{\text{Si}}.\text{cm}^{-2}$. The electrodes were not calendered and their porosity at the pristine state was estimated at around 60%.

Table 1 Composition of the electrode for the ZnSO₄ and reference (Zn-free) formulations.

Formulation name		Electrode composition (w%)					
<i>Salt</i>	<i>Coord. ratio</i>	<i>Silicon</i>	<i>Graphene</i>	<i>NaCMC</i>	<i>Citric acid</i>	<i>KOH or NaOH</i>	<i>Zn precursor</i>
Zn-free	0	73.4 73.6	11	7.2	7.4	1.0 0.8	0
ZnSO ₄	0.22	69.9 70.1	10.5	6.8	7	1.0 0.7	4.8 4.9

Cu current collector mechanical properties and their influence on electrochemical performance

Figures 1a to 1d present the evolution with cycling of the specific discharge capacity and coulombic efficiency (CE), of the reference (21.4 % SF) and the ZnSO₄ (22.3 % SF) electrodes (averaged on 3 to 8 cells), made with either a cold rolled (C.-R.), an annealed (Ann.) or textured (Txt.) Cu CC. When the last two are used, the capacity retention is significantly enhanced compared to the C.-R. Cu CC for the Zn-free formulation. Respectively, the 60th cycle capacity is approximately 2230 and 1930 vs. 1740 mAh.g_{Si}⁻¹. The coulombic efficiency (CE) is also affected by the nature of the current collector for this formulation. The 1st cycle CE is 82.8 and 84.9 vs. 81.1 %, and the CE plateaus at around 99.5 vs. 99.4 % from the 20th cycle, for the Ann. and C.-R. Cu CC, respectively. The average CE between the 20th and 65th cycle was not obtained for the Txt. Cu CC. Because, the CE was over 100 % for most of the cycles, supposedly due to parasitic reactions at the Li counter-electrode during the charge. In contrast, for the formulation containing ZnSO₄, the impact of the Cu CC's nature is very limited since the 60th cycle capacity is approximately 2550 and 2320 vs. 2520 mAh.g_{Si}⁻¹, the 1st cycle CE is 86.2 and 85.5 vs. 84.5 % and it stabilizes at around 99.4 and 99.5 vs. 99.2 % from the 20th cycle for the Ann., Txt. and C.-R. Cu CC, respectively. Complementary information on electrochemical performance is gathered in Table S1 for every formulation tested in this study. In summary, it clearly appears that the Ann. and Txt. Cu CC improves the capacity retention over the C.-R. Cu CC for the Zn-free formulation, while this is not the case for the ZnSO₄ one. These results also show that whatever the grade of Cu CC, the cyclability and the CE are increased by the crosslinking of the binder with Zn. Remind that the latter formulation has better mechanical properties than the former, *i.e.* superior cohesion, hardness, and elastic modulus, which ultimately lead to a reduced expansion of the electrode during electrochemical cycling.¹²

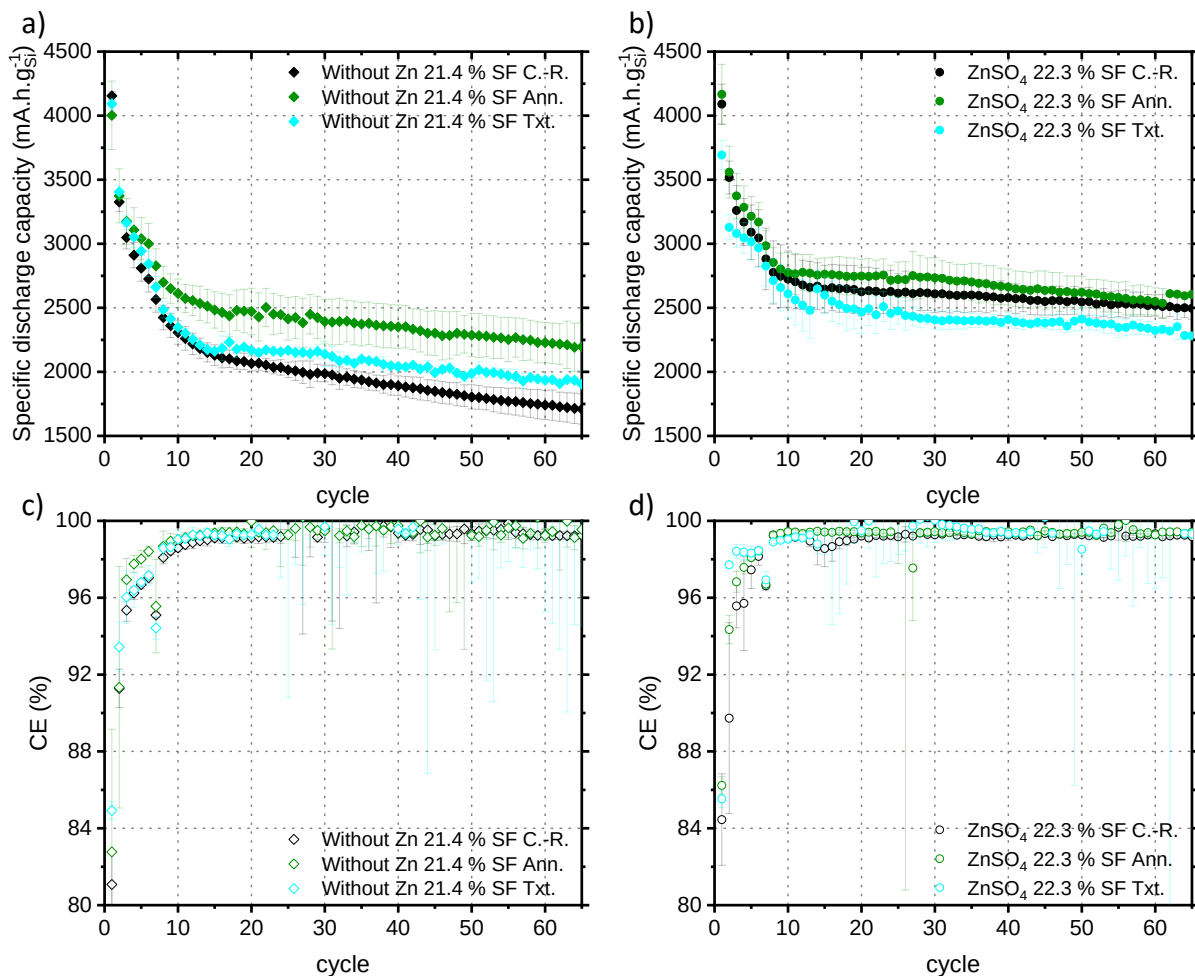


Figure 1 Mean specific discharge capacity and CE as a function of cycle number of electrodes with either a cold rolled, an annealed or a textured Cu current collector: (a, b) Zn-free formulation; (c, d) ZnSO₄ formulation. The electrodes were cycled at C/40 for the 1st cycle, then C/20 for 5 cycles, and C/10 for the remaining cycles. The mean and standard deviation values were determined with a minimum of 3 electrodes for each formulation.

In complement, the cracking patterns of Zn-free and ZnSO₄ electrodes on the different Cu CC. were observed after 1 cycle with a scanning electron microscope (SEM), as shown in Figure 2. The study of cracking after only 1 cycle is relevant since the *operando* optical microscopy analysis did not reveal any further crack formation or propagation after a couple further cycles (see Figure S1). This is also in accordance with our previous *operando* optical microscopy observations on Si-based electrodes, showing that the larger cracks form during the first delithiation and then close and open at the same places in the electrode film upon successive lithiation/delithiation cycles.¹³ This means that most of the electrode mechanical degradation in the forms of large cracks happen in the first cycle. This is expected since the lithiation and delithiation reach their maximum for the 1st cycle and so does the corresponding strain, and therefore induced stress. Nonetheless, additional mechanical damage may be anticipated

after repeated cycling because of material fatigue¹⁴ and also because of the accumulation of SEI products in the pores and cracks of the electrode,¹⁵ reducing the free space for electrode expansion. This additional damage may be the cause of the more gradual decrease in capacity observed after the first cycle. The latter can also have as a complementary origin the growth of the SEI electrically insulating the active material.¹⁶

The crack pattern on each electrode resembles that of mud cracking. The cracks run in different directions, which merge into a network and in doing so form islands of electrode coating. Even if it is not so obvious for the Zn-free electrode with a C.-R. Cu CC, cracks running in various directions can be seen. Such seemingly random crack orientation indicates that the stress which generates them is multiaxial.^{4,17} Interestingly, the formation of such cracks in coatings, (thin) films, and layered material happen when under tension.^{4,17} This is consistent with the cracks apparition during the delithiation, as observed by operando optical microscopy in Figures S1a and S1c and in previous work.¹⁸ It is due to the constraint imposed by the current collector in the x and y (in plane) directions to the electrode retraction. In these directions, the electrode is strongly contracting but not the collector. This leads to large deformation incompatibilities in the x and y directions while nothing constrains the electrode in the z (out of plane) direction. This is the reason why the cracks are occurring in planes perpendicular to the electrode. A study by X-Ray tomography on the standard (Zn-free) electrode showed that cracks preferentially initiate from porosity (which is equivalent to a flaw) at the bottom of the electrode near to the current collector interface, and then propagate first in the z direction (toward the top of the electrode) and then grow in the x-y plane.¹⁸ SEM observations of cracks presented Figure S2 also show that the cracks do not reach the Cu CCs, whatever the formulation or Cu CC type. However, crack could be kinking out of their initial propagation direction during their growth.⁴ From Figure 2, the spacing between adjacent and parallel cracks (equivalent to the island dimensions) were estimated for the six samples over several regions of interest (each ROI's surface is equal to 0.4 mm²) and the results are displayed in Table 2.

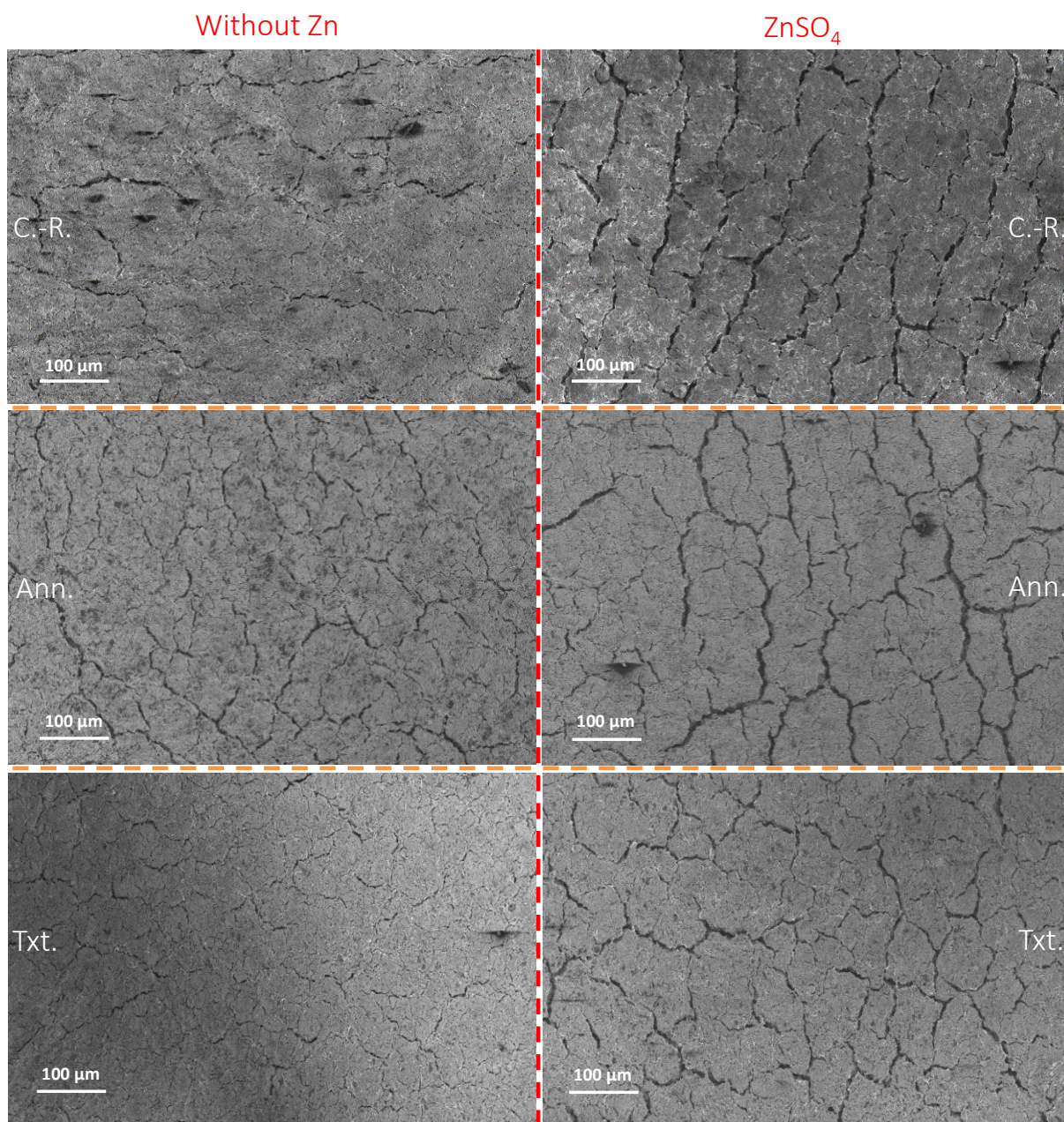


Figure 2 SEM observations of electrodes surface, after 1 cycle; Left side from top to bottom: Zn-free formulations (21.4 % SF) with a C.-R., then an Ann. and finally a Txt. Cu CC; Right side from top to bottom ZnSO₄ formulations (22.3 % SF) with a C.-R., then an Ann. and finally a Txt. Cu CC. For the Ann. and Txt. Cu CC electrodes, the brightness and contrast were modified with the software ImageJ.

The crack spacing is rather similar for the ZnSO₄ formulation with every Cu CC, e.g. in between 74 and 84 μm for the mean value. This can be correlated to their similar electrochemical performance as seen in Figure 1. This at first sight seems to indicate the ZnSO₄ formulation electrode cracking is firstly controlled by its mechanical properties and not by the Cu CC. Actually, electrodes made with a cross-linked binder show much superior mechanical strength, with higher resistance to indentation and scratching than the reference electrodes.^{11,12} Thus, the higher cohesion of such electrode could

explain the fact that the Cu CCs' grade has no major impact on the mechanical and electrochemical properties for the ZnSO₄ formulation. In contrast, there is approximately a one-half and a one-third ratio for the Zn-free formulation between the C.-R. (98 µm) and respectively, the Ann. (55 µm) or Txt. (37 µm) Cu CC space between two adjacent cracks. Thus, in this case, the electrode cracking depends strongly on the Cu CC for the Zn-free formulation and thus depends on the interface between the electrode and the Cu CC.

Table 2 Electrode crack spacing (equivalent to the island dimension) for the ZnSO₄ (22.3 % SF) and its Zn-free reference (21.4 % SF) formulations with either a C.-R., an Ann. or a Txt. Cu CC.

		Spacing between cracks (µm)	Std. Dev. (µm)	Number of Measurements (Nb. of ROIs)	Film thickness (µm)
ZnSO ₄	Cold rolled	84	18	44 (2)	33
	Annealed	81	24	162 (4)	38
	Textured	74	21	260 (6)	33
Without Zn	Cold rolled	98	35	28 (2)	33
	Annealed	55	18	208 (5)	29
	Textured	37	15	214 (6)	29

For better understanding, the Cu CCs' were investigated through nano-indentation experiments, profilometry and XPS spectroscopy. Nano-indentation and profilometry results are displayed in Table 3. The Cu CCs used present a relatively narrow range of elastic modulus (E) with 100, 90 and 70 GPa for the C.-R., Ann. and Txt. Cu CC, respectively. However, there is a stark difference in terms of hardness (H), which are equal to 2, 1 and 1.3 GPa for the C.-R., Ann. and Txt. Cu CC, respectively. This parameter can be used to determine the Cu CCs' yield strength (YS) and ultimate tensile strength (UTS) with a fairly good precision as they are linearly correlated.¹⁹ To do so, the hardness is first converted to the Vickers hardness number (VHN) using eq. (1)²⁰:

$$VHN = H \times \frac{1000}{9.81} \quad (1)$$

Then, applying the eq. (2) and (3) for respectively the YS and UTS¹⁹:

$$YS = 2.874 \times VHN \text{ (MPa)} \quad (2)$$

$$UTS = 3.353 \times VHN \text{ (MPa)} \quad (3)$$

Those equations were obtained by a linear regression analysis over 120 data points from copper alloy samples.¹⁹ The validity range of those equations span from 50 to 425 VHN, which includes our data range (see Table 3). Results in Table 3 show that the calculated yield strength and the ultimate tensile strengths are 2 and 1.5 times lower for the Ann. and the Txt. Cu CC, than for the C.-R. one, respectively. One can observe that the capacity retention for the Zn-free electrodes increases when the yield strength of the current collector decreases, *i.e.* when its deformability increases, while for the electrode with ZnSO₄ the cyclability is on the other hand independent of the mechanical properties of the collector. These trends are depicted in Figure 3a, where the capacity retained at the 60th cycle is plotted as a function of the yield strength of the Cu CC.

Table 3 Main mechanical characteristics and roughness, average (Ra) and quadratic average (Rq) of the C.-R., Ann. and Txt. Cu CC. The mean roughness values and their standard deviation were determined from 6 measurements over a distance of 2 mm for each Cu CC.

Current collector	Elastic modulus (Gpa) (Measurement depth (μm))	Hardness (Gpa) (Measurement depth (μm))	Vickers hardness number	Yield strength (MPa)	Ultimate tensile strength (MPa)	Ra (nm)	Rq (nm)
Cold rolled	100 (0.3)	2 (0.6)	204	586	684	45 ± 4	60 ± 6
Annealed	90 (0.2)	1 (0.3)	102	293	342	193 ± 4	266 ± 13
Textured	70 (0.3)	1.3 (1)	133	381	444	389 ± 14	479 ± 25

Figure S3 shows SEM images of the different Cu CCs surface over a distance of around 20 μm and their respective roughness over a distance twenty times bigger. The aspect of the roughness is similar for the C.-R. and Ann. Cu CCs, as can be seen respectively on Figures S3a and S3c and takes the form of parallel stripes, most likely coming from the lamination process. However, the roughness measurements show that the amplitude of those stripes are much bigger, but less frequent for the Ann. Cu CC (Figure S3d), compared to the C.-R. Cu CC (Figure S3b). The Txt. Cu CC presents a completely different roughness in the form of grains Figure S3e, which results in roughness with high amplitude and high frequency, as can be seen Figure S3f. Unfortunately, the texturing process of the Txt. Cu CC is unknown. Quantitative values of roughness were obtained from Figures S3b, S3d and S3f for the different Cu CCs and are given Table 3. The average (Ra) and quadratic average (Rq) roughness is approximately 4 times higher for the Ann. than for the C.-R. Cu CC and around 2 times higher for the Txt. than for the Ann. Cu CC. Interestingly, the standard deviation is at maximum around 10 % for the

Ra or Rq value of the different Cu CCs meaning that their roughness is rather homogeneous over their whole surface. The relation between the cracks spacing and the roughness of the Cu CC is shown in Figure 3b. It is observed that this cracking mechanism of the electrode is relatively independent of the roughness of the Cu CC in the case of the ZnSO₄ containing electrodes. On the contrary, the cracks spacing clearly appears to decrease with the increase in the roughness of the Cu CC for the Zn-free electrodes. These trends suggest again that the ZnSO₄ containing electrodes' damage mechanisms are independent on the substrate properties and thus, are controlled by the electrode cohesion. While for the Zn-free electrodes these mechanisms depend on the interface between the electrode and the Cu CC.

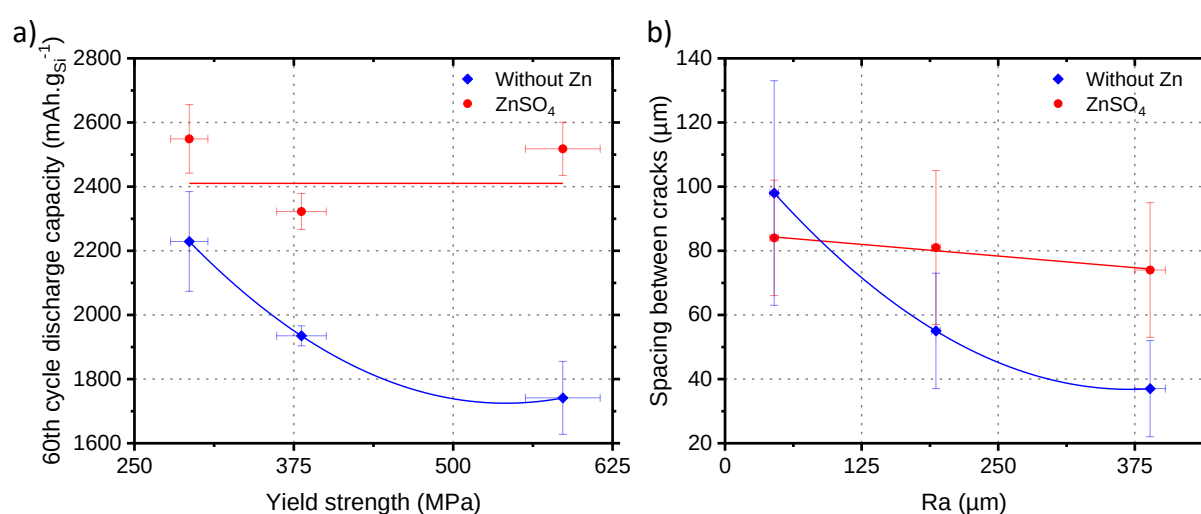


Figure 3 (a) 60th cycle specific discharge capacity as a function of the Cu CC yield strength for both formulations; (b) Spacing between cracks as a function of the average roughness for both formulations.

The chemical composition of the different Cu CCs surface was investigated by X-Ray photoelectron spectroscopy (XPS) and is presented Figure S4 (the peaks position are available Table S2). Interestingly, the surface composition of the C.-R. and Ann. Cu CCs are similar and composed of a layer of Cu(OH)₂ and Cu₂O, which for the former can form copper carboxylate bonds with the binder,¹¹ thus favoring the adhesion between the film and the Cu CC. However, the Txt. Cu CC's surface is composed of CuCr₂O₄. It is known that the of metal surfaces chromating increases the adhesion of polymeric materials with it, so we think that the surface composition of Txt. Cu CC is favorable to an equal and even superior adhesion of the electrodes to that of the other Cu CC.

To summarize, the Zn-free formulation electrodes cyclability and fracture behavior shows a significant dependence on the Cu CC grade. On the contrary, such dependence is not visible for the Zn cross-linked electrodes, which possess a much higher cohesion. Therefore, for the reference

formulation of lower cohesion, it appears that the increase in adhesion at the CC's interface, via the roughening of the surface of the current collector and/or the decrease of its yield strength, contributes to mitigate the electrodes' film mechanical damage, therefore preserving its cyclability.

An elegant way to modulate the adhesion at the interface as well as the mechanical properties of the collector in contact with the electrode is to cover the surface of the collector with a buffer layer. Thus, Xu et al.,²¹ and Li et al.²² showed that the insertion of a soft and conductive layer of conductive carbon and PVDF is beneficial to the cyclability of silicon-based electrodes. The more conventional approach is to increase the roughness of the current collector. However, the benefit of this approach decreases when the binder content in the electrode (i.e. its cohesion) increases, as shown by Jeon et al.,²³ and also as observed here with the Zn cross-linked electrodes. On the contrary, Basu et al.²⁴ observed that the introduction of a conductive layer, which at the same time promotes the sliding of the silicon electrode, can bring about a remarkable improvement in the cyclability of silicon-based electrodes. Literature's results and ours, point out that there is an urgent need to comprehensively and systematically study the role of the surface properties of the CC and its interface with the coating on the mechanical and electrochemical behavior of electrodes, when its active material presents volume variations during the (de)insertion of lithium.

The yield strength is an important parameter for a substrate as it influences the cracking behavior of a film adhering to it, when there is sliding at the interface⁵ (i.e. shear-lag mechanism). Then, for a film coated on a relatively ductile substrate, the spacing between cracks is proportional to the stress and inversely proportional to the substrate yield stress (or to the friction at the interface¹⁷). The ratio between those two parameters also indicates the transition between the shear-lag and the small scale yielding mechanism⁵ (which is also dependent of the film to substrate ratio of elastic modulus). When the small scale yielding mechanism dominates (i.e. for a sufficiently rigid substrate), the crack spacing is inversely proportional to the stress but proportional to the coating fracture toughness.^{17,25} The nano-indentation experiments showed that the yield strength is lower for the Ann. and Txt. Cu CC, which means that they are more ductile (i.e. more prone to plastic deformation). A greater ductility/deformability of the substrate makes it possible to better accommodate the strain of the electrode and then mitigate/buffer the stresses within the electrode. The sensitivity of the Zn-free electrodes to the ductility of the substrate can be explained by its lower toughness (and higher volume variation), whereas as written above, the higher toughness (and lower volume variation) of the Zn cross-linked electrodes can render it less or insensitive to the substrate ductility.

Now, looking into thin film on substrate cracking theories help to gather more insights on the Zn-free and ZnSO₄ electrodes cracking behaviors. First, it is necessary to know the critical stress σ^* at

which the cracking occurs. This stress is the sum of the residual stress from electrode shrinking during its drying on the CC (whose manifestation can be the cracking or bending observed on uncycled electrode²⁶) and the stress arising from delithiation. Applying the theory of Beuth Jr J.,²⁷ it is possible to obtain an estimation of the critical stress for the formation of non-interacting cracks reaching the CC interface, in a film on an infinitely thick substrate. This theory has the advantage of taking into account the full range of elastic mismatch between the electrode coating and Cu CC. One can apply it using eq. (4)²⁷:

$$\sigma^* = \frac{\delta(h) \times \bar{E}_1}{\delta^*(\alpha, \beta) \times h} \text{ (MPa)} \quad (4)$$

With $\delta(h)$ (μm) being the width of the cracks at the top surface of the electrode, which span from a few to about ten microns for both formulation as can be seen Figure 2; $\delta(\alpha, \beta)$ is a nondimensionalized crack opening displacement which is tabulated²⁷ for different value of the “Dundurs parameters”^{4,27} α and β . For plane strain problems α range between -0.9 to -1 for both formulations on the three different Cu CC (which negative value indicates a relatively compliant film on a relatively stiff substrate). β is approximately equal to $\alpha/4$; $\bar{E}$ (MPa) is the material plane strain tensile modulus (the appendix 1 in eq. (4) correspond to the film); μ (MPa) is the material shear modulus equal to $\frac{E}{2 \times (1+\nu)}$. For both formulations electrode coating, the Poisson ratio is hypothetically equal to 0.3 as it is a common value for composite materials, and the Cu CCs’ Poisson ratio is 0.33. The elastic modulus are respectively 3.75 and 1.25 GPa for the ZnSO_4 and its reference formulations, as previously determined by nano-indentation for pristine electrodes soaked in “electrolyte”;¹² h (μm) is the film thickness.

For the Zn-free electrodes on the different Cu CC the resulting critical crack stresses range from tens of MPa to around 100 MPa, while for the the ZnSO_4 formulation the stresses range from 100 Mpa to a few hundreds of MPa. What makes the difference between the critical stress for cracking of these two electrodes in our calculation is essentially there different elastic moduli. Those critical stress values are obviously approximations as for example the film thickness at which the cracking occurs is most likely different from its pristine thickness (because of silicon volume expansion) and also since the electrode’s elastic modulus depends on its state of charge.²⁸ Nonetheless, those order of magnitude are probable, considering previously reported values.^{12,29} Now, considering the electrodes’ critical crack stress over Cu CCs’ yield strength ratio (*e.g.* approximately 0.1 to 1.5) and the films’ over substrates’ elastic modulus ratio (*e.g.* approximately 0.01 to 0.05),⁵ the cracking behavior of the ZnSO_4 and Zn-free electrodes, on the three different Cu CCs most likely follows the shear-lag mechanism (see Table 1 and Figure 4⁵). However, it is hard to evaluate, as the transition point with the small scale yielding mechanism for our range of material properties is not well defined in Hu and Evans’s publication.⁵

Nevertheless, for the Zn-free electrode on the C.-R. the sliding interface is most likely accompanied by interface delamination because of the Cu CC high yield strength (in the contrary, a low one increase the ability of the substrate yielding to blunt the crack propagation at the interface and thus reduces the risk of delamination) and its poor adhesion to the electrode film.⁵ Indeed, apart from the poorer adhesion intrinsic to the Zn-free formulation compared to the ZnSO₄ one, the C.-R. presents the lowest roughness of all three Cu CC, see Figure S3, with a Ra and Rq of only 45 ± 4 and 60 ± 6 μm (Table 3), respectively.

Cracks are not necessarily detrimental to the electrode cyclability if they are vertical (in the z-direction). This is exemplified by the Zn-free (21.4 % SF) on Ann. or Txt. Cu CC electrode, which delivered better performance while having more and or larger cracks than the same formulation electrode but with a C.-R. Cu CC. Their presence could offer more space to buffer the volume expansion and consequently reduce the delamination risk during lithiation. The multiplication of cracks might also reduce the impact of pores clogging by SEI. On the opposite, delamination is more detrimental to the electrode cyclability as it results in the electrical contact loss of electrode pieces, which becomes electrochemically inactive. As seen previously, delamination could be a consequence of the sliding interface cracking mechanism if the CC yield strength is high and the adhesion to the film is poor. It can also originate from neighboring islands pressing onto each other during lithiation, as observed here by operando optical microscopy on the reference formulation (21.4 % SF) electrode with a C.-R. Cu CC (Figure S1), and in previous work.¹³ Thus, delamination likely explain the poorer capacity retention from the Zn-free electrodes on C.-R. Cu CC (Figure 1) compared to the other two Cu CCs.

Ink solid fraction modification and its influence on electrode properties

Figure 4 shows the viscosity as a function of the shear rate for the Zn-free and ZnSO₄ inks at different SFs. Similar studies were conducted for inks formulated with ZnO as well as the related references (see Table S3 for the composition). The corresponding results are shown Figure S5a. The inks exhibit a shear-thinning behavior, which means that the viscosity decreases with increasing shear rate. The solid fraction significantly enhances the ink viscosity (easily up to an order of magnitude) when it is increased, mostly because the solvent volume is reduced such that particles interactions are favored. This makes the SF adjustment a simple way to tune ink viscosity without modifying the electrode formulation. Interestingly, both formulations have similar viscosity at the tape casting shear rate of either 37 or 56 s^{-1} (*i.e.* at the blade gaps $h = 150$ or 100 μm , with a casting speed of 5.6 mm.s^{-1}). Therefore, both formulations should show comparable behavior under the blade gap during electrode preparation. At a shear rate of 0.01 s^{-1} , *i.e.* nearly in rest condition, the ZnSO₄ formulation ink viscosity is always slightly inferior, whichever the SF, to the Zn-free ink viscosity (see Figure S5b). This could originate from a denser binder ad/absorption on the silicon particles, which reduces the steric hindrance and the liquid phase viscosity, or from an increased interparticles electrostatic repulsion induced by

ZnSO₄ salt adsorption at the surface of the particles. The same behavior is also observed for the inks formulated with ZnO and its reference, whichever the SF, as can be seen Figure S5a. However, the magnitude of this effect is much larger. In a general manner, the ink viscosity above 22 % SF for the ZnO and its reference formulation is higher than the ZnSO₄ and its reference, as summarized in Figure S5b. This highlights that there is a complex interplay between pH, concentrations and presence of divalent cations. Such complexity was previously observed in binder solutions.¹²

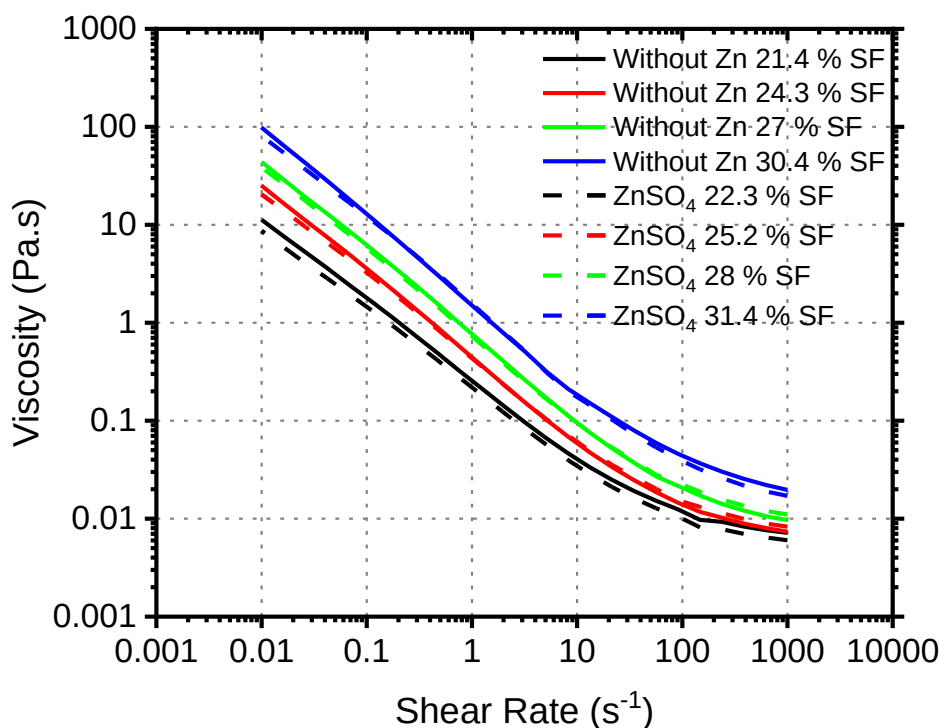


Figure 4 Viscosity as a function of shear rate for inks without Zn or with ZnSO₄ at different SF.

The ink yield stress as well as storage (G') and loss (G'') modulus are gathered Table 4 for the Zn-free and ZnSO₄ formulations at different SF. The former represents the minimal stress required for the fluid to flow and is obtained by multiplying the viscosity by the shear rate at the first measurement point, around 0.01 s⁻¹. For both formulations the yield stress increases with the SF, up to 9-fold when passing from the lowest to the highest SF. However, as for the viscosity, the yield stress growth with the SF for the ZnO and its reference formulations is much greater. Namely, for the former it increases 9-fold, just from 21.8 to 27.5 % SF to reach 1.81 Pa and for the latter it increases 17-fold, from 21.5 to 27.1 % SF to reach 3.54 Pa. All the data are summarized Figure S5c. The yield stress is associated to ink stability during drying (at rest), such that the higher the yield stress, the less prone the ink is to sedimentation and phase segregation. As such, increasing the SF reduces those risks.

Table 4 Yield stress, storage modulus, and loss modulus for inks without Zn or with ZnSO₄ at different SFs.

	Zn-free				ZnSO ₄			
Solid fraction (w%)	21.4	24.3	27	30.4	22.3	25.2	28	31.4
Yield stress (Pa)	0.11	0.25	0.44	0.98	0.09	0.2	0.38	0.81
Storage modulus (Pa)	3	28	54	193	1.8	15	42	120
Loss modulus (Pa)	0.8	10	20	88	0.6	6	15	62

The G' and G'' values are taken from their plateau at low strain amplitude (not shown) for a 1 Hz solicitation frequency. For both formulations at every SF, $G' > G''$ which proves that the ink behaves as physical gel, *i.e.* there is interconnected matter throughout the whole ink volume. The storage modulus increases with SF, *i.e.* the matter network in the ink fortifies, which is consistent with the yield stress evolution with SF.

In order to evaluate the magnitude of silicon particles/binder interactions,³⁰ depending on ink's SF and formulation, thermogravimetric analyses (TGA) of silicon particles contacted with the binders solution were carried out. The inks were here prepared with a binder:Si mass ratio of 8:1 (for comparison the ratio is 1:8 in the ink formulations used to manufacture the electrodes) in order to exacerbate the ad/absorption of the binder and thus facilitate its detection by TGA. Si particles were suspended in the binder solutions, recovered by centrifugation, and then dried at room temperature and further at 60 °C (see supporting information for details). Figure 5 illustrates the mass loss of dried Zn-free or ZnSO₄ binders on silicon particles prepared at different SFs (averaged from 3 measurements). The first mass loss from 30 to 150 or 160 °C for the Zn-free and ZnSO₄ samples, respectively, is associated with dehydration. This mass loss is 0.9 and 1.2 % for the Zn-free samples at 21.4 and 27 % SF, respectively. For the ZnSO₄ samples, the mass loss is 1.4 and 2.3 % at 22.3 and 28 % SF, respectively. The second mass loss is associated with the decomposition of the organic moieties and span between 150 to 340 °C for the Zn-free samples, and between 160 to 450 °C for the ZnSO₄ samples. This mass loss is 3.9 and 4.6 % for the Zn-free samples at 21.4 and 27 % SF, respectively. For the ZnSO₄ samples, the mass loss is larger, 5.7 and 8.2 % at 22.3 and 28 % SF, respectively.

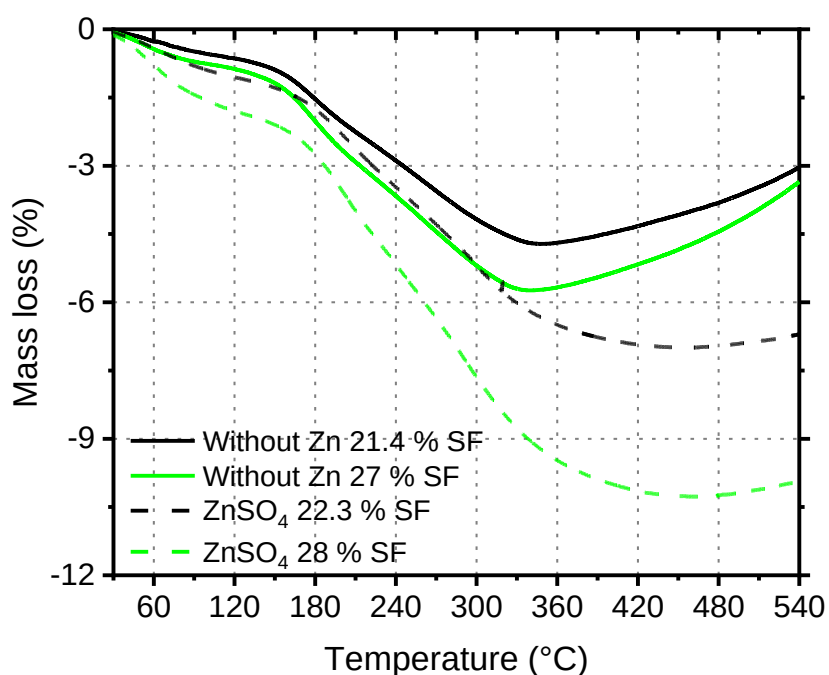


Figure 5 Mass loss of silicon particles covered by dried binder, either without Zn or with ZnSO₄, at different SFs.

Whatever the SF, the mass loss related with the organic component is higher for the ZnSO₄ binder. The fact that more binder is readily ad/absorbed on the particles in the ink suggests a higher affinity with the Si particles. The CMC and citric acid are ad/absorbed to the silicon particles through Van der Waals interaction, or hydrogen or ionic bonds^{31–33}. The Zn(II) cations are expected to adsorb to the silicon particles surfaces through electrostatic interactions. The presence of Zn(II)-carboxylate coordination bonds for the ZnSO₄ formulation should cause more binder to be retained onto the particles. Also, the amount of binder ad/absorbed increases with the SF because as the liquid volume is reduced the binder/particles interactions are favored. The difference in binder ad/absorption between both formulations could explain the viscosity difference seen in Figure 4, with the hypothesis of lower ink's liquid phase viscosity being favored due to enhanced ad/absorption in the presence of ZnSO₄ species. Interestingly, the silicon oxidation which appears as a mass gain at high temperature, is delayed by around 110 °C with the ZnSO₄ binder compared to the Zn-free binder (around 440 and 330°C, respectively). This delay in the silicon oxidation can reflect a better silicon coverage by the binder. Indeed, the carbonization of the binder layer may prevent the direct contact between the silicon surface and the air until it is oxidized as CO₂. Importantly, the “spontaneous” binder ad/absorption on the particles in the ink was only representing around 4 to 8 % (for a binder volume 8 times higher than in a typical ink formulation), whereas the binder proportion in the electrode is around 15 to 20 % (as can

be seen in Table 1). Therefore, most of the binder is dissolved in the ink liquid phase rather than readily adsorbed of the silicon, and deposits at the particles surface and interparticle junctions during drying.³⁴

The electrical resistivity of the Zn-free and ZnSO₄ coatings at different SFs is illustrated in Figure 6. The ZnSO₄ coating resistivity is higher than the Zn-free ones, whichever the SF. The electrical conductivity of composite electrodes made with active material, conductive additive, and binder has a first-order dependence on the binder layer thickness ad/absorbed between the conductive additive particles^{35,36}, because the electric conduction is made by tunneling (once the electric percolation is achieved in the electrode, *i.e.* above a critical volume fraction of conductive additive, which is the case for those electrode formulations). Thus, and in agreement with the picture coming out from the TGA measurements, the ZnSO₄ binder might also be more ad/absorbed on the graphene particles. Another cause could be the trapping of electrons (negatively charged) or the hindering of their transfer through and between graphene particles due to their attractive interaction with the adsorbed Zn²⁺ cations (positively charged).³⁷ Additionally, the resistivity increases with the SF; this is again in complete agreement with the increase of the amount of ad/absorbed binder on the Si particles with the SF (Figure 5), as the trend will be similar for the binder ad/absorption on graphene. The electrode conductivity is quite low, only around one order of magnitude higher than the ionic conductivity of the electrolyte (LP30 Li⁺ conductivity is 0.015 S.cm⁻¹ ³⁸) for the Zn-free electrodes and approximately the same order of magnitude for the ZnSO₄ electrodes. This could induces non-negligible impedance from the conductive additive networks, as compared to the electrolyte.³⁹ Fortunately, upon silicon lithiation, its electric conduction increases by several orders of magnitude⁴⁰ which will reduce the impedance. As a matter of fact, previous work⁴¹ showed that it is possible to reduce the conducting carbon content down to 6 w%, which increases the resistivity to about 400 Ohm.cm, without suffering any increase in the electrode resistance nor decrease of the cyclability.

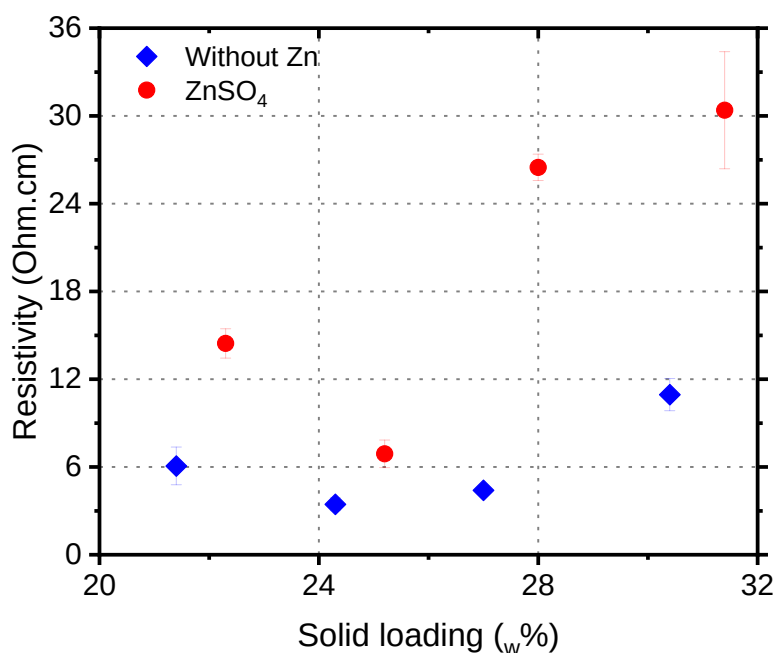


Figure 6 Electrode coating (without Cu CC) resistivity for Zn-free and ZnSO₄ formulation at different SF.

Figures 6a to 6d present the specific discharge capacity and CE of the formulations with ZnSO₄ at 22.3 and 28 % SF and Zn-free formulations at 21.4 and 27 % SF, all with a C.-R. Cu CC. When a higher SF is used, both the capacity retention and CE are enhanced for both formulations. The performance enhancement is however much more significant for the Zn-free formulation. In details, for the latter, the 60th cycle capacity is approximately 2470 vs. 1740 mAh.g_{Si}⁻¹ and the 1st cycle CE is 87.0 vs. 81.1 %, for the 27 and 21.4 % SF, respectively. For the ZnSO₄ formulation, the 60th cycle capacity is approximately 2550 vs. 2520 mAh.g_{Si}⁻¹ and the 1st cycle CE is 86.9 vs. 84.5 % (but within std. dev. range), for the 28 and 22.3 % SF, respectively. The average CE between the 20th and 65th cycle was not compared because the CE was over 100 % for most of the cycles, supposedly due to parasitic reactions at the Li counter-electrode during the charge.

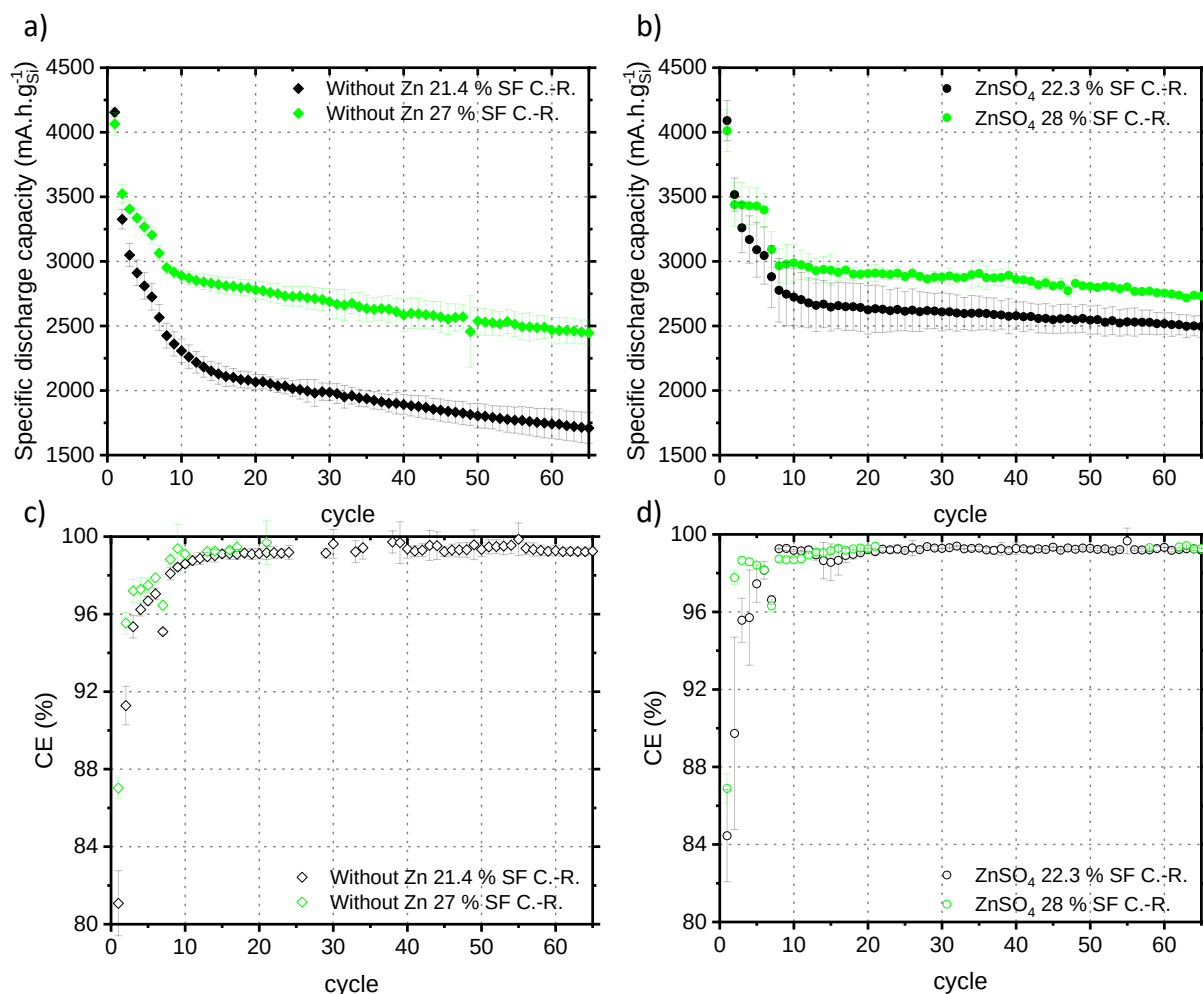


Figure 7 Mean specific discharge capacity and CE as a function of the cycle number of electrodes prepared with different ink SFs and with C-R. Cu CC: (a, c) Zn-free formulation; (b, d) ZnSO₄ formulation. The electrodes were cycled at C/40 for the 1st cycle, then C/20 for 5 cycles, and C/10 for the remaining cycles. The mean values and their standard deviation were determined from a minimum of 3 electrodes for each electrode formulation.

It clearly appears that increasing the SF improves the electrochemical performance of both formulations with a C-R. Cu CC. The difference is particularly visible for the Zn-free formulation so we characterized those electrodes further (also for the Zn-free + LiOH formulation with a C-R. Cu CC, as can be seen in Figure S6). First, the binder distribution on particles could be modified by the SF, as suggested by the enhanced ad/absorption of binder on particles with increasing SF. However, its preliminary investigation on electrode 3D analysis by focused-ion beam (FIB)-SEM was not conclusive because the binder was barely discernable. Second, phase segregation and binder accumulation on top of the electrode^{7,8} is a possibility at 21.4 % SF considering the rather low value of the ink yield stress. Also, the higher binder concentration at 27 % SF could have provoked a larger Cu CC corrosion and

consequent Cu-carboxylate bonds formation, the core phenomenon of the electrode “maturation” process, inducing a significant improvement of its electrochemical performance.¹¹ EDX was used to evaluate the distribution of the binder (through the analysis of Na/K) and extent of the Cu CC corrosion. Values below one percent were obtained. EDX quantifications of Na/K at the electrode surface render similar atomic percentage (within std. dev. range) for both Zn-free 21.4 % SF and 27 % SF formulations, suggesting that the distribution of the binder may not vary with the SF. This conclusion should however be taken with caution, because the underlying hypothesis is that the Na and K ions (introduced with the CMC and the citric acid buffer) are localized in the polymer phase, as a counter ion of the carboxylates of CMC and citric acid. However, these functions can be involved in bonds with the surface of the silicon or be neutralized, in the form of carboxylic acid functions. Then, Na⁺ and K⁺ ions can simply be adsorbed on the surface of the silicon, not reflecting the exact distribution of the binder. Further, Cu EDX quantification at the coating/Cu CC interface shows similar atomic percentage (not shown) for both Zn-free formulations, suggesting similar extent of corrosion. We thus believe the more likely explanation for the better electrochemical performance at higher SF is due to the enhanced ad/absorption of binder on silicon particles with increasing SF, which could be at the origin of better electrode mechanical stability. Anyway, the SF should be tuned to maximize the electrochemical performance of silicon-based electrodes.

Unfortunately, the electrochemical performance enhancements with the other two Cu CCs than the C.-R. one, do not seem systematic at higher ink SF. Indeed, increasing SF to 27 and 28 % for respectively the Zn-free and ZnSO₄ formulations, with an Ann. or a Txt. Cu CC yielded scarce (as can be seen Figure S8) or even no improvement (Figure S7). It is such that the interplay between both SF and Cu CC influence parameters, still need to be better understood to systematically improves the electrochemical performance of silicon electrodes. Nevertheless, these results attest once again of the Zn cross-linked electrodes superiority, which whatever the collector and/or the SF of the ink, show superior electrochemical performance (and are nearly independent on the Cu CC grade and ink’s SF).

Conclusion

The influence of solid fraction and current collectors, comparing cold rolled vs. annealed and textured copper, was evaluated for silicon based negative electrode for Li-ion batteries. The C.-R. Cu CC appears to have a high hardness which translates to high yield strength, whereas the Ann. and Txt. Cu CCs are softer. The former also has a poor roughness compared to the other two, which reduces the adhesion between the film and the Cu CC. Those properties have a significant impact on the cracking behavior of the Zn-free electrodes most likely because the intrinsic film cohesion and adhesion to the Cu CC of this formulation is relatively weak (compared for example to the ZnSO₄ formulation). Eventually, the Zn-free electrode with a C.-R. Cu CC at low SF present the lowest electrochemical

performance for this formulation likely because of film delamination during cycling. Whereas, the latter is reduced or even prevented for Zn-free electrode on Ann. or Txt. Cu CCs and for all tested ZnSO₄ electrodes. Then, increasing the SF led to improved electrochemical performance for three of the four formulations tested on C.-R. Cu CC (*i.e.* both reference and ZnSO₄ formulations), which could be related to different binder conformation on the silicon and/or graphene particles. However, the effects were limited when an Ann. or Txt. Cu CCs were used. For both parameters (SF and Cu CC), the mechanisms which affect electrochemical performance are complex, multi-factorial, and not yet fully rationalized. Nevertheless, in light of the possible performance differences, both ink SF and Cu CC grade should be more systematically addressed in the research field of batteries.

Experimental

Material preparation

Binder solutions

First, a pH 3 buffer solution (0.171 M of citric acid + 0.084 M of KOH or NaOH) was prepared by dissolving citric acid (99 %; Sigma-Aldrich) and KOH or NaOH salt (> 98 %; Sigma-Aldrich) in ultra-pure water. Then, 5 mL of buffer plus a variable amount volume of ultra-pure water was used to dissolve 160 mg of NaCMC (Mw $\approx$ 700 000 g.mol⁻¹, D.S. 0.9; Sigma-Aldrich). The as-obtained solution was the reference binder solution (Zn/RCO₂H = 0). Finally, upon NaCMC complete and homogeneous dissolution, the Zn(II) precursor was added all at once, and left until homogenization. For the reference containing LiOH, LiOH•H₂O ($\geq$ 98 %; Sigma-Aldrich) was also added at once. For every step, solutions were magnetically stirred at room temperature.

The salts coordination water was counted as a part of the binder water volume, whereas, the approximately 15 %_w ad/absorbed water in NaCMC was not taken into account.

For this study, different precursors of Zn(II) were used: ZnSO₄•7H₂O (Pure cryst.; Alfa Aesar), (99.99 %; Alfa Aesar) and ZnO (99.99 %; Alfa Aesar). Their quantity was adjusted to systematically reach the predefined theoretical molar coordination ratio of 0.22:

$$\text{Coordination ratio} = \frac{n_{\text{Zn}}}{n_{\text{COOH(citric acid+CMC)}}} \quad (5)$$

Electrodes

The Si powder used as active material was obtained by ball-milling Si powder (325 mesh, 99.96 %; Materion) using a HD-01 attritor (Union Process). The milling was performed under argon atmosphere for 20 h at 600 rpm with a ball-to-powder mass ratio of 10:1. The as-milled Si powder was composed of micrometric agglomerates as primary particles ($d_{50} \approx 10 \mu\text{m}$, $S_{\text{BET}} \approx 20 \text{ m}^2.\text{g}^{-1}$) and

secondary particles were under the micron. Its oxygen content determined by a LECO analyzer was approximately 1 w%.

160 mg of Si powder, 24 mg of graphene platelets used as conductive additive (xGnP M15 grade from XGSciences, average thickness ≈ 7 nm, average diameter = 15 μm , surface area $\approx 120\text{-}150\text{ m}^2\cdot\text{g}^{-1}$, according to supplier data) and a variable volume of binder solution (by weight) were set in a vial with three balls (diam. = 9.5 mm), both made of silicon nitride. The whole was mixed using a Pulverisette 7 (Fritsch) planetary mixer for 1 h at 500 rpm. Then, the as-prepared ink was tape casted with a doctor blade on a Cu current collector (Cu CC), either cold-rolled (C.-R.) (99.9 %, thickness $\approx 20\text{ }\mu\text{m}$, cold rolled; PI-KEM), annealed (Ann.) (99.8 %, thickness $\approx 25\text{ }\mu\text{m}$; Alfa Aesar) or textured (Txt.) (thickness $\approx 14\text{ }\mu\text{m}$). For the Txt. Cu CC the ink was tape casted on the face presenting the rugosity (the other face has a flat surface). The blade gap was $h = 150\text{ }\mu\text{m}$ (model 3540, $s = 5.6\text{ mm}\cdot\text{s}^{-1}$; Elcometer) or $h = 100\text{ }\mu\text{m}$ for the inks having a 27 % SF or higher in order to obtain the desired silicon loading (see below). As-prepared films were dried at room temperature for 12 h. Finally, electrodes were punched (diam. = 1 cm) and dried 2 h at 100 °C under vacuum ($P \approx 10\text{ mbar}$), prior to mass ($\Delta m = \pm 0.01\text{ mg}$; OHAUS) and thickness ($\Delta e = \pm 1\text{ }\mu\text{m}$; Mitutoyo) measurements. Then, they were dried again for 1 h under the same conditions prior to assembly. Electrodes were selected if their active mass loading reached $1.75 \pm 0.1\text{ mg}_{\text{Si}}\cdot\text{cm}^{-2}$.

Solid fraction

The ink dry matter percentage, as defined by eq. (6), corresponds to the ink solid fraction (SF):

$$SF = \frac{m_{dry}}{m_{dry} + (V_i \times \rho_{H2O})} \times 100\text{ (}\% \text{)} \quad (6)$$

With m_{dry} (mg) the total mass of the dry components used for the composite electrode, *i.e.* the active material, the graphene and binder. The solvent mass (*i.e.* water) is calculated by multiplying V_i (ml) the binder volume used for the ink, by ρ_{H2O} the water density which is equal to 997 $\text{mg}\cdot\text{ml}^{-1}$. Thus, the SF is modified by changing the binder volume used for the ink formulation. The weight fractions of the electrode components are preserved thanks to the modification of the binder solution concentration. This is achieved by varying the amount of ultra-pure water added to the 5 mL of buffer solution. For example, a standard binder solution contains 8.2 mL of water (5 mL of buffer plus 3.2 mL of ultra-pure water), and then 0.8 mL of binder solution is used for the ink formulation. The corresponding SF are 21.4 and 22.3 % for the Zn-free and ZnSO_4 formulation, respectively, with the difference coming from the addition of ZnSO_4 . Then for example, both 24.3 % SF Zn-free and 25.2 % SF ZnSO_4 inks have the same volume of binder solution, *i.e.* 0.68 mL, etc...

Material characterization

XPS

XPS spectra were recorded using an AXIS Ultra (Kratos) equipped with an Al monochromatic source ($E_{K\alpha} = 1486.6$ eV). The pass energy was fixed to 20 eV to measure the regions of interest, allowing a 0.1 eV resolution. The C 1s signal from adventitious carbon was used for energy calibration, setting its position at 284.8 eV. For reproducibility, 14 measurements were performed per ROI's energy range (Cu 2p, Cu LMM etc...) for each Cu CC samples, and the spectra were summed. For the Txt. Cu CC the face presenting the rugosity was analyzed.

SEM

The surface and coating/current collector interface of the electrodes (after removal with adhesive tape) were metallized with carbon and then analyzed with an EDX SDD probe (SAMx) in a SEM 5800LV (Jeol) with a voltage and gun current of 15 kV and 0.5 nA.

Current collectors' surface images are obtained using a SEM JSM 7600F (Jeol) with an in-lens SE detector. The gun voltage was 5 kV. For the Txt. Cu CC the face presenting the rugosity was analyzed.

Electrodes surface images are obtained after one cycle, using only the SEM part of a FIB-SEM 550 L (ZEISS), with the in-lens SE detector. The gun voltage and current were 6 kV and 5 nA. To avoid any air exposure, a sealed sample transfer shuttle (SEMILAB) was used between the glove box (where the cells were dismantled) and the FIB-SEM.

Profilometry

The current collectors' surface roughnesses were measured using a stylus profiler P-7 (KLA) using a diamond tipped stylus with a radius of curvature of 2 μm . For the C.-R. and the Ann. Cu CC the stylus was passed orthogonally to the stripes direction, because of their preferred orientation. For both of them the stylus load was 2 mg and 0.5 mg for the Txt. Cu CC. In all cases the stylus was passed six times over 2 mm (for the sake of reproducibility and the results were averaged) at a speed of 100 $\mu\text{m} \cdot \text{s}^{-1}$ and the sampling rate was 1 kHz. For the Txt. Cu CC the face presenting the roughness was analyzed.

Rheology

Electrode ink flow properties were determined with a MCR101 (Anton Paar) rheometer. The geometry used was plane-plane configuration (upper plate diam. = 50 mm, gap between both plates $h = 300$ μm). The temperature was regulated to 20 °C with a Peltier probe. Storage (G') and loss (G'') modulus were measured with increasing strain from 0.01 to 100 % at a frequency of 1 Hz. Shear stress and viscosity were measured with increasing shear rate from 0.01 to 1000 s^{-1} and then back down to 0.01 s^{-1} . The back scan was taken for the ink viscosities as tape casting occurs after the high-shear planetary mixing step.

TGA

The amount of ab/adsorbed binder on the surface of the silicon particles was evaluated using a thermo-gravimetric analysis. Inks containing 80 mg of silicon plus 3.2 mL of binder solution were prepared identically to those used for the coatings, with the exception of the number of silicon nitride balls placed in the jar for planetary mixing (which was increased to 6 instead of 3). Additional samples were made with 2.36 mL of more concentrated binder solution to increase the SF. In fact, the binder:Si mass proportion was selected to be 8:1 contrarily to classic ink formulation, for which the proportion is 1:8. Next, the inks were centrifuged in a glass vial for 5 min at 5000 rpm⁻¹. The supernatant fluid was removed and the remaining powder was allowed to dry, first for 12 h at room temperature and then for 12 h at 60 °C. Finally, the samples were analyzed with a STA 449F3 Jupiter (NETZSCH), between 30 and 540 °C at 5 °C.min⁻¹ under air. For reproducibility, 3 measurements were performed per formulation.

Indentation

The mechanical properties of the Cu current collectors were analyzed using a nano-indenter NHT³ (Anton Paar). The system coupled a sinusoidal load to the standard one to render a hardness and elastic modulus depth profile. The head (Berkovich) applied a maximum force from 0.1 to 400 mN. The oscillating contribution amplitude was 5 % of the force at any moment, and a frequency of 5 Hz and an acceleration coefficient (CSR strength ramp) of 0.1 s⁻¹ were used. The Oliver and Pharr⁴² method was used to determine the hardness and elastic modulus. For the latter calculus, the Poisson coefficient was taken to be 0.33. In addition, 9 measurements were performed for each sample, for the sake of reproducibility. For the Txt. Cu CC the face presenting the flat surface was analyzed.

Conductimetry

The electrical resistivity of the electrode coatings was measured with a 280SI 4-point measuring head (Four Dimensions Inc.). The films were coated on Mylar, which is an insulating polymer, to prevent any current collector contribution during the measurement. The rest of the protocol was identical to the coating of conventional electrodes. The distance between the probes was about 1 mm each and the mass applied to the measuring head is 60 g. For reproducibility, the resistance was measured at 100 different locations on a 3x3 cm² coating square, and the test was repeated twice on 3 samples per formulation. Finally, the resistivity was determined according to eq. (6):

$$r = \frac{R \times S}{e} (\Omega \cdot \text{cm}) \quad (7)$$

With R (Ω) the measured resistance, S the contact area between the probe and the electrode coating, which is equal to 0.283 cm², and e (cm) the coating thickness.

Electrochemistry

Electrodes were assembled in Swagelok cells in Ar filled glove box (O_2 and $H_2O < 1$ ppm) in half-cell configuration. The counter and reference electrode were metallic Li disc (diam. = 10 mm, thickness = 380 μm , 99.9 %; Aldrich) placed on a Cu current collector (diam. = 12 mm, thickness = 250 μm). Two layers of glass microfiber membranes were used as separator (grade GF/D, diam. = 13 mm, thickness = 670 μm ; Whatman). For some cells, an extra monolayer of polypropylene (PP) separator in contact with the Si electrode (grade 2500, diam. = 13 mm; Celgard) was used. As such, electrodes were protected from fiber inclusion coming from GF/D separators, which made easier their post-cycling observation by SEM. The separator layers were soaked with 300 μL of electrolyte made of 1 M LiPF_6 in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v:v) plus 10 % of fluoroethylene carbonate (FEC) (99.9 %; Solvionic). Si electrodes were cycled at room temperature using a multichannel VMP system (Biologic) in galvanostatic mode between 0.005 to 1 V (vs. Li^+/Li^0). The C-rate was C/40 for the 1st cycle, C/20 for the next 5 cycles, and C/10 for the subsequent cycles ($1\text{C} = 3820 \text{ mA.g}_{\text{Si}}^{-1}$). Prior to cycling, cells were rested for 2 h at open circuit voltage (OCV). This period was set to 8 h for cells containing the extra PP layer in the separator (because of wetting issue with the electrolyte blend DMC). Cells were also relaxed at OCV for 10 s and 1 min after each discharge (lithiation) and charge step, respectively. For the sake of reproducibility, three to eight cells were tested for each Si electrode formulation, and the results were averaged.

Operando optical microscopy

The morphological evolution of the electrode surface during cycling was observed *operando* using an ECC-Opto-Std-Aqu cell (EI-cell). The electrodes were cycled following the same protocol as the Swagelok cells, except that a C/20 regime was applied. The potentiostat/galvanostat was an SP-300 (Biologic). The images were acquired with a DFC320 camera (LEICA) installed on a MEF4 M microscope (REICHERT). The cell had an observation window of 2 mm in diameter.

The electrode/separator stack was modified for the cell to work properly. In particular, some elements of the stack are holed to free the field of view up to the silicon electrode surface. In detail, from the stack bottom to top, there was the quartz window, then an Li counter-electrode (diam. = 10 mm) with a hole in its center (diam. = 3.5 mm). Next, two layers of GF/D (diam. = 10 mm), also holed in the center (diam. = 2.5 mm), were used as separator. The hole in the separator was smaller in order to hinder the Li dendrite propagation. Finally, the silicon electrode was set with a Cu spacer on its back (thickness = 250 μm), followed by a stainless-steel spring. The spring kept the stack compressed while the spacer protected the electrode which was too thin to support the spring pressure without any deformation.

During the first discharge, a gas bubble was generated by the SEI formation which blocked the field of view. Consequently, it was not possible to acquire sharp images over this period of time. To eliminate the bubble, the cycling was stopped after the first discharge (lithiation) and the cell electrolyte was renewed in the glove box. Only about 200 images could be opened simultaneously with the Image-Pro Plus 5.1 software due to the limited computer performance. To circumvent this issue, OCV steps were added to have enough time to save them and restart the acquisition. An in-house macro made with the Super Macro software was used to acquire images automatically every 5 to 10 minutes. The electrode surface was very regular such that it lacked in contrast at x20 magnification. As such, the CLAHE (local contrast enhancement) function (block size = 127, maximum slope = 2) of ImageJ was used to improve the contrast.

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Impact of the Cu Current Collector Grade and Ink Solid Fraction on the Electrochemical Performance of Silicon-Based Electrodes for Li-Ion Batteries

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Table S1 List of the electrodes and their mean 1st cycle electrochemical performance of every formulation cycled in Swagelok cells.

Formulations			Electrode dimensions		1 st cycle electrochemical performance			
Salt	Coord. Ratio	Solid fraction (w%)	Current collector	Pores (v%)	Discharge capacity (mAh.g _{Si} ⁻¹)	Charge capacity (mAh.g _{Si} ⁻¹)	CE (%)	Nbr. of electrodes
Without Zn	0	21.4	Cold rolled	61 ± 0.3	4160 ± 30	3400 ± 80	81.1 ± 1.7	4
Without Zn	0	21.4	Annealed	60 ± 4	4000 ± 270	3360 ± 240	82.8 ± 6.4	6
Without Zn	0	21.4	Textured	63 ± 0.6	4090 ± 40	3470 ± 40	84.9 ± 0.5	3
Without Zn	0	27	Cold rolled	64 ± 1	4070 ± 90	3540 ± 40	87.0 ± 0.5	8
Without Zn	0	27	Annealed	73 ± 1	3830 ± 130	3300 ± 140	85.7 ± 2.4	7
Without Zn	0	27	Textured	63 ± 2	3900 ± 60	3390 ± 60	86.9 ± 0.6	3
ZnSO ₄	0.22	22.3	Cold rolled	61 ± 2	4090 ± 160	3350 ± 170	84 ± 2	3
ZnSO ₄	0.22	22.3	Annealed	63 ± 7	4170 ± 230	3590 ± 190	86.2 ± 0.4	4
ZnSO ₄	0.22	22.3	Textured	62 ± 3	3690 ± 110	3160 ± 100	85.5 ± 0.5	3
ZnSO ₄	0.22	28	Cold rolled	63 ± 1	4010 ± 160	3490 ± 170	86.9 ± 0.7	4
ZnSO ₄	0.22	28	Annealed	59 ± 11	4100 ± 40	3620 ± 300	85.0 ± 1.1	4
ZnSO ₄	0.22	28	Textured	59 ± 0.6	3690 ± 70	3140 ± 60	85.3 ± 0.3	3
W/o Zn+LiOH	0	21.5	Cold rolled	65 ± 0.7	4280 ± 130	3460 ± 90	81.8 ± 1.8	4
W/o Zn+LiOH	0	25.8	Cold rolled	65 ± 2	3940 ± 130	3610 ± 60	87.9 ± 0.9	4
ZnO	0.22	21.8	Cold rolled	62 ± 0.8	4140 ± 70	3610 ± 60	87.3 ± 0.5	3
ZnO	0.22	27.5	Cold rolled	66 ± 3	3950 ± 80	3390 ± 90	85.8 ± 1.5	8

Figure S1a shows the morphological evolution during cycling of the surface of the Zn-free electrode (21.4 % SF) with a C.-R. Cu CC, as observed by *operando* optical microscopy. Unfortunately, the particle contrast is very poor even at a magnification of 20x. At lower magnification of 10x (not shown), even the cracks were barely visible. The first signs of crack appearance happen around 250 mV during the delithiation. The electrode shrinkage is also visible on the coating island formed in the middle of the observed area. The left corner blurriness may come from the Li dendrite growth from the counter electrode. The hole in counter electrode creates an edge where the current density is higher. Therefore, during charge, dendrite growth occurs preferentially at this spot and thus is visible with the microscope. This blurriness could also be due to gas bubbles resulting from SEI formation. The region of interest (ROI) was changed before the second cycle lithiation. Cracks are also clearly visible in this ROI, and they close gradually during lithiation due to the coating volume expansion until a tension of around 50 mV is reached where they are completely closed. At the very end of the lithiation, the surface shakes and then protrude out of focus. This was already observed and is due to the electrode delamination.¹ In fact, when the crack close and the islands merge, the electrode volume expansion induces extra stress. It concentrates at the coating/current collector interface at the islands edges and might induces delamination,² which happened for our reference formulation.

The surface morphological evolution of the ZnSO₄ electrode (22.3 % SF) with a C.-R. Cu CC, also acquired during cycling by *operando* optical microscopy, is presented in Figure S1c. Unfortunately, the first delithiation images were lost after computer crash during acquisition. At the beginning of the second cycle lithiation, one can see a bright spot on the right-hand top corner. This is a lithium dendrite on the counter electrode which appears blurry since it is out of focus. The silicon electrode Li⁺ consumption during lithiation causes the dendrite to disappear. The cracks close completely around 70 mV and no delamination occurs after that. Some particles are bright, which we believe to be the lithiated graphene platelets. At the end of the lithiation, these get even brighter, which could come from the fact that graphene turns gold during the last lithiation stage (LiC₆).³ During the second delithiation, the first cracks appear at approximately 250 mV, similarly to the Zn-free formulation electrode. Then, cracks keep widening without sign of new cracks appearance. For the third cycle, the ROI was changed. Cracks opened and closed from the same positions at each cycle, and the overall electrode behavior remains the same.

Figure S1b shows the electrochemical performance of the *operando* optical microscopy tests for the Zn-free and ZnSO₄ electrodes observed in Figures S1a and S1c, respectively. The specific discharge capacities and CE are lower than the ones obtained for electrodes cycled in Swagelok cells (by 14.9 and 8.6 % points of CE, for the ZnSO₄ and its reference electrodes, respectively). The optical microscopy cell configuration degrades the electrodes and separator stack (holed counter electrode and separator),

which is probably responsible of the poorer performance. Nonetheless, the electrodes deliver full discharge capacity for both formulations, but the charge capacities are much lower, as shown by the CE. Cracking formations shown in Figures S1a and S1b represent those of highest stress/strain during lithiation and reduced stress/strain during delithiation. Finally, delamination is only observed in the case of the Zn-free electrode. Unfortunately, we cannot see if the rupture happens at the coating/ Cu CC interface or in the coating bulk and therefore determine which fracture toughness is concerned.

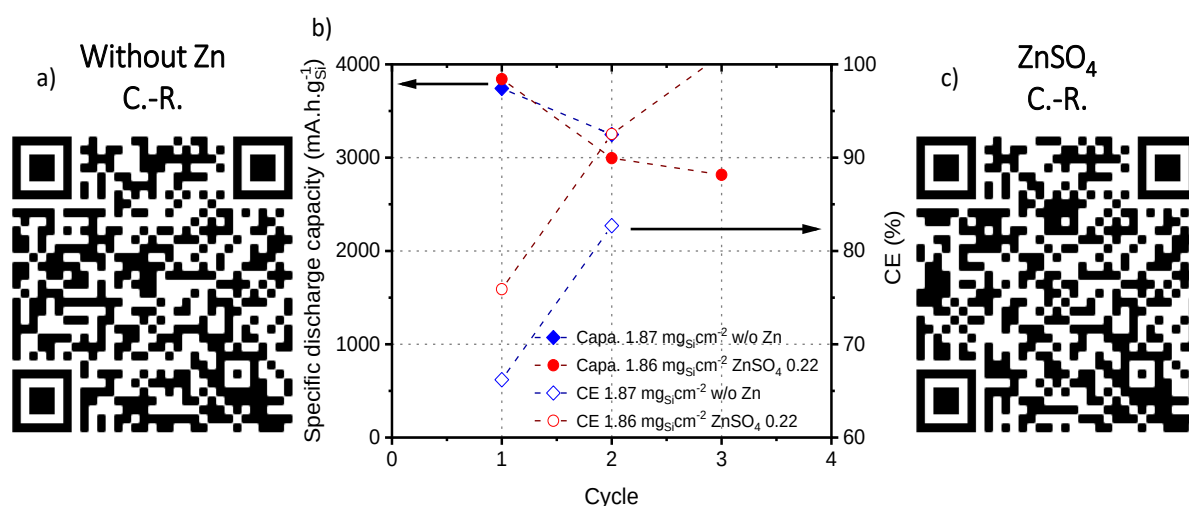


Figure S1 Operando optical microscopy surface observations of electrodes with a C.-R. Cu CC: (a) Zn-free formulation (21.4 % SF) and (c) ZnSO₄ formulation (22.3 % SF); (b) Electrochemical performance associated with experiments (a) and (c).

Beuth Jr J. L.⁴ studied two types of cracks, one of which reaches the substrate interface and the other that propagates towards it but never reaches it. For the latter, which prevails in the case of compliant film on stiff substrate, the crack driving force becomes lower than the coating fracture resistance as the crack progress towards the interface. The in-depth cracks observations on ZnSO₄ (22.3 % SF) and its reference (21.4 % SF) electrodes on an Ann. Cu CC Figures S2a and S2b, respectively, seems to agree with this result. This phenomenon was also observed with a C.-R. and a Txt. Cu CC, but not shown here.

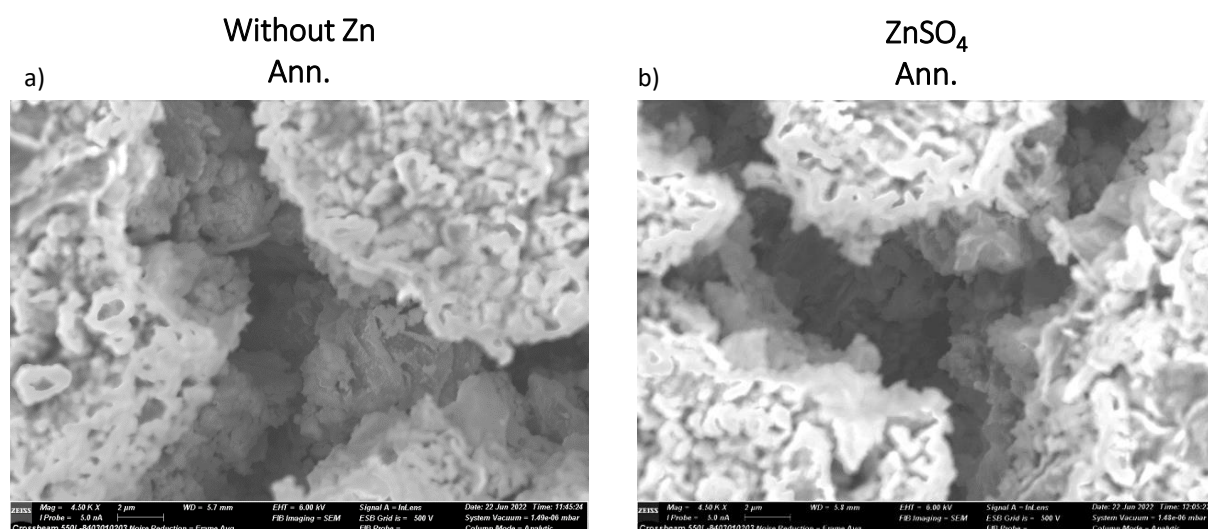


Figure S2 SEM observations inside surface cracks of electrodes with an Ann. Cu CC, after 1 cycle: (a) Zn-free formulation (21.4 % SF); (b) ZnSO₄ formulation (22.3 % SF).

Figure S3 shows SEM images of the different Cu CCs surface over a distance of around 20 µm and their respective roughness over a distance twenty times bigger. For interpretation of those results, the reader is referred to the discussion accompanying Table 3 in the main text. Quantitative values of roughness were obtained from Figures S3b, S3d and S3f for the different CuCCs and are available Table 3.

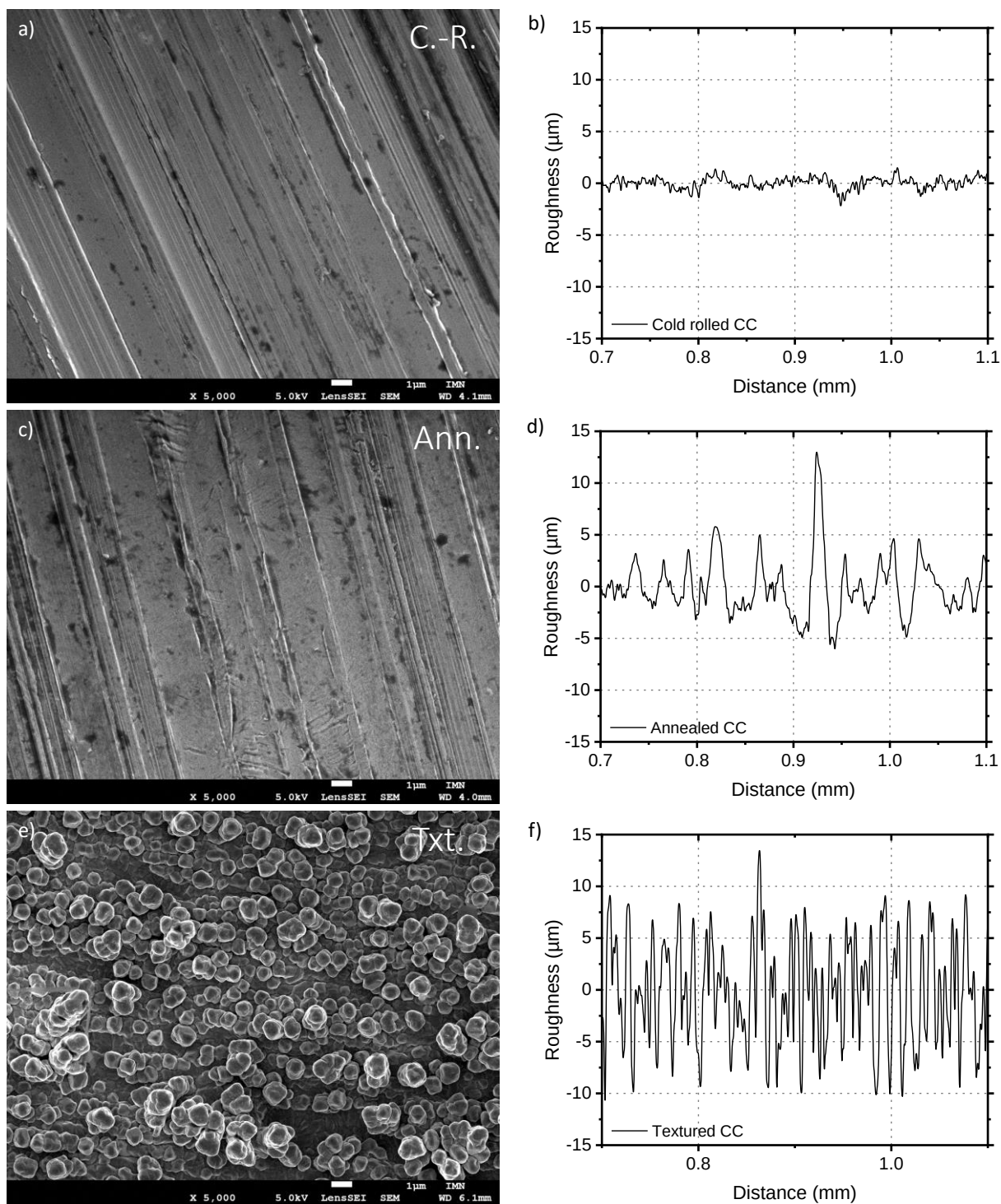


Figure S3 Cu CCs' surface SEM observations and roughness: (a, b) Cold rolled Cu CC; (c, d) Annealed Cu CC; (e, f) Textured Cu CC.

Figure S4 shows the XPS spectra, with an analysis depth estimated to 10 nm, of the 3 different Cu CCs focused on the Cu 2p and Cu L₃M_{4,5}M_{4,5} regions. The different peaks positions were obtained graphically and are presented Table S2. No fitting was performed as only qualitative information on the surface

composition was needed and also because some Cu CC suffered surface composition evolution under the beam. Indeed, the C.-R. and Ann. Cu CCs' surfaces present evolution over time as can be seen with increasing intensity of the Cu 2p_{3/2} peak at 932.09 and 933.23 eV and of the Cu 2p_{1/2} peak at 951.98 and 952.97 eV respectively (Figures S4a and S4c), the red curves being the sum of the 5 first spectra and the blue ones being the sum of the 9 last spectra. For the C.-R. and Ann. CCs Cu LMM regions (Figures S4b and S4d, respectively), only the sum of the 5 first spectra is presented. For those samples the Cu 2p and Cu LMM peaks position (Table S2)⁵ and the samples evolution⁶ correlates well with the presence of Cu(OH)₂ (presence of Cu 2p shake up structure peaks typical of Cu(II) species) and Cu₂O. However, for the Ann. Cu CC the Cu(OH)₂ layer is much thicker as the Cu₂O Cu 2p_{3/2} and Cu 2p_{1/2} peaks are almost undiscernible. The Txt. Cu CC surface composition is different than for the other two Cu CCs and did not evolve during the spectra acquisition. First, there is the presence of Cr(III) 2p_{3/2} and 2p_{1/2} peaks at respectively 576.21 and 586.14 eV in Figure S4f, which could be the signature of either CuCr₂O₄⁷⁻⁹ or CuCrO₂¹⁰⁻¹² (the presence of Cr was also verified by EDX but is not shown). There is also the presence of two discernible Cu LMM peaks at around 916.85 and 918.5 eV (kinetic energy), which can be attributed to Cu₂O⁵ and CuCr₂O₄,⁹ respectively. The position of the two Cu 2p_{3/2} peaks Figure S4e at 932.49 and 934.36 eV also correlates very well with Cu₂O⁵ and CuCr₂O₄,⁷⁻⁹ respectively. For the latter the copper is in a +2 oxidation state which again matches perfectly with the presence of shake up structure peaks in the Cu 2p region.

X-ray diffraction measurement with a grazing incidence ($1\theta = 1^\circ$, 15 to 60 2θ and 15 h of acquisition) was also performed on the Txt. Cu CC (not shown). But, no diffraction peaks except those of copper were present, such that no more information on the Cu CCs surface composition was obtained.

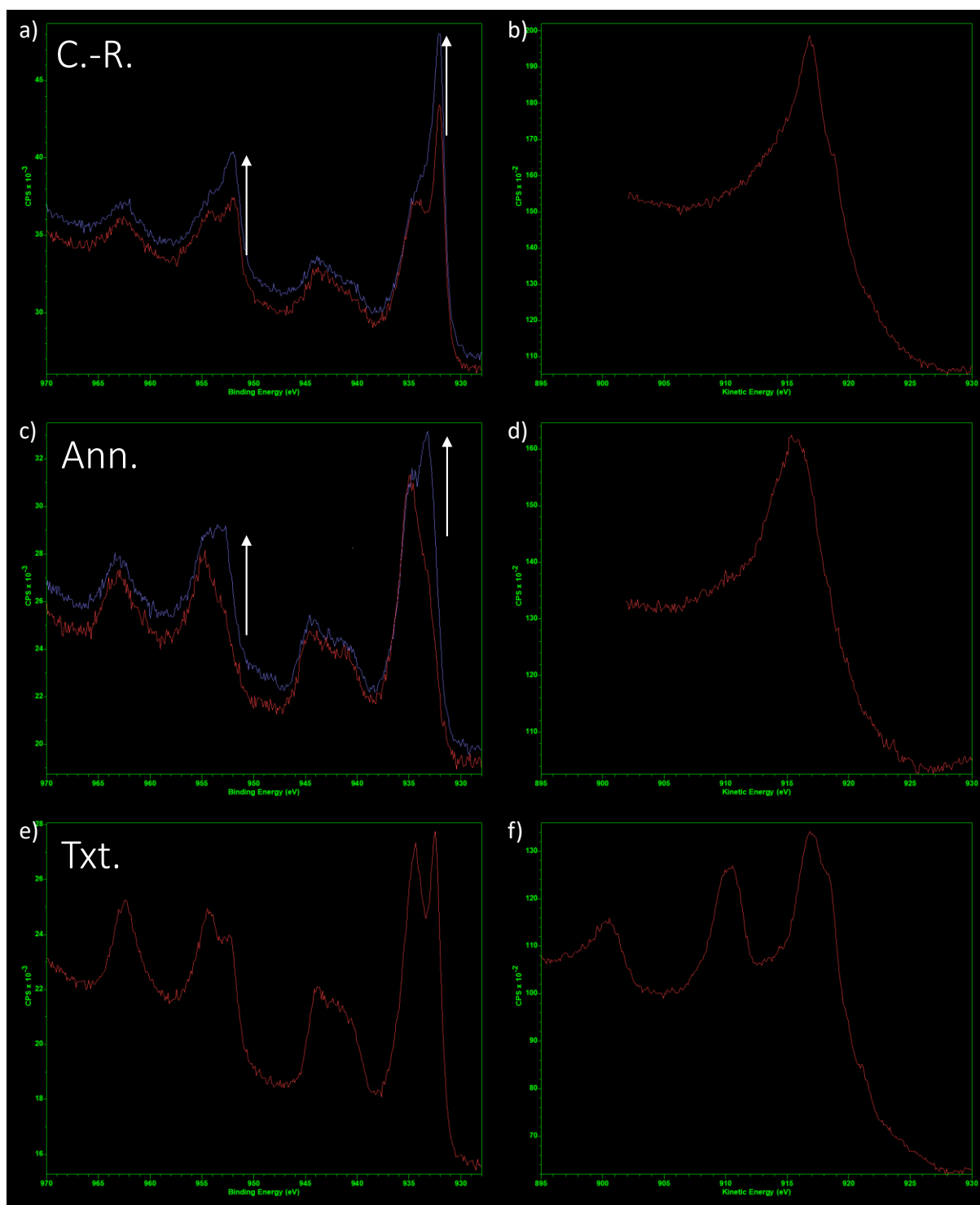


Figure S4 Cu CCs' XPS spectra focused on the Cu 2p and Cu LMM regions: (a, b) Cold rolled Cu CC, in red the sum of the 5 first spectra, in blue sum of the 9 next spectra; (c, d) Annealed Cu CC, in red the sum of the 5 first spectra, in blue sum of the 9 next spectra; (e, f) Textured Cu CC.

Peaks positions obtained graphically from Figure S4 are presented Table S2. For the Cu LMM peaks the position is expressed in terms of kinetic energy. For peaks attribution details see Figure S4.

Table S2 XPS peaks position and their respective attribution to chemical species.

	Cu 2p _{3/2}	Shake up peaks	Cu 2p _{1/2}	Shake up structure peaks	Cr 2p _{3/2}	Cr 2p _{1/2}	Cu L ₃ M _{4,5} M _{4,5}	Peak attribution
Cold rolled Cu CC	932.09		951.98		/	/	916.78	Cu ₂ O
	934.3	944.01	954.18	962.62				Cu(OH) ₂
Annealed Cu CC	933.23		952.97		/	/	915.63	Cu ₂ O
	934.95	944.59	954.77	963.03				Cu(OH) ₂
Textured Cu CC	932.49		952.37		576.21	586.14	916.85	Cu ₂ O
	934.36	943.83	954.33	962.4				CuCr ₂ O ₄

Table S3 summarizes the ZnO and respective reference formulations which are used in this study, and the corresponding electrode compositions. The ZnSO₄ being replaced with ZnO is particularly interesting because it significantly reduces the dead weight in the electrode composition, which is otherwise brought on by the sulfates. It also raises the binder pH solution up to 4.3 (compared to approximately 3.4 and 2.9 for the Zn-free and ZnSO₄ formulations, respectively). Therefore, LiOH was used in its reference binder formulation to similarly raise the pH (at around 4.4).

Table S3 ZnO and its reference formulations and their corresponding electrodes composition.

Formulation name	Electrode composition (w%)						
Salt	Coord. ratio	Silicon	Graphene	NaCMC	Citric acid	NaOH (+LiOH)	Zn precursor
Zn-free + LiOH	0	73.1	11	7.2	7.3	0.7 +0.7	0
ZnO	0.22	71.8	10.8	7	7.2	0.7	2.5

Inks viscosity as a function of the shear rate for the Zn-free and ZnSO₄ formulation at different SF are illustrated in Figure S5a. The inks exhibit a shear-thinning behavior, which means that the viscosity decreases with increasing shear rate. The solid fraction significantly enhances the ink viscosity when it is increased, mostly because the solvent volume is reduced such that particles interactions are favored. Note that for example, both 21.5 % SF Zn-free + LiOH and 22.3 % SF ZnO inks have the same volume of

binder solution (*i.e.* 0.8 mL) and that both 27.1 % SF Zn-free + LiOH and 27.5 % SF ZnO inks have the same volume of binder solution (*i.e.* 0.59 mL), etc... There are significant viscosity differences between the ZnO and its reference inks for “equivalent” SF at 0.01 s^{-1} , which was not the case between ZnSO_4 and its reference inks (see Figure 4). Interestingly, the difference is reduced at the tape casting shear rate, of either 37 or 56 s^{-1} (*i.e.* $h = 150$ or $100\text{ }\mu\text{m}$, with a casting speed of 5.6 mm.s^{-1}). The ink structure is destroyed by the shear rate and the polymer chains align with flow, such that most of the formulation’s effect on the ink is likely smoothed. Figures S5b and S5c summarize the viscosities and yield stresses, respectively, which were obtained around 0.01 s^{-1} , for every ink formulation at the different SFs. For descriptions, the reader is referred to the discussion accompanying Figure 4 and Table 4 in the main text.

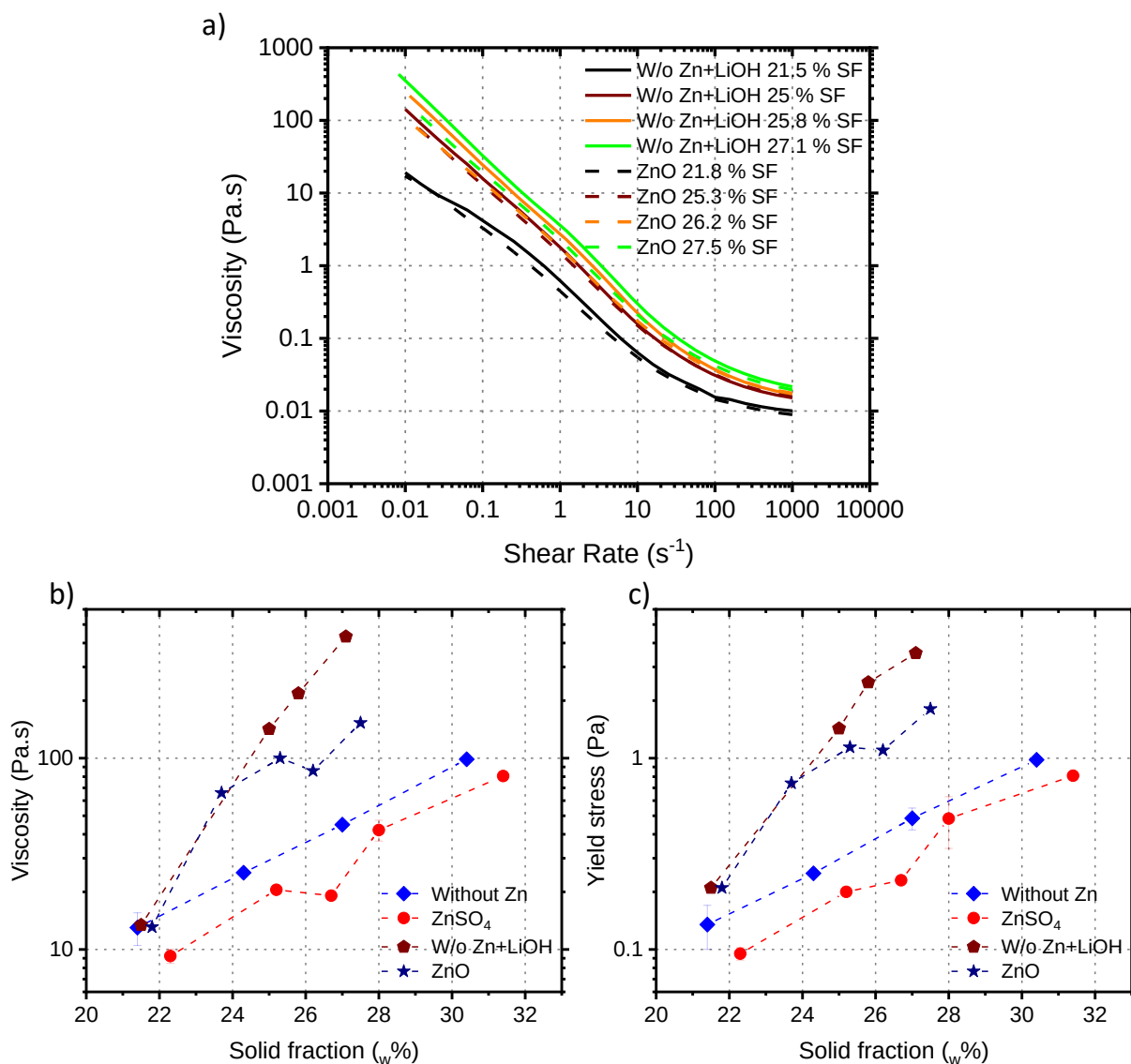


Figure S5 (a) Viscosity as a function of shear rate for Zn-free + LiOH or ZnO inks at different SF; (b) Summary of the viscosity obtained at a shear rate of approximately 0.01 s⁻¹ as a function of the SF, for every formulation; (c) Summary of the yield stress calculated at a shear rate of approximately 0.01 s⁻¹ as a function of the SF, for every formulation.

Figure S6 present the specific discharge capacity and CE of the formulations with ZnO at 21.8 and 27.5 % SF and Zn-free with LiOH at 21.5 and 25.8 % SF on a C.-R. Cu CC. When a higher SF is used, both the capacity retention and CE are enhanced for the Zn-free + LiOH formulation, but not for the ZnO electrodes. Namely, for the Zn-free formulation, the 60th cycle capacity is approximately 2180 vs. 1930 mAh.g_{Si}⁻¹ and the 1st cycle CE is 87.9 vs. 81.2 for the 25.8 and 21.5 % SF, respectively. For the ZnO formulation, the 60th cycle capacity is approximately 2310 vs. 2530 mAh.g_{Si}⁻¹, the 1st cycle CE is 85.8 vs. 87.1 %, and it stabilizes at around 99.3 vs. 99.3 % from the 20th to the 65th cycle, for the 27.5 and 21.8 % SF, respectively (but within std. dev. range for every parameter). Increasing the SF appears

only beneficial for the Zn-free + LiOH electrodes in this case. Nevertheless, whatever the SF is, the cyclability of the ZnO-based formulation remains superior.

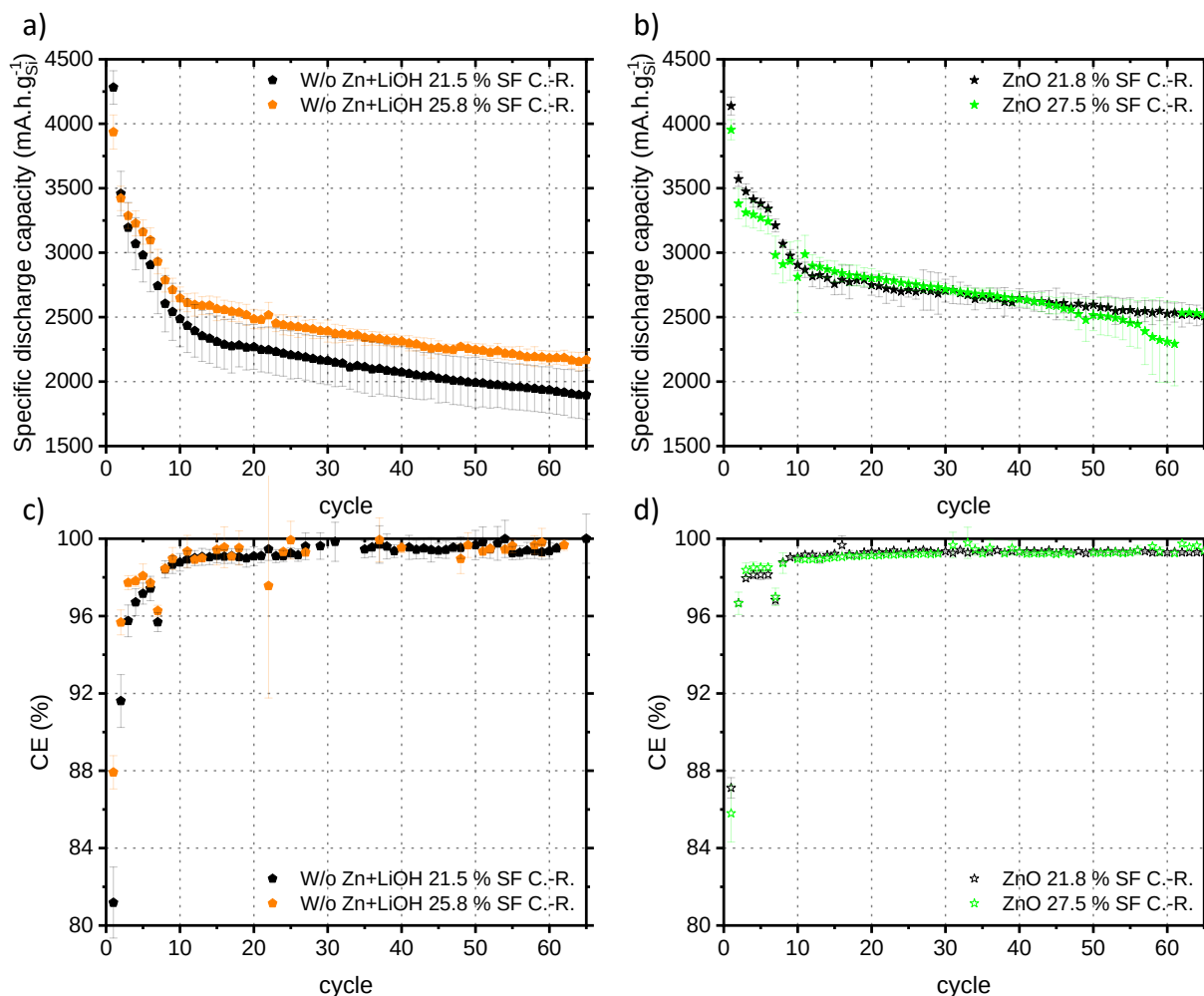


Figure S6 Specific discharge capacity and CE by cycle of electrodes prepared with different ink SFs and with a C.-R. Cu CC: (a, c) Zn-free + LiOH formulation; (b, d) ZnO formulation. The electrodes were cycled at C/40 for the 1st cycle, then C/20 for 5 cycles, and C/10 for the remaining cycles. The mean values and their standard deviation were determined from a minimum of 3 electrodes for each electrode formulation.

Figure S7 present the specific discharge capacity and CE of the Zn-free formulation at 21.4 and 27 % SF and the ZnSO₄ formulation at 22.3 and 28 % SF, both coated on an Ann. Cu CC. For both formulations no clear SF impact was observed as the capacity retention and CE are very similar or within std. dev. range. In details, for the Zn-free formulation, the 60th cycle capacity is approximately 2300 vs. 2230 mA.h.g_{Si}⁻¹ and the 1st cycle CE is 85.7 vs. 82.8 %, for the 27 and 21.4 % SF, respectively. For the ZnSO₄ formulation, the 60th cycle capacity is approximately 2680 vs. 2550 mA.h.g_{Si}⁻¹ and the 1st cycle CE is 85 vs. 86.2 %, for the 28 and 22.3 % SF, respectively.

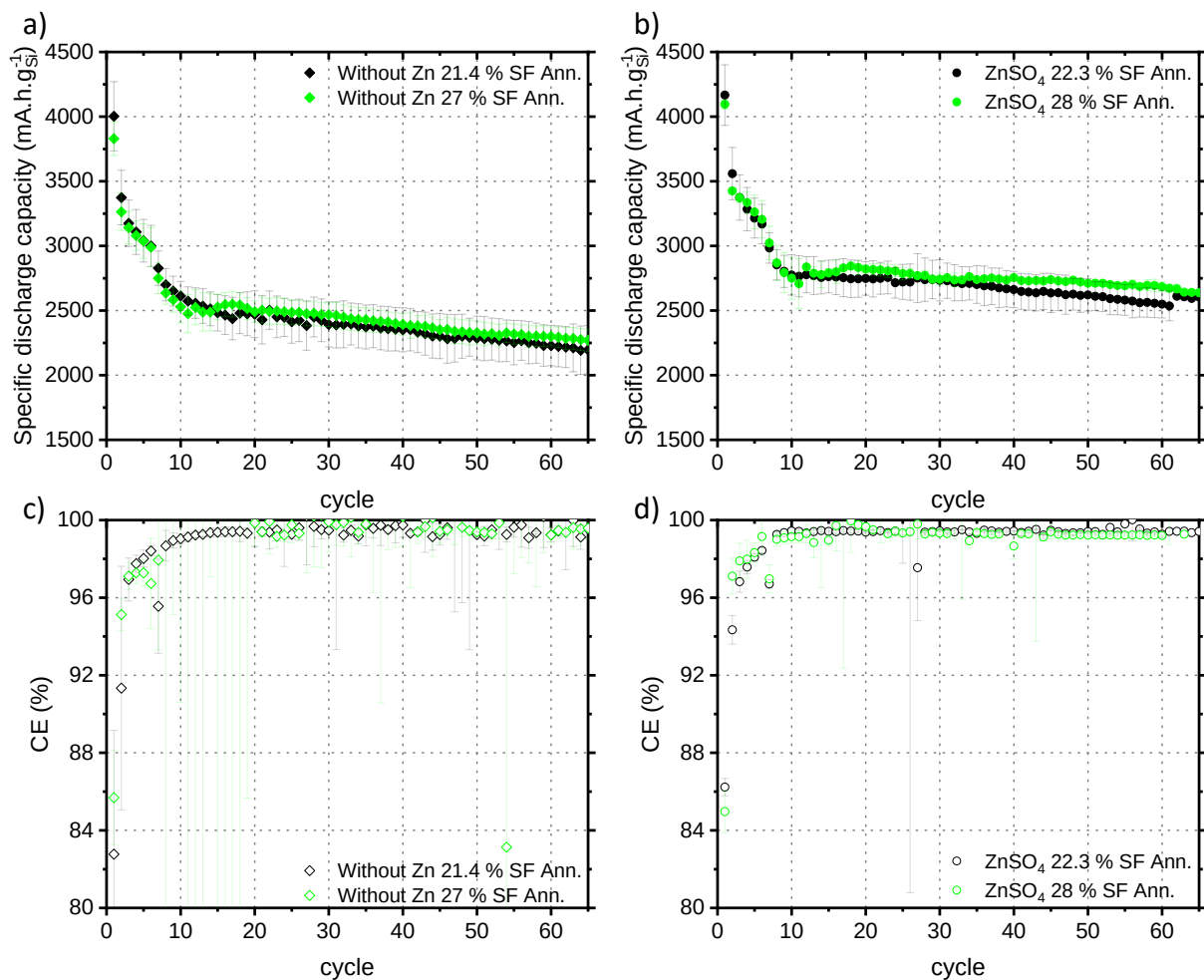


Figure S7 Specific discharge capacity and CE by cycle of electrodes prepared with different ink SFs and with an Ann. Cu CC: (a, c) Zn-free formulation; (b, d) ZnSO₄ formulation. The electrodes were cycled at C/40 for the 1st cycle, then C/20 for 5 cycles, and C/10 for the remaining cycles. The mean values and their standard deviation were determined from a minimum of 3 electrodes for each electrode formulation.

Figure S8 present the specific discharge capacity and CE of the Zn-free formulation at 21.4 and 27 % SF and the ZnSO₄ formulation at 22.3 and 28 % SF, both coated on a Txt. Cu CC. For both formulations, a slight improvement was observed on the capacity retention with increasing SF. In details, for the Zn-free formulation, the 60th cycle capacity is approximately 2150 vs. 1930 mA.h.g_{Si}⁻¹ and the 1st cycle CE is 86.9 vs. 84.9 %, for the 27 and 21.4 % SF, respectively. For the ZnSO₄ formulation, the 60th cycle capacity is approximately 2460 vs. 2320 mA.h.g_{Si}⁻¹ and the 1st cycle CE is 85.3 vs. 85.5 %, for the 28 and 22.3 % SF, respectively.

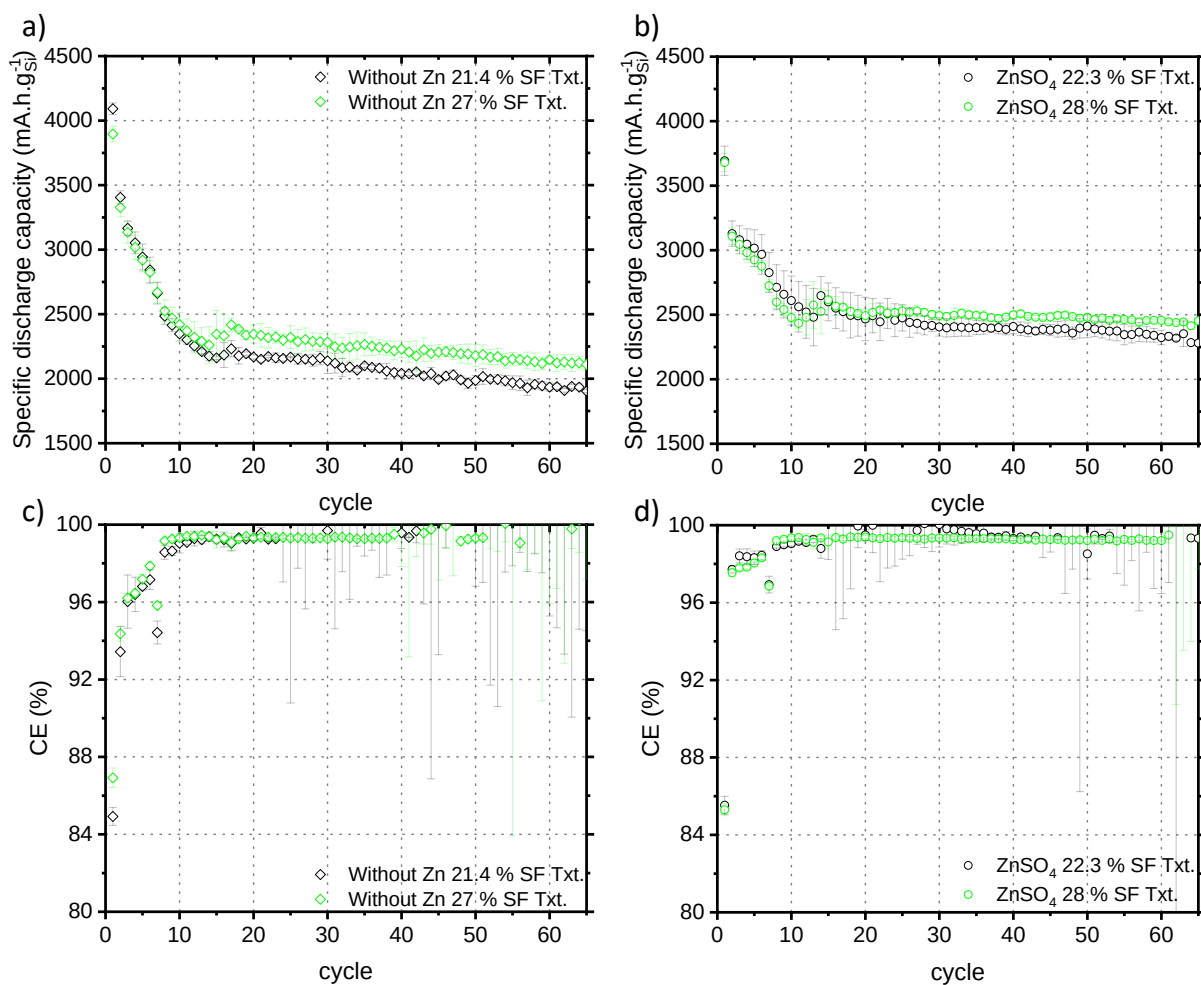


Figure S8 Specific discharge capacity and CE by cycle of electrodes prepared with different ink SFs and with a Txt. Cu CC: (a, c) Zn-free formulation; (b, d) ZnSO₄ formulation. The electrodes were cycled at C/40 for the 1st cycle, then C/20 for 5 cycles, and C/10 for the remaining cycles. The mean values and their standard deviation were determined from a minimum of 3 electrodes for each electrode formulation.

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5. Conclusion et perspectives

Cette thèse a permis l'exploration d'une petite partie des opportunités offertes par la chimie de coordination, à travers la préparation de liants pour électrodes négatives à base de silicium pour LIB. Celle-ci s'appuie sur des liaisons intermoléculaires entre un ligand organique, qui peut être négativement chargé (carboxylate, phosphonate, sulfonate, phenolate...) ou neutre (amine, pyridine, phosphine...), et un cation métallique multivalent. Notre point de départ est une solution de liant poly(acides carboxyliques) de référence dans l'équipe, pour laquelle l'ajout d'un simple précurseur de Zn(II) induit la formation de liaisons de coordination Zn-carboxylates. Cette méthode de formulation est très versatile comme le témoigne l'ensemble des précurseurs utilisés durant cette thèse : ZnSO_4 , $\text{Zn}(\text{NO}_3)_2$ et ZnO . Il est aussi possible de moduler le ratio de coordination théorique, c'est-à-dire le nombre de mol de Zn sur le nombre de mol de fonction acide carboxylique portée par les molécules organiques du liant, qui sont la carboxyméthylcellulose et l'acide citrique.

Les liants de coordination ont été étudiés en solution par rhéologie et un premier résultat intéressant a été observé. Seule la solution de liant ZnSO_4 ($\text{Zn}/\text{CO}_2\text{H} = 0,22$) montre des signes de réticulation en solution. En effet, elle présente une viscosité nettement plus élevée à bas gradient de cisaillement et se comporte comme un gel physique (module de stockage > module de perte), contrairement aux autres solutions contenant du Zn(II). À plus haut ratio de coordination *i.e.* (0,66) la solution de liant devient vraisemblablement biphasique avec des agrégats nanométriques de CMC maintenus par des liaisons Zn-carboxylates intra-chaînes. Quant à la solution de ZnO (0,22), son pH d'environ 4.3 est plus proche du $\text{pK}_{\text{a}2}$ de l'acide citrique (*i.e.* 4,76) que du pK_{a} de la CMC (*i.e.* 3,4), de sorte que la formation de complexes moléculaires (plutôt que de motifs étendus) avec le premier est vraisemblablement favorisée. Ainsi, la formation d'un réseau de coordination percolant à travers l'ensemble du volume de liant ZnO (0,22) n'a pas lieu. Il y a donc des interactions complexes entre le pH, le Zn(II) et les molécules d'acide citrique et de CMC. Une fois sec, les carboxylates des échantillons de liant ont été étudiés par spectroscopies IR et NMR (^{17}O et ^1H - ^{13}C en polarisation croisée). Cependant, les résultats ont été peu concluants, du fait de la composition complexe des liants : plusieurs cations *i.e.* K, Na, Zn et molécules complexantes *i.e.* acide citrique, CMC couplé à l'état amorphe des échantillons qui engendrent des signatures en spectroscopie difficilement interprétables. Au final, seule l'analyse IR indique qu'il y a bien formation de carboxylates de Zn. Une étude par STEM-EDX sur de la poudre d'électrodes (sans additif conducteur xGnP15) montre que le zinc est dispersé de manière totalement homogène à l'échelle nanométrique dans la phase de liant (sans particule, de Zn(0) ou de ZnO par exemple), que ce soit pour les échantillons préparés avec ZnSO_4 ou ZnO . Ainsi, le réseau de réticulation est parfaitement distribué dans la phase de liant, qui lui-même couvre en partie les particules de silicium.

L'intérêt des liaisons de coordination Zn-carboxylates est que leur énergie de liaison est plus élevée que celles des liaisons hydrogènes entre acide carboxyliques, qu'elles remplacent. En conséquence, les électrodes avec le liant de coordination sont plus résistantes, comme l'a confirmé les différentes caractérisations mécaniques. Tout d'abord, la cohésion du film d'électrode et son adhérence au collecteur de courant sont plus élevées. Cependant, Il y a là encore une différence entre la formulation ZnSO_4 et ZnO (0,22), la première étant plus efficace que la seconde. Cela est vraisemblablement dû à la présence de liaison covalente silyl-ester entre le liant et la surface des particules de silicium et de liaison Cu(II) -carboxylate entre le liant et le collecteur de courant, qui sont favorisées au pH plus acide du liant ZnSO_4 (*i.e.* 2,9). Les électrodes préparées avec ce dernier ont une dureté et un module élastique plus élevés que des électrodes non coordonnées. De plus, ces propriétés mécaniques sont préservées dans les conditions opérationnelles d'une batterie, du fait d'une faible absorption de l'électrolyte par le liant de coordination. Au final, en condition *operando*, cela se traduit par une expansion atténuée du film d'électrode. La microscopie optique *operando* a ainsi permis d'observer la délamination d'un îlot de film d'électrode, préalablement formé par l'apparition des craquelures lors de la délithiation. Par ailleurs, cette délamination n'a été observée que sur une électrode sans zinc, et pas sur l'électrode avec du ZnSO_4 .

De telles propriétés mécaniques sont à l'origine des meilleures performances électrochimiques obtenues pour les électrodes de silicium avec un liant de coordination. Dans le détail, l'efficacité coulombique est améliorée pour les premiers cycles, avec par exemple environ + 3 % et + 6 % au premier cycle pour le liant ZnSO_4 et ZnO (0,22), vis-à-vis de leurs électrodes de référence respective. Au 60^{ème} cycle cela se traduit par environ une nette amélioration (+ 45 % et + 30 %) de la rétention de capacité de décharge pour le liant ZnSO_4 et ZnO (0,22), vis-à-vis de leurs électrodes de référence respective. Une brève étude avec une molécule non complexante utilisée à la place de l'acide citrique a permis de conclure que la coordination de la CMC et la présence de l'acide citrique (également sous forme coordonnée) sont toutes deux nécessaires aux si bonnes performances de ces électrodes. Enfin, l'étude de la SEI par STEM-EDX après le premier cycle a montré que le liant de coordination a aussi un impact sur celle-ci. Tout d'abord, le liant de coordination agit comme une SEI artificielle réduisant la surface de silicium disponible à la dégradation de l'électrolyte et au dépôt des composants de la SEI (particulièrement pour la partie inorganique de celle-ci c'est-à-dire les sels LiF et $\text{Li}_x\text{PO}_y\text{F}_z$). Ensuite, la SEI formée est plus stable grâce aux meilleures propriétés mécaniques générales des électrodes, ainsi elle reste plus fine et donc son impédance est moindre (comparée à celle qui se forme dans les électrodes sans liant de coordination).

Une étude sur la fraction de solide de l'encre a montré que cette dernière permet de modifier la distribution des éléments au sein de l'électrode composite, et qu'ainsi un optimum en termes de

performance électrochimique peut être atteint. Cela avait déjà été identifié dans la littérature mais jamais pour les électrodes négatives à base de silicium. Une influence des propriétés mécaniques du collecteur de courant sur les craquelures a été clairement identifiés, particulièrement pour les électrodes à base de liant non coordonné, grâce à l'observation de la surface des électrodes au MEB après 1 cycle. Dans certains cas les performances peuvent être significativement augmentées, en passant par exemple d'un collecteur de courant laminé à froid à un collecteur de courant recuit (ou texturé) pour des électrodes formulées avec environ 21-22 % de fraction solide. Toutefois, à plus haute fraction de solide ces améliorations ne sont pas systématiques, de sorte qu'il existe une interdépendance entre les effets du collecteur de courant et de la fraction de solide, dont la nature n'a pour l'instant pas été totalement appréhendée.

Enfin, les performances électrochimiques des électrodes contenant un liant de coordination au Zn ont été systématiquement supérieures à leurs électrodes de référence (mais à condition que les paramètres soient similaires pour les deux formulations), ce qui témoigne de la robustesse de cette approche.

Les perspectives de cette thèse suivent principalement deux axes, le premier concerne les techniques de caractérisations et le second le développement des formulations de liants de coordination.

Tout d'abord, concernant les techniques de caractérisation *operando* utilisés durant cette thèse, c'est-à-dire la dilatométrie et la microscopie optique, qui se concentrent généralement seulement sur les premiers cycles des électrodes. La raison sous-jacente est que les performances électrochimiques sont moindres ou diminuent très rapidement, ce qui rend assez rapidement les analyses peu représentatives d'un cyclage classique. Il est alors nécessaire de développer et/ou d'améliorer ces cellules et montages *operando* pour obtenir des cyclages performants et donc pouvoir caractériser le comportement des électrodes de manière plus aboutie. Par exemple, pour des plans de cellule de microscopie optique il est possible de s'inspirer des travaux de Dasgupta N. P. et al¹ et d'utiliser l'impression 3D de matériau polymère comme le polyétheréthercétone pour les fabriquer (résistant aux conditions opérationnelles d'une LIB).

Ensuite, la tomographie au rayons X est particulièrement intéressante, car elle permet de reconstruire le volume d'une électrode avec un contraste de phase, en étant assisté par un ordinateur. Il est ainsi possible dans nos électrodes de segmenter/identifier la phase de gaz, d'électrolyte, de liant plus graphène et les plus grosses particules de silicium. Lorsque cette technique est couplée au dispositif expérimental *in situ* développé par Vanpeene V. et al², il devient possible de suivre la dynamique de ces éléments au cours du cyclage. Au cours de cette thèse, des expériences avec les formulations sans zinc,

ZnSO₄ et ZnO (0.22) ont été menées aux synchrotrons PSI (ligne de lumière TOMCAT) et ESRF (ligne de lumière ID16B); elles feront prochainement l'objet d'une publication. De plus, une étude préliminaire sur le marquage du liant et de la SEI (permettant de les segmenter séparément) a été réalisé sur ID16B. Combiné à la résolution élevée de cette expérience (jusqu'à une taille de voxel d'environ 25 nm), cela pourra permettre à terme de décrire plus finement l'évolution des électrodes au cours du cyclage.

Enfin, un travail préliminaire a été amorcé sur la substitution par dialyse³ du Na de la NaCMC par un autre cation, comme le zinc afin de simplifier la composition des solutions de liant et donc faciliter leur analyse. Des expériences préliminaires ont également montré qu'il est possible d'étendre l'approche du liant de coordination à d'autres cations métalliques (par exemple, Al³⁺ et Fe³⁺), ce qui pourrait à la fois permettre de moduler les propriétés des liants, via la modification des forces de liaison cation-ligand, et donner accès à des techniques de caractérisation permettant de sonder localement l'environnement des cations (spectroscopie NMR pour Na et Al, et Mössbauer pour Fe). Ainsi, des résultats électrochimiques obtenus avec des électrodes formulées avec des liants de coordination non optimisés à base de Al₂(SO₄)₃ ou de Fe₂(SO₄)₃/Fe₂O₃ sont prometteurs.

5.1. Références

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Titre : Étude de liants de coordination pour électrodes négatives au silicium de batteries lithium-ion

Mots clés : Batteries lithium-ion, silicium, liant, coordination

Résumé :

Le silicium est un matériau prometteur pour augmenter la densité d'énergie des batteries lithium-ion. Il délivre une capacité gravimétrique et volumique respectivement 10 et 3 fois supérieure à celle du graphite, qui est le matériau d'électrode négative de référence. Cette différence vient de la quantité de lithium qui réagit avec le silicium, allant jusqu'à l'alliage c-Li₁₅Si₄. Cependant, cela s'accompagne d'une expansion atteignant jusqu'à 280 % du volume initial du matériau. Outre les problématiques de fissuration et porosification intrinsèques au silicium, deux mécanismes de défaillance majeurs des électrodes se manifestent alors au cours de leur cyclage :

- La dégradation continue de l'électrolyte, à cause de la déstabilisation de la couche de passivation à l'interface avec l'électrolyte ;
- La fragmentation et/ou délamination du film d'électrode, en raison de la défaillance du liant.

Dans ce contexte, l'amélioration des propriétés physico-chimiques du liant, utilisé dans la fabrication des électrodes, est cruciale pour atténuer leur dégradation mécanique. Pour cela, un liant de type poly(acide carboxylique), classique pour les électrodes de silicium, est réticulé par des liaisons de coordination grâce au simple ajout d'une source de cation divalent (ex. ZnSO₄, ZnO). Le réseau de coordination ainsi formé améliore significativement le comportement mécanique des électrodes. Le liant de coordination semble aussi agir comme une couche de passivation artificielle, limitant ainsi la dégradation de l'électrolyte à la surface du silicium.

Ces effets combinés améliorent grandement la tenue au cyclage des électrodes.

Title: Study of coordination binder for silicon negative electrodes of lithium-ion batteries

Keywords: Lithium-ion batteries, silicon, binder, coordination

Abstract:

Silicon is a promising material to enhance the lithium-ion batteries energy density. It delivers a gravimetric and volumetric capacity respectively 10 and 3 times higher than graphite, which is the reference negative electrode material. This difference comes from the amount of lithium that reacts with silicon, up to the c-Li₁₅Si₄ alloy. However, it comes an expansion of up to 280% of the initial volume of the material. Thus and besides the intrinsic silicon problematics (cracking/porosification), two major electrode failure mechanisms are experienced upon cycling:

- A continuous electrolyte degradation, due to the passivating solid electrolyte interphase (SEI) layer destabilization;
- The electrode film fragmentation and/or delamination, due to binder failure.

In this context, improvement of the physico-chemical properties of the binder, used for the electrode manufacturing, is crucial to mitigate their mechanical degradation. For this purpose, a poly(carboxylic acid) binder, which is typical for silicon electrodes, is reticulated by coordination bonds thanks to the simple addition of a divalent cation source (e.g. ZnSO₄, ZnO). The resulting binder cross-linked network significantly improves the electrode mechanical behavior. It also appears that the coordination binder acts as an artificial SEI, limiting the electrolyte degradation on the covered silicon surface.

Combined, these effects greatly improve the electrode capacity retention.