

Conception et développement de nouveaux matériaux d'électrodes organiques pour batteries Lithium-ion et Sodium-ion

Roberto Russo

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Thèse de Doctorat

Mention Chimie Spécialité Chimie-Électrochimie des Systèmes organiques

présentée à l'Ecole Doctorale en Sciences Technologie et Santé (ED 585)

de l'Université de Picardie Jules Verne

par

Roberto Russo

pour obtenir le grade de Docteur de l'Université de Picardie Jules Verne

Design and development of new organic electrode materials for Lithium-ion and Sodium-ion batteries

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Alla mia famiglia, per il vostro amore

List of Publications and Patents

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- 2) Environmentally Friendly Lithium-Terephthalate/Polylactic Acid Composite Filament Formulation for Lithium-Ion Battery 3D-Printing via Fused Deposition Modeling.
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- 3) Experimentally Validated Three-Dimensional Modeling of Organic-Based Sodium-Ion Battery Electrode Manufacturing
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- 6) Substituted Molecular thianthrene as active material for positive electrode in all-organic Dual-ion battery <u>R. Russo</u>, J.N. Chotard, G. Gachot, C. Frayret, G. Toussaint, P. Stevens & M. Becuwe In preparation
- 7) Unraveling the redox mechanism and material microstructure and crystal structure of dilithium benzonquinone dioxime as positive material for lithium-ion battery
 <u>R. Russo</u>, C. Davoisne, A. Urrutia, Y. Danten, C. Gatti, G. Toussaint, P. Stevens, C. Frayret & M. Becuwe In preparation
- 8) Nouvelles électrodes organiques et leur utilisation dans des systèmes électrochimiques <u>R. Russo</u>, P. Stevens, G. Toussaint, M. Becuwe.
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"Dilexit veritatem" Marc Bloch

Abbreviations/Acronyms

ACN : Acetonitrile AQ : Anthraquinone TGA-DSC : Thermogravimetric Analysis – Differential Scanning Calorimetry BET : Theory for monolayer molecular adsorption Brunauer, Emmett & Teller **CE** : Coulombic efficiency C^{theo}: theoretical capacity **BQ** : Benzoquinone KB600 : Carbone Ketjenblack EC-600JD **CNT**: Carbon Nanotubes Csp: Carbone Super P DEC : Diethyl carbonate DMC : Dimethyl carbonate EC : Ethylene carbonate PC : Propylene carbonate DMF: N,N-dimethylformammide **XRD** : X-ray Diffraction EDS (or EDX) : Energy Dispersive X-Ray Spectrometry FTIR : Fourier-transform Infrared NMR : Nuclear magnetic resonance GC/MS : Gas chromatography–mass spectrometry Li-ion : Lithium-ion Na-ion : Sodium-ion SEM : Scanning Electron Microscopy **TEM : Transmission Electron Microscopy** NMP: N-Methyl-2-pyrrolidone CMC : Carboxymethyl cellulose PVdF : Polyfluorene de vinylidene PVK : Poly(N-vinylcarbazole) NMR : Nuclear Magnetic Resonance THF : Tetrahydrofuran VGCF : Vapor Growth Carbon Fiber Li₂-BQD : Dilithium *p*-benzoquinone dioxime DNB: Dinitrosobenzene PNDD: 1,4-phenyleneazine-N,N-dioxide CZA : Carbazole LiCZA : Lithium 2-(9H-Carbazol-9-yl)acetate Li-4-BACZ : Lithium 4-(9H-carbazol-9-yl)benzoate DCZP : 1,4-Di(9H-carbazol-9-yl) benzene **TNT**: Thianthrene DMTNT: 2,7-dimethylthianthrene DFTNT: 2,7-difluorothianthrene Li₂-NDC : Dilithium Naphthalene Dicarboxylate Na₂-NDC : Disodium Naphthalene Dicarboxylate NVPF : Sodium Vanadium Fluorophosphate

General introduction

Today, the topic of climate change has become central in the political and social debate. In recent decades, the research of the scientific community has studied the impact of human activities on the ecosystem in our planet, underlining that the emission of some gases has a negative impact on the natural balance of the planet. Specifically, a series of gases capable of modifying the climate have been identified and named "climate-altering gas". The main effect of these gases is to increase the "Greenhouse effect" of the earth, which results in an increase in the average temperature of the planet, a phenomenon that takes the name of global warming; among the Greenhouse Gas (GHG), scientists agree that the predominant role is played by carbon dioxide (CO₂), a molecule produced by all combustion processes between materials based on carbon and oxygen. Global warming can have extremely negative impacts on our ecosystem: it can lead to imbalances on a local scale, as heavy rains out of season or long periods of drought, but it has also effects on a global scale, as the melting of glaciers, rise in the level of seas and desertification of large regions. These phenomena have been studied by the UN Intergovernmental Panel on Climate Change (IPCC), which developed different projections on the possible increase in the Earth's temperature, shown in Figure I.1. Some of the scenarios, in which the emissions of climatealtering gases are not mitigated in any way, envisage an average increase of 5 degrees by 2100: this hypothesis would, if it came true, have catastrophic effects for the planet, humans, animals and plants[1]. However, projections show that the temperature increase can be limited to +1.5 °C thanks to measures to reduce emissions of climate-altering gases. In order to keep the temperature increase below +2 °C, the IPCC has developed a plan called Net Zero Emissions by 2050 Scenario (NZE): the main purpose of this plan is to reduce net emissions to zero of CO_2 by 2050[2]. To achieve this target, a path has been proposed that focuses on the modification of energy sources (energy transition or ecological transition), to replace energy sources with high carbon dioxide emissions with sources characterized by low (or zero) CO₂ footprint (decarbonization of energy sources). This objective, albeit well outlined in scientific papers, is characterized by a socio-political-economic complexity of huge entity: the replacement of fossil energy sources to minimize the CO₂ emissions could impact the ever-increasing need for energy, which is linked to the development of humanity's wellness.



Figure I.1: Global surface temperature change. Increase relative to the period 1950-2100. Reproduced from ref [1].

The energy transition is focusing mainly on two main domains, the production of electricity and the transport sector. These two sectors are accounted to be responsible for at least 50% of the total CO₂ emissions in the world[3]. The replacement of gas and coal-fired power plants with renewable energy sources, such as photovoltaic and wind power plants, could abate CO₂ emissions from electricity production (Figure 1.2). However, renewable energy sources are characterized by a strong intermittency: they depend on atmospheric factors (as sunlight, wind, *etc.*), which are difficult to predict and manage. To optimize the electricity production from renewable energy sources, and make them advantageous in replacing fossil sources, it is necessary to develop efficient energy storage systems, to store electricity when photovoltaic panels and wind turbines are in operation and use it when the systems are unable to produce.



Notes: TWh = terawatt-hours; gCO₂/kWh = grammes of CO₂ per kilowatt-hour, STE = solar thermal electricity; PV = photovoltaic; CCUS = carbon capture, utilisation storage. Other includes geothermal power, ocean energy and hydrogen.

Figure I.2: Global power generation by fuel/technology in the Sustainable Development Scenario, 2019-2070. Reproduced from

About transport sector, the solution that is taking place is the replacement of internal combustion engine (ICE) cars with electric vehicles, where there is a battery capable of powering an electric engine. According to estimation provided by the international energy agency (IEA), the automotive sector is responsible for 25% of total CO_2 emissions[3–5]. To minimize emissions from road transport, massive electrification of the sector is required, which however requires highperformance energy storage technology: unlike consumer electronics (mobile phones, laptops), energy density and power density requirements for electric cars are highly challenging. To date, the only technology capable of meeting the energy storage needs of renewable energy sources (called stationary storage) are very limited. One option is the use of pumped hydroelectric energy storage: although it is a very efficient and low-cost method, this technology requires a particular morphology of the territory; therefore, this option is not versatile and can only be used in specific and limited cases. Electrochemical storage technologies more suited to stationary applications such as redox-flow batteries are yet mature enough, it may take a decade before it becomes mature enough to be used extensively. The most efficient and versatile solution is the one proposed by lithium-ion batteries, capable of guaranteeing high performance and being used in various situations. Even for electric cars, batteries based on lithium-ion technology are the only ones that can start to approach performances comparable to ICE cars. Although lithium-ion batteries are at the center of enormous efforts by the scientific community, to achieve continuous improvement in terms of performance and costs, there are still several limitations that do not make them ready to support the required energy transition on a global scale. The inorganic active materials used suffer from the supply of raw material and their location, as well as the costs of manufacturing, CO₂ footprint and recyclability. Figure I.3 shows the demand for metals for lithium-ion batteries up to 2030.



Source: BloombergNEF. Note: Metals demand occurs at mine mouth, one-year before battery demand. All metals expressed in metric tons of contained metal, except lithium, which is in lithium carbonate equivalent (LCE).

Figure I.3: Metals demand from Lithium-ion batteries 2020-2030. Reproduced from ref [6].

Inorganic materials are based on transition metals such as cobalt, nickel and manganese, which are affected by supply and recyclability problems: 1) the abundance of these resources is strictly limited while the demand for energy storage systems is strongly increasing[6–8]; 2) their extraction and processing cost is very high; 3) LIB using inorganic materials are reported to be poorly recyclable[9]. In the future, the high costs and ecological issues related to these materials could be the bottlenecks in the massive production of batteries, due to the enormous increase in demand for energy storage systems from the automotive and industrial fields[10,11]. Considering all these limitations, some research groups re-orientated their efforts toward innovative organic-based materials (made up of very abundant elements such as carbon, nitrogen, sulfur, oxygen and hydrogen) reported to be promising candidates for the manufacturing of batteries with an extremely low environmental footprint. Organic batteries are indeed particularly promising due to their easy material retrieval and recycling, as well as their low temperature manufacturing requiring less energy. In the next chapter, the history and state of the art of organic materials used in energy storage systems will be illustrated, mainly for lithium-ion batteries, but also "post-lithium technologies" and "metal-free" technologies will be dissected.

Chapter I. State-of-art of Organic materials for energy storage applications

In this chapter, rechargeable electrochemical accumulators will be introduced, describing how they work and the main systems developed. In particular, a focus will be made on accumulators based on lithium-ion technology. To date, this technology is the one that provides the best performance in electrochemical terms: the history of development and large-scale production of the first lithium-ion battery will be retraced. Next, a brief overview of the state of the art of commercially available battery materials will be made.

Afterward, the development of organic materials for applications in energy storage systems will be illustrated. Starting from the first attempts reported in the literature, different classes of molecules will be analyzed in detail, discussing the strategies implemented to improve the performance of these materials. The chapter will be concluded with the positioning of this thesis work with respect to the panorama of organic materials for batteries.

State-of-art of secondary electrochemical generators

A **Galvanic cell** or **Voltaic cell** (in honor of the Italian scientists Luigi Galvani and Alessandro Volta, respectively), commonly named battery, is an electrochemical cell in which an electric current is generated by spontaneous Oxidoreduction reactions. The electrochemical cell consists of two electrodes: one electrode is called Cathode and is the reducing electrode corresponds to the positive pole of the battery on discharge, while the other is called Anode and corresponds to the oxidating electrode, the negative pole on discharge. The two electrodes are immersed in an electrolytic solution, which has the function of allowing the transfer of ions between the two electrodes. Furthermore, the electrodes are separated by a separator, which allows the passage of ions but not that of electrons, which are conveyed into an external circuit.

Alessandro Volta is universally considered the inventor of the first primary battery: despite the previous work of Galvani about the electricity generated by electrochemical reactions, in 1799 Alessandro Volta was the first reporting the assembly of an electrochemical cell, consisting of a stack of two discs of Zinc and Copper, separated by brine-soaked paper (as electrolyte).

Electrochemical cells can be divided into two groups, based on the reversibility or irreversibility of the electrochemical reactions at the electrodes:

1. Primary electrochemical generator (pile): the redox reactions involved are irreversible, the charged system can deliver the stored electrochemical energy only once.

 Secondary electrochemical generator (accumulator): it can be charged and discharged several times, thanks to the reversible electrochemical reactions involved in the electrodes.

The object of this thesis is the study of secondary electrochemical cells; therefore, the functioning of the primary cells will not be explored. Electrochemical accumulators are so that the chemical energy of the redox reaction is released in the form of electricity: during discharge, the electrochemical reaction between cathode and anode takes place spontaneously on discharge, releasing the electrons in an external circuit; during the charge, the accumulator is connected to a source of electricity, which acts as a driving force for the electrochemical reaction in the non-spontaneous reverse direction; in this phase, the electrical energy is stored in the form of chemical energy.

The basic elements of an accumulator do not differ much from the pile conceived by Volta. As showed in Figure I.1, it consists of two electrodes, where there is the electroactive material involved in electrochemical reactions. Both the electrodes are immersed in an electrolyte (which can be solid, liquid or a combination of these two states, such as gel electrolytes), which ensures the transport of ionic species (anions and cations) from one electrode to another, and assure the electroneutrality of the system. A separator (soaked with the electrolyte) is placed between the two electrodes, which allows the passage of ions, but not electrons (electronic insulator): the separator serves to avoid short circuits resulting from the contact of the two electrodes. It must be electro-/chemically stable to resist battery electrolytes and applied voltages.



Figure 1.1: Working scheme of secondary electrochemical generator (accumulator) in charge and in discharge phase.

The first accumulator was invented by the French scientist Gaston Planté in 1859, called "Leadacid" cell. The cell consisted of two Lead-based electrodes separated by a linen ribbon and immersed in a solution of sulfuric acid. Despite the successive evolutions of the cell structure, the electrochemical process remained unchanged. Even if the Lead-acid accumulator is characterized by a low energy density, the high power and the low production cost led to a wide diffusion of this system, that is still used for thermal vehicles, security supply in nuclear power stations and storage solutions for PV production in non-grid connected installations.

In 1899, Waldemar Jungner invented the first rechargeable alkaline battery of the Nickel-Cadmium (Ni-Cd) type. Finally, in 1967, cadmium was replaced by metal hydrides (Ni-MH) for reasons of cadmium toxicity. This type of accumulators gained great popularity as rechargeable batteries for consumer electronics before the arrival of LIB, given their good volumetric energy density. The chemical species involved at the base of the electrochemical reaction and the metrics of the different cells are summarized in Table I.1.

	Lead-Acid	Nickel-Cadmium	Nickel-metal hydride
Positive electrode	PbO ₂	NiOOH	NiOOH
Negative electrode	Pb	Cd	Metal Hydride
Voltage (V)	2.1	1.2	1.2
Energy den. (Wh kg⁻¹)	40	60	80
Cycling life	>750	>1500	>1000
Advantages	Low cost	High power density	High energy density
Disadvantages	Low energy density	High toxicity (Cd)	High self-discharge

Table I.1: Electrodes and characteristics of commercially available accumulators.

In the 1970s, Whittingham and coworkers were the first to propose a paradigm shift in accumulator electrochemistry: the use of intercalation chemistry for energy storage systems[12]. The first attempts to develop rechargeable Li batteries were focused on Lithium metal as anode, with LiTiS₂, LiMoS₂ and LiMnO₂ as the cathode. However, lithium batteries based on LiMoS₂ and LiTiS₂ *vs.* metallic Lithium showed huge safety problems: the frequent cases of battery fires discouraged further commercialization attempts. In 1980, the development of new cathode material, the LiCoO₂ (LCO) by Goodenough and coworkers gave new impetus in the field of lithium-ion technology[13]. Nowadays, LiCoO₂ based materials are still one of the most used cathode materials, especially for application in electronics (mobile phone, laptops, cameras, *etc.*).

The quest of high-performance anode material had long remained a challenge in the development of high performance and safety lithium-ion battery. Attempts by Whittingham and coworkers to use metal lithium have highlighted major safety problems, due to the formation of dendrites, responsible for short-circuits and battery fires. In 1987, Yoshino proposed a new anode material, the petroleum coke, a soft carbon that demonstrated a reversible capacity of ≈ 200 mAh g⁻¹ (out of a theoretical 372 mAh g⁻¹), with excellent capacity retention[14]. Then, Yoshino moved to the development of a full battery, coupling the LiCoO₂ cathode discovered by Goodenough with the anode based on petroleum coke, with Propylene Carbonate (PC) as electrolyte solvent. In 1991, Sony Co. commercialized the battery developed by Yoshino for consumer electronics. This battery showed an energy density of 200 Wh L⁻¹ (volumetric) and 80 Wh kg⁻¹ (gravimetric): it was at the same time small, light and durable, while being reasonably priced. The three aforemetioned scientists, Whittingham (development of insertion materials for batteries), Goodenough (development of LiCoO₂ as cathode material) and Yoshino (development of carbon coke as anode material and development of the full-cell LiCoO₂//Carbon coke) were awarded the Nobel Prize for Chemistry in 2019 "for the development of lithium-ion batteries".

The first lithium-ion battery paved the way for a new field of research. The search for materials capable of working at high potential, with a better specific capacity has extended to a huge number of new materials. For simplicity, in this paragraph we will report the materials that have shown excellent electrochemical performances and that have been developed up to the commercialization stage. These materials have been reported in Table I.2.

Electrodes	Materials	Structure (type)	Redox mechanism	Potential (V)	Capacity (mA h g^{-1})	Commercia- lization
	LiCoO ₂	Layered	$LiCoO_2 \leftrightarrow CoO_2 + Li^+ + e^-$	3.7	274	Y
Cathode	LiFePO ₄	Olivine	LiFePO₄↔FePO₄+Li ⁺ +e ⁻	3.45	170	Y
	$LiMn_2O_4$	Spinel	$LiMn_2O_4 \leftrightarrow 2MnO_2 + Li^+ + e^-$	4.0	148	Y
	$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_{2}$	Layered	$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_{2} \leftrightarrow Ni_{1/3}Mn_{1/3}Co_{1/3}O_{2} + Li^{+} + e^{-}$	3.6	277	Y
	$LiNi_{0.80}Co_{0.15}Al_{0.05}O_{2}\\$	Layered	$LiNi_{0.80}Co_{0.15}Al_{0.05}O_{2} \leftrightarrow Ni_{0.80}Co_{0.15}Al_{0.05}O_{2} + Li^{+} + e^{-it}$	3.6	278	Y
Anode	Graphite	Insertion	6C+Li ⁺ +e ⁻ ↔LiC ₆	0.1	372	Y
	$Li_4Ti_5O_{12}$	Insertion	$Li_4Ti_5O_{12}+3Li^++3e^-\leftrightarrow Li_7Ti_5O_{12}$	1.55	175	Y
	Si	Alloving	Si+4.4Li ⁺ +4.4e ⁻ ↔Li _{4 4} Si	0.25	4212	Y

Table I.2: List of cathode and anode inorganic material for lithium-ion batteries currently available on the market.

As for cathode materials, $LiMn_2O_4$ (LMO)[15,16] was introduced a few years later. The LMO is characterized by a higher mean redox potential, 4.0 V against the 3.7 V vs. Li⁺/Li of the LCO but showed a specific capacity of only 148 mAh g⁻¹, corresponding to 54% of LCO capacity. To date, LMO has a significantly lower application than LCO and is mainly used as an additive in cathode mixtures.

Two other layered materials have been developed for lithium battery applications, LiNi_{1-x-y}/Al_xCo_yO2 (NCA)[13] and LiNi_{1-x-y}Mn_xCo_yO2 (NMC)[17,18]. The NCA material showed improvements in specific energy and durability compared to LCO, while NMC significantly improved durability and safety, but at the expense of lower energy density. NMC111 was the first material of this family put on the market. Thereafter, NMC compounds with a high Nickel content, such as NMC532, NMC622 and NMC811, were developed. The increase in the quantity of Ni offers two important advantages: 1) a reduced Co content and therefore a reduction in production costs; 2) a significant increase in the specific capacity and consequently in the energy density. These Ni-rich NMC materials are already available on the market or in a close stage to commercialization.

In recent years, some companies have begun to opt for different chemistry for electric vehicles. The high production costs of NMC/NCA and the scarce availability of raw materials has led some companies to choose LiFePO₄ (LFP) as cathode material[19,20]. Discovered by researchers at the University of Texas by Goodenough and coworkers in the mid-1990s, the LFP cathode offers numerous benefits, including long cycle life, superior thermal stability, and low raw material cost[21]. On the other hand, LFP is characterized by lower specific capacitance and nominal voltage, which results in lower specific energy than other mentioned cathode materials. Furthermore, the LFP is characterized by an olivine structure, which allows a diffusion of the ions in 1-D: as a result, LFP exhibits low conductivity and low rate performance. This problem has been partially solved by using nanosized[22] carbon coated[23] LFP particles.

The breakthrough in lithium-ion battery technology was triggered by the replacement of lithium metal with carbon based materials as anodic material, now mostly graphite[24–26]. The graphite exhibit excellent electrochemical properties: with a theoretical specific capacity of graphite is 372 mAh g⁻¹ and an intercalation potential between 0.25 V and 0 V vs. Li⁺/Li, it is still today the most performing anodic material[24]. Despite the high energy density, carbon based materials have shown limitations. The most important is the lithium plating phenomenon[27] due to the low average potential of graphite (approx. 0.1 V vs. Li⁺/Li), which limits its functioning at high C-rates[28]. Titanium oxides and especially lithium titanate (Li₄Ti₅O₁₂, LTO) have substantially higher working potentials, around 1.55 V versus Li⁺/Li for the redox pair Ti₃⁺/Ti₄⁺ and are interesting alternatives to overcome the safety problems caused by lithium plating[29]. However, the high

insertion potential significantly lowers energy density; moreover, the LTO is characterized by a specific capacity of 175 mAh g⁻¹, half that of graphite. Therefore, it is an inherently structurally stable material with excellent reversible Li⁺ de-/insertion;[30–32] it also has an extremely flat potential plateau on both charge and discharge step, which is characteristic of a two-phase reaction mechanism.

In addition to insertion anodes, research has also focused on another type of negative material, which is based on alloying[33]. Of the metals and metalloids capable of alloying with lithium, silicon is the most promising candidate for real-world applications[34]. Si is characterized by a series of advantages: 1) it is abundant, environmentally friendly and non-toxic, 2) it offers extremely high gravimetric and volumetric capacities (3579 mAh g⁻¹ as gravimetric capacity) shows an appropriate average voltage of approx. 0.4 V vs. Li⁺/Li[35–37]. However, it suffers from poor cycling due to the large volume variation (280% during the cycle at full capacity at room temperature), which leads to subsequent mechanical and chemical degradation. Mechanical degradation occurs as pulverization of the silicon particles, loss of electronic contact between the Si particles and the conductive network of the electrode, and delamination from the current collector[38][39]. Chemical degradation occurs together with the irreversible consumption of the electrolyte and active lithium due to the continued growth of an unstable SEI, which lowers the coulombic efficiency (CE).

Characteristic of energy storage systems

Battery performance can be evaluated through a series of electrochemical parameters. Here below are listed the main parameters that must be taken into consideration in the design of a battery system.

Voltage: generally speaking, voltage is defined as the "pressure" from a power source that pushes charged electrons (current) through an electric circuit; it is measured in Volts (V). In the case of batteries, the voltage can be seen as the difference in electric potential between the positive and negative electrodes.

Specific Capacity: It defines the amount of energy that is stored per unit mass or volume. The theoretical specific gravimetric capacity can be calculated by the following formula:

$$C^{theo}(C) = \frac{n \cdot F(C \cdot mol^{-1})}{MW(g \cdot mol^{-1})}$$

where the theoretical capacity is expressed in Coulombs (C), n is the number of electrons involved in the electrochemical process and F is the Faraday constant (96485 C mol⁻¹); in the dominator we have the molecular weight (MW) expressed as g mol⁻¹. For simplicity, in general it is preferred to express the capacity in Ah kg⁻¹ or in mAh g⁻¹, depending on the scale of the battery system (e.g., battery pack for vehicles or single battery in laboratory scale). Based on the conversion 1 mAh = 3.6 C, the specific capacity can be re-written as:

$$C^{theo}(mAh\ g^{-1}) = \frac{n \cdot 26801}{MW}$$

It is important to note that the theoretical specific capacity, calculated with the aforementioned formula, hardly coincides with the real specific capacity, as in a real energy storage system several parasitic reactions could take place, decreasing the storage capacity of the material.

Energy density: is defined as the amount of energy stored by an accumulator for mass or volume unit. It is usually expressed in mass unit (Watt-hour per kilogram, Wh kg⁻¹) in the research field, while for applications in electric cars it is preferable to express it as volumetric density (Watt-hour per liter, Wh L⁻¹). The energy density of a battery can be calculated using this formula:

$$Energy \ density \ (Wh \ kg^{-1}) = \frac{Nominal \ Voltage \ (V) \cdot Battery \ capacity \ (Ah)}{Battery \ weight \ (kg)}$$

Cycle life: the cycle life of batteries is the number of charge and discharge cycles that a battery can complete before losing acceptable performance. By convention, for mobile applications a battery with less than 80% of its initial capacity is considered to have reached the end of cycling life.

Rate capability: it corresponds to current applied to the discharged battery in order to fully charge it in a given time. The rate 1C means the battery is fully charged in 1 hour, 2C in half an hour and C/2 in two hours.

Coulombic efficiency: is the capacity yield of each cycle of the battery. It refers to the ratio of the discharge and charge capacities of the same cycle. It is usually a fraction less than 1.

Voltage efficiency: is determined by the difference between the charging voltage and voltage of the battery during discharging.

Energy efficiency: The energy efficiency is a measure of energy loss in the entire charge/discharge cycle.

In the introduction, some of the advantages of using organically derived materials for energy storage applications were mentioned. In the next paragraph, the mains advantages and disadvantages about this class of compounds will be summarized, in comparison with the inorganic materials.

High energy density: Organic materials are characterized by a tunable potential, which in some cases can reach up to 4.0 V *vs.* Li⁺/Li, and by a high specific capacity, since most of the organic molecules are characterized by a low molecular weight. The combination of these two parameters lead to a high energy density compared to inorganics: an example is given by benzoquinone, one of the most studied organic molecules for energy storage, which exhibits a potential of 2.8 V *vs.* Li⁺/Li and a specific capacity of *ca.* 500 Ah kg⁻¹, for an overall energy density of about 1400 Wh kg⁻¹, almost three times higher than that of commercial LiCoO₂ (550 Wh kg⁻¹), one of the most employed cathode material for commercial batteries.

High power density: the redox reactions of organic materials intrinsically have a faster kinetics than the inorganic intercalation process, therefore organic-based electrodes can work at higher power density. Several organic structures can achieve outstanding rate performances: among these, those that have shown the best speed capabilities are phenothiazine, thianthrene and triphenylamine derivatives.

Structural flexibility: organic materials are characterized by a wide variety of molecular structures: this allows to design structures with different chemical and mechanical properties. The latter can potentially open the way to different methods of manufacturing electrodes, currently closed to organic materials. Among these, casting, printing and vapor deposition can be mentioned, due to their characteristics of solubility, film-forming ability and sublimability. The variety of manufacturing techniques may allow the development of flexible and wearable devices in the future.

Sustainability: Currently, the inorganic materials used in the batteries manufacturing are based on transition metals, such as Co, Mn, Fe, Ni, *etc.* These metals, despite showing exceptional electrochemical properties, suffer from some drawbacks such as 1) high production costs, due to their scarcity and energy-intensive manufacturing processes; 2) the processing of these materials has a great environmental impact, both in terms of CO₂ emissions and for the scarce recyclability. On the contrary, organic compounds are essentially composed of atoms abundant on the earth's crust, such as C, N, O, S and F which do not necessarily require extraction processes (*i.e.* mining); moreover, the synthesis is often cheap, low temperature and does not involve high carbon dioxide emissions (soft chemistry). Finally, in some cases they can be extracted directly or possibly synthesized from biomass or other waste from the chemical industry and are easily recyclable through the carbon dioxide cycle. Therefore, it can be concluded that organic materials are good candidate for an eco-friendly production of energy storage systems.

Despite the advantages listed above relating to organic materials, such as low production costs and environmental impact among all, academic research relating to the applications of organic molecules for energy storage has highlighted some limitations, some of which represent important challenges on the way to commercialization of these batteries.

Low Mass Density: Organic materials are in most cases characterized by a marked lower mass density compared to inorganics. Low density is not a drawback for energy systems working on gravimetric energy density, but it can be a limiting factor for applications that require a high volumetric energy density. For example, lithium batteries for mobile phones, laptops and electric vehicles require high energy density in a relatively small volume. To overcome this issue, it is important to develop organic materials characterized by a high gravimetric energy density, to compensate the low mass density.

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Low electronic conductivity: Organic electrode materials are electrical insulators, which impedes the circulation of electrons inside the electrode (also called electronic percolation). Poor conductivity therefore implies a limitation to the rate performance. For inorganic materials, as LiFePO₄ (LFP), adding conductive carbon through an appropriate method (carbon coating) can significantly improve electron transport in the electrode and ensure a good performance at high C-rate. However, compared to what has been reported in the literature for LFP, the quantity of conductive carbon necessary for organic materials is markedly greater. The percentage amount (by weight) of the conductive carbon in the entire composite electrode is around 20-50% in most organic-based electrodes. This high quantity leads to a strong decrease in volumetric energy density, as well as to several rheological and formulation problems (higher quantity of binder, solvent for slurry, etc). Several strategies have been developed to overcome this drawback: electroactive organic molecules with extended conjugated structure, the use of conductive polymers as polymeric backbone and mixing active materials carbon with excellent conduction (eg CNT or graphene) at the molecular level.

Solubility: Most of the small organic molecules are highly soluble in the electrolyte solvent and the dissolution of the active materials in the electrolyte reduces markedly the cycling life. Several strategies have been developed to avoid dissolution of the active materials: the most efficient strategy is the polymerization of organic molecules, to form an electroactive polymer that exhibits reduced solubility in organic solvents. In addition to the synthesis of covalently bonded polymers, there is also another type of polymer, the coordination polymers, which connects the electroactive parts with the coordination bonds between the metal ions and the atoms of N, O or S. Another way to decrease solubility is the use of substituents of an ionic nature, often using lithium organic salts.

Self-discharge: This is a phenomenon where, due to parasitic (electro-) chemical reactions inside the battery, the energy of the battery is dissipated chemically. These reactions often occur at high operating temperatures. It is expressed as a percentage of capacity loss per unit of time: for inorganic materials, it is estimated at around 3% per month on average for lithium-ion batteries.

In the 1978, Hünig proposed a classification of organic materials based on their energy storage mechanisms[40], reported in Figure I.2. The first type of mechanism is called "*n*-type": the

oxidation reaction leads to the formation of a negative charge on the electroactive group, compensated by the acquisition of a positive charge, or cation (C⁺); the most common types of cations in organic batteries are Li⁺, Na⁺, K⁺, Mg²⁺, *etc.* For this first group, the quinone derivates, organodisulfides, diimmides and pteridines for positive electrodes are examples, and carboxylates, azobenzene for negative electrodes. The second type of mechanism is called "*p*-type": in this case, the oxidation of the active material leads to the formation of a positive charge, which is compensated by the insertion of a negative charge, an anion (A⁻). In the *p*-type group, aromatic amines (such as phenothiazine and phenoxazine) have gained popularity, together with conjugates amines, thianthrene-based polymers and carbazole derivates. The last group of electroactive molecules is called "Bipolar": an oxidation step leads to the loss of a negative charge with the consequent loss of a C⁺ cation (*n*-type), whilst the second oxidation step creates a positive charge, with the relative acceptance of a negative charge A⁻ (*p*-type); an example is the nitroxide derivates (as PTMA).



Figure I.2: General notation of the main reversible redox systems in organic chemistry according to the Hünig classification. X/Y: functional groups based on N, O, S, P or other π -conjugated groups; R and R' being potentially fused into a single ring system. Reproduced from ref [41].

Organic materials as positive electrode

N-type molecules

Quinones

Quinone derivatives are undoubtedly one of the most studied classes of organic compounds for energy storage applications. The enormous interest on quinone derivates has several explanations: quinones show a reversible two-electron redox reaction, with very rapid electrochemical kinetics and an average potential between 2 and 3 V (vs. Li⁺/Li), depending on their molecular structure [42]. In addition to their interesting electrochemical properties, which make them promising candidates for battery applications, quinones are characterized by chemical flexibility, due to their simple molecular structure [43,44]. This versatile structure allows to easily modify the (electro-)chemical and mechanical properties, often via simple synthetic routes[45]. The aromatic ring can be substituted in many ways, to modify its solubility in different media through the synthesis of polymers, or it is possible to enrich the structure with functional groups able of improving the reaction kinetics, etc. This variety of structural modification possibilities has been extensively studied and reported in the literature and will be the subject of an in-depth discussion in the next paragraph. Last, but not least, quinones are widely present in biological systems, for example in the form of plastoquinone and ubiquinone, where they play an important role as electron carriers in the respiratory chain in the chloroplast and mitochondria. This massive presence in natural bio-organic sources, as biomass or from waste from the agri-food industry, making them advantageous in term of production costs. Finally, quinones and its derivates can be used with a vast number of metal ions, such as lithium[45], sodium[46], potassium[47,48] and recently also bivalent cations[49,50]. Considering their promising electrochemical performances, their versatile structure and their wide availability, quinones can be considered a milestone in this research field.

The redox mechanism can be generalized as an enolization reaction of the carbonyl group, which can be promoted by a conjugated structure[51]. The redox mechanism of the simplest of quinones, 1,4-benzoquinone, is showed in Figure I.3. After the two reduction steps, both carbonyl groups are transformed into -C-O⁻, followed by the acceptance of a cation to balance the negative charge. This process leads to an overall decrease in the energy of the system, because it restores

the aromaticity of benzene[52]. Going in the opposite reaction direction, the oxidation process leads to an increase in energy due to the breakage of aromaticity. This concept underlies the rational design of quinone derivatives: the potential can be tuned by using substituents that stabilize (or destabilize) the aromatic ring, following the rules that electron-withdrawers increase the potential, while electron donors decrease the potential.



Figure I.3: Redox mechanism of 1,4-benzoquinone. The proposed mechanism can be extended to all quinone derivates.

In 1972, Alt et *al.* studied chloranil molecule as active material for rechargeable batteries[53]. This molecule showed a reversible redox reaction, providing the 85% of its theoretical capacity (C^{theo} = 218 mAh g⁻¹) in half-cell *vs.* lithium metal anode, using LiClO₄ in propylene carbonate (PC) as electrolyte. In 1984, Tobishima and coworkers reported a study on 1,4-benzoquinone[54]: this molecule is characterized by a high theoretical capacity (496 mAh g⁻¹ for two-electrons exchanged), thanks to its low molecular weight (108 g mol⁻¹). However, 1,4-benzoquinone exhibited a low redox potential, around 2.50 V *vs.* Li⁺/Li, much lower than inorganic materials. Moreover, this molecule showed poor cyclability, characterized by a marked capacity drop after 10 cycles: this is due to the high solubility of benzoquinone in the electrolyte solvent. This study highlighted several issues common to all quinone derivatives: 1) the instability of the radical intermediate, 2) the strong solubility in organic solvents conventionally used as electrolytes, responsible for poor cycling and 3) the low electronic conductivity, which requires enormous quantities of conductive carbon. To address these problems, it is therefore necessary to implement the extensive molecular engineering of quinone structure in order to achieve, at the same time, high specific capacity, high potential and a good electrochemical stability.

Since quinones are small non-polar organic molecules, these molecules result in being soluble in the commons carbonate solvents used for electrolytes. To avoid dissolution and therefore overcome the problem of poor cycling life, two different strategies were explored: one is the polymerization of quinone, the second is the substitution of benzene with ionic groups, such as lithium salts, to obtain the so called "lonic organic salts".

Concerning the polymerization approach, Song and colleagues presented a quinone polymers, polybenzoquinonyl sulfide (PBQS, Figure I.4a)[55]. After polymerization, PBQS cathode exhibits a reversible capacity of 275 mA h g⁻¹ with an average redox potential of 2.67 V vs. Li⁺/Li (Figure I.4b). The PBQS also showed a dramatic improvement in cycling stability: a capacity retention of 86% after 1000 cycles was observed, as showed in Figure I.4c. This result proves that polymerization is a simple but effective approach to guarantee the cycling stability without marked loss of specific capacity.



Figure I.4: a) Molecular structure of Polybenzoquinonyl sulfide (PQBS), b) potential-capacity profile at different current density and c) evolution of the specific capacity as a function of cycle number cycled in half-cell vs. metallic Li. Reproduced from ref [55].

The second method to suppress dissolution is by using substituents of the aromatic ring. The most effective approach is based on ionic groups, often lithium salts, able to reduce drastically the solubility in organic solvents. These compounds are called "ionic organic salts": an example of this approach was reported in the literature Lakraychi and coworkers[56]. The authors reported the synthesis of tetralithium 2,5-dihydroxy-1,4-benzenedisulfonate (Li₄-DHBDS), where two sulfonate groups were added via 2-steps synthesis. This quinone derivate showed a good capacity retention: a specific capacity of 100 mAh g⁻¹ was displayed after 10 cycles at a rate of C/20, which then stabilizes at 90 mAh g⁻¹ after 40 cycles (Figure I.5a,b). Furthermore, for Li₄DHBDS an operating potential of 3.2 V vs. Li⁺/Li is observed, that means a voltage gain of +650 mV compared to other benzoquinone-based electrode reported in literature.



Figure I.5: a) Potential-composition profile at different current density (inset: molecular structure) and b) evolution of the specific capacity as a function of cycle of Li_4DHBDS in half-cell vs. metallic Li. c) Positioning of substituent groups based on their electrochemical electronegativity (electropositivity) nature. Reproduced from ref [56].

Interestingly, this approach not only improves the cycling life, but also permits to tune the electrochemical performance, e.g. the redox potential: in the aforementioned example, the electron-withdrawing nature of the sulfonate groups led to an increase of the average redox potential. Based on the electronegativity of the substituent groups (reported in Figure I.5c), it is possible to obtain an overall improvement of the electrochemical properties. In Table I.3 were listed different examples of 2,5-disubstuited benzoquinone reported in the literature.

Substituents	Potential (V	C^{theo} (m Λ h σ^{-1})	Spec. Cap (mAh g ⁻¹)	Spec. Cap (mAh g ⁻¹)	Deference
(2,5 pos)	vs. Li⁺/Li)	C (MANg)	- 1st cycle	- (N cycle)	Reference
-SO₃Li	3.25	180	175	100 - (50)	[56]
-C ₆ F ₁₃	3.10	66	177	98 - (20)	[57]
$-C_4F_9$	3.10	99	100	58 - (20)	[57]
-CF ₃	3.00	219	162	60 - (20)	[57]
-OCH₃	2.60	319	312	255 - (10)	[58]
-H	2.53	496	N/A	N/A	[54]
-CH₃	2.50	394	226	129 - (15)	[59]
-OH	2.50	382	270	80 - (10)	[60]
$-OC_{10}H_{21}$	2.50	127	125	88 - (20)	[58]
-iPr2	2.2	279	128	94 - (15)	[59]

State-of-art of Organic materials for energy storage applications					
-tBu2	2.0	243	165	158 - (15)	[59]
-OLi	1.90	352	176	135 - (10)	[61]

Table I.3: Energy metrics of 2,5-disubstituted 1,4-benzoquinone derivates.

Natural compound - Quinones

Another interesting research field about quinone derivates concern the development of biosourced material as active material for organic batteries. Rhodizonic acid was one of the first bioderived organic compound studied for electrochemical energy storage applications[62]. It can be easily derived from myo-inositol, a sugar alcohol presents in many foods, as cereals, nuts and several fruits. Myo-inositol accounts about 8% of dry weight of corn-steeping liquor[63], a byproduct of agricultural production: thus, Rhodizonic acid can be derived from recycling of agriculture waste. The lithium salt can be obtained through a one-step acid-base reaction of lithiated base and rhodizonic acid, an easy chemical reaction that does not require polluting solvents or energy-intensive synthesis processes. The scheme process is reported in the Figure I.6a. Dilithium rhodizonate was extensively studied by Tarascon and coworkers[63,64] to obtain a lithium battery derived from renewable source. The organic electrode showed impressing electrochemical performances: the molecule can reversibly exchange 4 Li⁺/e⁻ per unit formula, for a specific capacity of 580 mAh g⁻¹ (87% of retention in the first cycle, divided into 4 different plateaus, one for each lithium exchanged during the reaction. However, the authors identified in 2.8 V vs. Li⁺/Li the overall average potential of lithium rhodizonate, for an energy density of 1100 Wh kg⁻¹, comparable with the energy density of inorganics materials. Despite the high specific capacity measured in the first cycle, a marked capacity fading was observed after few cycles, with ca. 50% less capacity after only 14 cycles; furthermore, the insertion mechanism showed a great polarization, due to the large amount of energy involved in the mechanism of breakdown/formation of aromaticity of the benzene ring. These two problems, together with the need to use a large amount of conductive carbon in the composite electrode, make this molecule unsuitable for applications in commercial batteries.


Figure I.6: a) Synthesis of Dilithium Rhodizonate ($Li_2C_6O_6$) starting from myo-inositol; Potential-composition profile (inset: evolution of the specific capacity as a function of cycle number) of dilithium rhodizonate in b) extended potential window 3.5 – 1.5 V and c) reduced potential window of 2.5-1.5 V in half-cell vs. Li. Reproduced from ref [63].

Nevertheless, Lithium rhodizonate became a milestone in the field of organic electrodes: the concept of organic molecules resulting from abundant, low cost and easy recyclability bio sourced raw materials has revived the interest of many electrochemists in the development of a new organic materials for energy storage applications.

Natural compound - Naphthoquinone

After the pioneering work of Tarascon and coworkers, a growing interest on bio-sourced materials led several battery groups to extend the research to Naphthoquinone-based material for energy storage applications. Among the different naphthoquinone available in natural products, two specific molecules have attracted the attention of researchers: Juglone and Lawsone (Figure I.7a,b), which can be find by leaves, roots, fruits and plants. **Juglone** was proposed as active material for sodium ion batteries by Chen et colleagues[65]. The composite Juglone/RGO showed an insertion potential ranging from 1.1 to 1.4 V *vs.* Na⁺/Na and a reversible capacity of 440 mAh g⁻¹ (58% of reversibility after the first cycle), that slightly decreases and stabilizes at 280 mAh g⁻¹ after 10 cycles.



Figure 1.7: Chemical structure of naphthoquinone-based natural molecules.

In 2017, Lee and Park proposed **Lawsone** as active material for organic batteries[66]. In this study, Lawsone was compared to **Naphthoquinone**, from which it differs for presence of lithiated hydroxyl group. The -OLi group led to herringbone packing configuration with π - π interactions between adjacent molecules: it gives Lawsone an excellent charge transport property, resulting in good rate performance. On the contrary, the presence of hydroxy group lowers the insertion potential by 200 mV (2.3 V *vs.* Li⁺/Li) compared to Naphthoquinone.

Based on these results, which marks significant progress over previously reported performances of quinones, Lawsone has been extensively studied by the John George group: to improve electrochemical performance, the design of a dimer[67] and tetramer[68] structures was proposed. The dimer, also called **Bis-Lawsone** (BL, Figure 1.7c), exhibited two voltage peaks, localized at $2.1-2.5 \vee vs$. Li⁺/Li, with a specific capacity of 130 mAh g⁻¹ at C/5 (85% of theoretical capacity). Li₂BL electrodes exhibited moderate rate performance, only 61% of the specific capacity was retained passing from C/5 to 2C rate, and poor cycling life (30% of capacity retention after 35 cycles).

To obtain better structural stability and overcome the solubility of Lawsone, Miroshnikov and coworker proposed a new oligomer composed by four Lawsone units, connected through a benzene moiety, called **TetrakisLawsone** (Li₄-TKL, Figure I.7d). This Lawsone tetramer can take up four Lithium ions (1 Li⁺ per formula unit), as confirmed by solid state NMR/FTIR spectroscopy analysis, but it showed only two reduction/oxidation peaks, located at 2.3 V and 2.0 V vs. Li⁺/Li. In the first cycle, the Li₄TKL electrode exhibited an excellent specific capacity of 240 mAh g⁻¹ at a current rate of C/10, but a poor capacity retention, only 48% after 300 cycles (116 mAh g⁻¹). Interestingly, the electrode showed a good rate capability: 160 mAh g⁻¹ at 1C rate, corresponding

to 67% of the capacity at low C-rate (Figure I.8a,b). These results were also observed with sodium ion batteries[69]: the reversible intercalation of 4 sodium ions, for a specific capacity of 237 mAh g^{-1} in the first cycle, which quickly drop to 163 mAh g^{-1} (69% capacity retention) after 10 cycles (Figure I.8c,d).



Figure I.8: a) Potential-capacity profile and b) evolution of the specific capacity as a function of cycle number for Li₄-TKL; c) Potential-capacity profile and d) evolution of the specific capacity as a function of cycle number for Na₄-TKL. Reproduced from ref [68] and [69].

Natural compound – Anthraquinone

Purpurin (1,2,4-Trihydroxyanthraquinone, Figure I.9a) was investigated as an organic active material for lithium-ion batteries by John George et al[70]. Purpurin showed a two-electron step redox mechanism, which in the charge phase are located at 2.5 V and 3.0 V, while in the discharge the two plateaus are at 2.2 V and 2.7 V. The strong polarization between the charge and discharge phase (300 mV) indicates a very slow redox reaction kinetics. Regarding the specific capacity, the Purpurin/Li cell showed a capacity of 196 mAh g⁻¹ after the first discharge at C/20 rate (Figure I.9c), which decreases dramatically to 90 mAh g⁻¹ of reversible capacity after 50 cycles (Figure I.9a inset): according to the authors, the capacity fading is linked to the irreversibility of lithium de/insertion process. Furthermore, the current density tests showed a notable decrease in the specific capacity (100 mAh g⁻¹ after 1 cycle at C/2 rate), confirming the low kinetics of the lithium-ion intercalation reaction in the Purpurin.

Another anthraquinone-like structure is called **Emodin** (6-methyl-1,3,8-trihydroxyanthraquinone, Figure I.9b). This molecule, present in various plants and easy to extract, is mainly used as an

active ingredient in the pharmaceutical sector. In 2016, Hu and coworkers presented a novel study on Emodin as cathodic material for lithium-ion battery[71]. Emodin electrode showed only 157 mAh g⁻¹ during the first cycle (C^{theo} = 199 mAh g⁻¹), together with a poor capacity retention after 100 cycles (60 mAh g⁻¹). The exchange of 2 Li⁺ per formula unit takes place in a single redox step, with an average de-/insertion potential of 2.39 V vs. Li⁺/Li. To improve the cycling stability of the Emodin, the authors prepared an electrode composite using Single-walled carbon nanotube (SCNT). Carbon nanotube provides a stable anchorage of the active material, preventing the dissolution, but also a fast electronic path, improving the rate performance. The Emodin/SCNT electrode architecture exhibited a good capacity retention in half-cell vs. lithium metal, with 120 mAh g⁻¹ after 80 cycles, and 72 mAh g⁻¹ at high current density (Figure I.9d).



Figure I.9: Molecular structure of a) Purpurin and b) Emodin. c) Potential-capacity profile of Purpurin electrode in half-cell vs. Li, cycled at a C/20 rate (inset: evolution of the specific capacity as a function of cycle number)[70]; d) Potential-capacity profile of Emodin/SCNT hybridized electrodes in half-cell vs. Li. Reproduced from ref [71].

Diimmides

The carbonyl functions are electroactive not only in quinones, as showed in the previous paragraph, but also in the form of anhydride in aromatic diimide systems (CDI). The *n*-type redox mechanism is based on the reduction of the carbonyl groups of the imide and the consequent reoxidation of the enolate[42,72]. Despite the presence of four carbonyl groups per unit formula, the diimides can exchange reversibly only two lithium ions per structure, in a potential window of 2-3 V (*vs.* Li⁺/Li); which implies a theoretical capacity between 50 and 200 mAh g⁻¹. The reduction of the other two carbonyls requires a potential lower than 1.5 V *vs.* Li⁺/Li, which can

lead to the degradation of the molecular structure. The study of diimide aromatic systems has mainly focused on three different structures, which different aromatic core: pyromellitic diimide (PMCDI), naphthalene diimide (NTCDI) and perylene diimide(PTCDI)[73], reported in the upper part of Figure I.10, respectively. The pyromellitic diimide has a redox potential of 1.8 V vs. Li⁺/Li and a specific capacity of 200 mAh g⁻¹ after 25 cycles, as showed by Renault *et al.*[74]. Moving towards an extended aromatic core, from benzene to naphthalene (Li₂-NTCDI), the insertion potential increased to 2.5 V vs. Li⁺/Li, 700 mV greater than Li₂-PDMI (Figure I.10b). However, the Naphthalene core increases the molecular mass, resulting in a decrease in specific capacity, measured at 135 mAh g^{-1} [75,76]. The difference in redox potential can be explained by a lower LUMO energy level for naphthalene than for benzene derivative (PMDI). Finally, the perylene diimide (Li₄-PTDCI) showed a further reduction of the specific capacity (80 mAh g⁻¹), with no benefits in terms of insertion potential [77,78] showed an average redox potential identical to that of naphthalene (2.5 V vs. Li⁺/Li): this means that the energy density of Li₄-PTDCI is lower than the naphthalene derivative, having its same potential and a lower specific capacity. Despite the loss in terms of energy density, Perylene diimide derivate could be interesting for some specific applications, as for high power density system: since the greater extension of the conjugation results in a better intrinsic electronic conductivity and therefore a better electrochemical reversibility at high C-rates[79]. Naphthalene-tetracarboxidiimide derivatives proved to be the best trade-off in terms of specific capacity, redox potential and rate performance: for this reason, this molecule was deeply investigated as positive organic material.



Figure I.10: Diimmides derivates based on aromatic core. Molecular structures and potential-capacity profile of a) pyromellitic diimide, b) naphthalene diimide and c) perylene diimide in half-cell vs. Li. Reproduced from ref [74], [75] and [77].

Regarding the potential tuning, Vadehra et al. showed the influence of the substituent groups of the aromatic core, developing a series of derivatives of the naphthalene diimide[75]. The use of aryl substituents with electron donor group character (–NMe₂) leads to a decrease in the insertion potential (2.3 V *vs.* Li⁺/Li), while the use of electron withdrawal groups (–F and –CN) leads to redox potentials around 2.9 V (*vs.* Li⁺/Li). This study shows the good tunability of the voltage of the organic carbonyls of the diimide: however, the use of these substituents, often with a high molecular weight, led to a decrease in the theoretical capacity due to the increase in molecular mass. Generally, the gain obtained in terms of potential is not favorable compared to the loss in terms of capacity.

In addition to the aromatic ring, the nitrogen substitution of the imide function (N-substitution) plays a very important role in the design of these compounds: this substitution allows the synthesis of a polymerizable unit or the introduction of ionic functions. Both approaches are well known in countering the phenomenon of solubilization and preserve the stability of active material along cycling. The first structures studied were the polyimides[79] (poly NTCDI): these polymers were synthesized by polycondensation reactions of naphthalene tetracarboxylic acid anhydride with various diamine derivatives [78,80,81]. The use of a polymeric structure has shown an increase in cycling stability, as these polymers are not very soluble, unlike single-molecule NTCDI. Furthermore, the polymerization does not lead to a noticeable molecular weight increase: these poly-NTCDIs have reasonable specific capacities of the order of 130 to 170 mAh g⁻¹, with excellent capacity retention after 100 cycles, or even more. To circumvent the use of polymers and use single-molecules, N-substitution of diimide with permanent anionic functions, such as carboxylates and sulfonates (in the form of lithium salts) or cationic functions (such as quaternary ammonium), have been successfully tested. These strategies have made it possible to obtain cells with a stability around 50-200 cycles, with a gravimetric capacity between 110 and 180 mAh g⁻ ¹.[76,82–84] To limit the solubility of NTDCI, Stoddart and collaborators proposed a NTCDI derivative with a triangular structure (NTCDI- Δ), able to deliver a specific capacity of 86 mAh g⁻¹ at a rate of 10C, stable up to 300 cycles [85]. This remarkable result was attributed by the authors to the good distribution of electrons (electronic sharing) through interactions between the molecular orbitals of NTCDI units very close to each other in the molecular prism NTCDI-A. Similarly, a nanoporous structure NTCDI-COF (Covalent Organic Framework) still provides 60 mAh g⁻¹ after 700 cycles at 1C rate[86]. This strategy, in addition to increasing the life of the cell, allows for significant improvements in terms of high-power density applications.

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Figure I.11: Classification of naphthalene diimide (NTDCI) redox unit by topology. One single organic redox unit can be assembled into different molecular assemblies so that the electrochemical and battery performances are affected. Reprinted from ref [87].

Pteridines

In the quest for new electroactive organic molecules, the researchers focused their attention on the molecules involved in bio-electrochemical processes. Among these molecules, Riboflavin, also called vitamin B2, collected much interest, as involved in the transport process of protons and electrons in the energy chain of mitochondria[88]. Moreover, Riboflavin and its derivatives are very abundant in nature: it can be extracted from various vegetables, almonds and eggs.

Riboflavins was firstly studied in 2013 as positive material for Li-ion battery by Lee et *al.*[89] The Riboflavin showed a reversible capacity of 105 mAh g⁻¹ in half-cell, which results in a 74% of the theoretical capacity. Furthermore, the galvanostatic tests showed an average insertion potential divided into two distinct plateaus, at 2.4 V and 2.65 V *vs.* Li⁺/Li, indicating a process in two consecutive one-electron reduction steps.

Following the study on Riboflavin, Park and coworker[90] developed a series of derivatives based on Pteridine electroactive moiety. The authors' idea was to tailor riboflavin, by removing nonelectroactive substituent groups, to reduce weight and increase specific capacity. Three different molecular systems were presented, Lumichrome (LC), Alloxazine (ALX) and Lumazine (LMZ), illustrated in Figure I.12. Passing from Lumichrome to Lumazine, the molecular structure is increasingly simplified, first by removing two methyl groups and then by removing the third condensed ring of the aromatic core.



Figure I.12: Molecular structures of pteridine derivatives as bioinspired redox compounds for energy storage. Reprinted from ref [90].

In the GITT test, reported in Figure I.13, Lumichrome showed a specific capacity of 169 mAh g⁻¹, corresponding to 76% of the theoretical capacity ($C^{\text{theo}} = 221 \text{ mAh g}^{-1}$ for 2 Li⁺ exchanged), which grows to 84% by switching to Alloxazine, which displayed a specific capacity of 211 mAh g⁻¹. Both electrodes showed a very similar galvanostatic profile, with two plateaus located at 2.52 and 2.42 V vs. Li⁺/Li.

As regards the third molecule investigated, Lumazine, the electrochemical profile was characterized by a strong polarization, much greater than the two previous examples (Figure I.13a). Furthermore, LMZ exhibited a specific capacity of only 193 mAh g⁻¹, corresponding to the half of its C^{theo}. Galvanostatic tests performed at high temperature showed a good improvement in the capacity (251 mAh g⁻¹): this result, together with the phenomenon of strong polarization, can be explained by a low kinetics of the insertion reaction of the lithium ions, which in fact limits the ability of the molecule to store energy under operating conditions.



Figure I.13: GITT profile obtained for a) Lumazine, b) Lumichrome and c) Alloxazine electrodes in half-cell vs. metallic lithium. Reprinted from ref [90].

Benefiting from the extensive aromatic structure of pteridine derivatives, the authors fabricated a composite electrode using nanocarbons, with the double purpose of 1) immobilizing the active material by exploiting the strong π – π interactions and 2) improve its properties of electrical conductivity. Thanks to this engineering of the electrode architecture with the carbon nanotubes, multiple improvements in electrochemical performances were observed: the capacities delivered

by the LC-based and ALX-based electrodes were measured as 215 mAh g⁻¹ and 236 mAh g⁻¹, respectively. Furthermore, the interaction with the nanotubes improved the cycling stability: after 500 cycles, these composite electrodes maintained respectively 96% and 91% of their initial capacities, thanks to the decrease in the electrolyte dissolution phenomenon. Nevertheless, only limited improvements were observed with Lumazine/CNT nanohybrid, due to the marked dissolution of the active material: the π - π interactions decrease with the size of the aromatic core. This result showed the trade-off between the energy density, resulting from the reduction of the molecular structure, and the solubility of the active material in the electrolyte.

Other chemistries

In the preceding paragraphs, classes of compounds have been described that have been studied for a long time. However, in recent years, new electroactive groups have been published in order to improve the electrochemical performance and avoid some recurrent issues of the organic materials (e.g. dissolution, poor electronic conductivity, *etc.*). In this section, two new classes of molecules recently reported in the literature will be illustrated, as promising new materials for positive electrode exceptional electrochemical properties.

In 2021, Vlad and collaborators proposed for the first time a series of electroactive molecules belonging to the family of conjugated sulfonamides (CSA)[91]. The first designed CSA molecule was the dilithium 1,4-phenylenebis((methylsulfonyl)amide), hereafter Li₂-p-PDSA (Figure I.14a, left). The electrochemical characterization showed the reversible exchange of 2 Li⁺/e⁻ for formula unit: the Li-ion can be inserted on the nitrogen atom of a sulfonammide group, which leads to a change in the aromaticity of the benzene ring. Driven by the exceptional properties of Li₂-p-PDSA, the authors extended the family of CSA derivates, they designed and studied other members of the CSA family, which emphasizes the influence of stereoisomerism (Figure I.14a), multiredox centres (Figure I.14b) and substituent effects (Figure I.14c) on the electrochemical properties and charge-storage performances. The formal redox potential of the uncovered CSA chemistries spans a wide range between 2.85 V and 3.45 V vs. Li⁺/Li, finely tunable through electrostatic or inductive effects. Among the various derivatives reported, tetralithium benzene-1,2,4,5-tetrailtetrakis ((sulfonyl) amide) (Li₄-PTtSA) showed the best electrochemical performances. The cell Li₄-PTtSA in half cell showed an average potential around 3.0 V vs. Li⁺/Li, with a low polarization of \sim 80 mV (Figure I.14d). At the slow cycling rate of C/10, the specific capacity was 115 mAh g⁻¹, with less than a 5% capacity loss over 50 cycles (Figure I.14e). At 1C rate, Li₄-PTtSA reached the 80% of the C^{theo}, with a capacity retention of 75% after 1.000 cycles (Figure I.14f).



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Figure I.14 - The first generation of conjugated sulfonamides derivates reported in ref [91], regrouped for a) stereomerism, b) multiredox centers and c) substituents. d) Potential-composition profiles of Li4-PTtSA electrodes in half-cell vs. metallic lithium. Evolution of the specific capacity as a function of cycle number cell attained with a cycling rate of e) C/10 and f) 1C rates.

In 2022, again Vlad and coworkers published in pre-printing a study on conjugated Oximate as new electroactive group for organic materials[92]. The authors reported a series of five oximate derivates, spanning from cyclic (aromatic), acyclic (non-aromatic), aliphatic and tetrafunctional stereotypes, to investigate the modulation of electroactivity based on the molecular structure (Figure 1.15a). Interestingly, these materials were characterized by reversible solid-state polymerization by intermolecular azodioxyl coupling (-ONNO-) and to the intramolecular cyclization of furoxan of their oxidized forms. Concerning their electrochemical performance, the oximate derivates exhibited an average redox potential ranging from 2.5-3.2 V vs. Li⁺/Li, which allows to have lithiated materials stable under air, and a specific capacity between 210-360 mAh g⁻¹ (Figure 1.15b). Among the different derivates, Li₂-BQDO displayed high reversible capacity (357 mAh g⁻¹) at good redox potential (3 V vs. Li⁺/Li), with a good stability over cycling.

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Figure I.15 – a) The first generation of conjugated oximate derivates reported in ref [92] *; Reversible capacity, average redox potential and corresponding energy density comparison of lithiated positive organic materials.*

P-type molecules

Nitroxides

Nitroxide radicals are well known compounds as oxidizing agents of alcohols to aldehydes and ketones. In the last 20 years, nitroxide radicals have also been studied as redox units for energy storage materials. Nitroxides are characterized by stable radical structure, due to the delocalization of the unpaired electron along its N-O bond. Nitroxides radicals are the only electroactive function that does not require an aromatic nucleus to stabilize the radical, because the latter is chemically stable within the nitroxide function, which provides an excellent resistance to cycles, generally greater than 1000 cycles[93–96]. As regards its electrochemistry, the nitroxide radical exhibits a double redox mechanism (Figure I.16a): it can be reduced at a low potential to an aminoxyl anion, through an *n*-type mechanism which involves the insertion of a C⁺ cation; or it can be oxidized at a high potential to an oxoammonium cation (*p*-type), with the insertion of an A⁻ anion[97]. Despite its bipolar nature, most of the studies reported in the literature concern its *p*-type reactivity. Nitroxide radical showed a high redox potential value (> 3 V vs. Li⁺/Li) and is therefore used as positive electrode materials.



Figure I.16: Redox mechanism for a) nitroxide and b) proxyl molecules.

The nitroxide radical was first reported by Nakahara et al. in 2002 as a new generation of organic materials for rechargeable batteries[98]. The structure presented was the poly-(2,2,6,6-tetramethylpiperidinyl-oxy methacrylate), also called PTMA. In this work, the authors started from the polymerization of the commercially available PTMA monomer and then they characterized the electrochemical properties of PTMA as the positive electrode in a half-cell *vs*. Li. The cell showed an average potential of 3.5 V *vs*. Li⁺/Li, with a reversible capacity of 77 mAh g⁻¹, which corresponds to 70% of the theoretical capacity; additionally, the electrode exhibited excellent capacity retention for over 500 cycles. Finally, a good rate capability was also observed: passing from a current density of 0.1 to 1.0 mA cm⁻², 91% of specific capacity was retained.

Based on this first work on PTMA, in 2005 the Japanese company NEC Corporation proposed the first organic radical battery (ORB)[99]. ORBs can be full organic type (both electrodes based on organic materials) or lithium battery type, where the anode is lithium metal. In 2007 Nakahara and collaborators proposed a water-based slurry to prepare a homogeneous PTMA composite electrodes[93], which led to an improvement of the specific capacity (111 mAh g⁻¹, Figure I.17a). Furthermore, full cells were assembled with graphite as anode material, which displayed an output voltage of 3.5 V *vs.* Li⁺/Li, as already observed in the previous work. In the first cycle, a large irreversible capacity was observed, mainly due to graphite, but after the 10th cycle, Coulombic efficiency reached 97%. The cell also exhibited decent capacity retention, with 87% of the initial capacity was obtained after 100 cycles (Figure I.17b). These first experiments on nitroxide radicals have opened the way to a new line of study: many polymeric backbones have now been used to modify the electrochemical, chemical and mechanical properties of the active material. Among the different screened polymers, we can mention polymethacrylate[98,100],

poly (vinyl ether)[101] and polyether[102] among the most promising polymeric structures for radical nitroxides.



Figure I.17: a) Potential-capacity profile and b) evolution of the specific capacity as a function of cycle number for PTMA electrode in half-cell vs. Li; c) Positioning of proxyl polymer and d) potential-capacity profile of PEO-PROXYL electrode in half-call vs. Li. Reprinted from ref [99] and [103].

Another derivative based on the nitroxide radicel group is 2,2,5,5-tetramethylpyrrolidin-N-oxyl (PROXYL, Figure I.16b)[96,103]. Although it has been less investigated than PTMA, this material is characterized by very interesting electrochemical properties. For example, the PROXYL derivative grafted onto an ethylene glycol (PEO) polymer has a higher theoretical capacity (147 mAh g⁻¹, Figure I.17c)[96]. Furthermore, the average redox potential is 100 mV higher than PTMA, as well as an excellent stability over cycling (stable for >1000 cycles, Figure I.17d). However, in the studies reported by Nishide and coworkers[103], it was observed that the specific capacity in half-cells *vs.* Li⁺/Li is only 70% of the theoretical capacity. Added to this is the need to use a large amount of carbon (often greater than or equal to 50%) to obtain a good electronic conductivity in the PROXYL-based electrode. This large amount of carbon conductor negatively affects the energy density by weight and volume, making it far from a possible industrialization.

Phenothiazine

Phenothiazine and its derivatives have been an important class of organic molecules used in many fields, such as in pharmacology, photoluminescence, semiconductor organic electronic devices (light-emitting diodes), thin-film transistors and photovoltaic cells. Phenothiazine is characterized

by an angular structure along the axis of the Nitrogen-Sulfur atoms, called the "butterfly structure"; when oxidized, a cationic radical species with a planar structure is obtained. An EPR study of oxidized phenothiazine showed that it is the the nitrogen atom that is involved in the formation of the cationic species after the loss of one electron. The radical species can therefore undergo a new oxidation to give the di-cationic species thanks this time to the sulfur doublet. Given their good intrinsic conductivity and their ability to form a stable cationic radical, as well as their low molecular weight and modulable oxidation potential, the phenothiazine derivatives have received great interest as an electrode material for energy storage. However, despite its excellent electrochemical properties, phenothiazine is a highly soluble molecule in organic solvents: this characteristic makes it unsuitable for use in common organic liquid electrolytes. To overcome this problem, a series of derivatives have been developed using two different approaches: the single-molecule phenothiazine substituted with ionic groups and the polymerization of phenothiazine moiety.

The first approach, based on N-substitution of phenothiazine to form an ionic organic salt, was reported by Becuwe and collaborators[104] in 2020. By exploiting the reactivity of nitrogen, phenothiazine was N-substituted with a lithium benzoate group (lithium 4-(10H-phenothiazin-10yl) benzoate, LiPHB). LiPHB exhibited a high insertion potential (3.7 V vs. Li⁺/Li) in half-cells vs. Lithium, with one-electron reversible exchange, for a specific capacity of 86 mAh g⁻¹. The rate performance is not as good, the cell displayed a specific capacity of 82, 55 and 26 mAh g^{-1} at C/5, C/2 and 1C at C-rates, respectively (Figure I.18a). However, the half-cell showed an excellent cycling stability over 500 cycles at C/5 rate, for an overall 72% of capacity retention (Figure I.18b). Most studies were focused on the use of phenothiazine-based polymers as electrode materials. Polymers can be distinguished into two types: the synthesis of polymeric backbone with PT as a pendant active molecule[105–109] and synthesis of polymers using a phenothiazine-base, in order to have the active group directly incorporated into the polymer backbone.[110–112] Among the polymers synthesized using the first strategy, poly (3-vinyl-N-methylphenothiazine) (PVMPT) aroused much interest, thanks to its excellent cycle stability and capacity retention at very high current densities (up to 100C). The authors explain both results by π interactions between neighboring oxidized (and neutral) phenothiazine units[106,107]: the interactions between vicinal phenothiazines enables a rapid passage of electrons, as well as providing an anchoring effect, which avoids a dissolution of the active material in the electrolyte. The result is that the electrode is able to cycle up to 100C and maintain its specific capacitance during long-

40

term cycles, with only 7% loss of capacitance after 10,000 cycles at 10C[106]. However, the specific capacity is affected by the strong π interactions between the phenothiazine groups[107,113]: the PVMPT shows a capacity of about 50 mAh g⁻¹, corresponding to half the theoretical value. In order to reduce this type of interactions, Esser and coworker have developed a different type of polymer, with a higher degree of cross-linking, called X-PVMPT, in order to improve the specific capacity without losing the benefits in terms of stability and kinetics[108]. This new polymer made it possible to obtain a specific capacity of 112 mAh g⁻¹(Figure I.18c), equivalent to the theoretical capacity, combined with an excellent capacity retention: after 1000 charge/discharge cycles, a capacity of 102 mAh g⁻¹ was retained, corresponding to a specific capacity loss of 9% (Figure I.18d).



Figure I.18: a) Potential-capacity profile and b) evolution of the specific capacity as a function of cycle number for LiPHB-based electrode in half-cell vs. Li; c) Potential-capacity profile and d) evolution of the specific capacity as a function of cycle number for X-PVMPT electrode in half-cell vs. Li. Reprinted from ref [104] and [108].

Regarding the approach with the direct polymerization of phenothiazine, an interesting example was proposed by Acker et al[112]. The proposed polymer is formed by monomers which contain both phenothiazine and two thiophene rings, to obtain a conjugated backbone. This structure provided an improved performance at high C-rates compared to the above: the phenothiazine-

based polymer demonstrated more than 30,000 cycles at 100C rate, with a capacity retention of 97%. However, despite this outstanding performance, the large amount of inactive side groups and co-monomers reduced the specific capacity of Poly (PT-T2) to only 30 mAh g⁻¹. This example conceptually shows that intrinsic conduction through the polymer backbone in the doped state enables high charge/discharge rates.

Thianthrene

Due to the interesting electrochemical properties observed with Phenothiazine, another *p*-type compound with a similar structure was investigated as an electroactive material, the Thianthrene (TNT): indeed, this molecule differs from phenothiazine by replacing the nitrogen with a sulfur atom. Despite this difference, all the aforementioned considerations for Phenothiazine remain valid for thianthrene derivates: the butterfly structure upon redox reaction (Figure I.19, right), the possibility of reaching a dicationic structure, the intrinsic high conductivity and modulable oxidation potential, as well as the high solubility in organic solvent.



Figure I.19: P-type redox mechanism of thianthrene molecule. Reprinted from ref [114].

In 2015, Speer et al. firstly reported thianthrene-based materials in the framework of lithium-ions batteries technology[114]. Thianthrene-functionalized polynorbornene polymers were investigated as *p*-type organic cathode materials. A composite electrode containing thianthrene polymer, carbon black (Super P) and PVDF binder in a ration 50:47:3 wt% was prepared and its electrochemical performance were tested in a half-cell *vs.* metallic lithium. The thianthrene polymers showed reversible oxidation reactions at a high potential of 4.1 V *vs.* Li⁺/Li with a reversible capacity of 66 mAh g⁻¹ after 14 cycles (Figure I.20a). After that, an irreversible loss of specific capacity was observed, down to ca 25 mAh g⁻¹ after 100 cycles (Figure I.20b). On the heels of the encouraging results obtained by Speer, the research group of Schubert also

reported a study carried out on thianthrene polymers[115][116]. The positive electrode was prepared using 2-vinyl thianthrene as active material, mixed with carbon Super P and PVDF in ratio 40/55/5 %wt; the electrode was formulated in NMP and casted on aluminum foil by doctor blading. Electrochemical tests were performed in a half-cell versus metallic lithium disk, using 1 M LiClO₄ in EC/DMC (3/7 %vol) as electrolyte. The composite electrode showed 4.05 V for charging and 3.95 V vs. Li⁺/Li for discharging at 1C rate (Figure I.20c). In the first cycle a discharge capacity of 105 mAh g⁻¹ could be obtained (78.6% CE), corresponding to 95% of theoretical capacity. Moreover, the stability of these systems is good: after 250 charge/discharge cycles at 1C, 86 mA h g⁻¹ of reversible capacity was measured, for an 82% of capacity retention (Figure I.20d)



Figure I.20: Potential-capacity profile and evolution of the specific capacity as a function of cycle number for a) Polynorbornene thianthrene and b) Polyvinyl thianthrene based electrode in half-cell vs. Li. Reproduced from ref [114] and [115].

In 2020, Masuda et al. showed the electrochemical properties of two thianthrene-based polymers, named poly thianthrene-1-ylmethyl 4-ethynylbenzoate and poly (thianthrene-1-ylmethyl)-4-ethynylphthalate[117]. The first polymer displayed a low reversible capacity (35 mAh g⁻¹) in the first cycle, corresponding to only 49% of its theoretical capacity, but with a good capacity retention along cycling. The second polymer gave a higher reversible capacity, even higher than the theoretical capacity one (100 mAh g⁻¹ vs. 83 mAh g⁻¹): for the authors, this phenomenon is due to the participation of the polymer backbone in the discharge process; in

both cases, a high redox potential (4.1 V vs. Li⁺/Li) was observed. As drawback, this polymer showed low coulombic efficiency in the first cycles and it is also affected by strong capacity fading.

Carbazole

In last decade, several studies on the carbazole moiety as *p*-type electroactive group have been reported in the literature. In 2012, Yao and coworker studied polyvinyl carbazole (PVK) as a high potential positive material[118]. The charge/discharge curves showed a high average potential, around 3.7 V *vs.* Li⁺/Li, among the highest in organic molecules. The reversible capacity obtained in the first cycle corresponds to 125 mAh g⁻¹ (Figure I.21a), very close to the theoretical value of 139 mAh g⁻¹; despite this high reversible capacity, the PVK was affected by a low Coulomb efficiency, due to parasitic reactions as the coupling between the side-rings of the carbazole moiety that take place during the first oxidation of the electroactive material. Nevertheless, the overall electrochemical performances of polyvinyl carbazole were comparable, both in terms of potential and capacity, to those obtained with conventional positive-electrode materials such as LiCoO₂ or LiFePO₄. Lastly, the study highlighted good stability over cycling, with a capacity of 117mAh g⁻¹ after 50 cycles (Figure I.21b). In 2015, Yao's group reported an example of all-organic battery with PVK as a positive electrode and viologen as a negative material, as an example of entirely *p*-type battery[119]. The cell exhibited an average potential of 1.8 V and a specific capacity of 100 mAh g⁻¹, which slowly decreases to the 65% of the initial capacity, after 100 cycles.



Figure I.21 : a) Potential-capacity profile (inset: molecular structure) and b) evolution of the specific capacity as a function of cycle number for Polyvinyl carbazole in half-cell vs. Li. Reproduced from ref [118].

Recently, the study of Polyvinyl carbazole has been extended to other metal-ions technologies. Li and collaborators reported a PVK-based electrode in the framework of potassium-ion battery: this polymers showed the highest redox voltage for an organic KIB, with an average redox potential of 4.05 V vs. K⁺/K; the main drawback of this K-ion battery was the poor Coulombic efficiency[120]. In the same year, this polymer was employed in a dual-intercalation Na-ion batteries[121]. The authors reported an average intercalation potential of 3.5V vs. Na⁺/Na and a discharge capacity of 130 mAh g⁻¹ after the first cycle, very close to the theoretical value (138 mAh g⁻¹). The material showed a good cyclability, with 110 mAh g⁻¹ of reversible capacity after 100 cycles. An interesting capacity was observed also at high C-rate: 62 mAh g⁻¹ of capacity were measured after 900 cycles under a high current density (0.5 A g⁻¹).

In 2020, Dai *et al.* reported a combined computational/experimental study on 5,11-diphenyl-5,11dihydroindolo[3,2-b]carbazole polymer[122]. In this work, the authors focused on the effect of a phenyl group as an N-substituent of carbazole, highlighting many advantages: firstly, the phenyl substituent improved the diffusion of PF_6^- anion along the active material; moreover, the substitution with electron withdrawer help strengthen the global p-electron conjugation throughout the molecule. Compared to other carbazole derivates, the presence of a benzene ring also brings advantages at the level of interactions with the surrounding environment: it protects the active site, the nitrogen atom, from direct contact with the electrolyte. Finally, the computational calculation confirmed the stabilization of free radical electrons: a marked increase in HOMO/LUMO energy level was calculated in the case of phenyl carbazole. Both the higher delocalization and stability of free radical electrons makes N-substituted carbazole very promising for high potential electrodes.

In the same year, Xu *et al.* proposed the in-situ electro-polymerization of carbazole trimer (Figure I.22a), the 4,4',4"-Tris-(carbazol-9-yl)-triphenylamine (TCTA), as strategy to avoid dissolution of active material and stabilize the capacity[123]. The electropolymerized TCTA electrodes demonstrated excellent electrochemical performance with a high discharge voltage of 3.95 V *vs.* Li⁺/Li (Figure I.22b), with 92 mAh g⁻¹ of reversible capacity, which was retained even at ultrafast rate capability >200C, 20 A g⁻¹ (Figure I.22c). Moreover, the material exhibited an outstanding capacity retention after 5000 cycles at 1 A g⁻¹ (Figure I.22d).



Figure I.22: a) In-situ electropolymerization mechanism of 4,4',4''-Tris-(carbazol-9-yl)-triphenylamine (TCTA); Potential-capacity profile of Poly TCTA electrode in half-cell vs. Li, cycled at b) different potential window and c) different current density; d) evolution of the specific capacity as a function of cycle number for Poly TCTA electrode. Reproduced from ref [123].

Recently, Zhao and coworkers published a study where a machine learning algorithm was employed to predict electrochemical properties of different carbazole derivates[124]. From first principles, the authors linked the reversibility of the electron exchange process with the nature of the substituent of the nitrogen atom: an electron-withdrawing substituent can stabilize the structure with a consequent increase of redox potential of carbazole. Furthermore, the planarity of 5-member heteroatomic ring improves the dilution of the electron density, leading to an overall increase in the potential. Based on these deductions, the authors synthesized and characterized a dimer of carbazole, the para-bicarbazole phenyl (p-BCz-Ph), where the two carbazoles are connected through a bond on the side-ring and each had a benzene ring as N-substituent. The galvanostatic test on p-BCz-Ph were performed in half-cell versus metal Lithium at 2C. After the first cycles, the cell showed a specific capacity of 120 mA h g⁻¹, approximately the 90% of the Q^{theo}. A capacity fading was observed after 100 cycles, with a remaining 90 mAh g⁻¹, corresponding to a capacity retention of 70%, coupled with a low coulombic efficiency (90%).

Organic materials as negative electrode

N-type molecules

Dicarboxylate derivates

Carboxylate derivatives are considered promising candidates as negative electrode materials for organic Li-ion batteries, due to their low working potential typically between 1.5 and 0.5 V compared to Li⁺/Li. Similar to most of the organic redox functions, *e.g.* quinones derivates, an aromatic core unit is required for reversible storage using conjugated dicarboxylates. In this case, the lithium ion is taken up by the carboxylate group (mechanism shown in Figure I.23a), which leads to a low redox potential. Walker and *coll.* investigated a series of aliphatic carboxylates, comparing derivatives characterized by 1) different lengths of the aliphatic chain, 2) different stereochemistry (*cis/trans*) and 3) a different amount of unsaturation along the chain. In this study, *trans* isomers exhibited the best electrochemical performances, while no differences were noted in the redox potential of all aliphatic derivatives analyzed: the position and nature of the unsaturated groups do not influence the reaction potential. However, it was observed that only one Li-ion can be reversibly exchanged during the electrochemical process. For this reason, aliphatic dicarboxylate have not been thoroughly investigated.

In 2009, Armand and coworkers published their work on dilithium benzene-1,4-dicarboxylate, also known as dilithium terephthalate (Li₂-TP). The half-cell Li₂-TP/Li showed a plateau located at 0.9 V vs. Li⁺/Li and a reversible specific capacity of 300 mAh g⁻¹ at a rate of C/20, corresponding to a reversible exchange of 2 Li⁺ per molecule. After 50 cycles, a reversible capacity of 234 mAh g⁻¹ was observed, reflecting a good cycling stability (Figure 1.23b). In terms of rate capability, the dilithium terephthalate showed 240 mAh g⁻¹ (70% of the theoretical capacity) at 1 C rate. Together with the excellent electrochemical performances showed by Armand, this molecule is also characterized by 1) chemical flexibility of the molecular structure, 2) availability, as it can be obtained through the simple (bio-)degradation of a polyethylene terephthalate (PET), and 3) recyclability of Li₂-TP.



Figure I.23: a) Redox mechanism of dilithium terephthalate. b) Potential-composition profile (inset: evolution of the specific capacity as a function of cycle number). Reproduced from ref [125].

For the reasons listed above, terephthalate derivates were deeply investigate in the last years: firstly, its application has been extended to a wide range of cations, listed in Table I.4, to study the influence of the counter-cation on the electrochemical properties. As it can be deduced from the data, the choice of cations does not significantly influence the redox potential: all M-TP's (with M = Li, Na, K, Ca, Sr and Ba) showed an average potential of 0.8 V vs. M^{n+}/M . However, the counter ion seems to play an important role for both the specific capacity and stability over cycling. Potassium, Calcium and Strontium showed low capacity, far from the theoretical value, while the Lithium, Sodium and Barium terephthalates were close to C^{theo} in the 1st cycle. Regarding the capacity after 50 cycles, Lithium [125] and Strontium [126] derivates showed a poor capacity retention, with a loss of 22% and 28% of capacity, respectively. On the contrary, the use of sodium (Na₂-TP)[127] and calcium (Ca-TP)[126] show high retention of capacities. The authors explained these result with the ionic nature of the O-Na and O-Ca bonds.

Active material	Potential (V vs. M ⁿ⁺ /M°)	Q ^{theo} (mAh g ⁻¹)	Spec. Cap (mAh g ⁻¹) 1 st cycle	Spec. Cap (mAh g ⁻¹) 50 cycles - (Cap retention)	Reference
Li ₂ TP	0.80	301	300	234 - (78%)	[125]
Na ₂ TP	0.80	255	200	200 - (99%)	[127–129]
K ₂ TP	0.85	221	150	130 - (86%)	[128,129]
Ca-TP	0.80	263	170	155 - (91%)	[126]

State-of-art of Organic materials for energy storage applications									
Sr-TP	0.85	213	125	91 - (72%)	[126]				
Ba-TP	0.80	178	150	135 - (86%)	[126]				

Table I.4: Energy metrics of the corresponding M^{n+} Terephthalate dicarboxylate ($M=Li^+$, Na^+ , K^+ , Ca^{2+} , Sr^{2+} and Ba^{2+}) retrieved from various reported papers.

As seen in the case of benzoquinone, the substituents of the benzene ring can influence the energy required to break the aromaticity or for its reconstitution, changing the redox potential of the derivates. Therefore, the researchers have designed and synthesized several mono or disubstituted terephthalates, playing with the nature of the substituent (electron-donor or electron-withdrawer groups) to decrease the redox potential and consequently increase the energy density, as illustrated in Figure I.24. The first work on the substitution of the aromatic ring of terephthalate was proposed by Lakraychi et *al.* in 2017[130]. The authors reported the synthesis of dilithium 2,5-dimethylterephthalate (Li₂-DMT), where the methyl groups act as electron donors for the inductive effect. Li₂-DMT showed an average potential of 0.65 V vs. Li⁺/Li, 110 mV lower than Li₂-TP. Furthermore, this active material showed a reversible specific capacity of 160 mAh g⁻¹, stable for over 50 cycles with a coulombic efficiency of 99%. Despite these promising results, several critical issues were identified for Li₂-DMT: 1) the synthetic route requires high temperatures and toxic reactants; 2) the first cycle was characterized by a high irreversibility (39%), due to the formation of SEI and to the non-planarity of the molecule, caused by substituent group.



Figure I.24: Energy metrics for disubstituted terephthalate dicarboxylates.

In 2018, Lakraychi and coworkers extended the study to other functional groups. In the paper, the author synthesized derivates using -Br (dilithium dibromoterephtalate, Li₂-DBT), -OCH₃ (dilithium dimethoxyterephtalate, Li₂-DMoT) and -NH₂ (dilithium diaminoterephtalate, Li₂-DAT) as substituents[131]. The three groups can act as an electro-donator group *via* a mesomeric effect, but also as an electron-withdrawing group due to electronegativity (inductive effect). The

dibromoterephtalate showed the highest redox potential, measured as 1.08 V vs. Li⁺/Li, while dimethoxy- and diamine- terephthalate exhibited 0.81 V and 0.75 V vs. Li⁺/Li, respectively (Figure I.25a): none of the substituents led to a lowering of the potential compared to Li₂-TP. This result may be due to the strong electrostatic interaction between the heteroatom of the substituent and the inserted lithium, which cancels the effect due to the nature of electron donors. However the three compounds displayed a great irreversibility and loss of capacity during the first cycle, about 70% for Li₂-DBT and 60% for Li₂-DMoT and Li₂-DAT. Furthermore, the terephthalate molecules displayed a low reversible capacity after 50 cycles (Figure I.25b), corresponding to the half of their theoretical capacities. An explanation proposed by the authors is that irreversibility can be linked to the trapping of a Li-ion in the active material after the first discharge, preventing its subsequent extraction. However, to validate this hypothesis, it is necessary to study the crystal structure at different charge states using a coupled diffraction technique and electron microscope imaging, which is not reported by the authors.



Figure I.25: a) Potential-composition profile and b) evolution of the specific capacity as function of cycle number for Li_2 -DBT (blue curve), Li_2 -DMoT (red curve) and Li_2 -DAT (green curve). Reproduced from ref [131].

Brandell's research team studied monosubstituted terephthalate with primary amine (Li₂-MAT)[132]. The molecule exhibited an average operating potential of 0.85 V versus Li⁺/Li, with a high capacity of 443 mAh g⁻¹ after the first discharge; however, only 200 mAh g⁻¹ were delivered in the charge phase, for an overall reversibility of 45% in the first cycle. After 50 cycles, the reversible specific capacity stabilizes at 180 mAh g⁻¹ for the electrodes obtained through lyophilization; this value corresponds to 65% of the theoretical capacity.

After the first pioneering work reported for the terephthalate derivates, several research groups have methodically investigated the effect on the electrochemical properties of a variation of the aromatic group. Figure I.26 were illustrated the series of dicarboxylate derivatives: naphthalene (NDC), biphenyl (BPDC) and anthracene (ADC) dicarboxylate, and perylene tetracarboxylate (called PTC), characterized by presence of 4 carboxylate groups.



Figure 1.26: Molecular structure, theoretical capacity and measured values of the first reduction potential for different extended conjugated dicarboxylates employing aromatic extension. Reprinted from ref [133].

The first example of dilithium naphthalene dicarboxylate (Li_2 -NDC) as a positive material was reported in the literature by Fedele and collaborators in 2014[134]. The Li₂-NDC showed a monoclinic crystal system, with a space group of P21/c, with an increase in the distance between the two terminal carboxylates, from 5.7 Å for Li₂-TP to 8.3 Å, due to the larger size of naphthalene core. The derivative Li₂-NDC showed an average redox potential of 0.80 V vs. Li⁺/Li, about 100 mV lower than di-lithium terephthalate: this result can be ascribed to the π -conjugation enhancement destabilizing the LUMO orbitals of the molecule. The naphthalene dicarboxylate displayed a reversible capacity 200 mAh g^{-1} after the first cycle at C/20, corresponding to 85% of the theoretical capacity. Despite this good result, this material showed poor cycling, with a marked capacity fading after just 10 cycles. This phenomenon can be addressed to 1) structural degradation of the material, 2) exfoliation of the organic electrode from current collector contact 3) bad formation of the SEI layer. Concerning the rate performance, at 1 C Li₂-NDC delivered 176 mAh g⁻¹ of reversible capacity in first cycle (75% of the Q^{theo}, Figure I.27a) which stabilizes at 115 mAh g⁻¹ after 50 cycles. It can be explained by better delocalization of the negative charge on the naphthalene structure compared to terephthalate, and by an improved ionic conductivity, due to the greater distance between the intercalation sites.

In the same year, Ogihara *et al.* published a hybrid full-cell $LiNi_{0.5}Mn_{1.5}O_4//Li_2$ -NDC, with a gel polymer as the electrolyte[135]. The full cell provided an output voltage of 3.9 V, with a discharge capacity of 360 mAh g⁻¹ and 220 mAh g⁻¹ in the first two cycles, based on the anodic active material mass. In addition, the full cell showed a good capacity retention after 100 cycles at C/5 rate: the authors attributed this high cycling stability to the quasi-solid electrolyte, which avoids degradation processes of the liquid electrolyte.

In 2017, Biphenyl dicarboxylate (BPDC) was investigated for energy storage applications[136]. The biphenyl core consists of two aromatic rings connected through a single bond, rather than being fused together as in naphthalene: the presence of an extra bond increased the distance between two adjacent carboxylate groups, reaching an interlayer distance of 9.84 Å. However, Li₂-BPDC has the same crystal structure as Li_2 -NDC (monoclinic, P21/c), with a planar molecular structure. Regarding electrochemistry, Li₂-BPDC is able to insert two Li-ions reversibly at an average potential of 0.7 V against Li⁺/Li, with a specific capacity of 211 mAh g⁻¹ after 1 cycle, equivalent to its theoretical capacity; moreover, the capacity remained stable at 200 mAh g⁻¹ (95% of Q^{theo}) after 25 cycles. Furthermore, biphenyl dicarboxylate exhibited a good rate capability, with 186 mAh g⁻¹ (88% of Q^{theo}) and 182 mAh g⁻¹ (86% of Q^{theo}) of reversible capacity at C/2 and 1C rate (Figure I.27b), respectively. Li₂-BPDC displayed superior rate performance and low polarization (100 mV in these conditions), compared to terephthalate and naphthalene dicarboxylate. Ogihara and coworkers published in 2020 a comparative study on Li₂-NDC versus Li₂-BPDC. This work showed two different intercalation mechanisms: for Li₂-NDC, a mix of two-phase transition and solid-state solution mechanisms was observed, as well as an energetically stable Li⁺-intercalated state; the corresponding diffusion coefficient of lithium (D_{Li}) was calculated around 10⁻¹⁴-10⁻¹² cm² s⁻¹. On the contrary, Li₂-BPDC showed a pure solid solution type mechanism, with a Li⁺ diffusivity around 10^{-12} - 10^{-8} cm² s⁻¹. The higher D_{Li} coefficient for Li₂-BPDC can be explained by weak interactions with Li⁺, which leads to an energetically unstable Li⁺ intercalation. This difference in Li⁺ diffusivity between the two molecules is the basis of the different rate performance.

In 2013, Zhao et al. employed hyperconjugated perylene as an aromatic core with four carboxylate groups, called Li₄-PTC[137]. This molecule was easily synthesized through a alkaline hydrolysis of 3,4,9,10-perylenetertracarboxylic acid dianhydride (PTDCA), followed by an acid-base reaction with lithium salt. This derivative should theoretically be able to store 4 lithium ions per formula unit, providing a theoretical capacity of 237 mAh g⁻¹: however, Li₄-PTC was able to exchange reversibly only 2 Li⁺/e⁻ per molecule, delivering half of its Q^{theo} (108 mAh g⁻¹ at C/20).

The average potential is higher than previous dicarboxylates (1.1 V vs. Li⁺/Li, Figure I.27c), because the insertion sites intramolecular interactions with the vicinal carboxylic sites, with a consequent variation of the redox potential.

In 2014, Fedele and coworkers investigated the performance of perylene tetracarboxylate lithium salt at high C-rates[138]. Li₄-PTC sustains a reversible insertion capacity of *ca.* 105 mAh g⁻¹ at 2.5C, with a stable capacity of 90 mAh g⁻¹ (coulombic efficiency >99%) over 50 cycles. The capacity slightly decreases to 82 mAh g⁻¹ at 5C and rapidly fades at higher cycling regime. The authors reported these results as non-optimized electrode composites, both in terms of electronic and ionic percolation, non-ideal for high current density application. Starting from these observations, lordache et *al.* worked on the engineering of the electrode architecture, in order to make it suitable for high power density applications[139]. In this paper, the carbon Super P was replaced by the highly percolating MWCNTs as conductive additive, using only 0.5 wt.% of MWCNT in the electrode composite. This optimization was possible thanks to the particular affinity between Li₄-PTC and MWCNT, therefore this approach cannot be easily extended to other organic materials, including the dicarboxylate derivatives showed above. This new electrode architecture led to a significant increase in active material mass loading to 12 mg cm⁻² (95 wt.% of the electrode), with an aerial capacity up to 1.2 mAh cm⁻². In addition, this electrode also exhibited good cycling stability, with 87% of capacity retention after 70 cycles.

Recently, Fedele and coworkers published a study on anthracene dicarboxylate, called Li₂-ADC[140]. From a geometric point of view, the presence of the anthracene core (composed by three fused benzene rings) leads to a further increase in the distance between the carboxylate layer, reaching an interlayer distance of 10.31 Å. The different aromatic structure slightly influences the average redox potential, measured as 0.81 V vs. Li⁺/Li (Figure I.27d). A marked improvement was observed for the rate performance: at 10C, the reversible capacity was 162 mAh g⁻¹, corresponding to 84% of the Q^{theo}. Furthermore, the anthracene dicarboxylate showed a remarkable stability over cycling: after 50 cycles, the capacity stabilizes at 144, 134, and 133 mAh g⁻¹ for 2.5C, 5C and 10C rates, respectively. However, Li₂-ADC exhibits low stability at low C-rates: the authors measured a rapid capacity fading when cycled at C/5 rate. The authors attributed this capacity drop to the partial dissolution of the fully reduced form (Li₄-ADC): by the visual analysis of the separator, a blue fluorescence attributable to the active material dissolution phenomenon were reported.



*Figure I.27: Potential-composition profile for a) Li*₂*-NDC b) Li*₂*-BPDC c) Li*₄*-PTC and d) Li*₂*-ADC electrode cycled in half-cell vs. metallic lithium at 1C as C-rate. Reprinted from ref* [134], [138] *and* [140].

The study of Dicarboxylate Naphthalene was also extended to sodium ion batteries. Cabañero and coworker published a work on Na₂-NDC as a negative material for sodium ion cells[141]. Through diffraction analysis, the authors were able to calculate the cell parameters (a= 12.1 Å, b= 3.6 Å, c= 11.36 Å, β = 103.88°) and refined structural parameters, and found a monoclinic unit cell, with *P*21/*c* as the space group, the same found for the lithium salt. Na₂-NDC reversibly exchanges 2Na⁺/2e⁻ for unit formula, with an average potential of 0.45 V vs. Na⁺/Na. The disodium naphthalene dicarboxylate displayed a specific capacity of 200 mAh g⁻¹ in the first cycle at C/10 rate (Figure I.28a), with a capacity retention of 76% at 2C rate.

Considering these interesting performances in half cells *vs.* Na, Medabalmi *et al.* reported a hybrid sodium ion full cell, using Na₂-NDC coupled with an inorganic cathode, consisting of Na₃V₂O₂(PO₄)₂ grafted on rGO (reduced graphene oxide)[142]. After the first cycle, the whole cell was able to deliver a reversible specific capacity of 150 mAh g⁻¹ (based on the mass of Na₂-NDC) at an output voltage of \approx 3.2V, but with low reversibility (*ca.* 30%) and strong capacity fading, with only 100 mAh g⁻¹ (based on the mass of Na₂-NDC) after just 20 cycles.

Choi and coauthors reported the electrochemical properties of disodium biphenyl dicarboxylate (Na₂-BPDC) in half cells *vs.* Na[143]. The Na₂-BPDC showed a reversible specific capacity of 200 mAh g⁻¹ at C/20 rate, *via* a reversible transfer of two Na⁺ ions at a potential of \approx 0.5 V *vs.* Na⁺/Na

(Figure I.28b), with excellent cycling stability over 150 cycles. Moreover, Na₂-BPDC demonstrated a superior rate capability: it showed full capacity up to 2C and about half the capacity at 20C, which is better than the lithium salt. The authors hypothesized that the planarity of the BPDC²⁻ molecule was responsible for the speed of the sodium ion transfer observed for the Na₂-BPDC.

The tetrasodium perylene tetracarboxylates (Na₄-PTC), published in 2015, showed an improvement in terms of rate performances[144]. Half-cell vs. Na tests revealed a first discharge capacity of 267 mAh g⁻¹ at 2C, corresponding to 4 sodium ion insertion, but only 2 Na⁺ were reversible deintercalated, for a reversible capacity of 119 mah g⁻¹ (CE = 44%, Figure I.28c). However, the Na₄-PTC showed excellent stability and rate capability: a reversible capacity of 94 mAh g⁻¹ and 83 mAh g⁻¹ was observed after 300 cycles at 2C and 10C, respectively. After 100 cycles at 50C, Na₄-PTC exhibited a reversible capacity of 57 mAh g⁻¹, 50% of its Q^{theo}; interestingly, the electrode exhibited a low polarization, measured as 5-10 mV at 2C. As in the case of lithium salts, the extension of the aromaticity of the core involves a significant improvement in the reaction kinetics, which is directly reflected in a better power density, but also affects the average redox potential, which increases with larger aromatic core.



Figure I.28: Potential-capacity profile for a) Na₂-NDC b) Na₂-BPDC and Na₄-PTC electrodes cycled in half-cell vs. metallic Na. Insets: evolution of the specific capacity as function of cycle number.

To conclude, in this section three strategies for improving the electrochemical performance of dicarboxylated derivatives were evaluated, precisely the role of the cation, the effect of both the substituents and the aromatic core. In summary, the results reported in the literature show that the cation directly influences the cycling stability, whilst the substituents can tune the redox potential of the dicarboxylate derivatives. Finally, the aromatic core showed a marked effect on the rate performances, allowing the development of derivatives able to work at high power density. These three factors enable a rational design of the dicarboxylate derivatives, in order to adapt them to different applications, in the event that these require better performance in terms

of cell duration, energy density or power density. Starting from these premises, it will be possible in the future to reach a wide diffusion of this class of compounds for energy storage applications.

Azo compounds

in 2018, Wang and coworkers presented a new class of active redox molecules, based on the diazo functional group (-N=N-)[145]. This functional group showed an average insertion potential of approximately 1.5 V compared to Li⁺/Li. This class of molecules can be classified with an n-type mechanism: the redox mechanism involves the insertion of two lithium ions on the nitrogen atoms, with the simultaneous reduction of the double bond of the single-bond di-azo group; the reverse occurs on reoxidation. The authors first report the azobenzene (AB) molecule, characterized by two substituted aromatic rings on each nitrogen. First, the electrochemical properties of simple azobenzene were investigated in a half cell vs. metallic lithium. In the reduction phase, it exhibits two plateaus at 2.0 and 1.7 V, which are slightly different from those in the oxidation phase, located at 2.2 to 1.6 V vs. Li⁺/Li. Azobenzene showed only 200 mAh g⁻¹ of reversible capacity in the first cycle (Q^{theo} = 295 mAh g⁻¹), together with a low coulombic efficiency (55%). In addition, azobenzene showed low stability over cycling, due to its solubility in the electrolyte solvent: after 50 cycles, only 50 mAh g⁻¹ of reversible capacity were measured. To reduce the dissolution phenomenon, a mono-substituted azobenzene was synthesized and studied. the 4-(phenylazo) benzoic acid lithium salt (PBALS).[146] PBALS showed a significant improvement in terms of reversibility in the first cycle (CE=78%), capacity retention (89% after 100 cycles), average redox potential (ca. 1.30 V vs. Li⁺/Li) and rate performance (up to 20 C). However, it was necessary to use a high concentrated electrolyte (7 M LiTFSI in DOL/DME) to limit the dissolution of PBALS, as well as the need for a high quantity of conductive carbon (30%) and binder (10%) in the composite electrode. Wang and coworkers extended the study to disubstituted azobenzene, specifically to azobenzene-4,4'-dicarboxylic acid lithium salt (ADALS, Figure I.29a). In half-cells with Li metal, ADALS showed an average potential of 1.5 V vs. Li⁺/Li, with a capacity of 190 mAh g^{-1} and 77% of reversibility in the first cycle at C/2 (Figure I.29b). Moreover, it showed a good rate performance, with 90%, 71%, and 56% of retained capacity at 2C, 10C, and 20C rates, respectively; at 20C, ADALS retained 89% of initial capacity after 5000 cycles. ADALS has two redox groups able to reversibly exchange Li ions: the di-azo group and the two dicarboxylate substituent. However, since the redox potential of the diazo group is higher than carboxylate groups, they are reduced first, interrupting the conjugation and deactivating the electroactivity of the carboxylates.



Figure I.29: a) Redox mechanism of azobenzene-4,4'-dicarboxylic acid lithium salt (ADALS). b) Potential-composition profile and b) evolution of the specific capacity as a function of cycle number of ADALS-based electrode in half-cell vs. metallic Li. Reprinted from ref [147].

In a later work, Zhang's group used ADALS as a negative electrode in full hybrid cells, coupled with both LiFePO₄ (LFP) and LiCoO₂ (LCO) as positive electrodes[147]. The hybrid cells displayed an output voltage of 1.7 and 2.5 V with LFP and LCO, respectively; the specific capacity was measures as 129 mAh g⁻¹ for LFP/ADALS and 121 mAh g⁻¹ for LCO/ADALS. Furthermore, Wang et al. presented another paper in which they demonstrated the possibility of extending the electroactivity also to sodium ion technology[148], using a sodiated azobenzene dicarboxylate (ADASS). The ADASS was able to reversibly intercalate 2 Na⁺ per molecule in a potential range of 1.2/1.4 V vs. Na⁺/Na, with a reversible capacity of 170 mAh g⁻¹ of capacity after 500 cycles at 1C.

Few examples of azobenzene derivatives were reported in the literature to date, but the chemically flexible structure is suitable for a molecular engineering approach, *in primis* to decrease the redox potential and then to increase stability over cycling by decreasing the solubility of the azobenzene in organic solvents.

P-type molecules

Viologen

The main negative *p*-type material is the quaternized-N,N'-bipyridyl salts, also known as Viologen. This class of compound have been extensively studied as a negolyte in organic redox flow batteries, where the active material is dissolved in an aqueous solution[149–151]. Viologen is characterized by a 2-step redox mechanism: the completely oxidized form (indicated as V^{2+}) can be reduced to the intermediate radical cation (indicated as V^{*+}), then reduced to the neutral form (V). Viologen derivates exhibit the lowest redox potential among of the *p*-type materials and the oxidized state (anion-inserted state) is stable under air.

Yao et al. first reported the poly-(1,1'-pentyl-4,4'-bipyridinium dihexafluorophosphate) (denoted by $[PBPy](PF_6)_2)[119]$, as a negative material able to exchange 2 anions per formula unit (Figure 1.30a). The electrochemical properties were evaluated in an n-Bu₄N·PF₆/PC electrolytic system. The anion insertion takes place at -0.7 and -1.2 V vs. Ag⁺/Ag, with an initial specific capacity equal to 79 mAh g⁻¹ (corresponding to 76% of Q^{theo}, Figure I.30b). However, over cycling, stability was poor: after 20 cycles, the reversible capacity dropped to 38 mAh g⁻¹ (Figure I.30c) due to the dissolution of polymer in the electrolyte. In order to reduce the solubility of viologen, Cadiou et al. synthesized a cross-linked viologen polymer, called ([c-PV](ClO₄)₂)[152]. This polymer exhibits two redox plateaus located at 2.5 and 2.1 V vs. Li⁺/Li, with a theoretical capacity of 88 mAh g⁻¹ (Figure I.31a). However, [c-PV] (ClO₄)₂ showed good cycling stability only when cycled on the second plateau (38 mAh g⁻¹ capacity at redox potential 2.1 V vs. Li⁺/Li), while a rapid capacity drop was observed when the polymer was cycled on the first redox plateau, located at 2.5 V vs. Li⁺/Li (Figure I.31b). The authors attributed this phenomenon to the steric/electronic hindrance in the polymer during the insertion of the second anions (reoxidation at 2.5 V vs. Li⁺/Li), as this behavior was also reported on other cross-linked polygenic hydrogels in aqueous electrolyte. To prevent the viologen dissolution and increase the cycling life, Jouhara and coworker used a different strategy, where the viologen molecules were disubstituted with a lithium acetate group, to obtain the already mentioned ionic organic salt[153]. Two different zwitterionic forms of viologen were designed, the Li₂diacetate-4,4'-bipyridinium di-perchlorate (Li₂[diacetate-V](ClO₄)₂) and the Li₂(E)diacetate-1,2-bis (4-pyridyl) ethylene di-perchlorate (Li₂[diacetate-bpe](ClO₄)₂).



Figure I.30: a) Potential-capacity profile (vs. Ag⁺/Ag) and b) evolution of the specific capacity as a function of cycle number of poly-(1,1'-pentyl-4,4'-bipyridinium diheafluorophosphate) (PBPy) in half-cell vs. Li. c) Redox mechanism of PBPy derivate. Reprinted from ref [119].

Both molecules showed two plateaus, related to anionic insertion, located at a potential of 2.4 and 1.4 V vs. Li⁺/Li. Moreover, the viologen diacetates exhibited a reversible de-/intercalation of two CIO_4^- ions, corresponding to a specific capacity of 130 mAh g⁻¹ for Li₂[diacetate-V](CIO₄)₂ (Figure I.31c) and 110 mAh g⁻¹ for Li₂[diacetate-bpe](ClO₄)₂ (Figure I.31d). Despite the ionic substituents, the two compounds showed a capacity fading with cycling: the dissolution can be attributed to an intramolecular (self-charged) compensation in the zwitterionic form, which leads to the formation of a neutral compound after complete oxidation, which makes the molecule soluble in organic solvents. To decrease the insertion potential of viologens, Kato and coworkers designed a series of derivates, characterized by an extended π -conjugation, by adding aromatic rings to the structure in order to increase electron density[154]. This approach does not affect the electroactivity of the viologen, as it does not interrupt the conjugation along the viologen structure, preserving redox reaction. The extension of the conjugation led to a decrease in the average redox potential to ca. 2 V vs. Li^+/Li , as well as decrease in the difference between two plateaus, from 500 mV to 200 mV: this result can be explained by a reduction of the interaction between the two pyridinium moieties. The two synthesized molecules displayed a specific capacity of 54 to 70 mAh g⁻¹, close to the theoretical capacity; however, a poor capacity retention was observed due to the high solubility of the species in the reduced form (neutral form).



Figure I.31: a) Potential-capacity profile and b) evolution of the specific capacity as a function of cycle number of $[c-PV](ClO_4)_2$ in half-cell vs. Li. Potential-capacity profile of c) (Li₂[diacetate-V](ClO₄)₂) and d) (Li₂[diacetate-V](ClO₄)₂), two zwitterionic forms of viologen test in half-cell vs. metallic Li. Reprinted from ref [152] and [153].

To summarize, the use of viologens as negative *p*-type materials showed several limitations, such as the relatively high potential and high solubility in electrolytic solvents, which results in low capacity retention. However, a rational design of the viologens structure, such as polymerization or the use of charged substituents to form organic salts, can still be explored, in order to enable a high performance full organic battery based with an anionic rocking chair mechanism.

Full organic batteries

After having illustrated the different classes of organic compounds, assembled in half-cells versus lithium metals or coupled with inorganic materials, in this paragraph the topic of so-called "Full organic batteries" will be addressed. "Full organic" cell refers to electrochemical cells in which both electrodes, cathode and anode, are based on organic materials. Full organic cells can be divided into three categories, depending on the type of mechanism used to store energy: Cationic rocking chair, Anionic rocking chair and Dual-ion[155]. "Rocking chair" mechanism indicates a cell where the cation (or anion) moves back and forth between the electrodes, de-inserting from one to insert into the other; in this case, the electrolyte therefore acts as an ionic conductor, where the ions navigate between the reduced electrode and the oxidized electrode. This mechanism, on which commercial lithium ion batteries are based, is called "Cationic" if the ion involved is the

cation (Figure I.32a) or "Anionic" (Figure I.32b), when it is the negative ion involved in the electrochemical process.

The Dual-ions configuration, on the other hand, is characterized by another electrochemical process: it involves two reversible mechanisms, namely the insertion of cations on an electrode, in conjunction with the insertion of anions on the opposite electrode. In this case the electrolyte, always composed of a dissolved salt of anions and cations (for example Li⁺ and PF₆⁻ forming LiPF₆), therefore plays the role of ionic reservoir (Figure I.32c).



Figure 1.32: Schematic of fundamental cell configurations obtained by playing with both n- and p-type organic electroactive materials shown during the discharge process. (a) All-organic cell incorporating n-type electrode materials only (cationic rocking-chair). b) Symmetric situation with p-type electrode materials (anionic rocking-chair). c) Mixing both n- and p-type electrode materials (dual-ion configuration). Reprinted from ref [155].

Cation rocking-chair batteries

The first full organic cell configuration explored was based on the mechanism called "Cation rocking chair" (Figure I.32a). These cells base their energy storage capacity on the exchange of Li⁺ ions (or other cation Cⁿ⁺) between the cathode and anode, both of which are *n*-type materials. The cathode, containing the reserve of lithium ions, transfer the ions to the anode, where they are inserted into the negative material. The first example of a completely organic cell cation rocking chair was proposed by Tarascon in 2009[64], as a continuation of the previous study on lithium rhodizonate[63]. The authors used tetralithium tetrahydroxybenzoquinone (Li₄-THQ) as the active material for both the positive and negative electrode (symmetrical battery), thanks to its amphoteric behavior. The authors showed that Li₄-THQ can be oxidized to the intermediate Li₂-THQ around 2.7 V (*vs.* Li⁺/Li) and after it can be completely reduced to Li₆THQ at 1.8 V, for an overall working potential of 1 V; both redox steps involve the exchange of two Li⁺/e⁻ per formula unit, for a resulting specific capacity of *ca.* 200 mAh g⁻¹. However, the cell exhibited poor capacity retention: after 50 cycles, the capacity drops to 120 mAh g⁻¹ (60% of capacity retention). To

increase the output voltage, several research groups tried to disubstitute hydroxyquinone with carboxylic acid groups, the latter being able to de-/intercalate lithium at a low potential.

In 2013, Chen et *al.* reported a full cell based on tetralithium 2,5-dihydroxy terephthalate (Li₄-p-DHT) as both cathode and anode materials (symmetric cell). The amphoteric behavior was linked to two different electroactive groups: carbonyl groups (Li₄-p-DHT/Li₂-p-DHT at 2.55 V *vs.* Li⁺/Li) and carboxylates groups (Li₄-p-DHT/Li₆-p-DHT at 0.8 V *vs.* Li⁺/Li)[156]. The symmetric battery (Li₂-p-DHT/Li₆-p-DHT) showed an average output voltage of 1.8 V, with a discharge capacity of 223 and 145 mAh g⁻¹ at C/10 and 5C, respectively. Furthermore, the cell showed a good retention capacity, with 95% reversible capacity after 50 cycles at C/10 rate: this improvement can be explained by the presence of carboxylate groups which decreases the solubility in organic solvents. In addition, Chen's group extended the p-DHT study to the corresponding sodium[46] and potassium[157] ion technology, creating the first sodium and potassium full organic cell, respectively. Tetrasodium-2,5-dihydroxy terephthalate (Na₄-p-DHT), in the symmetric cell Na₂-p-DHT//Na₆-DHT, displayed an output voltage (1.8 V *vs.* Na⁺/Na), identical to the lithium derivate, but with the half of energy density, 65 Wh kg⁻¹ for Na₄-p-DHT against 130 Wh kg⁻¹ obtained with lithium-ion technology; in the case of potassium ion technology, the energy density decreased to 35 Wh kg⁻¹.

The study of full organic cells based on the cation rocking chair was not only focused on quinone and its direct derivatives, but it was extended towards other classes of molecules. Iordache and his collaborators[158] assembled a lithium-ion full cell using two different chemistries, both based on a perylene structure: perylene polyamide (PTCI) as cathode, while lithium perylene tetracarboxylate (Li₄-PTC) was used at the anode. The cell provided an average voltage output of approx. 1.2V, with a capacity around 80 mAh g⁻¹, and was stable for over 200 cycles (81% of capacity retention). Shaijumon and co-workers[159] coupled perylene polyimide with disodium terephthalate (Na₂-TP) to obtain a full organic sodium cell. The cell delivered an initial capacity of 73 mAh g⁻¹, with an average voltage of 1.35 V; however, a marked capacity fading was observed after only 20 cycles.

Hu et al proposed for the first time the preparation of a green battery, where both the active materials, cathode and anodic, are directly obtainable from biosourced materials, demonstrating its potential for applications as energy storage devices. For the cathode material, the authors proposed **Emodin** (6-methyl-1,3,8-trihydroxyanthraquinone), an anthraquinone-like molecule,
present in various plants. For the anode material, Humic acid was used, a natural biopolymer derived from microbial degradation of dead plants: the electrochemical activity of Humic acid comes from carbonyl, carboxylic and phenolate groups present on the biopolymer structure. In the first cycle, the full cell Emodin/SCNT electrode *vs.* lithium humate was characterized by a specific discharge and charge capacity of 127 and 210 mAh g⁻¹, respectively (based on the active mass of emodin). However, even in the case of full-cells, capacity retention remains a critical parameter, with only 60 mAh g⁻¹ of reversible capacity after 100 cycles (99% coulombic efficiency). The average voltage of full cells was approximately 1.5 V, consistent with the potential difference between the Emodin (≈ 2.39 V *vs.* Li⁺/Li) and lithium humate (≈ 1.1 V *vs.* Li⁺/Li).

More recently, Vlad's group proposed a full cell using tetralithium benzene-1,2,4,5-tetrailtetrakis ((sulfonyl) amide) (Li₄-PTtSA), belonging to conjugated sulfonamide family, as a positive active material coupled with Li₂-NDC and ADALS as negative electrodes[91] (Figure I.33a). The Li₄-PTtSA//Li₂-NDC cell showed a higher average cell voltage of 1.6 V, with a reversible specific capacity of 80 mAh g⁻¹ (based on the cathode mass) in the first cycle. However, a capacity decrease was observed in the first 5 cycles, then stabilizes at 60% of the initial capacity after 50 cycles (Figure I.33b). The Li₄-PTtSA//ADALS full-cell exhibited a lower average output voltage than the previous case (1.2 V) but is able to deliver its theoretical capacity (113 mAh g⁻¹, based on the cathode mass) in the first of capacity was observed: after 80 cycles, the full cell retains only the 60% of the initial capacity (67 mAh g⁻¹, Figure I.33c).



Figure 1.33: a) Full organic cell configuration of tetralithium benzene-1,2,4,5-tetrailtetrakis ((sulfonyl) amide) (Li₄-PTtSA) with dilithium naphthalene dicarboxylate (Li₂-NDC, left) and with azobenzene-4,4'-dicarboxylic acid lithium salt (ADALS, right). Potential-capacity profile and (up) evolution of the specific capacity as a function of cycle number (down) of b) Li₄-PTtSA//Li₂-NDC and c) Li₄-PTtSA//ADALS full organic cell. Reprinted from ref [91].

Anion rocking-chair batteries

The Anionic rocking chair configuration (Figure I.32b) is composed of a positive and a negative electrode, both *p*-type, which exchange anions reversibly on charge-discharge, keeping the electrolyte concentration constant during cycling.

Generally, *p*-type negative materials are characterized by more positive redox potential (usually between 1.5 and 2.0 V *vs.* Li⁺/Li) compared to the inorganic counterparts, and the cell therefore results in a low energy density. The first studies on anodic clear rocking date back to the 1990s, when Lee et al. proposed a cell composed of polypyrrole/polyaniline (PAni) followed by the complete symmetrical PAni/PAni cell, but the reported results were unsatisfactory[160].

Yao and coworker reported in 2015 a full organic cell based on a carbazole polymer (poly (N-vinylcarbazole), PVK) as the positive electrode and a viologen polymer (poly (1,1'-pentyl-4,4')-bipyridinium dihexafluorophosphate) as the negative electrode, with an electrolyte composed of 1 M n-Bu4NPF₆ in propylene carbonate (PC)[119] (Figure I.34a). The full cell showed an average output voltage of 1.8 V and a capacity of 100 mAh g⁻¹ (based on the mass of the positive electrode) after the first cycle (Figure I.34b). However, the capacity decreases to 60 mAh g⁻¹ after 100 cycles for 60% capacity retention (Figure I.34c).



Figure I.34: a) Full organic cell configuration of poly (N-vinylcarbazole) (PVK) with poly (1,1'-pentyl-4,4')-bipyridinium dihexafluorophosphate) (PBPy). b) Potential-capacity profile and c) evolution of the specific capacity as a function of cycle number of PVK//PBPy full organic cell. Reprinted from ref [119].

In 2019, Poizot's group reported an example of an organic full cell based on a small molecule approach, rather than using polymers[153]. The cell was assembled using dilithium 2,5-(dianilino) terephthalate (Li₂-DAnT) as the cathode and dilithium [diacetate-V](ClO₄)₂ as anode materials (Figure I.35a). The organic cell exhibited an average output voltage of about 0.7 V, with a specific capacity of only 20mAh g⁻¹ (based on the mass of both electrodes, Figure I.35b,c): the limited capacity was due to the cathode material, the Li₂-DAnT[161], whose operation were limited to the exchange of a single electron to avoid the dissolution of the active material in the electrolyte[44].



Figure I.35: a) Full organic cell configuration dilithium 2,5-(dianilino) terephthalate (Li₂-DAnT) with Li₂-diacetate-4,4'-bipyridinium di-perchlorate (Li₂[diacetate-V](ClO₄)₂). b) Potential-capacity profile and c) evolution of the specific capacity as a function of cycle number of Li₂DAnT//Li₂[diacetate-V](ClO₄)₂ full organic cell. Reprinted from ref [153].

The positive aspects are inherent to the excellent cycling stability, as the cell showed a good capacity retention over 400 cycles; furthermore, the use of a low quantity of conductive carbon in the composite electrode, 15% for the cathode and 5% for the anode, compared to previous cases where it exceeded 30%. In the same year, Oyaizu and coworkers[162] reported a metal-free full cell, based on aliphatic polyethers with high density of 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) and viologen moiety, acting as positive and negative material, respectively. The whole cell provides an average output voltage of ≈ 0.9 V and a specific capacity of 80 mAh g⁻¹ at 1C, which decreases to 48 mAh g⁻¹ at 5C as C-rate. Furthermore, thanks to the plasticity and polymeric nature of the electrodes, as well as the electrolyte (solid state), the authors were able to assemble flexible cells and showed motivating results towards free-form 3D printable batteries.

Dual-ions batteries

By definition, the "dual-ions" configuration is based on the acceptance/release of both ions constituting the electrolytic salt (cation and anion) during the electrochemical process. An electrode accepts the anion (p-type material) and simultaneously the other electrode will the cation (*n*-type material) from electrolyte. Thus, the electrolyte acts as both an ion conductor and an ion reservoir for charge compensation in the electrode materials. The first example reported of an organic dual ion cell dates back to the 1980's and was reported by MacDiarmid and his collaborators. It was based on the bipolar nature of polyacetylene (PAc)[163]. However, the authors did not reporte the electrochemical performance of the cell. In 2009, the first all-organic battery made used poly (PTIO-norbornene) (*p*-type) as the positive material and poly (galvanoxylstyrene) (*n*-type) for the negative electrode, using a mixture of 0.5 M n-Bu₄NClO₄ and 0.01 M n-Bu₄NOH in acetonitrile as electrolyte. The cell displayed a voltage of 0.66 V, with a specific capacity of 32 mAh g⁻¹ (92% of Q^{theo}) at 10C; in addition, the cell exhibited outstanding rate performances, cycling up to 360C (charge in 10 seconds). However, after 250 cycles the cell capacity dropped to 57% of the initial value. A second cell was published by this group in 2011, using the same electrolyte but with poly-(4-(nitronylnitroxyl) styrene) as both positive and negative electrodes, thanks to its amphoteric nature[164]. The output voltage was measured as 1.3 V, with a reversible capacity of 44 mAh g⁻¹ at 10C rate, and a stability over 250 cycles. Moreover, the cell showed good rate capability up to 60C. Despite the improvements compared to the previous cell, the electrodes composition was made with only 10 wt.% of active material (AM:VGCF:PVDF=10:80:10). Zhu et al. [165] developed an all-organic Na dual-ion battery, again using polytriphenylamine (PTPAn) as the *p*-type cathode material, coupled with poly (anthraquinonyl-sulfide) (PAQS) as the *n*-type negative electrode[166] (Figure I.36a). A solution of saturated NaPF₆ in a DOL-DME mixture (v/v = 1:1) was used as the electrolyte, allowing here the exchange of Na⁺ and PF₆⁻ ions between the two electrodes. The cell exhibited an average voltage of 1.8V, with a specific capacity of 200 mAh g⁻¹ after the first cycle, based on the anode mass (Figure I.36b). Furthermore, the cell was characterized by an excellent rate capability, with a capacity of 130 and 118 mAh g⁻¹ at 16C and 32C, respectively (Figure I.36c). Finally, the cell revealed an outstanding stability at 8C rate, with a high capacity retention for 500 cycles (Figure I.36d).



Figure I.36: a) Full dual-ions organic cell configuration with polytriphenylamine (PTPAn) with poly (anthraquinonyl-sulfide) (PAQS). b) Potential-capacity profile, c) rate performance test and d) evolution of the specific capacity as a function of cycle number of PTPAn//PAQS full organic cell. Reprinted from ref [166].

Schubert and coworkers reported a complete cell composed of two redox polymers[115]. Poly (2-vinyltianthrene) is used as the positive electrode material, prepared by the polymerization of 2-vinylthianthrene and tested in a half-cell against lithium. It shows a discharge potential located at 3.95 V vs. Li⁺/Li and a capacity of 105 mAh g⁻¹. Poly (2-methacrylamide-TCAQ) is used as the negative electrode material (Figure I.37a). In a half-cell configuration in front of a lithium electrode, this material has an estimated discharge capacity of 130 mAh g⁻¹, as well as a 2.4 V vs. Li⁺/Li. The complete cell was assembled in a button cell, then tested for more than 250 cycles, with an EC-DMC (v/v=3:7) 1 M LiClO₄ mixture as the source of Li⁺ and ClO₄⁻ ions. This cell displayed an average discharge voltage of 1.35 V and a discharge capacity of 105 mAh g⁻¹ of active material (Figure I.37b).



Figure 1.37: a) Full dual-ions organic cell configuration with Poly (2-vinyltianthrene) (PVT) and Poly (2-methacrylamide-TCAQ) (PTCAQ). b) Potential-capacity profile, c) evolution of the specific capacity as a function of cycle number and d) rate performance test of PVT//PTCAQ full organic cell. Reproduced from ref [115].

In 2019, Casado and coworker proposed a symmetric battery using a homopolymer (PI1, Figure I.38a), a copolymer composed by 3,7-diamino-methylphenothiazine (DAMPT), which works as a positive material, and naphthalene tetracarboxylic dianhydride (NTCDI), as a negative material[167], as illustrated in Figure I.38a. The CV curve showed two oxidation-reduction peaks associated to the naphthalene di-imide moiety, at 2.33 and 2.51 V vs. Li⁺/Li, while the third peak (3.73 V) is related to phenothiazine moiety; the full cell shows two peaks, a 1.25 V and 1.6 V vs. Li⁺/Li, in agreement with the individual redox processes. The cell delivered 128 mAh g⁻¹ at 50 mA g⁻¹ and 124 mAh g⁻¹ at 1000 mA g⁻¹, equivalent to a one-electron redox reaction in the phenothiazine moiety (Figure I.38b). Although a poor coulombic efficiency was measured at low current densities (50 mA g⁻¹), it increased to 97% for higher current densities (800 mA g⁻¹). Long cycling stability was studied at high current density (800 mA g⁻¹) for 1000 cycles: the initial discharge capacity of 77 mAh g⁻¹ decreased to 72 mAh g⁻¹, *ie* a capacity retention of 94% (Figure I.38c).



Figure I.38: a) Amphoteric redox mechanism of 3,7-diamino-methylphenothiazine (DAMPT)-naphthalene tetracarboxylic dianhydride (NTCDI) co-polymer. b) Potential-capacity profile and c) evolution of the specific capacity as a function of cycle number of DAMPT-NTCDI// DAMPT-NTCDI full symmetric organic cell. Reprinted from ref [167].

In 2022, Jia and coworker reported a high-voltage full organic cell, based on a nitroxide radical polymeric cathode and a silver terephthalate anode[168]. The cathode polymer was a TEMPO polymer modified with AQ: the anthraquinone moiety was added to graft the polymer to CNT. The grafting was used to reduce the electronic resistance and enhance the mass transport of the electrolyte along the electrode. The Ag₂-TP anode demonstrated better conductivity and higher rate performance compared to other dicarboxylate-based materials. The full cell PTMA_{0.95}-co-AQ_{0.05}/Ag₂-TP displayed an average voltage of 2.8V, with a specific capacity of 133 mAh g⁻¹ (based on anode mass) over 100 cycles at 1C (capacity retention of 98%). based on the weight of the active material, an energy density of 157 Wh kg⁻¹ was calculated. However, the cathode composite requires a large amount of carbon nanotube (60 .wt% of the electrode), therefore the real energy density is much lower.

Electrode (+)	Electrode (–)	Electrolyte	Voltage (V)	Specific Cap. 1 st cycle	Reference
ΡΤΜΑ	C _{gr}	1M LiPF ₆ in EC/DEC 3:7	3.5 V	0,23 mAh	[169]
Poly (PTIO- norbornene)	Poly (galvanoxyl- styrene)	n-BuNClO4 (0.5 M) + n- Bu4NOH (0.01 M) in ACN	0.66 V	32 mAh g ⁻¹	[170]
Poly (PTIO- norbornene)	Poly (4-nitronyl- nitroxyl) styrene	BuNClO4 (0.5 M) + Bu4NOH (0.01 M) in ACN	1.3 V	44 mAh g ⁻¹	[164]
ΡΤΡΑ	PDHT	1M LiPF ₆ in EC/DMC/DEC 1:1:1	2.35 V	250 mAh g ⁻¹	[165]
ΡΤΡΑ	PAQS	NaPF ₆ sat. in DOL/DME 1:1	1.8 V	200 mAh g ⁻¹	[166]
ΡΤΡΑ	NTCDA	2M LiTFSI in Ethyl Acetate	1.2 V	200 mAh g ⁻¹	[171]
Poly(2-vinyl thianthrene)	Poly TCAQ	1M LiClO4 in EC/DMC 3:7	1.35 V	105 mAh g ⁻¹	[115]
PTPAn	PI5	1M EMITFSI In EC/DMC 1:1	1.5 V	mAh g⁻¹	[172]
DAMPT	PI1	1M LiPF ₆ in EC/DMC 1:1	0.8 V	128 mAh g ⁻¹	[167]
ΡΤΜΑ	Ag ₂ TP	3.5 M LiTFSI in TEGDME	2.8 V	mAh g ⁻¹	[168]

State-of-art of Organic materials for energy storage applications

Table I.5: Summary of energy metrics for Dual-ions organic cells reported in literature.

Positioning of the thesis work

The intense research on electroactive organic molecules in the last decade has made possible to take a step towards a solid base of high-performance materials, even reaching the production of the first "all-organic" full-cell. However, the all-organic cells reported in the literature showed a series of limitations, such as the low active material loading in the electrode and a nominal voltage of <3 V, markedly lower than those of inorganic-based lithium batteries (3-4 V).

The objective of my thesis work is based on the identification and development of new high performance organic materials, both for the positive and the negative electrode, with the aim of designing an all-organic battery with an output voltage higher than 3 V, for both Lithium-ion and Sodium-ion technologies.

To achieve this goal, several strategies were developed:

- The development of new *n*-type positive material for Lithium batteries, based on a benzoquinone molecular structure, but with an oxime as electroactive group.
- The rational design of the molecular structure of *p*-type positive materials already reported in literature; the approach consisted in the screening of substituents group with (electro-)chemical/physical properties able to improve the electrochemical performance and reduce the dissolution phenomena of the active material in the electrolyte. Then, the best performing active material was assembled into an "all-organic" full-cell in a Dual-ion configuration.
- Optimization of the Na₂-NDC-based electrode as anode for Sodium-ion batteries, in order to improve their electrochemical performance through the improvement of the electrode structure. Thus, the best electrode architecture was then assembled in a hybrid full-cell, coupled with an inorganic material as a cathode.

A total of 7 papers and a patent have been published or submitted during the thesis work and will used to construct and organize the thesis manuscript.

Chapter 2 takes elements of the paper to be published "Unraveling the redox mechanism and material microstructure and crystal structure of dilithium benzonquinone dioxime as positive material for lithium-ion battery" in preparation and discusses the redox mechanism of the Dilithium 1,4-benzoquinone dioxime as new *n*-type positive materials.

Chapter 3, uses the paper « N-Substituted Carbazole Derivate Salts as Stable Organic Electrodes for Anion Insertion" published on ChemNanoMat (https://doi.org/10.1002/cnma.202200248) and describes the design, synthesis and electrochemical characterization of a set of carbazole derivatives as *p*-type positive materials with redox potential around 4 V *vs.* Li⁺/Li.

Chapter 4, uses the filed patent "Nouvelles électrodes organiques et leur utilisation dans des systèmes électrochimiques" (FR2208778) and decribes a new set of single-molecule Thiantrene derivates which were investigated as p-type positive materials with redox potential above 4 V *vs.* Li⁺/Li.

Chapter 5, uses the paper "Disodium Naphathalene Dicarboxylate Negative Electrode for Organic-Inorganic Hybrid Sodium batteries" submitted to J. of Power Sources and discusses the optimization of the disodium Na₂-NDC negative electrode.

Introduction

As we have already mentioned in the first chapter, to produce an "all organic" battery with an high output voltage (>3 V), it is necessary to have positive organic material characterized by a redox potential around 3.5-4 V vs. Li⁺/Li.

Benzoquinones are undoubtedly one of the most studied organic materials for energy storage application[42], providing high gravimetric capacity (496 mAh g⁻¹ of specific capacity for 1,4-benzoquinone[173]) and an average redox potential in the range 2.5-3.0 V vs. Li⁺/Li[45]. Furthermore, benzoquinones are characterized by a chemically flexible structure , which can be easily modified through the facile addition of substituent on the aromatic ring, in order to improve electrochemical properties (potential and capacity), create more stable molecular systems (e.g. polymers) or to tune the (electro-)chemical properties[174].

Despite the interesting advantages, quinones derivates reported in literature also showed a high solubility in electrolyte solvent, which lead to poor cyclability due to active material dissolution. Moreover, as the redox potential is below 3 V in most of the cases studied, lithiated quinones are unstable under air as they can be oxidized by oxygen; only few quinone derivates have showed a potential greater than 3 V, as the tetralithium 2,5-dihydroxy-1,4-benzenedisulfonate (Li₄-DHBDS), which displayed an operating potential 3.2 V *vs.* Li⁺/Li, as reported by Lakraychi and coworkers[56].

In order to overcome the problems related to quinone materials, without losing its advantageous aspects, such as an extremely flexible molecular structure from a chemical point of view, a good approach is the development of similar molecular structures using a new electroactive group, characterized by better electrochemical performances.

With this philosophy in mind, in the present work, a new class of organic molecules easily derived from benzoquinones are presented, known as Dioximate. Electrochemical properties of benzoquinone dioxime were studied by Rathore et al[175]: the authors reported a reversible redox reaction with an average potential of 1.3 V vs. Satured Calomel Electrode (SCE), it is therefore possible to estimate a redox potential around 4.5 V vs Li⁺/Li. These electrochemical tests were performed with 0.1 mol dm⁻³ TBAH in ACN as electrolyte; the reactivity in the solid state, using a different electrolyte, can influence the redox potential: however, it is legitimate to hypothesize that the average redox potential is higher compared to benzoquinone/dihydroxyquinone couple (2.6 V vs. Li⁺/Li).

Starting from this outstanding performance in solution, lithiated benzoquinone dioxime was investigated as active material for lithium-ions batteries: this would allow to combine all the benefits related to benzoquinones, i.e. the ease of availability, the enormous variety of modification, with an electroactive group, the oxime, capable of working at higher potentials with a consequent increase in energy density.

In a study by Vlad et al.[92], proposed as pre-printing scientific article in 2022, lithiated oxymate derivates were reported new positive material for Lithium-ion batteries. The authors proposed five derivatives of dioxime through a rational design of the molecular structure: starting from the dilithium benzoquinone dioxime (Li₂-BQD), a series of derivatives have been developed, based on both aliphatic and aromatic. About the electrochemical performance, the oximate derivates exhibited an average redox potential spanning in the range 2.5-3.2 V *vs*. Li⁺/Li, which allows to have lithiated materials stable under air, and specific capacity between 210-360 mAh g⁻¹. In addition to the electrochemical investigation, this work elucidated the reversibility of the redox reaction through Ex-situ infrared spectroscopy and X-ray diffraction technique.

In the first part of the present work, the redox mechanism giving rise to the Li₂-BQD system was investigated through a computational study thanks to a molecular approach. This preliminar study was aimed at providing a first insight of possible structure-property relationships of this compound. The simulation involved both Density Functional Theory (DFT) computations and subsequent accurate electronic structure examination. Thanks to this modelling, it was possible to provide a first estimation of the redox potential for the couple involving Li₂BQD and its oxidized counterpart, the dinitrosobenzene (DNB). Moreover, by using delocalization indices some further clues toward the understanding of electrochemical behaviour were gained. This thorough examination at the molecular approach both allowed to identify the most probable lithium intercalation location sites and to elucidate the changes occurring in terms of aromaticity during the molecular redox reaction. While these observations/interpretations could be modified when considering the crystalline state – which may involve some specific stacking, different kinds of interatomic distances between the redox centers and Li⁺ ions, etc. – this kind of approach has the merits of paving the way towards a first rough estimate of intercalation features along with an understanding of the electrochemical phenomena. Secondly, both Li₂-BQD and the dinitrosobenzene were synthesized and electrochemically characterized. The galvanostatic tests performed in half-cell vs. metallic lithium showed an average potential of 3.0 V vs. Li⁺/Li, with a specific capacity of 330 mAh g⁻¹ in the first cycle, starting from both Li₂-BQD and DNB electrodes.

Additionally, XRD analyses were performed to study the role of crystal structure in the energy storage process. The impact of the microstructure on electrochemical performance for both reduced and oxidized states has been elucidated using TEM and EELS coupled techniques: these analyzes led to a better understanding of the electrochemical process, confirming its full reversibility, as well as explaining the differences observed over long cycling.

Computational study of Li₂-BQD and DNB

In the quest for new redox-active systems serving as electrodes, computational modelling may contribute to complement the characterization of experimental works or even to take part in elucidating the mechanisms. DFT calculations may for instance be involved in research investigations performed either on crystalline phases already identified experimentally or on molecular/complex moieties for which the sole knowledge of the structural molecule is sufficient to predict the redox properties as a first step able to propose a ranking among several systems [176–179]. For a redox-active system containing two redox centres as it is the case here, electrochemical phenomena may potentially arise on only one side (*i.e.* single reduction) or by calling to either two successive one-electron/one Li⁺ steps or by direct double reduction. A thorough description of the electrochemical features for this kind of systems is thus reached by focusing on three species: the initial (oxidized) form fully devoid of neighbouring Li⁺, an intermediate (singly reduced) form and a final form exhibiting an environment of two Li⁺, each of them being located in the vicinity of each of the redox centres.

As a first insight, as previously stated, a molecular DFT modelling complemented by a thorough electronic structure analysis was undertaken to investigate the redox phenomena in this class of materials. This study was performed by calling to the same methodology as the one used previously for considering the case of quinones, using an implicit SMD solvation model in acetonitrile [180]. In the present investigation, the DFT calculations were performed by using the Gaussian code with the M06-2X functional. Focusing on such molecular approach not only enables to elucidate at least partly the involved electrochemical phenomenon by providing some guess of peculiar properties but is also particularly suited in the present case owing to the amorphous character of dilithium benzoquinone dioxime, Li₂-BQD (as stated in the next section). At the molecular state, by considering two successive steps each involving one electron/one Li⁺, the redox mechanism can be envisioned similarly to the suggestion of Rathore et al.[175], as depicted in Figure II.1. Within this electrochemical process, the molecular species may evolve from the oxidized state (left side of the Figure II.1), *i.e.* DNB, containing two N=O redox centres, towards the fully reduced state, *i.e.* Li₂-BQD, characterized by an uptake of two electrons and involving a complex structure with two Li⁺, which are supposed to be located in the neighbourhood of each of the oxygen atoms, if one considers a direct double reduction. The present computational

present computational approach considers the two options of reaching either an uptake of one electron (single reduction) or two electrons (double reduction) starting from the oxidized DNB.



Figure II.1 Expected electrochemical mechanism of lithium insertion/de-insertion involving the p-dinitrosobenzene (DNB) (Left) / di-lithium benzoquinone dioxime (Li₂-BQD) (Right) redox moieties.

The DFT modelling first provides the geometrical structures along with involved interatomic distances of the two Li⁺ complexes of DNB (Figure II.2a,b). In view of gaining a preliminary insight on the way Lithium may locate in the vicinity of the molecule to form a complex entity upon reduction, the Electrostatic Surface Potential (ESP) maps, which may be plotted after the DFT calculation, have proven to constitute a precious tool [130]. The minima are more specifically meaningful since they constitute areas that are characterized by an accumulation of electron, where Li⁺ ions may lie. The ESP maps of the three species that are involved during the electrochemical process of reduction of DNB are gathered in Figure II.2c, which concomitantly presents the representation of relaxed systems along with the involved bond lengths.

Especially, focusing on the ESP map of DNB, it is straightforward to identify two minima, both located nearby each redox centre, at ~ -22.3 and ~ -26.7 kcal/mol, within the red area exhibiting an electron-rich area. Among these two minima, the highest absolute value is situated in the vicinity of the Oxygen atom while the other one is nearer to the Nitrogen atom. Each minimum is situated at a roughly equivalent distance from either the Oxygen or Nitrogen atom although the distance from the minimum at ~ -22.3 kcal/mol is slightly farther from Nitrogen compared to the distance between Oxygen and the minimum at ~ -26.7 kcal/mol. Upon successive electron uptakes or through single/double reduction, the initial molecular entity evolves towards a complex involving one/(and then) two Li⁺ interacting with the Oxygen(s) atom(s) of the mono-/dianion through electrostatic interaction, which is clearly reflected in the ESP landscape. This latter complex is indeed modified accordingly, ending up with the doubly reduced state Li₂-BQD characterized by a large red area covering the anion. The intermediate state corresponding to the

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singly reduced complex exhibits on the unreduced redox centre a single minimum at ~ -55.6 kcal/mol nearby the Oxygen atom. It is straightforward to identify that the Li⁺ positioning effectively takes place within this area forming an almost linear arrangement with the C-N chemical bond (Figure II.2b). It thus constitutes a kind of double chelation with Li⁺ interacting preferentially with Oxygen but also with Nitrogen located however a bit farther (and presumably being less charged than Oxygen).



Figure II.2 Evolution of systems from DNB towards Li2-BQD upon Lithium reduction according to the electrochemical mechanism proposed in Figure II.1: Initial state (left), intermediate state (middle, Li-BQD) and final state (right, Li₂-BQD) forms of DNB derivatives. a) DFT-computed structures b) interatomic distances of the optimized geometry and c) Electrostatic surface potential (ESP) maps. Color code: blue (red) to visualize electron depletion (electron accumulation) within the range of 30.0 (deep blue)/-30.0 (deep red) kcal/mol. Surface local minima and maxima are represented along with corresponding values.

One of the fundamental aspects that can be reached in order to confirm the hypothesis proposed in Figure II.1 is to examine the geometrical features and electron delocalization/ bonding pattern (Figure II.2a,b and Figure II.3a). According to what is envisioned for this material, the six-

membered ring (6MR) shall in principle be characterized by a transformation from the fully aromatic nature (for the initial oxidized state) towards a quinoidal character (for the final doubly reduced state), while the intermediate state shall recover a semiquinone type. In order to quantify these aspects, the HOMA and FLU indices were collected for the three entities [181– 184]. HOMA values allow to get an estimation of the deviation of the bond distances in the ring relative to an aromatic model, characterized by all bonds equal to the optimal value, for which a value of HOMA equal to 1 is expected, (while a HOMA = 0 is related to a model non-aromatic system). FLU index is related to the ring electron delocalization, and it is defined in terms of the delocalization indices of all bonds in the rings that, for a perfectly aromatic system like benzene, should all be equivalent. Contrary to HOMA, FLU approaches zero for highly aromatic systems and largely deviates from zero for non-aromatic systems. Concerning the oxidized initial state, the expected result is observed, with an extremely clear aromatic character demonstrated by both HOMA (0.995) and FLU (0.003) values. On the other hand, the fully reduced state for the complex (final state) clearly exhibits the loss in aromatic character, with a HOMA value approaching 0 and a FLU value of about ~ 0.05, the intermediate state being logically characterized by the intermediate values of 0.856 and 0.012 for HOMA and FLU, respectively. In terms of bond lengths, the evolution of C-C values is in perfect agreement with these trends, starting from ideally equalized bonding type (1.39 Å for all bonds) for the initial state and ending up with differentiated data (bond lengths consistent with a quinoidal moiety, with traditional features of double (1.34 Å) and single (1.45 Å) bond lengths). Accordingly, the C-N chemical bond is progressively passing from 1.44 Å to 1.36 Å and then to 1.30 Å for the initial, intermediate and final states, respectively while the N-O chemical bond is evolving from 1.20 Å to 1.30 Å and then to 1.33 Å for the same states, respectively. Such evolutions are in line with the expected change in bonding order (i.e. switching between double and single bonds before/after double reduction for N-O and C-N bonds) according to the proposed redox mechanism presented on Figure II.1. Therefore, such observations clearly evidence the passage from the two nitroso functional groups (i.e. C-N=O groups attached to an organic moiety) towards the two dioxime functional groups (=C-N-O⁻). It can also be observed that the interatomic distance between Oxygen and Lithium amounts to 1.78 Å while the distance between Nitrogen and Lithium it is about 1.90 Å for the final state, the interatomic distance Li-O being slightly higher for the sole reduced functional group in the intermediate state (i.e. 1.84 Å). In order to examine the mechanism more in detail, the Quantum Theory of Atoms in Molecules (QTAIM) [185] already used to evaluate the delocalization indices

may also be employed in view of getting further physical-chemical insight on the electrochemical phenomenon. In particular, it allows for the estimation of net atomic charges (NACs). These values amount to +0.93-0.94 for Lithium in the intermediate or final states. Apart from this expected almost +1.0 net atomic charge, the – 0.81 and – 0.65 values for Oxygen and Nitrogen atoms at the final state, respectively (against -0.43 and -0.01 for the initial state), respectively reveal a charge transfer upon reduction, Δq , of -0.38|e| and -0.64|e| for Oxygen and Nitrogen, respectively. All together, these charge transfer results provide a further elucidation with respect to the electrochemical mechanism proposed in Figure II.1. The actual procedure – at least for this potentially oversimplified view of molecular systems – departs from a formal (=C-N-O⁻) vision owing to the electrostatic type of interaction occurring with Li⁺, which seems to involve primarily the Oxygen but also significantly the Nitrogen atom (the Li-O distance, 1.78 Å, being just slightly shorter than the Li-N distance, 1.90 Å). Note however, that the situation could certainly be different by considering the electrochemical process within a crystal at least for these interatomic distances, which in turn may impact the redox potential. The simple representation of the redox process proposed in Figure II.1 can thus be inferred by this QTAIM analysis, provided that the participation of Nitrogen to the process is considered, therefore modifying the overall chemical link of the CNO subunit. Such situation with a slightly revised vision of the mechanism is consistent with the location of Li⁺ in between the two ESP minima nearby the NO group. As a further step towards mechanism comprehension, a partition of the total energy for all states was performed to estimate the contribution of each atomic or molecular molecular to the total molecular energy and to observe if it stabilizes or destabilizes the system upon the redox process (thus implying to focus on differences in energy between either the singly or doubly reduced and the initial oxidized compound) (Figure II.3b). In line with the HOMA/FLU trends, the ΔE relative to the 6MR variation is largely destabilizing (i.e. positive values). It is possible to notice that the situation is reversed compared with the case of benzoquinones [180,186], while obviously fully in agreement with the proposed mechanism. Despite this large destabilization, we clearly observe that it is counterbalanced and even strongly overcome by the large negative ΔE contribution of the NO group, which is therefore largely stabilizing).



Figure II.3 a) Variations of electron delocalization indices – harmonic oscillator model of aromaticity (HOMA) and aromatic fluctuation index (FLU) descriptors – upon one-electron (single reduction, SR) or two-electron (double reduction, DR) electrochemical process; i.e. Δ HOMA (left, green) or Δ FLU (right, blue); b) Variation in Bader's energy (Δ E values, in Hartree (Ha)). These Δ E values concern the benzenic ring (6MR, blue) and the functional group (NO, orange).

Accordingly, this is a sign that DNB should lie in the family of positive electrode materials, which is consistent with the molecular redox potential for the double reduction estimated to be ~2.4 V vs. Li⁺/Li by selecting the same methodology as already used in the case of benzoquinones for the sake of results comparison. Owing to the consideration of such system as a potential redox-active specie for use as electrode in batteries, we estimated – as a first rough indication – the band gap between HOMO and LUMO, in view of comparing the relative capabilities of this compound with the standard *p*-benzoquinone (*p*-BQ). By using the HSE06 functional (known to be more suited for such evaluation[187]) applied to the geometry obtained at the M062X level previously examined, it is straightforward to identify from Figure II.4 that the DNB compound seems to be characterized by a lower band gap than *p*-BQ, these oxidized initial systems being characterized by a differentiation amounting to ~1.13 eV in favour of the DNB compound. On the other hand, for

the two kinds of families, it can be noticed that lower gap values are observed for both singly and doubly reduced states compared to the corresponding oxidized states.



Figure II.4 Frontier molecular orbital energy levels and energy gap comparison between the para-benzoquinone (p-BQ) and DNB derivatives (calculations performed by using the HSE06 functional, based on M062X/6-311+G(2d,2p) optimized geometry).

Synthesis and characterizations of Li₂-BQD and PNND

Inspired by the modeling investigation, **dilitihum 1,4-benzoquinone dioxime** (Li₂-BQD) were synthesized via salt formation reaction. Corresponding benzoquinone dioxime (BQD) was reacted with LiOH·H₂O in methanol (Figure II.5a), using the same procedure reported for the lithiation of dihydroxybenzene[188].



Figure II.5 Synthetic routes of a) Dilithium benzoquinone dioxime (Li₂-BQD) and b) Dinitrosobenzene (DNB).

The synthesis of Li₂-BQD was confirmed by FTIR and NMR analysis. NMR spectrum (Figure VII.2 Experimental Part) after the lithiation showed the disappearance of O-H peaks located at 12.10

ppm (s, 2H), observed in the pristine material (Figure VII.1). Furthermore, the aromatic hydrogen located were shifted at upfield (7.00-6.58 ppm) due to the presence of lithium ions, compared to the peaks in the BQD spectrum, located in the 7.85-6.44 ppm range. FTIR spectra (Figure II.6a, blue curve) corroborate the complete lithiation of benzoguinone dioxime with the O-H stretching band disappearance after lithiation and the C-N stretching peak shifting from 991 ppm in BQD to 970 ppm in Li₂-BQD, due to the presence of lithium ions. Lithium content was measured using atomic absorption spectroscopy (AAS) analysis, giving a complete chemical formula of Li_{2.03±0.05}-BQD. Finally, a thermogravimetric analysis (TGA, Figure II.6b, blue curve) revealed absence of any remaining solvent (no loss between room temperature and 300°C), meaning that the synthesized molecule is not in a solvated state. The oxidized counterpart of dioxime, poly (1,4phenyleneazine-N, N-dioxide) (PNND), was synthesized through the oxidation of dioxime with FeCl·6H₂O (ratio 1:3 eq.) in water using the procedure reported by Muller and coworkers[189](Figure II.5b). Such reaction was found to be quantitative since broad peak in the range 3500-2500 cm⁻¹ due to O-H stretching and the shifting to 1306 cm⁻¹ of C-N band, as well as the appearance of 1251 cm⁻¹ band due to trans N-O, were observed by FTIR (Figure II.6a, green curve) and in perfect agreement with the spectrum reported in literature[190]. NMR spectrum of poly (1,4- phenyleneazine-N, N-dioxide) confirms the reaction with the entire disappearance of hydroxide peak at 12.10 ppm and shifting to upfield, from 7.85-6.44 to 7.23-6.65, for the presence of nitroso group (Figure VII.3). The thermal stability of poly (1,4- phenyleneazine-N, N-dioxide) was evaluated thanks to thermogravimetric analysis (TGA): no mass loss was observed up to 200 °C (Figure II.6b, green curve), before it starts to decompose/fragmentate; this result confirms the absence of solvent trapped in the molecular structure.



Figure II.6 a) FTIR spectra (transmission mode) of benzoquinone dioxime (BQD, red line), dilithium benzoquinone dioxime (Li2-BQD, blue line) and poly(1,4-phenyleneazine-N,N-dioxide) (PNND, green line); 2) Thermogravimetric analysis of Li2-BQD (blue line) and PNND (green line).

In term of morphology, while Li_2 -BQD appeared as irregular granules and varied in size from ~10 to 30 μ m as observed by SEM (Figure II.7a), **PNND** showed consisted of clusters of slender parallelepipeds with a thickness around 1 μ m and lengths ranging from 2 to 5 microns (Figure II.7b).



Figure II.7 Scanning electron microscope images of dilithium benzoquinone dioxime and poly (1,4- phenyleneazine-N, N-dioxide): a) Li₂-BQD particles with granular shape; b) PNND clusters of slender parallelepipeds.

Electrochemical characterization of Li₂-BQD and PNND

As a preliminary study, the electrochemical performance of Li₂-BQD salt were tested using a Swagelok-type[®] half-cells vs lithium metal disk, using LiPF₆ in EC/DMC (50:50) electrolyte (commercially named LP30, battery grade purity). The galvanostatic profiles have been measured at C/20 in 4.0-2.0 V potential window. All the electrodes were prepared using an active material/conductive carbon (KJ600) ratio of 70:30, using the procedure reported in the Experimental part (Electrode preparation for Swagelok-type cell).

Li₂-BQD molecule showed an average insertion potential of ca. 3.0 V (Figure II.9a), higher than what reported for various organic systems, such as quinones[45] and diimides[75]. A large polarization (400 mV) was also observed, a common feature for organic-based electrode which indicates an energy-expensive structural rearrangement during the redox process. The charge phase displayed a specific capacity of 320 mAh g⁻¹, close to the theoretical capacity of 388 mAh g⁻¹. 277 mAh g⁻¹ of capacity was observed after the discharge, for 87% of reversibility during the first cycle. Despite the excellent electrochemical properties shown in the first cycle, several

drawbacks were observed along cycling. First, in the second cycle, despite no change in the oxidation capacity (331 mAh g⁻¹), the discharge capacity drops to 146 mAh g⁻¹, for a coulombic efficiency of only 44%. Secondly, a poor capacity retention was observed along the first 10 cycles, with a residual reversible capacity of only 52 mAh g⁻¹ (21% of capacity retention). After that, the capacity stabilized, reaching 31 mAh g⁻¹ of reversible capacity after 100 cycles (Figure II.9b).

Such behavior could be explained by either the dissolution of the active material in the electrolyte, frequent phenomenon for small organic molecules or by a non-optimized electrode formulation since for the preliminary test a simple hand-milled electrode with active material and conductive carbon was employed. The addition of binder and another mixing process can significantly improve the electrochemical properties. A last option could be nested in side-reactions affecting the redox process, hindering the reversibility of the lithium intercalation process. About the dissolution of active material in the electrolyte, very common for molecular electrode, a visual analysis after 10 cycles showed no traces of active material in the separator. Note that the dissolution of the active material in the electrolyte should colored the separator in contact with the electrode. As further confirmation, both benzoquinone dioxime and poly (1,4-phenyleneazine-N, N-dioxide) were kept in a mixture of LP30 solution for one week, showing no dissolution (Figure II.8).



Figure II.8 Solubility test of PNND and Li₂-BQD after 1 week in LP30.

To investigate the effects of the formulation on electrochemical properties, a different formulation was prepared, with the addition of binder and changing the mixing method. In this formulation, 10% of PDVF binder was added in the electrode composite, for a final ratio of 60/30/10 (AM/KJ600/PVDF) and the powder was ball-milled for 30 minutes. The results obtained with this different formulation were illustrated in Figure II.9c-d. Nevertheless, the new formulation showed electrochemical performances almost identical to the previous one: the halfcell exhibited a specific capacity 338 mAh g⁻¹ after the first charge, with a reversible capacity of 233 mAh g⁻¹ (31% irreversibility). In second cycle, a marked capacity drop was observed, with 168 mAh g⁻¹ of reversible capacity), just slightly better than the previous case. After 100 cycles, the specific capacity was quantified in 40 mAh g⁻¹, corresponding to a capacity retention of 17%. This result represents only a small improvement compared to the electrode without binder: it can be concluded that the of presence of the binder in the electrode composite did not prevent the capacity fading. Therefore, excluding the hypotheses on the dissolution or on the formulation of the electrode, the loss of capacity could be acute to degradation phenomena of the active material or of the electrolyte. However, these phenomena require very sensitive post-mortem analyzes and will investigated the last part of the present work, through a coupled TEM/EELS analysis of the electrode after a long cycling.



Unraveling the redox mechanism and material microstructure of dilithium benzoquinone dioxime as new electroactive n-type positive material

Figure II.9 a) Potential-capacity profile of 1st, 2nd and 100th cycle of Li₂-BQD electrode (70:30 AM/KJ600) in half-cell vs. Li, galvanostatically cycled over a potential range of 4.0-2.0 V at C/20, with LP30 electrolyte; b) corresponding evolution of the specific capacity as a function of cycle number. c) Potential-capacity profile of 1st, 2nd and 100th cycle of Li₂-BQD electrode (60:30:10 AM/KJ600/PVDF) in half-cell vs. Li, galvanostatically cycled over a potential range of 4.0-2.0 V at C/20, with LP30 electrolyte; d) corresponding evolution of the specific capacity as a function of the specific capacity as a function of cycle number.

The oxidized equivalent of benzoquinone dioxime, poly (1,4-phenyleneazine-N,N-dioxide), obtained *via* chemical synthesis, was also tested in a half-cell vs. Li, using the same set-up described above. Contrary to dilithium benzoquinone dioxime, PNND has no Lithium ions in its structure, so the first electrochemical step was the intercalation of lithium, with relative reduction of the molecule. When the half-cell was connected to the potentiostat, a voltage of 3.2 V *vs.* Li⁺/Li was measured, above the potential where oxidation take place, confirming the stability of the molecule to exposure to air. The first discharge showed a specific capacity of 336 mAh g⁻¹, the same value observed for the lithiated benzoquinone dioxime. The reversible capacity was measured in 313 mAh g⁻¹, corresponding to 7% of irreversibility, an excellent result for organic materials. The average redox potential was measured in 3.0 V *vs.* Li⁺/Li, with a polarization in line with what was measured in the previous cases. The second cycle showed a decreasing in capacity

to 268 and 293 mAh g⁻¹ for discharge and charge, respectively. In the subsequent cycles, a constant loss of capacity was measured, with a consequent low retention of capacity (Figure II.10). However, after 20 cycles, the coulombic capacity increased significantly, and the capacity remained stable along cycling. After 100 charge/discharge cycles, the specific capacity remains constant at 90 mAh g⁻¹, with a coulombic efficiency of 99.5%: it is possible to conclude that, as in the case of Li₂-BQD, after a significant loss of capacity in the first 20 cycles, the cell stabilizes and can cycle for a long time without further losses.



Figure II.10 a) Potential-capacity profile of 1st, 2nd and 100th cycle of PNND electrode (70:30 AM/KJ600) in half-cell vs. Li, galvanostatically cycled over a potential range of 4.0-2.0 V at C/20, with LP30 electrolyte; b) corresponding evolution of the specific capacity as a function of cycle number.

Characterization of Li₂-BQD through *ex-situ* XRD and TEM/EELS

analysis

From the electrochemical tests performed on both the Li₂-BQD and PNND electrodes, a marked difference emerged in terms of capacity retention along cycling. Although the redox mechanism is identical, poly (1,4-phenyleneazine-N,N-dioxide) exhibited superior capacity stability over cycling. To investigate this important difference, *ex-situ* TEM/EELS analyses, coupled with *ex-situ* XRD diffraction, were performed on both materials, along the first complete cycle. The preparation of the samples analyzed with the mentioned techniques is explained in detail in the experimental methods section. Firstly, a complete cycle of dilithium benzoquinone dioxime, illustrated in Figure II.11a, was analyzed: starting from the pristine materials (black point in Figure II.11b), the diffraction and microscopy analysis were also performed after the 1st charge (red point) and at the end of the first cycle (blue point). Before cycling, Li₂-BQD displays in X-ray

diffraction (Figure II.11c, black line) a broad contribution with no Bragg peaks, indicating an amorphous structure. The TEM investigation of this sample (Figure II.11e) showed a microstructure composed of particles either round with a range diameter of 5-25 nm or needle-like with a width range of 5-25 nm and a length higher than 100 nm arranged in hollow-like agglomerates. The SAED pattern (Figure II.11e, inset) exhibited a diffuse ring indicating an amorphous contribution, in agreement with the XRD data. The chemical characterization of the pristine sample obtained by EELS is reported in Figure II.11d for the lithium edge and Figure II.13d for the carbon and nitrogen edge. The broad and asymmetric contribution with a maximum at ~ 62 eV corresponds to the Li-Kedge (Figure II.11d, full black line) and will be used as reference spectrum for the lithiated phase. The white line with a sharp peak at 285 eV followed by a broad contribution at 290 eV is related to the C K-edge (Figure II.13d, black full line) π^* and σ^* state, respectively. A sharp peak followed by a broader contribution is also visible at 400 eV and corresponds to N K-edge (Figure II.13d, black full line). The presence of the nitrogen contribution confirmed the presence of active material in the investigated area.



Figure II.11 (a) Redox mechanism, (b) Potential-capacity profile, (c) ex-situ XRD powder patterns and (d) EELS spectra on the Li Kedge of Li2-BQD throughout the first cycle in half-cell vs. Li. TEM bright field images of Li2-BQD e) pristine, after f) half cycle and g) one full cycle in half-cell vs. Li. The associated diffraction patterns are in inset (and in Figure II.13a-c).

After the charging stage, with the oxidation of benzoquinone dioxime, two main Bragg peaks appeared at $2\theta = 15.5^{\circ}$ (020 reflection plane) and $2\theta = 25^{\circ}$ (011 reflection plane), indicating the appearance of crystalline phase (Figure II.11c, red line).

This crystalline phase, obtained from the electrochemical oxidation of benzoquinone dioxime to poly (1,4-phenyleneazine-N,N-dioxide), was included in the Pseudo-Voigt profile function refinement (Figure II.12). The refined unit cell was monoclinic $P2_1/n$ with cell parameters a = 6.3913(3) Å, b = 11.29544(11) Å, c = 3.71269(5) Å, $b = 92.523(4)^\circ$, and V = 267.770(14) with Bragg *R-Factor* = 0.146, $R_p = 1.30$, $R_{wp} = 1.79$ and $R_{exp} = 0.72$ reliability factors. All refined parameters confirms the electro-oxidation of dioxime benzoquinone involves the formation of 1,4-phenyleneazine-N,N-dioxide (PNND), resulting from the polymerization of Dinitrosobenzene, as previously reported by Gallo and collaborators[191]. Due to the elemental nature of the composition of PNND and the presence of light elements such as H and Li, further investigation with synchrotron and/or neutron measurements are recommended for full structural refinement.



Figure II.12 X-ray powder diffraction pattern of 1,4-phenyleneazine-N,N-dioxide (PNND) with experimental data in red, the calculated fit in black and the Y_{obs} - Y_{calc} in yellow. The blue ticks indicate Bragg peaks of the monoclinic P21/n with cell parameters a=6.3913(3) Å, b=11.29544(11, c=3.71269(5) Å and β =92.523(4)° which closely correlates with previously reported cell parameters[191].

The microstructure of the active material in the oxidized state (Figure II.11f) exhibited marked differences: the presence of large particles of irregular shape and a size ranging from 500 nm and up to 2.5 µm was observed. They form relatively large and homogeneous masses as highlighted

by white area according the (00-1) (red circle in Figure VII.4b and arrow in Figure VII.4c, Experimental part) in the dark field image. By investigating them closely, some small, rounded grains (~ 5-25 nm) can be distinguished and seem to be "glued" to the big particles. The SAED pattern obtained on the large particles present a dots pattern (see inset in Figure II.11f), which is characteristic of mono-crystalline sample and the indexation of the direction can be in accord with (00I) interplanar distance from PNND[191] (Figure II.13b). The chemical characterizations obtained by EELS showed the absence of contribution in the Li-Kedge (Figure II.11d, black dot line) and the presence of white lines in the C-Kedge and N-Kedge (Figure II.13d, black dot line): it confirmed that the crystalline area was the active material and the complete lithium deinsertion after the charge process.

After the discharge state (1 cycle complete), the Bragg peaks nearly disappeared, faint peaks were visible at $2\theta = 15.5^{\circ}$ and $2\theta = 25^{\circ}$, indicating the remaining presence of a crystalline structure. The microstructure after discharged sample showed relatively large, serrated and porous area: the diffraction pattern collected in this area exhibited defined rings, indicating a polycrystalline character. The dark field image obtained on the discharged sample highlighted the presence of small white areas (red arrows in Figure VII.4f, Experimental part), which diffracts according to the red circles (Figure VII.4e, Experimental part) and were distributed randomly. The inter-reticular distances determined from the diffraction pattern (see Figure II.13c) are $d_1 = 4.2$ Å, $d_2 = 3.0$ Å et $d_3 = 2.52$ Å. The chemical characterizations of discharged sample obtained by EELS showed the presence of a contribution in the Li-Kedge (Figure II.11d, black dash-dot line) similar to the pristine sample; moreover, the presence of white lines in the C-Kedge and N-Kedge (Figure II.13d, black dot line) confirmed the lithium re-intercalation in the active material during the discharged process. The analysis of small crystalline area showed a fast amorphization under the electron beam, as well as the characterization *via* EELS was performed in an average way (see experimental section).



Figure II.13 Selected Area Electron Diffraction pattern (SAED) of Li₂-BQD a) pristine, after b) half cycle and c) one full cycle. d) EELS spectra on the C K-edge and N K-edge of Li₂-BQD.

Characterization of PNND through *ex-situ* XRD and TEM/EELS analysis

The same analysis on the first complete cycle (Figure II.14a) was performed starting from chemically synthesized poly (1,4-phenyleneazine-N,N-dioxide) electrode. As in the previous paragraph, the analysis was carried out on the pristine materials (black point in Figure II.14b), then on the 1st charge (red point) and at the end of the first cycle (blue point). The TEM image, reported in Figure II.14e, showed significant differences compared to the Dinitrosobenzene obtained via electro-oxidation. The microstructure was formed of needle-like particles, which were arranged to form rectangular parallelepipeds, with lateral dimensions between of 150-200 nm and lengths ranging up to 1-2 microns. The SAED patterns recorded on PNND parallelepiped particles showed similar pattern (Figure II.14e, inset), with arranged dots corresponding to a monocrystalline phase and their indexation in agreement with the PNND in the zone axis [001] (Figure II.15a), indicating a preferential orientation growth. The EELS reference spectra (Figure II.14d and Figure II.15d, dark blue full line) showed the absence of lithium, consistent with the oxidized form that does not have lithium ions in the structure, and the presence of carbon and nitrogen confirming the presence of the active material; however, the π^* state at 285 eV in the C-K edge is less intense compared to what observed with Li₂-BQD. After discharging the sample, the complete amorphization of the crystalline structure was confirmed by X-ray diffraction, where the disappearance of the Bragg peaks was observed in the powder pattern (Figure II.14c, red line). The microstructure at the discharged state was evolved: the visible parallelepiped particles showed a smoother edge, but also other particles with 30-65 nm thick wall were observed in the image; the latter can be connected or not by a thinner area in the middle, as little like trivia monacha (Figure II.14f). The associated diffraction pattern is composed of diffuse rings indicating an amorphous structure which is coherent with the X-ray diagram. The EELS investigation on the Li-K edge (Figure II.14d, dark blue dot line) highlighted the presence of lithium, for which the shape and position of the main peaks fit with what observed for Li₂-BQD. The presence of active material was confirmed by the presence of carbon and nitrogen peaks (Figure II.15d, dark blue dot line).





Figure II.14 (a) Redox mechanism, (b) Potential-capacity profile, (c) ex-situ XRD powder patterns and (d) EELS spectra on the Li Kedge of PNND throughout the first cycle in half-cell vs. Li. TEM bright field images of PNND e) pristine, after f) half cycle and g) one full cycle in half-cell vs. Li. The associated diffraction patterns are in inset (and in Figure II.15a-c).

After one complete cycle, in the XRD powder pattern (Figure II.14c, blue line) were observed the same Bragg peaks already found in the pristine material: this result confirmed the reversibility of the redox reaction, with the full recovery of the starting crystalline structure, which is also identical to what obtained after the oxidation of dilithium benzoquinone dioxime. The microstructure did not change after the charge phase: the shape and size of active material particles is similar to the discharged state, with particles with 30-65 nm thick wall connected or not by a thinner area in the middle, as can be seen in Figure II.14g. The associated diffraction pattern (inset Figure II.14g and Figure II.15c) is composed of dots arranged in a motif indicating a crystalline sample: this result is coherent with the XRD measurement, but the signal is less intense

compared to the pristine sample. The indexation of diffraction peaks is compatible with PNND crystalline structure, but with the modification in the intensity distribution can indicate a slight change in the orientation of the crystal structure particles. Finally, the EELS analysis on the Li-K edge (Figure II.14d, dark blue dash-dot line) showed the absence of lithium, confirming the reversibility of the lithium de-/insertion redox process. As in the previous case, the presence of the active material in the investigated zone was confirmed by C-/N-K edges (Figure II.15d, dark blue dash-dot line).



Figure II.15 Selected Area Electron Diffraction pattern (SAED) of PNND a) pristine, after b) half cycle and c) one full cycle. d) EELS spectra on the C K-edge and N K-edge of DNB.

Coupled TEM/EELS and XRD analyzes on a complete cycle of Li₂-BQD and PNND showed several fundamental results to understanding the electrochemistry of these materials, reported for the first time for lithium batteries. From the results obtained, it is possible to confirm the complete reversibility of the lithium ion exchange process, as hypothesized by the computational study in the first part of the work. The observed evolution of the crystal structure, both via X-ray diffraction and TEM microscopy, showed the complete reversibility of the redox mechanism during the, starting from both Li₂-BQD and PNND compound; furthermore, EELS spectroscopy showed the complete and reversible de-/insertion of lithium ions in the structure both materials. Additionally, the analysis of materials microstructure through TEM microscopy may also explain the differences, in terms of electrochemical properties, between the two materials. Although the crystal structure remained unchanged for all states involving poly (1,4-phenyleneazine-N,Ndioxide), as confirmed by TEM diffraction and *ex-situ* XRD analysis, the microstructure was strongly different depending on the type of process (chemical or electrochemical) used to obtain the PNND. These differences in the microstructures can profoundly affect the lithium de-/insertion process during the cycle. The microstructure obtained through direct chemical synthesis is more orderly and oriented than the Dinitrosobenzene polymer obtained by electrochemistry, resulting in an improvement in the diffusion and insertion of lithium ions in the active material, with a consequent improvement in electrochemical performance, especially for regarding retention of capacity.

TEM/EELS investigation of Li₂-BQD and PNND after 20 cycles

This work paves the way for future developments of dioxime-based materials for energy storage. The proven reversibility of the redox mechanism, together with the high specific capacity in the first cycles and the versatile chemical structure, which allows the fine-tuning of the electrochemical properties, make these materials promising candidates for the development of green organic electrodes. However, the galvanostatic tests also showed a marked loss of capacity in the first cycles for both materials, which then stabilized starting from the 20th cycle.

In order to preliminary investigate this phenomenon, TEM analysis was performed for the two electrodes after 20 charge and discharge cycles; the intention is to establish some hypotheses about the capacity loss and the difference in capacity retention observed between Li₂-BQD and DNB, which can be further investigated in future works. The TEM images of the benzoquinone dioxime electrode after 20 complete cycles (Figure II.16a), showed a microstructure composed of irregularly shaped particles, characterized by marked porosity, since the color scale in the particles is inhomogeneous (one of these areas is surrounded by the dashed line in Figure II.16a). Furthermore, the presence of thin sheets was also observed, as highlighted by the black arrow in Figure II.16a. The associated diffraction pattern in negative mode (Figure II.16b) is composed of a defined weak ring indicating the polycrystalline nature of this microstructure (irregular particles + thin sheets). The inter-lattice distances d₁ and d₂ are respectively approximately 4.4 Å and 2.6 Å, but the information was insufficient to obtain the adequate indexation.

About the PNND-based electrode after 20 cycles (Figure II.16c,d), it was also composed of irregular shape particles which also was characterized by porous structure. In the case of PNND 20 cycles, the presence of the thin sheets and their associated diffraction pattern was not observed; the diffraction showed diffuse rings indicating the amorphous nature of the material. A first hypothesis that can be formulated is that the phenomenon of amorphization of the PNND, deduced from the disappearance of the diffraction pattern, could partially hinder the diffusion of ions and electrons through the active material, leading to a decrease in the specific capacity. Furthermore, the EELS analysis of Li₂-BQD after 20 cycles shows the presence of phosphorus, lithium, carbon, oxygen and fluorine relative to the areas where the polycrystalline thin sheets are present: these elements, deriving from the electrolytic salt, may indicate the presence of derivatives from the degradation of electrolyte. Indeed, these polycrystalline structures and their

relative chemical composition were not detected in the poly (1,4-phenyleneazine-N,N-dioxide) electrode: it is possible to hypothesize a lower electrolyte degradation in the PNND case, which could explain the greater specific capacity exhibited by the latter.



Figure II.16 a) TEM bright field images and b) associated diffraction patterns of Li₂-BQD after 20 cycles; c) TEM bright field images and d) associated diffraction patterns of PNND after 20 cycles.

To summarize, the oxidized form (poly (1,4-phenyleneazine-N,N-dioxide)) showed an amorphization of the crystalline structure, which could have an impact on the ionic and electronic conductivity of the two materials, with a consequent loss of electrochemical performance. Moreover, in the case of the Li₂-BQD electrode it is possible to hypothesize a marked degradation of the electrolyte, not observed in the DNB, which would lead to a further loss of capacity, thus explaining the difference in terms of capacity retention observed between the two materials. As a future perspective, it will be possible first of all to study the possible degradation products observed with TEM, through *ex-situ* XPS, Raman or FTIR analysis, to understand if these species derive from the electrolyte or from side-reactions involving the active material: this will allow a rational design of the salt and the electrolytic solvent, as well as of the molecular structure of the
active material; this last approach can also lead to an improvement of the electrochemical properties, especially as regards the redox potential, in order to obtain performances comparable to today's inorganic materials.

Conclusions

In this chapter, a comprehensive study of the electrochemistry of dilithium benzoquinone dioxime (Li₂-BQD), and its oxidized form Dinitrosobenzene (DNB), was reported.

Given the novelty of the investigated material, as first step, a computational study was performed to confirm the redox mechanism for the Li₂-BQD/DNB couple; the simulation allowed to validate the proposed redox mechanism through the identification of the intercalation sites and the aromatic features evolution, but also to elucidate in deeper detail the relative role played by the 6MR and the oxime-nitrous group during the redox process. This latter aspect was enabled thanks to the evaluation of the energy partition tool, which allowed to estimate the variation of the energy quantity for these various molecular groups upon the electrochemical process. The distinct features between these systems and those involving p-BQ were established at the molecular state, thus highlighting the redox mechanism/gaps differentiation between these classes of systems.

Afterward, the synthesis and characterization of the benzoquinone dioxime were performed, both in the lithiated form (Li_2 -BQD) and in the delithiated form (DNB). Galvanostatic tests in half-cell vs. metallic Li showed an average redox potential of 3.0 V vs. Li⁺/Li, with an excellent specific capacity in the first cycle, measured in 277 and 313 mAh g⁻¹ for Li₂-BQD and DNB, respectively; however, both derivatives exhibited low capacity retention low over long cycling, with only 11% and 23% of capacity after 100 cycles.

Furthermore, TEM analysis with electron energy loss spectroscopy (EELS) was coupled with *exsitu* XRD to experimentally validate the reversibility of de-/insertion of lithium ions process. The results of the EELS spectroscopy confirmed the complete reversibility of the lithium de-/insertion process in both the active materials, in accordance with the evolution of crystal structure observed in both XRD/TEM diffraction patterns. Moreover, the TEM images showed a marked difference in microstructure between dinitrosobenzene synthesized chemically or electrochemically (by electrooxidation of Li₂-BQD). A more oriented microstructure was observed in chemically synthesized dinitrosobenzene, preserved for the entire first cycle, which leads to

Unraveling the redox mechanism and material microstructure of dilithium benzoquinone dioxime as new electroactive n-type positive material

better ionic and electronic conductivity of the active material, with consequent better electrochemical performances.

This work has provided a detailed description of the redox process, confirming its complete reversibility and reporting the main electrochemical properties of the dioxime derivatives: it paves the way for future development of benzoquinone dioxime as new eco-sustainable positive materials for lithium batteries.

As a future prospect, a preliminary TEM/EELS analysis of Li₂-BQD and DNB (/PDNN) was performed after 20 charge and discharge cycles, to understand the possible causes of low capacity retention. TEM images showed the amorphization of DNB along cycling, as well as a marked formation of salts originating from the degradation of the electrolyte in the case of the Li₂-BQD electrode. A better understanding of these two phenomena, for now only hypothesized as causes of the loss of capacity, could lead in future works to a rational design of both electrolyte and active material, to improve the (electro-)chemical/physical properties of dioxime-based materials.

Chapter III. Development of Nsubstituted Carbazole derivate salts as new *p*-type positive materials

Introduction

Whilst cation insertion mechanism is the most known one, organic materials offer the possibility to also use anions as charge carriers. In that case, electrode material is based on "*p*-type" molecules, which can be oxidized reversibly into a radical cation, inducing the migration and insertion of anion to balance the charge. One of the main advantage of p-type materials is the high insertion potential: Nitroxide[162,192,193], aromatic amines, such as phenothiazine and phenoxazine[104,194] and conjugates amines [195,196] are characterized by an redox potential higher than 3.5V vs. Li. In recent years, several reports on a new *p*-type functional group, based on carbazole moieties, have also been published in the literature. In 2012, Yao and coworkers studied polyvinyl carbazole (PVK) as a high potential positive material[118]. The charge/discharge curves showed a high average potential, around 3.7 V vs. Li, among the highest for organic molecules, with a reversible capacity of 125 mAh g⁻¹. Despite their interesting electrochemical properties, PVK materials were affected by a low Coulombic efficiency, due to parasitic reactions that takes place during the redox processes.

In recent years, Dai *et al* reported a combined computational/experimental study on the effect of the phenyl group as the N-substituent of carbazole, highlighting many advantages in terms of electronic structure [122]. From first principles, the authors linked the reversibility of the electron exchange process with the nature of the substituent of the nitrogen atom. An electron-withdrawing substituent can stabilize the structure with a consequent increase of redox potential of carbazole.

The molecular design impacts drastically the overall electrochemical performances of carbazole derivates. With this in mind, a new set of carbazole-based single molecules for energy storage applications is proposed. Various molecular structures have been synthesized following two strategies, to improve electrochemical performance in terms of redox potential and specific capacity (Figure III.1). The first strategy involves the adjunction of an insoluble fragment directly on the molecule backbone (Approach 1). Even if in some cases the presence of this type of fragment is not sufficient to completely prevent the solubility,[140] this strategy proved to be effective with various redox center such as quinones or phenothiazines.[104,197] A second less developed approach is based on the formation of well-defined oligomers like dimers or trimers (Approach 2). This is exemplified with quinones derivatives[198,199] and extend recently to phenothiazine/phenoxazine,[194] this strategy is applied for the first time for carbazole.



Figure III.1 Synthesized of molecular carbazole derivatives

Synthesis of and characterization of LiCZA, Li-4-BACZ and DCZP

Three different carbazole derivatives were synthesized from simple carbazole using insoluble fragment incorporation or by dimerization (Figure III.2). Lithium 2-(9H-Carbazol-9-yl)acetate derivate (LiCZA) was synthesized to obtain a salt insoluble in the electrolyte without increasing the molecular mass too much (230.94 g/mol), and to maximize the theoretical specific capacity of the active material (116 mAh g⁻¹). Note that in the present case, the electron donor nature of the acetate group should induce a slight decreasing of the insertion potential. On the contrary, the derivate Lithium 4-(9H-carbazol-9-yl)benzoate (Li-4-BACZ) presented an electron-withdrawing substituent, the lithium benzoate group, which could provoke an enhancement of the insertion potential; however, this group strongly increased the molecular mass (293.24 g/mol), with a consequent decrease in the theoretical capacity of the molecule (91 mAh g⁻¹). In order to combine the positive effects of the electron-withdrawing benzene group, without losing specific capacity, a dimer of carbazole was also designed and synthesized, 1,4-Di(9H-carbazol-9-yl) benzene (DCZP), to achieve a two-electron active molecule, with a higher specific capacity in relation with its weight (408.5 g/mol, for a C_{theo}=131 mAh g⁻¹).



Figure III.2 Synthetic route of LiCZA, Li-4-BACZ and DCZP.

Firstly, LiCZA was synthesized *via* N-substitution of carbazole with the acetate group, followed by the formation of a lithium salt, in order to obtain a 'small' carbazole derivate insoluble in carbonate-based liquid electrolytes. CZA was obtained by reacting carbazole with bromoacetic acid (Figure III.2), from an adapted synthetic procedure previously described.[200,201] The molecular structure of the carboxylic acid was confirmed by the NMR spectrum, which exhibits one peak at 12.99 ppm (s, 1H) due to the presence of -COOH hydrogen, and another peak at 5.23 ppm (s, 2H) corresponding to $-CH_2$ - of the acetate group (Figure VII.5 Experimental Part); furthermore, the infrared spectrum showed the disappearance of N-H stretching band at 3418 cm⁻¹ and N-H bending at 1600 cm⁻¹. Two bands due to carboxylic acid appeared, at 3051 cm⁻¹ (O-H stretching) and at 1720 cm⁻¹, due to C=O stretching.

The lithium salt is then obtained by the action of lithium hydroxide on carboxylic acid to give quantitatively the desired product. The complete lithiation is confirmed by the disappearance of the peak at 13 ppm of carboxylic acid proton, while the other peaks shifted upfield because of the presence of lithium ion. For example, -CH₂- peaks shifted from 5.23 to 4.78 ppm, due to its proximity with lithium atom (Figure VII.6). FTIR spectra show a broad peak at 3600-3300 cm⁻¹ due to Li-O stretching and a shift to 1605 cm⁻¹ from C=O stretching (Figure III.3a).

The benzoate derivative (Li-4-BACZ) was obtained by coupling first carbazole with methyl-4iodobenzoate to form 4-MBACZ. The synthesis of this intermediate was confirmed by NMR analysis, which showed the appearance of several peaks at 8.33 ppm (s, 1H), 8.30 ppm (s, 1H), 7.70 ppm (s, 1H) and 7.68 ppm (s, 1H), linked to the phenolic ring, and one singlet peak at 4.02 (s, 3H), due to the presence of methyl from ester group (Figure VII.7). Deprotection of the ester to form carboxylic acid is evidenced by the disappearance of methyl group signal at 3.92 ppm and the appearance of carboxylic acid peak at 13.17 ppm (Figure VII.8). Moreover, all the other peaks were shifted downfield by the presence of the carboxyl group. In the IR spectrum, both O-H and C=O stretching from the carboxylic group were founded, at 3026 and 1697 cm⁻¹ respectively (Figure III.3b). Lithium salt formation was realized by reacting the acid with lithium hydroxide, giving quantitatively Li-4-BACZ. This was confirmed by the disappearance of the peak at 13.17 ppm (Figure VII.9), after the replacement of hydrogen with lithium ion and the strong shift of the carbonyl band in FTIR (Figure III.3b). Furthermore, the lithium content in both LiCZA and Li-4-BACZ was measured using atomic absorption spectroscopy (AAS). The accurate chemical formula of the two compounds was Li_{1.03±0.05}-CZA and Li_{1.05±0.04}-4-BACZ.

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The carbazole dimer (DCZP) was synthesized through the modified Ulmann coupling reaction.[202] This reaction uses copper as a coupling catalyst, in the presence of 1,10phenantroline and a base (K_2CO_3). To obtain the DCZP, two equivalents of carbazole were reacted with dibromo benzene for 3 days at reflux and the reaction controlled with TLC until complete formation of the dimer. DCZP synthesis was confirmed by both NMR and IR spectra. On the NMR spectra, a peak at 7.86 ppm (4H) due to the benzene's hydrogens was observed (Figure VII.10). In the IR spectrum, the disappearance of N-H band at 3400 cm⁻¹ together with the appearance of C-C stretching from phenyl group appeared at 1514 cm⁻¹, and the two strong peaks at 750 and 723 cm⁻¹ characteristics of disubstituted phenyl ring (C-H bending), also confirmed the dimer formation (Figure III.3c). The thermal stability of carbazole derivates was evaluated via thermogravimetric analysis (TGA, Figure III.3d). As expected, lithium carboxylate derivatives exhibit good thermal stability with starting temperature decomposition of 393 °C and 417 °C respectively for Li-4-BACZ and LiCZA. Very first mass loss is attributed to residual solvent and have been remove by extra drying step (120°C under vacuum overnight before being transferred in the glovebox. TGA showed that the dimer is relatively less stable with a weight loss of about 2.95% between 240°C and 300 °C and a complete loss of the mass up to ca. 430 °C were observed, which is consistent with the absence of ionic fragment. Moreover, the plateau observed from room temperature to more than 200°C attests the absence of solvent molecules trapped in the molecular structure (solvation degree) coming from the synthesis, which is important for electrochemical tests.



Figure III.3 Comparison between FT-IR spectra of carboxylic acid (light color) and corresponding lithium salt (full color) for a) carbazole acetate and b) carbazole benzoate. c) Comparison between pristine carbazole (light red curve) and carbazole dimer (red curve) using transmission FTIR. d) Thermal analysis measurement (TGA) of LiCZA (green curve), Li-4-BACZ (blue curve) and DCZP (red curve) obtained under argon flow at a heating rate of 10 °C min⁻¹.

Crystals of DCZP were grown from slow evaporation of Cyclohexane/DCM solution in 10/1 ratio. Carbazole dimer was studied by single crystal diffraction. It crystallized in space group *Pbca* with cell constants a = 8.2206(14) Å, b = 16.372(3) Å, and c = 31.591(6) Å and angles $\alpha = \beta = \gamma = 90^{\circ}$, that perfectly match with those obtained from previous X-ray diffraction characterization.[203–205]. The structure is built from 8 molecules of DCZP in the unit cell (*Z*=8) with 30 independent carbon atoms (Figure III.4a). According with these parameters, the average C(benzene)-N(carbazole) bond length was found to be 1.410(3) Å, slightly smaller than the standard carbon-nitrogen bond length (1.47-1.50 Å)[206]. This suggests that the carbazole-phenyl bond energy is bigger than usual. Furthermore, the torsion angle between carbazole and benzene is 95.38(10)° from one side and 122.74(12)° for the other side: it means that DCZP dimer is characterized by a highly twisted structure, where each component is in different planes resulting in an array with one molecule per asymmetric unit (Figure III.4b).



Figure III.4 Crystal packing of DCZP, down the a) a-axis and b) representation of one dimer showing the twisted carbazole moieties toward the benzene. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group Pbca, with Z=8 for the formula unit, $C_{30}H_{20}N_2$. Relevant crystallographic parameters are available in the Experimental Part (Table VII.2 and Table VII.3).

Scanning electron microscopy (SEM) characterization of simple carbazole and its derivates revealed a clear distinction between their shape and size. CZ appeared as irregular granules and varied in size from ~10 to 30 μ m (Figure III.5a). The first synthesized derivate, LiCZA, consisted of clusters of slender parallelepipeds with lateral dimensions between of 2 to 5 μ m and lengths ranging up to several tens of microns (Figure III.5b). Li-4-BACZ and DCZP derivates differed from the LiCZA, by showing smaller length but a larger lateral dimension varying between 10 to 20 mm (Figure III.5c-d) and irregular aggregates of spheres and shards on their surfaces.



Figure III.5 Scanning electron microscope images of carbazole and their N-substituted derivates and salts: (a) carbazole particles with granular shape, (b) LiCZA clusters of slender parallelepipeds, (c) Li-4-BACZ) and (d) DCZP parallelepiped shapes with irregular aggregates of spheres on the surface.

Electrochemical characterization of LiCZA and Li-4-BACZ

The electrochemical performances of synthesized compounds were first studied using Swagelok[®]-type half-cells vs. lithium metal disk, cycled at C/5 rate in the potential range 4.2-2.7 V, using two different battery grade electrolytes, either 1 M LiPF₆ in EC/DMC (50:50) or 1 M LiClO₄ in propylene carbonate (PC). All the electrodes were prepared using an active material/conductive carbon (KJ600) ratio of 70:30, using the procedure reported in the Experimental part (Electrode preparation for Swagelok-type cell). The galvanostatic profiles of all carbazole derivatives do not show a well-defined plateau, making localization of the average redox potential more difficult. To overcome this problem, the oxidation and reduction potentials were calcu- lated by integrating the area under the curve (expressed in mWh/g) divided by the specific capacity (mAh/g). The overall mean potential was calculated as the arithmetic mean of the oxidation and reduction potentials, calculated as above.

Simple Carbazole without any modification was first studied and used as a reference: it showed an average insertion potential of 3.79 V vs. Li⁺/Li, higher than various organic systems, such as phenothiazine[109,207] and nitroxide derivates[195,208]. Despite the high redox potential, a poor coulombic efficiency during the first cycle and low-capacity retention along cycling have been observed. The first oxidation showed a specific capacity of 351 mAh g⁻¹, with only 94 mAh g⁻¹ capacity after the reduction, for a 27% of reversibility during the first cycle (Figure III.6a). The low coulombic efficiency could originate from carbazole electro-polymerization via N-N or side-ring bond, a side-reaction reported by Karon and co-worker[209]. Secondly, carbazole also showed poor capacity retention with only 74 mAh g⁻¹ of reversible capacity after 50 cycles (Figure III.6b): this capacity fading can be explained by the dissolution of the active material in the electrolyte. In order to improve the electrochemical properties, a test using LiClO₄ in propylene carbonate electrolyte was performed: as already reported in literature, the electrolyte salt and the solvent can deeply affect the electrochemical behavior[104] (Figure III.6c). However, no significant improvements in electrochemical properties were observed, since capacity retention was found to be as low as in the case of the LP30, with approximately 70 mAh g⁻¹ after 50 cycles (Figure III.6d), which corresponds to 46% of the theoretical capacity for the carbazole (based on 1-electron exchange). There is a little gain in terms of coulombic efficiency (35% of reversible capacity in the first cycle), but not enough to be to suggest that the parasitic reactions have been suppressed.



Figure III.6 (a) Potential-capacity profile of 1st, 2nd and 50th cycle and (b) corresponding evolution of the specific capacity as a function of cycle number of Carbazole electrode (70:30 AM/KJ600) galvanostatically cycled with LP30 as electrolyte. (c) Potential-capacity profile of 1st, 2nd and 50th cycle and (d) corresponding evolution of the specific capacity as a function of cycle number of Carbazole electrode (70:30 AM/KJ600) galvanostatically cycled with LP30.

To overcome the solubility issue observed in the case of simple carbazole, two new molecules were designed and synthesized, both N-substituted with a carboxylate group. The first molecule synthesized was Lithium 2-(9H-Carbazol-9-yl)acetate (LiCZA), where the methyl group - CH₂- of the acetate has an electron donating nature towards the carbazole moiety (a slight decrease of redox potential is expected). The second molecule, Lithium 4-(9H-carbazol-9-yl)benzoate (Li-4-BACZ), has a benzoate substituent on nitrogen atom, acting as an electro-attractor (a slight increase of the redox potential is expected). In both molecules, the lithium carboxylate group is used to avoid dissolution in the organic solvent of the electrolyte, while the properties of the two substituents groups can be used to tune the redox potential. The galvanostatic curve of the LiCZA is characterized by a solid-solution type curve without a well-defined plateau, with an average redox potential around 3.65 V vs. Li (Figure III.7a), lower than that observed with unsubstituted Carbazole. The average potential of carbazole substitued with benzoate counterpart is markedly higher, located at about 3.86 V (Figure III.8a). This difference

of 210 mV could be explained by the difference between the substituent's nature. In the case of LiCZA, the inductive electron-donating effect of the -CH₂- group of the acetate group leads to a decrease in the redox potential, while the benzoate group of Li-4-BACZ, with its electron withdrawing property, can better delocalize the electronic charge with a consequent stabilization of the free radical state, as showed in computational calculations of Dai *et al*,[122]. This result confirms what was reported by the previous computational calculations and follows the same trend than quinone-based system,[210] the redox process potential can be increased with electron-withdrawing substituent groups. Interestingly, both compounds show very stable performances over cycling, with a notable difference in terms of specific capacity, both in absolute value and in relation to their theoretical capacity (C_{theo}). In the case of the LiCZA, the specific capacity observed was 37 mAh g⁻¹ after 50 cycles at C/5 rate (with a CE of 97%, Figure III.7b), which correspond only to the 32% of the theoretical capacity C_{theo}= 116 mAh g⁻¹).



Figure III.7 (a) Potential-capacity profile of 1st, 2nd and 50th cycle and (b) corresponding evolution of the specific capacity as a function of cycle number of **LiCZA** electrode (70:30 AM/KJ600) galvanostatically cycled with LP30 as electrolyte. (c) Potential-capacity profile of 1st, 2nd and 50th cycle and (d) corresponding evolution of the specific capacity as a function of cycle number of Carbazole electrode (70:30 AM/KJ600) galvanostatically cycled with LP30.

Li-4-BACZ showed a capacity of 45 mAh g^{-1} after same number of cycles and C-rate, corresponding to half of its theoretical capacity (91 mAh g^{-1}), with a coulombic efficiency of 98%

(Figure III.8b). These results indicate that carbazole benzoate has a better ability to exchange PF₆⁻ anions, compared with the acetate counterpart, and can be explained by a better protection of the redox site (the nitrogen atom of carbazole moiety) from the solvent of electrolyte[122]. The higher capacity, combined with the higher potential, results in the greater ability of benzoate derivative to store electrochemical energy compared to the N-acetate derivate. As in the case of Carbazole, also the two carbazole derivates were investigated using LiClO₄ in propylene carbonate (Figure III.7c, d and Figure III.8c, d). Using the perchlorate electrolyte, no major modification in the redox potential was observed both in the case of LiCZA (from 3.59 to 3.65 V, Figure III.7c) and Li-4-BACZ, where the potential is still 3.79 V (Figure III.8c). For LiCZA the slight increase in redox potential is accompanied by a decrease in specific capacity, which drops from 38 to 28 mAh g⁻¹, after 50 cycles (Figure III.7d), while in the case of benzoate, the reversible capacity after 50 cycle is 50 mAh g⁻¹, greater than previously observed with LP30 electrolyte (Figure III.8d). This result balances the loss in terms of insertion potential, but the overall performances of the two active materials have not markedly improved using lithium perchlorate in propylene carbonate as electrolyte.



Figure III.8 (a) Potential-capacity profile of 1st, 2nd and 50th cycle and (b) corresponding evolution of the specific capacity as a function of cycle number of **Li-4-BACZ** electrode (70:30 AM/KJ600) galvanostatically cycled with LP30 as electrolyte. (c) Potential-capacity profile of 1st, 2nd and 50th cycle and (d) corresponding evolution of the specific capacity as a function of cycle number of Carbazole electrode (70:30 AM/KJ600) galvanostatically cycled with LP30.

The N-substitution of carbazole using carboxylate-based group has shown several advantages over unsubstituted carbazole. Indeed, the addition of a carboxylate group improved the electrode stability on cycling, preventing the dissolution of the electroactive material in the electrolyte. To confirm this phenomenon, the three carbazole-based molecule were added in LP30. As shown in Figure III.9, unsubstituted carbazole showed a consistent dissolution in the electrolyte solution, while LICZA and Li-4-BACZ were insoluble in the electrolyte.



Figure III.9 Solubility test in LP30 performed for Carbazole (left), LiCZA (center) and Li-4-BACZ (right).

Furthermore, the substitution with an electron-withdrawing group, as in the case of Li-4-BACZ, stabilizes the free radical state of carbazole and leads to an increase in the insertion potential, with a consequent increase of the energy density. This result was not observed in the case of LiCZA, where the electro donating nature of the acetate group led instead, to a decrease in the potential. However, the addition of a functional group to carbazole has a non-negligible drawback, it increases the molecular weight without an increase in the number of electrons that can be stored, so the theoretical capacity decreases.

Electrochemical characterization of DCZP

To keep the benefits of benzene substituents without losing specific capacity due to the increase in the molecular weight, a new design strategy was employed. Instead of using an electro-inactive group as a substituent, we opted for the design and synthesis of a carbazole dimer, di(carbazole-9-yl)phenylene (DCZP), where the two carbazole moieties are connected by a benzene ring in *para* position. This new molecule can theoretically store two electrons, one per carbazole unit, and the bridge consisting of an aromatic ring allows the stabilization of the oxidized state, as already observed in the case of benzoate derivative. As a preliminary study, the electrochemical properties of the DCZP dimer were studied using the same conditions as the previous molecular materials (Figure III.10). The carbazole dimer DCZP was tested using a half-cell vs Li, with the two different electrolytes, LP30 and 1M LiClO4 in PC, and a potential window of 4.2-2.7 V at C/5 rate (Figure III.10a and b). The dimer showed an average redox potential of 3.87 V with LP30 electrolyte, with a specific capacity of 45 mAh g⁻¹ after 50 cycles, whilst in the case of the LiClO₄ electrolyte the potential drops down to 3.5 V. This potential difference, more marked than in the cases of LiCZA and Li-4-BACZ derivatives, confirms a better insertion of the PF₆⁻ anion of LP30 in comparison with ClO₄⁻. In addition, the specific capacity with lithium perchlorate salt is also lower (36 mAh g⁻¹), for an overall lower energy density. To improve the electrochemical properties, further tests was carried out using the $LiPF_6$ salt in propylene carbonate solvent (PC), as this solvent was reported in the literature to be a better ionic carrier compared to EC/DMC 50:50 mixture of LP30.[104] An improvement with LiPF₆ in PC was observed both in the insertion potential (3.9V) and in reversible capacity, quantified in 54 mAh g⁻¹ after 50 cycles, with high coulombic efficiency (Figure III.10c). Therefore, LiPF₆ in PC proved to be the best electrolyte in relation to LP30 and LiClO₄ in PC used in the previous electrochemical tests. A low coulombic efficiency was also observed with the dimer in the first cycle. As discussed in the previous examples, this difference between charge and discharge capacity is attributable to electro-polymerization of carbazole moieties. To confirm that the dimer is also subject to this phenomenon, the pristine material and the DCZP electrode after a complete cycle were analyzed using infrared spectroscopy (Figure III.10d). For the single-molecule dimer, two peaks at 744 and 724 cm⁻¹ were observed, which are due to the disubstituted benzene ring in carbazole. The IR spectrum after a complete cycle (performed in a half cell vs. Li with LiClO₄ in PC electrolyte, 4.2-2.7 V at C/5), showed the disappearance of both the aforementioned peaks and the appearance of a very intense band at 799 cm⁻¹ which can be attributed to the trisubstituted benzene ring, in agreement with what was reported by Zhang[211]. These observations associated with the complete amorphization of the material during the first cycle (Figure VII.11) confirm the formation of polymeric DCZP during the first cycle and so corresponding low coulombic efficiency. [212,213].



Figure III.10 a) Galvanostatic profile of 1st, 2nd and 50th cycle of DCZP electrode (70:30 AM/KJ600), potential window of 4.2-2.7 V with (a) LP30, (b) 1M LiClO4 in PC and (c) 1M LiPF6 in PC at C/5 rate. (d) FTIR spectra of pristine DCZP (blue curve) and DCZP electrode after 1 cycle (red curve) with a potential window of 4.2-2.7 V with LiClO4 in PC.

The reversible capacity obtained in the preliminary tests at 54 mAh g⁻¹ with LiPF₆ in PC electrolyte was far from the theoretical capacity of a two-electron mechanism, only 41% of the theoretical capacity (C^{theo}=131 mAh g⁻¹). This difference can be explained by the exchange of only one electron during the redox process, as showed by Xu and coauthors[123]. To investigate this phenomenon, further electrochemical tests were carried out using a slightly larger potential range (4.5-2.5 V) in a half cell *versus* lithium, with LiPF₆ in PC as electrolyte (Figure III.11a). During the first cycle, a better reversibility was observed, 42% of compared to >70% measured in the previous cases. Furthermore, a strong increase in discharge capacity (110 mAh g⁻¹ in the first discharge) was observed, more than double compared with the cycling in the range 4.2-2.7 V. The reversible capacity turns out to be the 78% of C^{theo} calculated on two-electrons exchanged. Based on this result, it is possible to assume that in this potential range, both electrons are reversibly exchanged. Moreover, the retained specific capacity after 50 cycles was 104 mAh g⁻¹ with a coulombic efficiency of 95%, the loss is negligible compared to single carbazole (Figure III.11b).

The rate capability of the dimer was then investigated using LiPF₆/PC electrolyte (Figure III.11c). A reversible capacity of 103 mAh g⁻¹ was obtained at C/5, which decreases to 90 mAh g⁻¹ at C/2 and 80 mAh g⁻¹ at C-rate (1-hour charge) making this material quite interesting. At higher C-rate, the capacity drop is important, with values of 58 mAh g⁻¹ and 16 mAh g⁻¹ respectively at 2C and 5C, suggesting than a classical conductivity limitation appears.



Figure III.11 (a) Potential-composition profile of 1st, 2nd and 50th cycle of DCZP electrode (70:30 AM/KJ600) galvanostatically cycled over a potential window range of 4.5-2.5 V using 1M LiPF6 in PC as electrolyte and (b) corresponding evolution of the specific capacity as a function of cycle number and associated coulombic efficiency at C/5 rate.(c) Rate capability test performed at C/5, C/2, C, 2C and 5C rate using same electrolyte and potential window.

Post-mortem investigation of DCZP-based electrode

In order to go further, an anion storage mechanism in DCZP electrode was explored using *ex-situ* EDX and *ex-situ* FTIR analysis on the electrodes at different states of charge. The EDX analyses enabled the detection and quantification of the phosphorus (P) and fluorine (F), components of PF₆⁻ anions, at different oxidation states of DCZP. The results of the EDX measurements during the first cycle showed the prominent presence of P and F in the electrode after the first oxidation but their absence after the reduction, proving the intercalation and deintercalation of anion PF₆⁻ , respectively, into and from the DCZP cathode (Figure III.12a,b). Furthermore, the acquired EDX spectra and maps showed the same qualitative distribution patterns of the elements across the surface and in the cross-section areas of electrodes, indicating a uniform insertion of the salts within the bulk of the electrode (Figure III.13b-d). This result agrees with our SEM observation on the uniform dispersity of the constituent particles throughout the electrodes (Figure III.13a). The quantification of elemental distribution in the electrodes showed a similar pattern during the charge and discharge of the first and second cycles, indicating a complete reversibility of the process of insertion/disinsertion of the anion in this organic-based electrode. Table III.1 presents the results of quantitative elemental analyses in percentage of elemental concentration in weight (wt.%) for the two first cycles.



Figure III.12 (a) EDX spectroscopy of the DCZP electrodes on their cross sections during the first two cycles at C/5 rate. Spectra showing changes in the concentration of the detected elements indicated by the intensity of their corresponding peaks during charging and discharging. (b) Corresponding galvanostatic profile of DCZP in half-cell vs. Li. (c) CIO_4 - de-/insertion in DCZP followed by ex-situ FTIR spectroscopy.

The second method used to study the anion intercalation mechanism (ClO₄⁻ in this case) was an *ex-situ* Infrared spectroscopy (Figure III.12c). As in the case of EDX, cycling of DCZP electrode was stopped at different charge states during first cycle (1st oxidation and 1st reduction) and compared with pristine material. The corresponding Swagelok^ô half-cells were disassembled in an argon-filled glovebox to avoid any side reaction. The electrode was recovered and washed with dimethyl carbonate, to remove LiClO₄ salt, and dried under vacuum at 80 °C for 4 hours. The electrode powder was then mixed with KBr (spectroscopic grade) to prepare FTIR pellet in an argon filled glovebox. Contrary to the previous case, LiClO₄ electrolyte was used in this analysis, because the latter is more easily detected with IR spectroscopy than LiPF₆.[153] After the first oxidation of the electrode, two new peaks compared to the pristine material, at 1044 and 623 cm⁻¹ were observed, both assigned to the ClO₄⁻ anion. After the reduction, where the ClO₄⁻ deintercalation process takes place, the complete disappearance of the peak at 623 cm⁻¹ was observed, whilst the peak at 1044 cm⁻¹, intense after the oxidation, was reduced in intensity, confirming that a small amount of anion may remain embedded in the active material (maybe in association with carbazole polymer), which partly explains the low coulombic efficiency in the first cycle.



Figure III.13 a) SEM image of cross-section of DCZP electrode after the first charge; EDX maps of (b) F-kα and (c) P-kα recorded from the same cross-section in figure (a); (d) EDX spectrum acquired from the scanned area on the cross-section.

	1st cycle		2 nd cycle	
Element	oxidation	reduction	oxidation	reduction
	Wt% (σ)	Wt% (σ)	Wt% (σ)	Wt% (σ)
С	57.66 (0.24)	93.2	78.29 (0.14)	90.3 (0.02)
Ν	3.37 (0.23)	0.8	1,02 (0.02)	0.2 (0.01)
0	10.17 (0.10)	4.3	5.11 (0.06)	6.3 (0.02)
F	14.82 (0.10)	0.9	11.22 (0.06)	1.21 (0.01)
Na	2.93 (0.03)	0.1	0.14 (0.01)	0.3 (0.00)
AI	3.58 (0.02)	0.2	1.61 (0.04)	0.3 (0.00)
Si	1.95 (0.02)	0.5	0,14 (0.01)	1.06 (0.01)
Р	5.50 (0.03)	0.2	2.95 (0.03)	0.3 (0.00)
Total:	100.00	100.00	100.00	100.00

Table III.1 EDX quantitative elemental analyses of a DCZP electrode after 1^{st} oxidation, 1^{st} reduction, 2^{nd} oxidation and 2^{nd} reduction (percentage of elemental concentration in weight (Wt%) and corresponding standard deviation of calculated values (σ))

Conclusions

In this study, insoluble molecular carbazole derivatives have been proposed and studied as p-type positive materials for electrochemical energy storage. A reliable design and synthetic route by different N-substitution, either adjunction of an insoluble fragment (i.e. lithium carboxylate) or dimerization of the redox center, were carried out to counter the solubility phenomenon. The electrochemical properties of carboxylate-containing molecules have been evaluated and are comparable to simple carbazole. The insolubilizing effect of the two different N-substituents on the solubility is clear, together with the influence on the anion insertion/disinsertion process: depending on nature of the substituent, an electronic effect could deeply influence the redox potential observed in the electrochemical tests. The dimerization strategy revealed to be more interesting to improve carbazole reactivity. Thanks to a rational design, a carbazole dimer able of exchanging two electrons was studied. The dimer showed better performances in term of redox potential, specific capacity and rate capability especially using LP30 as electrolyte. Ex-situ EXD and ex-situ FTIR were also performed to study the intercalation mechanism for DCZP and confirm the complete reversibility of anion intercalation in the active material. This study thus reveals that active material performances can be tuned according by using a good combination between molecular structure of the material and electrolyte composition.

However, all three derivatives showed an electro-polymerization phenomenon, confirmed by both ex-situ FTIR and *operando* XRD, which lead to low coulombic efficiency in the first cycle.

Chapter IV. Design of substituted molecular Thianthrene as *p*-type positive material for Dual-ion battery

Introduction

Inspired by the electrochemical studies on phenothiazine derivates, Thianthrene (TNT) was recently investigated as *p*-type electroactive molecule for positive electrode[114,115,117]. This molecule differs from phenothiazine for the presence of a second sulfur atom instead of nitrogen; however, there are many similarities between these two compounds: as in the case of phenothiazine, also thianthrene is characterized by an angular structure along the axis of the Sulfur-Sulfur atoms, called the "Butterfly structure", which becomes planar after the oxidation and the consequent formation of a cationic radical species[214]. According to the Electron Paramagnetic Resonance (EPR) analysis[215], sulfur atom is involved in the formation of the cationic species after the uptake of one electron; the radical species can therefore undergo a new oxidation to give the di-cationic species thanks to the second sulfur atom.

Thanks to its ability to form a stable cationic radical, the low molecular weight and the reversible[216] and modulable oxidation potential, the thianthrene derivatives have received interest as an electroactive material for energy storage. However, despite its excellent electrochemical properties, thianthrene is highly soluble in organic solvents: this characteristic makes it unsuitable for use in common liquid electrolytes. In order to prevent the dissolution of thianthrene, the studies reported to date in the literature have focused on the use of thianthrene in polymeric form: this strategy, commonly adopted for other organic materials, reduces the losses of active material in the electrolyte solvent during cycling.

In 2015, Speer et *al.* firstly reported thianthrene-based materials in the framework of lithium-ions batteries[217]. The authors synthesized and tested the thianthrene-functionalized polynorbornene polymers: this material showed reversible oxidation reactions at a high potential of 4.0 V *vs.* Li⁺/Li, with a reversible capacity of 66 mAh g⁻¹ after 14 cycles. However, a marked irreversible loss of specific capacity was observed after 100 cycles. Schubert and coworker prepared Poly(vinyl-thianthrene) as positive material for full-organic cell[115]. Electrochemical tests showed a potential of 4.0 V for the oxidation and 3.95 V *vs.* Li⁺/Li in the reduction phase. Cycling at 1C rate, the half-cell exhibited a discharge capacity of 105 mAh g⁻¹ (CE = 78.6% CE) in the first cycle, corresponding to 95% of theoretical capacity. Moreover, after 250 charge/discharge cycles at 1C, a reversible capacity of 86 mAh g⁻¹ was measured for the cell, for an overall capacity retention of 82%.

Design of substituted molecular Thianthrene as p-type positive material for Dual-ion battery

Despite their interesting electrochemical properties, the polymers listed above were characterized by a high content of conductive carbon in the electrode composite, around 45-50% by weight: this results in a low active material loading, with a consequent low volumetric energy density. Furthermore, all the polymers developed showed a low capacity retention, except for the poly(2-vinylthianthrene), due to the dissolution of the active material in the electrolyte.

To overcome these issues, in this Chapter a new approach in the design of thianthrene-based electroactive materials are presented. Instead of using polymerized thianthrene compounds, two thianthrene derivates were design, synthesized and characterized, using disubstitution in 2,7positions to tune (electro-)chemical/physical properties of Thianthrene. Substituent with different nature (electron-withdrawing and donating effects) were screened to tune the redox potential: 2,7-dimethylthianthrene (DMTNT) and 2,7-difluorothianthrene (DFTNT) (Figure IV.1). The electrochemical properties of substituted thianthrene derivates, in terms of redox potential, reversible specific capacity and rate performance were evaluated compared to simple thianthrene. Furthermore, an in-depth analysis of crystal structure was carried out, to explain the difference in electrochemical properties. Moreover, a series of *post-mortem* analyzes were performed to evaluate the dissolution of the active material during cycling. Finally, the DFTNT was tested in all-organic full-cell configuration. Dilithium dicarboxylate naphthalene (Li₂-NDC), a wellknown *n*-type negative material[134,218,219], was used as anode in a Dual ion battery configuration. The all-organic dual ion cell showed an output voltage of 3.4 V and outstanding electrochemical performance: after 100 cycles, the all-organic cell exhibited an energy density of 80-100 Wh kg⁻¹ based on the electrode mass, one of the highest values reported in literature.



Thianthrene **(TNT)**



2,7-Difluorothianthrene **(DFTNT)**



2,7-Dimethylthianthrene **(DMTNT)**

Figure IV.1 Synthesized Thianthrene derivatives.

Synthesis and characterization of DMTNT and DFTNT

DMTNT and **DFTNT** were synthetized according to the procedure reported by Edson and Knauss[220]. In the first step of synthesis, fuming sulfuric acid was added to 4-methylbenzenethiol (for DMTNT, Figure IV.2a) and 4-fluorobenzenethiol (for DFTNT, Figure IV.2b), forming a purple solution that was stirred for 22 hours at room temperature. The second step consisted in the reduction of the S-oxide through Zinc powder in boiling acetic acid, refluxed for 18 h. All the details of the two syntheses were reported in the Experimental Part.

DMTNT synthesis was confirmed by NMR spectrum (Figure VII.13): the appearance of the peak at 2.11 ppm due to methyl protons; the other peaks result shifted to upfield, from 7.59 to 7.27 ppm and from 7.36 and 6.98 ppm, due to its proximity with methyl group; all the NMR peaks are in agreement with the spectrum previously reported by Casarini et *al.*[221]. FTIR spectrum showed the appearance of a broad band around 2900-2700 cm⁻¹ linked to methyl C-H stretching and a peak at 1456 cm⁻¹ due to methyl C-H bending; moreover, at 1697 cm⁻¹ to 1584 cm⁻¹ were observed the peaks due to C-C stretching of methyl group (Figure IV.3a, grey line).

DFTNT synthesis was confirmed by NMR spectrum, where the peak of aromatic hydrogen of Thianthrene, located at 7.36 ppm (Figure VII.12), was split in two signals located at 7.54 and 7.25 ppm (Figure VII.14), as already reported by Edson and coworker[220]. Moreover, FTIR spectrum (Figure IV.3a, red line) showed the appearance of C-F stretching located at 1255 cm⁻¹ and 1209 cm⁻¹, confirming the successful synthesis of 2,7-difluorothianthrene.



Figure IV.2 Synthetic route of a) 2,7-dimethylthianthrene (DMTNT) and b) 2,7-difluorothianthrene (DFTNT). Full synthesis details and characterization available in Experimental Part.

The thermal stability of the two thianthrene derivatives was investigated through the thermogravimetric analysis (TGA, Figure IV.3b). No weight loss was observed up to 200 °C for both materials, after which the DFTNT begins to decompose (red line), with a loss of about 90% of the

mass, while the DMTNT shows a slightly higher stability, up to 270 ° C (black line). Furthermore, the TGA confirms that there are no traces of solvent in the two chemical structures.



Figure IV.3 a) Comparison between Thianthrene (red line), 2,7-dimethylthianthrene (blue line) and 2,7-difluorothianthrene (black line) using transmission FTIR. b) Thermal analysis measurements of 2,7-dimethylthianthrene (black line) and 2,7-difluorothianthrene (red line) obtained under argon flow at a rate of 5° min⁻¹.

Scanning electron microscopy (SEM) characterization of simple thianthrene and its derivates revealed a clear difference in particle morphology, both in terms of shapes and sizes. TNT appeared as irregular granules, with a particle size ranging from 10 to 50 μ m (Figure IV.4a). The first thianthrene derivate, **DMTNT**, differs from TNT not only in the size of the particles, between 5 to 30 μ m (Figure IV.4b), but also for the presence of irregular aggregates of spheres and shards on the particle surface. **DFTNT** consisted in slender parallelepipeds with lengths between of 50 to 100 μ m and lateral dimensions ranging up to several tens of microns (Figure IV.4c).



Figure IV.4 Scanning electron microscope images of Thianthrene and its 2,7-disubstituted derivates: a) TNT particles with granular shape and irregular aggregates on the surface and c) DFTNT with slender parallelepiped shape.

Electrochemical characterization of TNT, DMTNT and DFTNT

As a preliminary study, electrochemical properties of both thianthrene derivates were studied and compared with non-substituted thianthrene. Galvanostatic tests were performed in Swagelok-like half-cell *vs.* metallic lithium, using LP30 as electrolyte, cycled in a potential window of 4.5-2.5 V at different C-rates, starting from C/5 up to 4C. All the electrodes were prepared using an active material/conductive carbon (KJ600) ratio of 70:30, using the procedure reported in the Experimental part (Electrode preparation for Swagelok-type cell).

Regarding the de-/insertion potentials, they were calculated by integrating the area under the oxidation/reduction curves (expressed in mWh g⁻¹) and divided by the specific capacity (expressed in mAh g⁻¹); the average redox potential was calculated as the arithmetic average of the oxidation and reduction potentials calculated with the above method. Non-substituted thianthrene showed an average potential of 3.95 V vs. Li⁺/Li, which decreases to 3.8 V in the case of DMTNT. This result can be simply explained by the electron donor (inductive) nature of the methyl substituents, which lower the anion de-/insertion potential as classically observed for organic-materials[130,131]. Contrary to methyl substituents, fluorine is characterized by an electron-withdrawing nature, due to the inductive effect deriving from its strong electronegativity. As result, an increase in the redox potential was observed in the case of DFTNT, with an average value of 4.10 V vs. Li⁺/Li. Therefore, a difference of 300 mV in the redox potential was observed passing from the methyl group to the fluorine as substituents, which results in a higher energy density for the DFTNT. This result confirmed that the substituents play an important role in tuning the redox potential and should be considered to propose rational design for maximizing the electrochemical performance.

In Figure IV.5a-c are illustrated the rate performance for Thianthrene, DMTNT and DFTNT, respectively. At the lowest C-rate (C/5), the three thianthrene derivates showed a poor coulombic efficiency (CE), as the charge capacities were much higher than discharge specific capacities. Unsubstituted thianthrene showed a coulombic efficiency of only 63%, with a discharge capacity of 70 mAh g⁻¹, while moving to DMTNT the CE is slightly higher, due to the increase of discharge capacity (74 mAh g⁻¹). Finally, DFTNT displayed a considerable increase in the discharge capacity (96 mAh g⁻¹), for an overall coulombic efficiency of 88%.

At higher C-rate test, despite a decrease of specific capacity, an improvement in coulombic efficiency for the three electrodes was observed Unmodified thianthrene showed the worst performance with increasing cycling rate with a reversible capacity of 52 mAh.g⁻¹ at C/2(CE of

84%). Moving to 1C rate, the capacity decreased to 37 mAh g^{-1} (CE = 93%) and then it was halved at 2C (only 17 mAh g^{-1} , CE = 96%) and vanish completely 4C.

the substitution of thianthrene with two methyl groups (DMTNT) showed a reversible capacity of 60 mAh g⁻¹ at C/2, with a coulombic efficiency which increased to 94%. Furthermore, the half-cell with the DMTNT showed a specific capacity of 48, 35 and 14 mAh g⁻¹ at 1C, 2C and 4C, respectively; in these last three cases, the coulombic efficiency was higher than 97%.

Finally, 2,7-difluorothianthrene exhibited the best electrochemical performances in half-cell with 98 mAh g⁻¹ (CE=90%) of specific capacity was measured after 5 cycles at C/2, which slightly decreased to 87 mAh g⁻¹ after 5 cycles at 1C (CE = 96%). Moving to 2C and 4C rates, the half-cell with DFTNT displayed 76 mAh g⁻¹ and 63 mAh g⁻¹ of reversible capacity after the 5 cycles, respectively, with a CE of approximately 97% in both cases.



Figure IV.5 Rate capability performed at C/5, C/2, 1C, 2C and 4C rate of a) TNT, b) DMTNT and c) DFTNT half-cell vs. Li, window range of 4.5-2.5 V with LP30 electrolyte.

Surprisingly, the three materials showed a poor coulombic efficiency at low C-rates: in view of a future in industrial application, it is necessary that the CE >96%, since lower CE values lead to a loss of energy between charges and discharge phases that do not meet battery industry standards. For this reason, long cycle tests were performed using 2C as C-rate, in which all three thianthrene derivates showed an average CE of around 96-97%.

In the first cycle in the long cycling at 2C rate, non-substituted Thianthrene showed a charge capacity of 63 mAh g⁻¹, with a reversible capacity of 58 mAh g⁻¹, for a coulombic efficiency of 94% (Figure IV.6a). After three cycles, a marked loss of capacity was observed, with only 35 mAh g⁻¹ of specific capacity, which corresponds to capacity retention of 60%. After the third cycle, the capacity remains stable for 450 cycles, as illustrated in Figure IV.6d. In the case of DMTNT, the half-cell displayed a specific capacity of 92 mAh g⁻¹ in the first charge, with a reversible capacity of 74 mAh g⁻¹ (coulombic efficiency of 80%). The CE increased to 94% after 50 cycles, and then reached the value of 98% after 100 cycles, with a reversible capacity of 66 mAh g⁻¹. Regarding the

cycling stability, DMTNT showed a constant loss of capacity along cycles (Figure IV.6e): after 450 cycles, the specific capacity was 52 mAh g^{-1} , corresponding to a capacity retention of 70% compared to the first cycle.

Lastly, the DFTNT showed a charge capacity of 97 mAh g⁻¹ with a reversible capacity of 90 mAh g⁻¹ after the first cycle (Figure IV.6c), with a stable reversible capacity for 200 cycles; after 450 cycles, showed in Figure IV.6f, the cell still delivered the 83% of the specific capacity observed in the first cycle, corresponding to 75 mAh g⁻¹ (CE= 98%).



Figure IV.6 Potential-capacity profile of the 1st, 2nd and 450th cycle for a) TNT, b) DMTNT and c) DFTNT in half-cell vs. Li, cycled in potential range of 4.5-2.5 V with LP30 electrolyte. Evolution of the specific capacity as a function of cycle number for d) TNT, e) DMTNT and f) DFTNT electrodes in half-cell vs. Li, using the same cycling conditions.

Two important results emerge from the electrochemical tests illustrated above. The first is the marked gap in rate performance between the simple thianthrene and DFTNT, to be ascribed to the role of the different substituents. Secondly, a poor coulombic efficiency was observed for all the three thianthrene derivates up to 1 C rate.

Characterization of TNT and DFTNT crystal structure

Regarding the differences in terms of performance at different C-rates, they are commonly related to differences in terms of morphology or crystalline structure of the material, which can profoundly affect the electrochemical properties[222]. Indeed, the ionic and electronic conductivity inside the material is strictly linked to the crystal structure: a different crystal packing of the molecules can facilitate the circulation of ions or electrons leads to better reaction kinetics

and consequently better performance at high current density. To investigate the impact of the structure on the electrochemistry of the investigated molecules, the crystal structures of thianthrene and DFTNT were compared. For unsubstituted thianthrene, the crystalline structure has already been reported in the literature[223]; the crystallographic structure of the DFTNT was refined for the first time using the single-crystal diffraction technique.

To do so, crystals of DFTNT were grown from slow evaporation of Cyclohexane/DCM solution in 10/1 ratio. The DFTNT structure was solved and refined using the Bruker SHELXTL Software Package. It crystallized in space group C2/c with cell constants a = 21.602(3) Å, b = 3.9479(6) Å, and c = 14.051(2) Å and angles $\alpha = \gamma = 90^{\circ}$ and $\beta = 119.310^{\circ}$ (7), for a cell volume of V = 1044.9(3) Å³. The structure is built from 4 molecules of DFTNT in the unit cell (*Z*=4), with 11 independent atoms (6 carbon, 2 sulfur, 2 fluorine and 6 hydrogen atoms). DFTNT exhibits a non-planar structure, with an angle centered on the Sulfur atoms of 135.0° (4) (Figure IV.7a,b).

The crystal structure of the 2,7-difluorothianthrene showed a different molecular packing compared to unsubstituted thianthrene. The DFTNT molecules shows the stacking of the molecules with a perfect overlap on top of each other along the b-axis, as shown in Figure IV.7a. This particular structure is due to the π - π -stacking interactions[224] between the aromatic rings of the DFTNT. Indeed, the distance between the adjacent aromatic ring in sandwich configuration was measured in 3.65 Å. This distance is consistent with the π - π -stacking interactions reported in literature, which estimated the distance in a range of 3.3-3.8 Å[225,226]. Thianthrene shows a different crystalline structure (monoclinic *P*21/*c*, unit cell in Figure IV.7c), with 129.33(7)° sulfurcentered angle and 3.49 Å between the two benzene rings of adjacent molecules. However, even if the distance is shorter compared to DFTNT, the π - π -stacking interaction occurs only between one ring of the TNT molecule, as illustrated in Figure IV.7d, rather than with both rings, as observed for the DFTNT.



Figure IV.7 Crystal packing of DFTNT (green box), a) down the b-axis and b) zoomed on the pair of molecules. Crystal packing of TNT (orange box), c) down the b-axis and d) zoomed on the pair of molecules, from crystal structure reported in literature[206]. Relevant crystallographic parameters are available on the Experimental part (Table VII.4, Table VII.5 and Table VII.6).

This difference in the molecular packing inside the crystal explains the difference also in terms of electrochemical performance. As widely reported in literature, the π - π -stacking interaction facilitates the transfer of electrons transfer[224,227] between adjacent molecules, creating an electronic conductive pathway; hence, it is possible to hypothesize that the better performance of DFTNT derives from its crystal structure. However, to confirm this hypothesis, it is necessary to perform further investigations. For example, a computational study can help to elucidate the crystal structure through the analysis of the molecular electronic structure, as already reported in the case of dilithium squarate[228]. Furthermore, from an experimental point of view, impedance and chronoamperometry measurements on the pristine material (TNT and DFTNT) in symmetrical cell configurations can provide information on the electronic conductivity of the two materials. As a perspective, a more in-depth study of the crystalline structure-conductivity relationship will provide fundamental information for the design of thianthrene derivatives for high power applications.

Post-mortem analysis of DFTNT electrode

Concerning the low coulombic efficiency at low C-rates, the explanation can be given by the high solubility of the active material in its oxidized form, *i.e.* after the insertion of the anions. The

Design of substituted molecular Thianthrene as p-type positive material for Dual-ion battery

dissolution of electroactive material during the oxidation phase (charge phase), leads to a slight decrease in the amount of active material in the electrode during the reduction phase (discharge phase). This phenomenon can explain the gap between charge and discharge capacity. To confirm the dissolution of the active material in oxidized form, a *post-mortem* gas chromatography analysis was performed. Two half-cells DFTNT//Li were assembled and charged to 4.5 V. The cells were kept at the cut-off potential for two different resting time: 5 hours and 15 hours, then the cells were disassembled and their separators analyzed in GC-MS. Both separators showed a purple spot due to oxidized DFTNT dissolved in the electrolyte (Figure IV.8, inset). The chromatograms from both separators (Figure IV.8) showed the presence of a peak relative to DFTNT, previously characterized by analyzing the pristine material. Increasing the resting time, an increase of the peak related to DFTNT was observed in the chromatograms. This result confirms the dissolution of the active material in the electrolyte and that this phenomenon increases proportionally with time. Therefore, this result explains the improvement of the coulombic efficiency increasing the C-rates. When the cell is cycled with high current density, the active material has less time to dissolve, leading to a lower gap between charge and discharge.



Figure IV.8 Gas-chromatography-MS analysis of separator recovered after 1 charge of DFTNT half-cell vs. Li, galvanostatically cycled over a potential window range of 4.5-2.5 V at 2C rate using LP30 as electrolyte after 5 hour of rest (light blue square) and 15 hour of rest (purple square).

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Despite the solubility of the active material in the electrolyte solvent, the galvanostatic tests illustrated above do not show significant loss of capacity in the case of DFTNT. A capacity retention of 83% was measured after 450 cycles. A possible hypothesis is that the solubilization phenomenon is reversible[113]. Once passed in solution, the oxidized form can be reduced reacting with the electrolyte solvent, passing back to the solid state. In order to confirm this hypothesis, self-discharge tests of the cell were carried out to investigate the reversibility of the dissolution process. Two half-cells versus Lithium were assembled, with TNT and DFTNT electrodes, and cycled up to the cut-off voltage of 4.5 V; then, the cells were kept at the cut-off voltage for different resting times (6, 12 and 24 hours); after that, the cells were discharged in order to measure the residual specific capacity. To evaluate the reproducibility of the experiment, 5 charge and discharge cycles were performed for each rest time. In the case of the TNT half-cell (Figure IV.9a), a residual capacity of only 27% was observed after the rest phase of 6 hours; as the rest time increased, the capacity retention dropped to 21% (after 12 hours) and 19% (after 24 hours). DFTNT exhibited a higher capacity retention, with 69%, 66% and 56% of reversible capacity after 6h, 12h and 24h, respectively (Figure IV.9b). The difference between the solubilities of the two materials, which determines the percentage of capacity retention in the self-discharge test, can be explained by the different intermolecular interactions since as mentioned in the previous paragraph, the DFTNT is characterized by stronger π - π -stacking interaction compared to unsubstituted thianthrene. These interactions can mitigate the dissolution of the active material in the electrolyte. Beyond the differences in capacity retention after the resting time, both the active materials showed a complete reversibility of the electrode capacity during the test. Despite the low discharge capacity after the rest phase, the cell displayed the same charge capacity in the following cycles. Moreover, the complete recovery of the capacity was not observed only in the 5 cycles with the same resting time, but also increasing the resting time between charge and discharge increases.



Figure IV.9 Self-discharge test of a) TNT and b) DFTNT electrodes in half-cell vs. Li using three different resting time: 6 hours (blue lines), 12 hours (red lines) and 24 hours (black lines).

The complete reversibility of the capacity can be explained by a mechanism of dissolution and reprecipitation of the active material on the electrode surface, as mentioned before. This phenomenon was already reported by Kolek and coworkers on phenothiazine polymers.[113] To verify this hypothesis, a coupled SEM/EDX analysis was performed on the DFTNT electrode before and after 100 charge/discharge cycles in half-cell *vs.* Li. The electrode before cycling (Figure IV.10a) is characterized by a smooth surface, without visible particles of active material, while after 100 cycles the presence of recrystallized particles was observed on the surface (Figure IV.10b). The morphology of the crystals corresponds to DFTNT (shown in Figure IV.4c), and furthermore the EDX spectroscopy, illustrated in Figure IV.10c, showed the presence of sulfur atoms on the particles deposited on the electrode. This analysis confirms the dissolution/recrystallization process of the active material on the surface electrode.



Figure IV.10 a) SEM image of DFTNT electrode surface before cycling. b) SEM image and c) EDX spectroscopy map of DFTNT electrode surface after 100 cycles at 2C rate.

The re-crystallization process of DFTNT is also confirmed by the *in-situ* XRD analysis, performed using a Swagelok-like cell, equipped with a beryllium window[229]. The powder patterns of the first two cycles are reported in Figure VII.15 (Experimental part) and shown the complete

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reversibility of the pristine crystalline phase (black line) after the charging process (red and green lines) and the discharge process (blue and pink lines). Given the quality of the powder patterns obtained from the *in-situ* analysis, it was not possible to refine the crystalline structure after the charging phase (DFTNT in the oxidized form).

Considering the results obtained for the three thianthrene-derivate molecules, it clearly emerged the marked improvement in the electrochemical performance using fluorine disubstituent (2,7difluorothianthrene). The presence of fluorine atoms, thanks to their electron withdrawing nature, leads to an increase in the redox insertion potential. Moreover, this molecule displayed a better capacity retention and rate performances, thanks to its crystal structure. Given the superior electrochemical properties compared to TNT and DMTNT, the DFTNT derivative was studied in more detail, to optimize its electrochemical properties.

Although preliminary analyses confirmed the dissolution of DFTNT in the oxidized form, this phenomenon does not interfere with capacity retention in short/medium cycling tests (up to 450 cycles). This aspect is ascribed to the fast-reversible dissolution/recrystallization of the active material on the electrode surface. Nevertheless, the solubility affects the CE and could lead to possible capacity fading in long cycling tests.

Therefore, reduce the solubility of the active material is a crucial step to improve the electrochemical performance and the cycling life of the cell. A common strategy to limit the dissolution of the electroactive material is the optimization of the liquid electrolyte, which plays a fundamental role in mediating the (electro-)chemical/physical properties of the active material[207].

Electrolyte optimization for DFTNT electrode

The first step in the rational design of an electrolyte is the choice of the electrolyte salt. In *p*-type materials, the redox process is based on the anion insertion, which involves the lithium salt counterion. Recently, a screening of different electrolyte salts for *p*-type materials was reported by Murugesan et *al.*, showing how electrochemistry can be greatly influenced by the choice of the anion.[104,230] In Figure IV.12a were reported the C-rate tests performed with three different lithium salts, Lithium hexafluorophosphate (LiPF₆), Lithium perchlorate (LiClO₄) and Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), which are among the most used in the lithium battery technology. To investigate only the effect of the electrolytic salt, the three electrolytes were prepared using the same concentration (1M) and type of solvent (mix of EC:DMC 1:1 vol.%). Concerning the redox potential, the galvanostatic curves (reported in Figure

IV.11) showed a slight lower oxidation potential using $LiClO_4$ (blue line), for an average redox potential of 4.05 V vs. Li^+/Li , while no differences were observed using $LiPF_6$ and LiTFSI (4.10 V vs. Li^+/Li).



Figure IV.11 Potential-capacity profile of the 1st cycle of the half-cell DFTNT vs. Li galvanostatically cycled at C/5 rate in a potential range of 4.5-2.5 V, using 1M LiPF₆ (blue line), 1M LiClO₄ (red line) and 1M LiTFSI (black line) as electrolyte salt in EC:DMC 1:1 vol.%.

A marked difference between the different electrolytes were observed in terms of specific capacity and rate performances. Despite the three cells showed the same charging capacity (125-130 mAh g⁻¹) at C/5 rate, the cell with LiTFSI electrolyte (Figure IV.12a, green squares) displayed a lower discharge capacity (63 mAh g⁻¹), associated with a coulombic efficiency of only 50%. On the other side, LiPF₆ exhibited a specific capacity of 107 mAh g⁻¹ (CE=82%, red circles) and LiClO₄ 104 mAh g⁻¹ (CE=83%, blue triangles). At 2C rate, the CE reached a value of 97% for all three salts, but with a significant difference in terms of specific capacity delivered. The half-cell with LiPF₆ as electrolyte showed a reversible capacity of 76 mAh g⁻¹, which drops to 54 mAh g⁻¹ with the LiClO₄ and to 39 mAh g⁻¹ in the case of the LiTFSI. These results show that LiPF₆ is the best salt both in terms of insertion potential, capacity retention and rate performance, compared to LiClO₄ and LiTFSI, the latter exhibiting poor performances at all the C-rates. This result may be related to the molecular structure of the electrolyte salt: the nature and size of the TFSI- anion is not adequate for insertion into the crystal structure of the DFTNT.

In addition to the electrolyte salt, the second element to optimize is the solvent where dissolve the salt to prepare the liquid electrolyte. Thanks to its dielectric properties, its ability to solvate ions and its chemical-physical properties, the solvent can deeply influence the electrochemical performance of an electrochemical cell. In this work, the mixture of organic solvents EC: DMC 1:1

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vol.%, the most common electrolyte solvent for lithium-ion batteries, is compared with propylene carbonate (PC) solvent. Figure IV.12b shows the specific capacities as function of the C-rate of the DFTNT, using 1 M LiPF₆ in EC:DMC (LP30, magenta/red circles) and 1 M LiPF₆ in PC (gray/black circles) as electrolytes.

At low cycling rate, from C/5 to 1C, PC-based electrolyte showed higher charge and discharge capacity than EC:DMC mixture. In the case at C/5, the cell with LiPF₆ in PC displayed 138 mAh g⁻¹ of charge and 117 mAh g⁻¹ of discharge, against 131 and 106 mAh g⁻¹ in the case of LiPF₆ in EC:DMC. Moreover, the coulombic efficiency is slightly better with the PC, calculated in 85% against 80% in EC:DMC solvent. The coulombic efficiency obtained with the two electrolyte solvents is equal starting from 1C rate (CE=95%). At higher C-rates (2C and 4C), the trend of the specific capacity was reversed since the half-cell with the LiPF₆ in EC:DMC exhibited a noticeable higher rate capability, with 76 mAh g⁻¹ of reversible capacity measured at 2C, against 58 mAh g⁻¹ of capacity obtained with Propylene Carbonate electrolyte. This difference becomes even more pronounced moving to 4C, where the electrolyte with EC:DMC mixture displayed 64 mAh g⁻¹ versus the 37 mAh g⁻¹ obtained with propylene carbonate. Therefore, it is possible to conclude that the half-cell with EC:DMC mixture as electrolyte showed better electrochemical performances compared to PC solvent.

The last parameter to consider in the design of the electrolyte is the concentration of the electrolytic salt. To investigate the effect of salt concentration, several galvanostatic tests were performed using different concentrations of LiPF₆ electrolyte. The comparison between 1 M LiPF₆ and 2 M LiPF₆ in EC:DMC 1:1 vol.% and in PC was reported in Figure IV.12c and Figure IV.12d, respectively. Both electrolyte systems exhibited the same tendencies changing the salt concentrations: the increase in concentration to 2 M leads to a better coulombic efficiency at low regimes, most probably thanks to the reduction of the active material dissolution. In the case of the EC: DMC, a coulombic efficiency of 94% at C/5 and 98% at C/2 of CE was measured, with a reversible capacity of 110 and 97 mAh g⁻¹, respectively. This is a 14% increase in efficiency values are 93% and 97% with the 2 M LiPF₆ in PC. The second result is the decrease in specific capacity at high C-rates as the electrolyte concentration increase. In the case of the 2 M LiPF₆ in EC:DMC, the specific capacity drops to 67 and 54 mAh g⁻¹ at 2C and 4C, respectively, lower than what measured for the 1 M concentration of LiPF₆ (76 and 64 mAh g⁻¹). A lower rate performance was also observed for the LiPF₆ in PC, albeit less marked. The different behavior at low and high C-
rates can be explained by the properties of the electrolytes as the salt concentration change. The increase in salt concentration leads to a reduction in the dissolution of the active material in the electrolyte, with a consequent improvement in coulombic efficiency. Indeed, as mentioned before, the dissolution phenomenon is responsible for the decrease of discharge capacity and the low CE. However, increasing the salt concentration leads to an increase in the electrolyte viscosity, slowing down ion diffusion through the electrolyte. As the C-rate increases, the lower diffusivity of the ions implies a limitation in the kinetics, with a consequent decrease in the specific capacity delivered.



Figure IV.12 a) Rate capability for different electrolyte salts: $LiPF_6$ (red circles), $LiClO_4$ (blue triangles) and LiTFSI (green squares) in EC:DMC 1:1 vol.%; b) Rate capability for different electrolyte solvents: $LiPF_6$ in EC:DMC 1:1 vol.% (red circles) and $LiPF_6$ in PC (black squares); c) Rate capability of 1 M LiPF₆ (red circles) and 2 M LiPF₆ (blue rhombuses) in EC:DMC 1:1 vol.%; d) Rate capability of 1 M LiPF₆ (red circles) and 2 M LiPF₆ (blue rhombuses) in EC:DMC 1:1 vol.%; d) Rate capability of 1 M LiPF₆ (purple triangles) in PC. All the tests were performed in half-cell vs. Li, in a window range of 4.5-2.5 V at C/5, C/2, 1C, 2C and 4C rates.

In this paragraph, a rational design of the electrolyte components was illustrated in order to improve the cycling conditions. From the comparison of the different electrolyte salts and solvents, $LiPF_6$ in EC:DMC exhibited the best electrochemical performances. Furthermore, by

increasing the concentration of the electrolytic salt, an improvement in the coulombic efficiency at low C-rates was observed, but also a decrease in the rate capability at 2C and 4C. Considering all these results, two electrolytes were selected for the tests in full organic cell: LiPF6 in EC: DMC (LP30) in two different concentrations, 1 Molar and 2 Molar, in order to maximize the cell performances both at low regimes (using 2 M LP30) and high regimes (using 1 M LP30).

Synthesis and electrochemical characterization of Li₂-NDC

Given the promising electrochemical properties shown in half-cell vs. metallic lithium, DFTNT was electrochemically studied as positive material for an all-organic full-cell. Concerning the organic active material for the anode, to the best of our knowledge only viologen has been studied as a p-type negative material. However, viologen and its derivatives are characterized by a high redox potential, around 2 V vs. Li⁺/Li, which significantly lowering the cell voltage. Therefore, the choice fell on a n-type negative material, the dilithium naphthalene dicarboxylate (Li₂-NDC), one of the most promising negative organic materials in the literature[134,218,231]. Indeed, this material is characterized by a low insertion potential (0.7 V vs. Li⁺/Li), high specific capacity (around 240 mAh g⁻¹) and good rate performance.

Li₂-**NDC** was synthesized *via* an acid-base reaction between naphthalene dicarboxylic acid and lithium hydroxide, as reported by Oghihara and coworkers;[135] details on the synthesis and characterization (NMR and FT-IT) are reported in the Experimental part.

The synthesis of **Li₂-NDC** was confirmed ¹H NMR spectrum exhibited the disappearance of O-H proton located at 13.27 ppm and the shift upfield of all the naphthalene protons, due to the presence of lithium ions (Figure VII.16). Furthermore, FTIR spectroscopy showed the disappearance of broad peak at 3600-3300 cm⁻¹, due to H-O stretching, and the shift from 1694 cm⁻¹ to 1560 cm⁻¹ of C=O stretching signal, due to the salt formation (Figure VII.17). Lithium content was quantified using atomic absorption spectroscopy (AAS) technique: the complete chemical formula of the two compounds was Li_{2.03±0.04}-NDC.

The assembly of full cell requires a precise balance between the capacities of the two electrodes, in order to maximize the energy that can be stored and avoid some problems such as lithium plating. Therefore, Li₂-NDC was electrochemically characterized, to obtain the exact specific capacity of the electrode composite. The electrochemical tests were performed in Swagelok-like half-cell *vs.* Li, in a potential window of 2.0-0.05V at C/5 rate, using LP30 as electrolytes. Figure IV.13a showed the galvanostatic profiles of the first 5 cycles and the evolution of capacity as function of cycles. The half-cell exhibited a capacity of 246 mAh g⁻¹ in the first discharge, with 165

mAh g^{-1} of reversible capacity, for an irreversibility of 33% after the first cycle, mainly due to the formation of the SEI layer. After 20 cycles the cell has a capacity of 140 mAh g^{-1} , for an overall capacity retention of 85% (Figure IV.13b).



Figure IV.13 Potential-capacity profile of the first 5 cycles and (b) evolution of the specific capacity as a function of cycle number for Li₂-NDC vs. Li, galvanostatically cycled at C/5 rate in a potential range of 2.0-0.05 V, using LP30 as electrolyte.

Assembly of all-organic Dual-ion full-cell DFTNT/Li2-NDC

The all-organic full-cell DFTNT//Li₂-NDC, illustrated in Figure IV.14, can be defined as Dual-ions cell configuration, where the electrochemical process involves the insertion of cations in the anode and the insertion of anions in the cathode. Concerning the electrolyte, always composed of a dissolved salt of anions and cations (for example Li⁺ and PF_6^- forming LiPF₆), it therefore plays the role of ionic reservoir.



Figure IV.14 Configuration of the all-organic full-cell DFTNT//Li₂-NDC.

Considering 246 mAh g⁻¹ as specific capacity for Li₂-NDC electrode, the full-cell was assembled using the ratio cathode mass/anode mass of 2.5:1 with LP30 electrolyte and 2:1 in the case of 2 M LP30. Galvanostatic tests were performed in Swagelok-like cell, cycled in a potential window of 4.0-2.V a different C-rates (C/5 and 1C). All the electrodes were prepared using an active material/conductive carbon (KJ600) ratio of 70:30, using the procedure reported in the Experimental part (Electrode preparation for Swagelok-type cell).

Regarding the output voltage, the DFTNT//Li₂-NDC full-cell showed an average voltage at 3.4 V with both electrolytes (Figure IV.15a,c,e). This is one of the highest values reported so far for an all-organic full-cell[232].

Concerning the capacities of the full-cell, Table IV.1 shows the specific capacity of the 1st and 100th cycles, calculated both on the mass of the active material (columns 2 and 3) and mass of the entire electrode (column 6); all values are calculated on the basis of the cathode masses. Firstly, the full-cells with 1 M LP30 and 2 M LP30 were compared at low C-rate (C/5 rate). In the first cycle, the cell with 1 M LP30 showed a charge capacity of 117 mAh g⁻¹, with a reversible capacity of 80 mAh g⁻¹, for a coulombic efficiency of 68% (Figure IV.15a,b). After 100 cycles, the cell showed a reversible residual capacity of 33 mAh g⁻¹ (CE = 87%), for an overall capacity retention of 36%. The full-cell with 2M LP30 electrolyte showed a higher coulombic efficiency of 72% in the first cycle, but with a lower specific capacity (65 mAh g⁻¹). However, the cell exhibited a better capacity

retention along cycling. After the first 10 cycles, the reversible capacity stabilized at 44 mAh g⁻¹, remaining constant up to 100 cycles, with a coulombic efficiency of 90%).

Electrolyte	C- rate	AM Charge capacity (mAh g ⁻¹)	AM Discharge capacity (mAh g ⁻¹)	CE (%)	Electrode Discharge capacity (mAh g ⁻¹)	Energy density (Wh/kg)		
1 st cycle								
1M LP30	C/5	117	80	68%	56	190		
2M LP30	C/5	90	65	72%	46	156		
1M LP30	1C	76	56	74%	39	133		
100 th cycle								
1M LP30	C/5	38	33	87%	23	79		
2M LP30	C/5	49	44	90%	31	105		
1M LP30	1C	38	35	92%	24	82		

Table IV.1 Energy metrics after the 100th cycle of full cell DFNT//Li₂-NDC using different electrolytes.

The results obtained are in line with what observed in half-cell test since the cell with 2M LP30 exhibited a better coulombic efficiency and capacity retention, thanks to the mitigation of the active material dissolution due to higher salt concentration. Although the cell with 1M LP30 showed a higher reversible capacity in the first cycle, the cell was characterized by low coulombic efficiency and capacity fading, as already observed in half-cell. To improve these two parameters, the full-cell with 1 M LP30 was cycled at 1C rate, to partially reduce the effect of the active material dissolution. The cell displayed a decrease in the specific capacity, both in the charge (76 mAh g^{-1}) and discharge (56 mAh g^{-1}) phases, but also a better coulombic efficiency (74%), consistent with the increase in cycling regime. After 100 cycles, the cell showed an improved stability over cycling, with 61% of capacity retention and 92% of coulombic efficiency, better than what observed at C/5 rate. Note that this results obtained in the full cell are consistent with what was observed for DFTNT in half-cell vs. Li. The poor coulombic efficiency and capacity retention exhibited at C/5 rate with 1 M LP30 as electrolyte, due to the partial dissolution of the active material in the electrolyte, can be improved with two different approaches: increasing the cycling rate or the electrolyte concentration. Both these strategies led to an improvement in efficiency, but it is important to note that only the increase of the salt concentration (2 M LiPF₆ salt in EC:DMC) leads to a stabilization of the specific capacity along cycling.

Regarding the energy density, the values obtained for the 1st and 100th cycle are reported in the last column of Table IV.1; all the values were calculated using the mass of the electrode. The design of single-molecule thianthrene derivates led to a considerable reduction of conductive carbon in the electrode composite (70:30 AM:CB) compared to the thianthrene polymers

reported in literature (40-50 wt.% of AM). In the first cycle, the energy density varies from 133 to 190 Wh kg⁻¹, while at the 100th cycle the values are between 80 and 105 Wh kg⁻¹. Therefore, thanks to the low carbon content in the electrode composite and the high output voltage, the all-organic cell DFTNT//Li₂-NDC exhibited a better energy density than polymeric thianthrenes all-organic cell[115].



Figure IV.15 Potential-capacity profile of 1st, 2nd and 100th cycle and evolution of the specific capacity as a function of cycle number for DFTNT//Li2-NDC full-cell, galvanostatically cycled in a potential range of 4.0-2.0 V: a,b) at C/5 rate using 1 M LP30 as electrolyte; c,d) at C/5 rate using 2 M LP30 as electrolyte and e,f) at 1C rate using 1 M LP30 as electrolyte.

The design of single-molecule thianthrene derivates led to a considerable reduction of conductive carbon in the electrode composite (70:30 AM:CB) compared to the thianthrene polymers reported in literature (40-50 wt.% of AM). In the first cycle, the energy density varies from 133 to

190 Wh kg⁻¹, while at the 100th cycle the values are between 80 and 105 Wh kg⁻¹. Therefore, thanks to the low carbon content in the electrode composite and the high output voltage, the all-organic cell DFTNT//Li₂-NDC exhibited a better energy density than polymeric thianthrenes all-organic cell[115].

Despite the outstanding performances exhibited in full-cell, the use of 2,7-difluorothianthrene as positive active material still requires some optimizations. At the material level, there are two feasible strategies. Firstly, the tetrasubstitution of thianthrene with electron withdrawing groups (e.g tetrafluorothianthrene), in order to further raise the anionic de-/insertion potential and obtain an even higher output voltage, with a consequent increase in energy density. Secondly, the substitution of thianthrene with polar groups, in order to reduce the solubility in organic solvents and increase the cycling life, as seen in previous works for n-type materials[210]. At the electrode level, it is possible to play with the morphology, the size of the active material particles and electrode thickness, in order to fine-tune the electrochemical properties and increase the active material mass loading. Finally, at the cell level, the optimization can be oriented towards the increasing of the electrolyte concentration beyond 2M: a screening of salt concentrations, to find a trade-off between coulombic efficiency at low C-rates and viscosity/diffusivity of the electrolyte system, can lead to a considerable increase in specific capacity and stability over cycling from the cell. Furthermore, as a future perspective, it will be very interesting to study the derivatives of thianthrene in all-solid state battery configuration: a solid state electrolyte will be beneficial not only in terms of better safety and conductivity, but also to avoid the phenomenon of dissolution of the active material in the electrolyte. However, to the best of our knowledge, a solid electrolyte for *p*-type materials has not yet been developed[233].

Conclusions

In the present work, a series of new p-type positive materials based on thianthrene have been designed and characterized. The synthetic approach was based on the 2,7-disubstitution of simple thianthrene, using substituent groups with different electrochemical characteristics: methyl (DMTNT, electron donor) and fluorine (DFTNT, electron withdrawing). Galvanostatic tests showed an improvement in performance thanks to both the substituents, in terms of specific capacity, capacity retention and rate performance. In the case of DFTNT, thanks to electron withdrawing nature of the substituent, the potential is increased by 150 mV with respect to the nonsubstituted thianthrene, reaching 4.10 V vs. Li⁺/Li. Furthermore, DFTNT showed better rate performances, which can be attributed to its crystalline structure, which facilitates electronic conduction within the active material. However, the *post-mortem* analysis (GC-MS and SEM/EDX) showed the dissolution of thianthrene derivates in electrolyte, which causes the poor coulombic efficiency at low C-rates: to overcome this problem, a screening of salts, solvents and electrolyte concentrations was performed. Half-cell tests have shown that the best electrolytes for DFTNT are 1 M LP30 at high C-rates and 2 M LP30 at low C-rates. DFTNT electrode was assembled in an all-organic full-cell, with *n*-type dilithium naphthalene dicarboxylate (Li₂-NDC) as anode. The fullcell, based on the Dual-ion mechanism, showed an outstanding output voltage of 3.4 V, one of the highest reported for an all-organic full-cell. Moreover, at C/5 the DFTNT//Li₂-NDC exhibited a reversible capacity of 80 mAh g⁻¹ and 65 mAh g⁻¹ with 1 M LP30 and 2 M LP30, respectively. After 100 cycles, the cell with 2M LiPF₆ showed a retention capacity of 68%. The full-cell with 1 M LP30 was also tested at 1C rate: an improvement of the coulombic efficiency was observed increasing the cycling regime, but no improvements were observed for capacity retention. Thanks to the low quantity of conductive carbon and the high output voltage of the cell, the dual-ion DFTNT//Li₂-NDC cell showed an energy density in the range 80-100 Wh kg⁻¹ (based on the mass of the electrode) after 100 cycles: this result is an improvement over the all-organic full-cell assembled with thianthrene polymers. This encouraging result that paves the way for a future industrialization of thianthrene-based organic materials.

Introduction

The dramatic increase in battery demands for the automotive sector and stationary energy storage applications[234,235] led the scientists to intensified the research on post-lithium technologies, able to combine high electrochemical performance, low production costs, with a low consumption of valuable and scarce raw materials[236–238].

Sodium batteries are considered as one of the most promising technology for post-lithium energy storage systems.[239,240] However, even though Na-ion batteries are approaching maturity, some unsolved problems are limiting the potential of this technology. Among these, the choice of hard carbon as an anode material leads to problems in terms of manufacturing cost and high volumetric energy density applications.[241,242]

In the quest of alternative materials to HC, part of the research is focused on organic redox-based materials, thanks their excellent theoretical electrochemical properties, low production cost, high recyclability and low environmental impact.[9,155,232] Among the organic compound, dicarboxylate derivates have attracted most of the attention for their promising characteristics as active material for negative electrode (low insertion potential, good specific capacity and stability over cycling), making them promising candidates to replace current anode materials for the construction of a more sustainable battery[125,133,243,244].

Given the scarcity of organic-based positive materials for Sodium-ion technology, part of the research has focused on the development of hybrid full-cell, which combine an inorganic cathode with an organic anode. The first hybrid sodium-ion battery was reported by Abouimrane and coworkers and use disodium terephthalate dicarboxylate (Na₂-TP) as a negative electrode and Na_{0.75}Mn_{0.70}Ni_{0.23}O₂ as the positive electrode[245]. The cell exhibited 3.6 V as its output voltage, with an initial specific capacity of 257 mAh g⁻¹ (based on the anode material). Additionally, the cell exhibited good cycling stability, with 93% capacity retention after 50 cycles. However, the full cell showed low reversibility (43%) in first cycle. Furthermore, the authors reported neither the rate performance at high C-rates nor the capacity retention after 50 cycles. Medabalmi and coauthors reported a cell using disodium naphthalene-2,6-dicarboxylate (Na₂-NDC), coupled with Na₃V₂O₂(PO₄)₂F/rGO as the positive electrode[142]. The cell provided a specific capacity of 150 mAh g⁻¹ (based on the mass of the anode), with an output voltage of 3.3 V. As in the previous case, this cell was characterized by a low reversibility (33%) in the first cycle and a strong capacity fading after only 20 cycles was observed. Despite the efforts made to improve the performance of electrodes based on dicarboxylates, these materials still suffer from some limitations, such as the intrinsically low conductivity.[246] As consequence, these materials require a considerable quantity of conductive carbon to create a good electronic percolation in the electrode. The large amount of carbon in the electrode negatively affects some electrochemical characteristics, as the formation of the SEI layer and the irreversibility during the first cycle notably. Considering all the above-mentioned problems, the optimization of the electrode architecture is a fundamental step for the organic materials.

In this chapter, a study on Disodium Naphthalene Dicarboxylate (Na₂-NDC, Figure V.1), as a negative organic material is presented. This molecule has been extensively studied for its interesting electrochemical properties, such as an average redox potential of 0.45 V vs. Na⁺/ Na and a reversible capacity of 200 mAh g⁻¹ in the first cycles,[141]. Furthermore, electrochemical performances of Na₂-NDC can be profoundly influenced by the crystalline structure and the morphology of the particles of active materials, depending on the synthesis conditions and/or recrystallization process[231,247]. In the first part, the crystal structure and the morphology of Na₂-NDC particles, by varying the synthesis steps and the formulation process, was investigated to optimize the electrode formulation. A screening of the electrolyte was also conducted in order to maximize the performance of the electrode. In the second part of the work, a complete Na-ion hybrid cell was assembled and tested, using the previously optimized Na₂-NDC electrode as the anode, coupled with Na₃V₂(PO₄)₂F₃ (NVPF), as the inorganic-based cathode[248–250]. An indepth electrochemical study of the full cell was performed to evaluate the stability after a long cycling and the rate capabilities for high power density applications. Finally, an investigation based on GC/MS analysis, UV-Vis spectroscopy and electron microscope (SEM-EDX) technique was performed to elucidate the aging mechanism in the hybrid cell in long-cycling test.





Figure V.1 Redox reaction mechanism for sodium insertion and extraction in Disodium naphthalene dicarboxylate (Na2-NDC)

Synthesis of and characterization of Na₂-NDC

Na₂-NDC was synthesized *via* an acid-base reaction between naphthalene dicarboxylic acid and sodium hydroxide, using methanol as solvent, as reported by Deng and coworkers[251]. The sodium salt showed a complete insolubility in carbonate-based liquid electrolytes. The synthesis of Na₂-NDC was confirmed by Infrared spectroscopy. FT-IR spectra showed the disappearance of broad peak at 3300-2300 cm⁻¹ due to H-O stretching and the shift from 1694 cm⁻¹ to 1560 cm⁻¹ of C=O stretching signal, due to the salt formation (Figure V.2a). Moreover, sodium content in Na₂-NDC was measured using atomic absorption spectroscopy and give a complete chemical formula of Na_{2.02±0.05}-NDC independently of the synthesis process. Finally, to investigate the thermal stability of Na₂-NDC, a thermogravimetric analysis (TGA) was performed (Figure V.2b). The measurement showed a weight loss of about 1.90% up to 600 ° C, which indicates a high thermal stability of the material; furthermore, the negligible mass loss indicates the lack of solvent molecules trapped in the molecular structure. Note that this aspect is crucial for electrochemical tests and samples were dried carefully before cycling.



Figure V.2 (a) Comparison between naphthalene carboxylic acid (NDC, blue line) and corresponding sodium salt (Na2-NDC, red line) using FTIR spectroscopy in transmission mode. (b) Thermogravimetric profile (TGA) of Na2-NDC obtained under argon flow at a heating rate of 10 °C.min⁻¹.

As previously mentioned, the anode material synthesis was performed using methanol as the reaction solvent, as reported in the literature[251], both NDC and Na₂-NDC were not soluble in this solvent. As to the crystal structure, this synthesis pathway leads to the formation of a monoclinic system (Figure V.3a), characterized by a space group P21/c, with cell parameters $\alpha = 12.1$ Å, $\beta = 3.6$ Å, $\chi = 11.36$ Å, with $\beta = 103.88^{\circ}$ and $\alpha, \gamma = 90^{\circ}$, in agreement with Armstrong and collaborators[141]. The morphology of Na₂-NDC synthesized in methanol (henceforth named Na₂-

NDC_{MeOH}) was studied using SEM. The SEM images showed an oriented agglomerate of platelets, with a thickness in the order of nanometers and a length around 2-3 microns, as illustrated in Figure V.3c. Finally, a specific surface area of 7.3 m²/g was measured for Na₂-NDC_{MeOH} through the BET analysis.

As disodium naphthalene dicarboxylate is highly soluble in water, therefore it is possible to dissolve and crystallize the molecule in an aqueous medium: this solubilization-precipitation process can modify the crystal structure and morphology of Na₂-NDC and affect the electrochemical performance of the material, as already observed in previous studies[231,247]. The Na₂-NDC crystallization step was carried out by dissolving 1 g of powder in 10 mL of water, followed by magnetic stirring for 1 hour. The solvent was then removed by heating the solution to 60 °C overnight. X-ray Diffraction analysis showed some difference in diffraction peaks, both in the position and intensity (Figure V.3b). Unfortunately, given the quality of acquired powder pattern related to the size of the crystallite, it was not possible to refine the structure of Na₂-NDC after recrystallization in water (hereinafter Na₂-NDC_{H2O}). Thus, it is only possible to conclude that the two molecules have a different crystalline structure, as also shown by Ogihara and Kishida in the case of lithium salts[231]. SEM images of Na₂-NDC_{H2O} showed a cluster of three dimensional morphology of cuboidal particles with lateral dimensions between 2 to 5 μ m and lengths ranging up to several tens of microns (Figure V.3d). Hence, the first conclusion is that the size of the particles of Na₂-NDC_{H2O} is much larger than what was observed in the previous case, and this is a crucial parameter for the electroactivity inside an electrode. This result was also confirmed by the BET analysis and by the comparison of the particle size distributions curves. The BET surface obtained after dissolution-crystallization is 2.5 m²/g, almost three times lower than the previous measurement. It is well-known that a reduction in specific surface area is directly linked to an increase in particle size. In addition, the Particle Size Distribution (PSD) analysis was performed for both materials. The curves obtained (illustrated in Figure V.3e,f), showed an increase in the average size of the particles after recrystallization, passing from a curve located entirely <1 micron (green line) to a curve centered between 2-4 microns (red line).

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Figure V.3 Comparison of Na₂-NDC_{MeOH} (green line) and Na₂-NDC_{H2O} (red line) by powder X-rays diffraction. Scanning Electron Microscopy of Na₂-NDC as-synthesized (b) in methanol (Na₂-NDC_{MeOH}) and (c) after recrystallization in water (Na₂-NDC_{H2O}).

Optimization of the Na₂-NDC electrode preparation

In order to understand the differences in terms of electrochemical properties between the two active materials obtained, with and without the crystallization step in water, the two active materials were prepared using an organic solvent (N-methyl pyrrolidone, NMP). Since the active material is not soluble in NMP, no change in morphology or crystal structure is expected from what is shown in Figure V.3. In addition to the two formulations in NMP, a preparation using water to make the slurry was formulated. In this case, the Na₂-NDC dissolves and recrystallizes during

the preparation process. The electrode was prepared using 60% by weight of active material, 25% of carbon C45, 13% of carboxymethylcellulose (CMC) binder and 2% of styrene-butadiene rubber (SBR), to improve the flexibility of the electrode.

The first formulation, Na₂-NDC_{MeOH} prepared in NMP, shows a homogeneous distribution of the active materials along the whole cross-section, which is composed of small particles well dispersed in the conducting carbon (Figure V.4a). The disodium naphthalene dicarboxylate morphology is similar to that of the pristine material shown in Figure V.3c. In the case of the Na₂-NDC_{H20} prepared in organic solvent, the electrode cross-section showed a non-homogeneous distribution of the active material. Indeed, the SEM observation revealed the presence of larger cuboids rods (tens of microns in length) that are composed of smaller recrystallized active material and covered with the conductive carbon and the binder (Figure V.4b). The third formulation, with aqueous solvent for the preparation of the slurry, leads to the dissolution of the active material and to a subsequent crystallization of this during the drying process of the electrode, carried out in 2 hours at 60 °C. This process can be defined as an *in-situ crystallization* of Na₂-NDC directly in the composite electrode (henceforward called Na₂-NDC_{insitu}). This procedure leads to the formation of the same crystalline structure observed for Na₂-NDC_{H2O} (as illustrated in Figure VII.19, Experimental part), *i.e.* the re-crystallized Na₂-NDC alone in water, with a similar but not identical morphology. In that case, the parallelepiped-shaped particles are smaller, between 2-3 microns (Figure V.4c). Furthermore, no large agglomerates were observed, and the active material particles are well dispersed along the electrode. The BET analysis of the three composite electrodes confirms the trend of the particle size observed in the SEM images of the cross-section. The first formulation shows the highest specific surface, with 13.2 m²/g, the second formulation exhibited a BET of 9.9 m^2/g and finally for the third formulation, the one with aqueous solvent, an intermediate value of 11.7 m^2/g was measured.

In order to compare the electrochemical properties of the three preparation of disodium naphthalene carboxylate, the three electrodes were studied using the same conditions. The electrochemical tests were performed in half-cell *vs.* Na, using 2023 Coin cells assembled in the glovebox under inert atmosphere. The galvanostatic test were carried out using a potential window of 2.0-0.05V at C/20 rate (1 Na⁺ exchange in 10hours). The electrochemical results for the three formulations were reported in Figure V.4d, e, f.



Figure V.4 SEM images of cross-section of three different Na₂-NDC electrodes a) Na₂-NDC synthesized in methanol and prepared in NMP (Na₂-NDC_{MeOH}), b) Na₂-NDC recrystallized in water and prepared in NMP (Na₂-NDC_{H2O}) and c) Na₂-NDC synthesized in MeOH and prepared in water (Na₂-NDC_{insitu}). d-f) Evolution of the specific capacity as a function of cycle number of the three Na₂-NDC electrodes, cycled in a half-cell vs. Na, in a potential range of 2.0-0.05 V with NP30 electrolyte at C/20 rate.

Both the formulation Na₂-NDC_{MeOH} and Na₂-NDC_{insitu} showed a specific capacity of *ca*. 300 mAh g⁻¹ after the first discharge, higher than the capacity observed for Na₂-NDC_{H2O}, measured in 202 mAh g⁻¹. Despite the lowest capacity, the latter preparation showed the highest reversibility after the charge step. The reversible specific capacity upon the first cycle was measured at 162 mAh g⁻¹, *i.e.* an overall reversibility of 80%, whereas the organic preparation of Na₂-NDC showed a high irreversibility, with only 57% of reversible capacity (171 mAh g⁻¹). The aqueous preparation exhibited an intermediate value in terms of reversibility (73%), but with the highest specific capacity after the first full cycle, at 214 mAh g⁻¹. Furthermore, this preparation also showed the best capacity retention along cycling: after 20 cycles, a reversible capacity of 185 mAh g⁻¹ was measured, corresponding to an 86% of the initial capacity. Organic formulations exhibited a capacity for Na₂-NDC_{MeOH} and 74% for Na₂-NDC_{H2O} after 20 cycles.

These electrochemical results are in good agreement with a previous study of Na₂-NDC-based electrode preparation[247] and can be explained by the electrode architecture described above. The NMP preparation using Na₂-NDC_{MeOH} showed the higher BET surface area due to the small particle size, which lead to a thicker SEI layer formation: the increase of the SEI layer results in

the high irreversibility observed during the first cycle of Na₂-NDC_{MeOH}. The counterproof is the low irreversibility measured in the case of Na₂-NDC_{H2O}, where the largest particle size was observed, with a consequent decrease in the specific surface and a minor formation of the SEI layer. This hypothesis is also confirmed by the trend of the BET surface for the three composite electrodes illustrated in the previous paragraph. On the other hand, the presence of particles of excessive size, as in the case of Na₂-NDC_{H2O}, can lead to a loss of electrode capacity. This phenomenon could be ascribed to the difficulty of the sodium ions to fully penetrate the active material. It can therefore be considered a kinetic limitation, which could be demonstrated with extremely low C-rate tests. In the design of an electrode, it is necessary to consider both drawbacks, to find a good balance between irreversibility and loss of capacity, both of which are related to the size of the particles. No substantial differences were observed regarding the insertion/de-insertion potentials between the different preparations, in terms of average redox potential (0.45 V vs. Na⁺/Na), as well as in terms of polarization, quantified as ca. 100 mV for all the electrodes. The aqueous preparation showed the best trade-off between the two effects. This electrode preparation reduced the irreversibility and increased the reversible capacity in the first cycle. Considering these results, the aqueous preparation was selected for the assembly of the full-cell vs. NVPF.

Synthesis and electrochemical characterization of NVPF

Na₃V₂(PO₄)₂F₃ (NVPF) was prepared using the synthetic route previously described by Tarascon *et al*[248]. The first step was the preparation of carbon-coated VPO₄ (C-VPO₄), mixing in water H₃PO₄, V₂O₅ and agar-agar rubber in water at 85°C. Then, the solid was annealed, to obtain carbon coated VPO₄ (C-VPO₄). NVPF was then obtained by heating a stoichiometric ball-milled mixture of 3NaF + 2C-VPO₄ at 700 °C for 1.5 hour under an argon atmosphere. The carbon coated NVPF was characterized using X-Ray Diffraction (XRD) analysis and SEM microscopy, to confirm the synthesis of one pure phase and analyze the morphology, respectively. XRD powder pattern (Figure V.5a) showed a crystal structure and cell parameters in very good agreement with those reported in previous works[252,253]. Furthermore, no peaks related to impurities derived from the synthetic route were observed, confirming the synthesis of pure active material. Scanning Electron Microscope (SEM) images of NVPF (Figure V.5b) showed a cluster of irregular-shape particules from size ranging between of 2 to 5 µm and lengths ranging up to tens of microns, and irregular aggregates of spheres and shards on their surfaces.



Figure V.5 a) XRD powder pattern and b) Scanning Electron Microscope (SEM) image of Na₃V₂(PO₄)₂F₃ (NVPF).

As a next step, the Na₂-NDC was incorporated in a full-cell configuration. Na₃V₂(PO₄)₂F₃ (also called NVPF), a well-studied active material, already used in sodium-ions batteries produced by the company TIAMAT, was selected as positive electrode to form a hybrid (inorganic/organic) full cell. Prior to the preparation of the complete cell, the electrochemical properties of NVPF were investigated in half-cell *vs.* metallic Na. To ensure consistency with the previous tests using Na₂-NDC, the same experimental set-up was used for the galvanostatic tests in half-cell. The results obtained after 100 cycles are shown in Figure V.6. NVPF exhibited a capacity of 125 mAhg⁻¹ after the first charge, divided into two plateaus of equal size of 62.5 mAh g⁻¹ each, the first located at 3.7 V *vs.* Na⁺/Na and the second at 4.2 V *vs.* Na⁺/Na. On the discharge, a specific capacity of 117 mAh g⁻¹ was measured, corresponding to 94% reversibility after the first cycle. Furthermore, the NVPF showed excellent stability over cycling with, after 100 cycles, a reversible capacity of 114 mAh g⁻¹, with a 97% of capacity retention.



Figure V.6 Potential-composition profile of 1st, 2nd and 100th cycle of NVPF electrode in half-cell vs. metallic Na, galvanostatically cycled over a potential window range of 4.25-1.75 V, using 1 M NaPF6 in EC/DMC 50:50 as electrolyte, at C/20 rate; ; b) corresponding evolution of the specific capacity as a function of cycle number at C/20 rate.

Electrolyte screening in half-cell Na₂-NDC/Na

In sodium ion cells, the type of electrolyte plays a fundamental role in the cyclic life of the cell, especially thanks to the improvement in the formation and degradation of the SEI layer. In recent years, several electrolytes and additives for sodium batteries were developed. In the present work three different electrolytes, already reported in the literature, were prepared and analyzed in order to maximize the electrochemical performance and cycling life of the organic electrode in such configuration. The electrolytes used are NP30, NP30 with the addition of 3% fluoroethylene carbonate (FEC), from now on called NP30+3%FEC and MAGIC electrolyte, which consists of NaPF₆ in EC/PC/DMC mixture with 4 additives: sodium oxalate (difluoro) borate (NaODFB), vinylene carbonate (VC), succinonitrile (SN), and tris-trimethylsilylphosphite (TMSPi). The latter electrolyte was reported by Tarascon and coworkers[254] as an optimized electrolyte for sodium-ion batteries. The composition and preparation of all three electrolytes was described in detail in the Experimental section.

The assembly of a full-cell requires a precise balance between the capacity of the cathode and the anode (and their respective masses), to avoid several issues as sodium plating phenomena. However, the capacity of the negative electrode can be strongly influenced by the type of electrolyte (and its additives). The difference mainly related to the formation process of the SEI layer, due to a different consumption of sodium ions (and consequently the irreversible capacity). Half-cell Na₂-NDC vs. Na with the different electrolytes were assembled to obtain the exact specific capacity of the electrode using different electrolytes. Electrochemical tests were performed using the conditions described for the previous tests. Figure V.7 shows the galvanostatic profiles of the first 5 cycles (formation cycles) of the Na₂-NDC half-cells vs. Na with the three different electrolytes: in the case of MAGIC electrolyte, the 5 formation cycles were carried out at 55 °C. Using the NP30 electrolyte, a specific discharge capacity of 293 mAh g⁻¹ was observed, which increases to 323 mAh g⁻¹ using the NP30 with the addition of 3% FEC, up to 350 mAh g⁻¹ of discharge capacity with the MAGIC electrolyte. This increase in discharge capacity is linked to the formation of a different SEI layer. The presence of additives leads to a greater consumption of sodium ions in the first discharge step, causing an increase of the irreversible capacity, but has the advantage of forming a more stable SEI, thus improving stability over cycling. Despite these differences, the reversible capacity in the first cycle was not affected. In the three cases examined, the reversible capacity was measured in a range between 220 and 240 mAh g⁻¹,

in agreement with what was observed in the preliminary tests reported in Figure V.4c. About the redox potential, all the curves showed an average value of 0.45 V vs. Na⁺/Na. It is interesting to note that the first discharge is 150 mV lower in potential than in subsequent cycles. This phenomenon was studied by Ogihara for the dilithium naphthalene dicarboxylate: the authors explained that a small amount of lithium ions remains irreversibly inserted into the active material structure, causing a negligible loss of capacity, but improving the ionic conductivity of the Li₂-NDC.[246] This could also be true in the case of Na₂-NDC, however, to confirm this hypothesis, a detailed characterization of the crystal structure along cycling will be necessary, to exclude that the phenomenon is linked to a change in the crystalline phase.



Figure V.7 Potential-capacity profile of the first 5 cycles (formation cycles) of half-cells Na2-NDC vs. Na, galvanostatically cycled over a potential window range of 2.0-0.05 V vs. Na+/Na at C/20 rate using a) NP30, b) NP30+3%FEC and c) MAGIC electrolyte (at 55 °C).

Electrochemical characterization of hybrid full-cell NVPF/Na₂-NDC

A full hybrid cell NVPF/Na₂-NDC was assembled and studied. The balance of the masses of the electrodes was calculated using 125 mAh g⁻¹ as the specific capacity of the NVPF-based cathode. Based on the capacities exhibited in half-cell with different electrolytes, an equally balanced full cell NVPF/Na₂-NDC requires an anode mass/cathode mass ratio of 1:2.4 using NP30, 1:2.6 with NP30+3%FEC and 1:2.8 with MAGIC electrolyte; however, an excess of 10% of anode mass was employed in the assembled full cells, to avoid plating phenomenon. The full cell NVPF/Na₂-NDC with MAGIC electrolyte were cycled at 55 °C during the formation step (5 cycles).

In terms of output voltage, the hybrid cell showed two different plateaus (characteristic of the NVPF, Figure V.6) located at 3.44 V and 3.93 V in the first cycle and then at 3.3 V and 3.8 V in the following cycles, as showed in Figure V.8. This variation is due to the Na₂-NDC anode, which in the half-cell versus Na showed a shift in the reduction potential after the first cycle.

Development of Disodium Naphthalene Dicarboxylate as negative electrode for Hybrid Sodiumion batteries



Figure V.8 Potential-capacity profile of the 1st, 2nd and 75th cycle of NVPF/Na₂-NDC full cell, galvanostatically cycled over a voltage range of 4.2-0.0 V at C/20 rate using a) NP30, b) NP30+3%FEC and c) MAGIC electrolyte; d) corresponding evolution of specific capacity as a function of cycle number for the three full-cell using NP30 (blue), NP30+3%FEC (green) and MAGIC (red) electrolyte.

Concerning the cells' capacities (Table V.1), the three cells showed similar values after the first charge, around 125 mAh g⁻¹ (based on the cathode material), with a discharge capacity of 88 and 85 mAh g⁻¹ for MAGIC and NP30, respectively, and only 77 mAh g⁻¹ for NP30+3%FEC (all based on cathode mass). The cells showed an irreversibility between the 30% (with MAGIC electrolyte) and 40% (with NP30+3%FEC), in line with what was observed in the previous tests on half-cell (irreversibility of 30%-35% in the 1st cycle for all the electrolytes). After the formation step (first 5 cycles), an almost identical capacity was observed for NP30 and MAGIC electrolyte, 74 and 75 mAh g⁻¹, respectively, while the cell with NP30+3%FEC showing a much lower capacity (only 65 mAh g⁻¹ of specific capacity, based on the cathode mass). Concerning the capacity retention, the presence of additives in the electrolyte shows an improvement in the stability of the cell capacity. After 75 cycles, the full cell with NP30 exhibited the lowest capacity retention, 81% compared

with the 5th cycles (60 mAh g⁻¹/144 mAh g⁻¹ based on cathode/anode mass), while NP30+3%FEC electrolyte showed 86% of capacity retention (55 mAh g⁻¹ based on cathode mass); the best result was obtained in the full cell with MAGIC electrolyte: after 75 cycles, the capacity retention was 93% compared to the specific capacity after formation step (70 mAh g⁻¹/196 mAh g⁻¹ based on cathode/anode mass).

Floctroluto	1 st cycle cap.	5 th cycle cap.	75 th cycle cap.	Capacity retention
Electrolyte	(cathode/anode)	(cathode/anode)	(cathode/anode)	after 75 cycles
NP30	85/204 mAh g ⁻¹	74/178 mAh g ⁻¹	60/144 mAh g ⁻¹	81%
NP30 +3%FEC	77/200 mAh g ⁻¹	65/169 mAh g ⁻¹	55/143 mAh g ⁻¹	86%
MAGIC	88/246 mAh g ⁻¹	75/210 mAh g ⁻¹	70/196 mAh g ⁻¹	93%

Table V.1 Specific capacity of the 1st, 5th (end of the formation step) and 75th cycle of NVPF/Na2NDC full cell, voltage of 4.2-0.0 V at C/20 with three electrolytes NP30, NP30+3%FEC and MAGIC; all the specific capacity (mAh g-1) were reported for both cathode and anode mass. The capacity retention is calculated using the reversible capacity of the 5th cycle (after the cell formation step) and 75th cycle.

However, the above values do not consider the loss of capacity observed during the formation step. Taking into account all the capacity losses, in the best case (full cell with MAGIC electrolyte) only 56% of capacity retention was measured after 75 cycles. The 30% of overall capacity fading derives from the first cycle, due to the first SEI layer formation and irreversible insertion in conductive carbon. However, an additional 14% loss was observed between the 2^{nd} and 75^{th} cycle. A first deduction can be made by looking at the galvanostatic profiles shown in Figure V.8. In all three curves, the length of the first plateau does not decrease, remaining constant at 63 mAh g⁻¹ along cycling: it is therefore possible to exclude that the loss of capacity derives from the cathode, but it is exclusively addressed to the organic anode.

There are two possible main explanations for the loss of capacity: the first is the degradation of the SEI layer along cycling. This phenomenon leads to an overconsumption of Na⁺ ions through the formation of sodium carbonates and other species belonging to the new SEI layer formed. The second cause is the loss of active material of the anode; the latter can be due to multiple causes, as the dissolution/degradation of the electroactive molecule or a cracking/delamination effect of the electrode. For these reasons, it is considered that the sole phenomenon responsible for the irreversible capacity during sodiation is the SEI formation and, during desodiation, is the loss of active material.

A first estimation of the capacity loss can be obtained through the analysis of the evolution of Coulombic Efficiency (CE) along cycling, reported in Figure V.9b for the three tested cells. The MAGIC electrolyte (magenta dots) showed the higher CE, higher than 99% after 10 cycles and> 99.6% after 20 cycles; the other two electrolytes, NP30 (blue dots) and NP30+3%FEC (green dots), reaching 99% after 30 cycles and do not exceed 99.5% for the entire cycling test. This result confirms that the cell with MAGIC have a better capacity retention at each cycle.

Regarding the contribution of electrolyte degradation or active material loss, the curve Voltage *vs.* Q reported in Figure V.9a for the cell with the MAGIC electrolyte confirms that both effects play a role in the loss of capacity. Indeed, it is possible to notice a shift during the cycling of the Q^C(blue arrow) due to a degradation/reformation of the SEI layer, but also a shift of the Q^D (red arrow), due to the loss of active material at the anode.

Using the method reported by Gutierrez and collaborators[255], it is possible to decompose the total loss of capacity (Q^{irr}_{tot}) into the contributions deriving from the SEI degradation/reformation process (Q^{irr}_{SEI}) and that deriving from the loss of active material (Q^{irr}_{AM}). Equation 1 illustrates the formulas for calculating the two contributions Q^{irr}_{AM} and Q^{irr}_{SEI} at the cycle n+1, while in Figure V.9c,d are plotted the cumulative values of Q^{irr}_{SEI} and Q^{irr}_{AM} as function of the cycles, calculated for both the full-cells with the NP30 and MAGIC electrolyte.

a) $Q^{irr}_{tot} = Q^{C}(n) - Q^{D}(n)$ b) $Q^{irr}_{AM}(n+1) = Q^{D}(n) - Q^{D}(n+1)$ c) $Q^{irr}_{SEI}(n+1) = Q^{C}(n+1) - Q^{D}(n)$

Equation 1 Formulas employed to calculate a) total irreversible capacity at cycle $n(Q^{irr}_{tot})$; b) irreversible capacity due to active mass loss at cycle $n+1(Q^{irr}_{AM})$; c) irreversible capacity due to SEI layer formation at cycle $n+1(Q^{irr}_{SEI})$.

From the two graphs it is possible to deduce that both phenomena play a role in the capacity loss: however, the contribution deriving from the degradation of the SEI layer and the consequent reformation is predominant, leading to double the loss of capacity both in the cell with the NP30 and the MAGIC. Another interesting observation is that the full cell with the NP30 shows a loss of capacity of more than double compared to the cell with the MAGIC, quantified at 32 and 14 mAh g⁻¹, respectively (Figure V.9c). This result can be explained by the formation of a more stable SEI layer in the case of hybrid full-cell with MAGIC electrolyte, because the additives form a stable polymer which avoids cracking or dissolution of the SEI layer. On the contrary, without polymerizable additives (NP30), the SEI layer showed a low stability, leading to a higher loss of

capacity: an unstable SEI layer leads to a greater consumption of sodium ions, because they are trapped in the solid electrolyte interface. The addition of FEC in the NP30 has only a small effect on the SEI stability, with a slight improvement of the capacity retention (86% of capacity retention in full cell NVPF/Na₂-NDC); as a drawback, this additive induces a large consumption of sodium ions to form the SEI (40% irreversibility in the first cycle only), with a consequent marked loss of capacity during the formation cycles. In the next paragraph we will focus on the SEI layer and electrolyte degradation, while subsequently the phenomena of the active material and of the electrode degradation will also be investigated.



Figure V.9 a) Evolution of Charge (Qc) and Discharge capacity (QD) for NVPF//Na₂-NDC full-cell with MAGIC electrolyte; b) Evolution of Coulombic Efficiency (CE) as function of the cycles for NVPF//Na₂-NDC full-cell with NP30 (blue dots), NP30+3%FEC (green point) and MAGIC (magenta dots). Evolution of capacity loss as function of the cycles deriving from: c) SEI degradation and d) loss of active material for NVPF//Na₂-NDC full-cell with NP30 (blue dots) and MAGIC (magenta dots).

In order to elucidate the effect of the electrolyte on the degradation of the SEI layer, a gas chromatography coupled with mass detector (GC/MS) analysis was performed. After cycling the cells with the three electrolytes, the separators were recovered and analyzed by GC/MS (Figure V.10). In the case of the cell with NP30, the presence a peak related to an organic specie deriving from the degradation of the electrolyte, the dimethyl 2,5-dioxahexane dicarboxylate (labelled 1₁),

was observed. This molecule, derived from the reduction of dimethyl carbonate and the following reaction between sodium salts and ethylene carbonate, is commonly used as an indicator of electrolyte degradation[256,257]. The chromatograms related to the cells with NP30+3%FEC and MAGIC electrolytes did not show visible peaks related to these two degradation products which indicated that in the presence of the additives the SEI formed during the first cycles is sufficiently stable and does not lead to an overconsumption of electrolyte.



Figure V.10 Gas-chromatography-MS analysis of the separator recovered after 100 cycles of NVPF/Na2-NDC full-cell, galvanostatically cycled over a voltage range of 4.2-0.0 V at C/20 rate using NP30(top), NP30+3%FEC (middle) and MAGIC (bottom) as electrolyte.

C-rate and long cycling test of hybrid full-cell NVPF/Na₂-NDC

Despite the formation of a stable SEI layer offer better capacity retention over cycling, such a layer can drastically disturb rate performances. A thicker SEI layer can affect the mobility of sodium ions across the interface, resulting a slowing down in the mobility of sodium ions involved in the redox process. This phenomenon was investigated through a C-rate test (Figure V.11a). At C/5, both the cells with NP30 and MAGIC electrolytes showed the same specific capacity, *ca* 70 mAh g⁻¹, whilst the cell with NP30+3%FEC exhibited a capacity of only 57 mAh g⁻¹. As the C-rate increased, the best performances were observed with the NP30 electrolyte displaying a reversible capacity of 58 and 27 mAh g⁻¹ at 1C and 5C, respectively. These capacities were higher than what was measured in the case of the MAGIC and NP30+3%FEC electrolytes at the same C-rates. This effect of reducing the rate capabilities is probably due to the different SEI layers, above all to their composition and thickness. As perspective, an in-depth analysis of SEI layer, using XPS technique and TEM microscopy, could in the future clarify its role in the kinetics and stability of the electrode.

The stability over long cycling of the two full-cells NVPF/Na₂-NDC with NP30 and MAGIC were evaluated after 400 cycles at C/5 as C-rate (Figure V.11b). After 400 cycles, the full cell with the MAGIC electrolyte displayed a specific capacity of 48 mAh g⁻¹ (based on cathode mass), corresponding to 67% of the capacity after the formation step (72 mAh g⁻¹), while the NP30 shows a 10% lower retention (57%, 41 mAh g⁻¹). The results obtained with the hybrid full cell NVPF/Na₂-NDC using the MAGIC electrolyte are encouraging for a future employment of organic materials since for the first time a full hybrid sodium-ion battery showed a stable capacity upon 400 cycles, with a capacity retention of 67% after the formation phase. In addition to the great stability over cycling, the hybrid cell also showed a good reversibility in the first cycle, around 70%. Both this two electrochemical features, capacity retention and reversibility in the first cycle, are a marked improvement compared the other hybrid cells reported in the literature[142,245], where the reversibility is around 40% and the capacity fades after 20 cycles.





Figure V.11 a) Rate capability performed at C/5, 1C, and 5C rate cycle of NVPF/Na2NDC full cell, using as electrolytes NP30 (blue), NP30+3%FEC (green) and MAGIC (red), voltage of 4.2-0.0 V; b) corresponding evolution of the specific capacity as a function of cycle number for the full-cell with NP30 (blue) and MAGIC (red) electrolyte at C/5 rate.

Taking into account the capacity loss during the formation cycles, the capacity retention after 400 cycles is around 40% compared to the first charge of the cell. As already pointed out in the previous paragraph, the disappearance of the capacity can be originated from multiple phenomena. The SEI degradation process, discussed above, play a non-negligible role in terms of capacity fading and is responsible for the difference in capacity retention observed between the two cells with NP30 and MAGIC electrolyte. However, the capacity fading could also be addressed to the loss of active material, due to dissolution or degradation of the active material, or mechanical stress phenomena, like particle cracking or electrode delamination from the current collector. To go beyond and to guide future investigations, a series of post-mortem tests were performed on cycled full-cell electrodes to understand more precisely what is happening upon cycling.

Post-mortem investigation of hybrid full-cell NVPF/Na₂-NDC

Firstly, to understand if the capacity is reversible or not, the full-cells NVPF/Na₂-NDC with NP30 electrolyte were disassembled after 100 cycles and each electrode was cycled in a new half-cell *vs.* Na with fresh electrolyte. In Figure V.12 were report the electrochemical curves of the original full cell and the two post-mortem half-cells NVPF *vs.* Na (Figure V.12, red line) and Na₂-NDC *vs.* Na (Figure V.12, blue line); to simplify the comparison, the capacity of the three cells was expressed directly in mAh. After the first cycle, the half-cell NVPF/Na showed the complete recovery of the specific capacity of the NVPF, indicating that the positive electrode did not lose

its ability to exchange the sodium ions (NVPF is therefore not involved in the capacity loss of the full cell). Regarding the Na₂-NDC-based anode, the specific capacity obtained after the first cycle in half-cell *vs*. Na was identical to the capacity measured in the 100th cycle for the full-cell. Then, contrary to what was observed for the cathode, the Na₂-NDC electrode showed a non-reversible loss of the specific capacity. This result indicates that most of the capacity loss observed in full cells derives from phenomena related to the active material: if electrolyte degradation were the only cause, a complete recovery of the capacity would have been obtained also for the anode. From this test, the reversible capacity loss due to only electrolyte degradation, cannot be identified: this may be due to the experimental errors intrinsic for this test. Indeed, the mass of the disassembled electrode which may not be precise, due to the presence of fibers of the separator, residual electrolytic salt, weight measurement error and other interferences.



Figure V.12 Potential-capacity profile of 1st and 100th cycle of NVPF/Na₂-NDC full cell (1st cycle full green line, 100th cycle dot green line), 1st cycle of NVPF vs. Na (red line) and Na₂-NDC vs. Na (blue line) post-mortem half-cells, with NP30 electrolyte.

Solubilization of the active material, a recurrent issue for organic-based electrodes[173,258], was our first hypothesis to explain capacity fading. Therefore, the dissolution of the active material in the electrolyte was investigated *via* UV-vis spectroscopy analysis, a highly sensitive technique able to detect very small concentration of aromatic compounds. After 100 cycles, the full cell was disassembled, the separator was recovered, placed in two different solvents (EC/DMC 50/50 and water) and the solution analyzed with UV-vis spectrometer. Comparing the spectra recorded for the separator with the pristine material prepared in water, no trace of Na₂-NDC were detected in

both solvent (all the spectra reported in Figure V.13). The insolubility of the active material in the electrolyte is an important characteristic of Na₂-NDC, because it allows to extend the life of the battery.



Figure V.13 UV-vis spectra of pristine Na2NDC in water (red line) and separator poured in water (blue line) and DMC (violet line).

Solubility issue eliminated, other origins of fading were investigated. Thus, SEM/EDX coupled analysis of Na₂-NDC electrode was performed in order to investigate the particle cracking or electrode delamination due to aging mechanism. Figure V.14 showed the cracking on the Na₂-NDC particles, due to the expansion/shrinkage they undergo following the dis-/insertion of sodium ions in the structure. Nevertheless, the cracking phenomenon does not lead to pulverization of the active material particles, as is observed for example in silicon particles[38,39]. The low volume expansion due to dis-/insertion process is a common feature for organic materials, as also shown by Ogihara and coworkers for Li₂-NDC[219], and it marginally affects the specific capacity fade of the organic-based electrode.



Figure V.14 High magnification SEM image of Na2-NDC particles after 100 cycles in full-cell vs. NVPF.

Surprisingly, by comparing SEM images before and after cycling, with NP30 or MAGIC as electrolyte, it was observed a clear delamination of the electrode from the current collector (void clearly observed in Figure V.15b,d). Thus, it is possible to deduce that continuous delamination of the electrode occurs during cycling and might provokes battery failure after complete delamination. This aspect was observed for the first times for carboxylate-based electrode and is useful for future development. In addition to SEM, EDX analysis was performed and reveals presence of high amount of fluorine over the current collector surface independently of the electrolyte (Figure V.15c and Figure V.15e). This fluorine layer can be attributed to the formation of the compound AIF₃, widely recognized as a side-product of aluminum reactivity toward PF₆, as already illustrated by Ma[259] for lithium ions and Konarov[260] for sodium and potassium ion batteries. In previous studies, it was observed that in presence of moisture, PF6⁻ is transformed into HF, which thus react with the Al-based current collector to form a passivation layer composed AlF₃. In general, the formation of a passive film of AlF₃ has beneficial effects, protecting aluminum from other chemical side-reactions that may occur during cycling. In this case, the formation of AlF₃ has a dramatical effect and leads to a thick layer responsible for the delamination of the electrode.



Figure V.15 SEM images of cross-section of Na2-NDC electrodes a) before cycling and after 100 cycles in full-cell configuration vs NVPF b) using NP30 electrolyte and c) related EDX color mapping; d) using MAGIC electrolyte and e) related EDX color mapping.

At this point, it is important to understand exactly why such behavior occurs. Intuitively, the presence of water in the electrode is the first natural option that comes to mind. Nevertheless, the TGA analysis performed on the formulated negative electrode indicates that there is no water remaining inside (Figure VII.20, experimental part), which is quite surprising but indicates that the problem does not come from a drying defect of the electrode. Another hypothesis would be to consider a reactivity between the electrode (or rather the active material) and the current collector. One option could be a chemical reaction between the active material and the aluminum. Such reactivity can make sense since carboxylate and carboxylic acid in general have a natural affinity with metals. To evaluate this, different types of current collectors like carboncoated AI and copper, widely employed in the battery industry to improve the electrical contact and decrease the resistance at the interface with the electrode, were used for the formulation of the electrodes (Figure V.16). For the aluminum current collector covered with a thin layer of carbon, a gradual decrease of the capacity is observed from the 2nd cycle. Moreover, the capacity displayed at the second cycle is lower than the one obtained with the collector without coating. On the other hand, using a copper current collector a better stability was observed during cycling whatever the electrolyte (198 mAh g⁻¹ of reversible capacity after 20 cycles compared with 185 mAh g⁻¹ for Al). The use of copper seems to be more suitable in terms of performance, since no delamination is also observed (Figure V.16c,d).





Figure V.16 Evolution of the specific capacity as a function of cycle number of Na2-NDC electrodes coated on a) carbon-coated aluminum and b) copper as current collector, cycled in a half-cell vs. Na, in a window range of 2.0-0.05 V at C/20 rate; c) SEM images and d) related EDX color mapping of cross-section of Na₂-NDC electrode on copper current collector after 20 cycles.

The results obtained with the copper current collector showed the absence of delamination effects and a good capacity retention, paving the way for a possible use of copper to enable the Na₂-NDC-based negative electrode. Nevertheless, it appears necessary to continue the investigations to avoid the delamination from Aluminum current collector, for example through chemical modifications of the surface or using different electrolyte additives able to prevent the uncontrolled growth of the AlF₃ layer. The perspective of these future development is to enable the use of aluminum as a current collector, to reduce the weight and manufacturing cost of the negative electrode.

Conclusions

In this paper, we presented the different prepration of an organic-based electrode composed of disodium naphthalene dicarboxylate (Na₂-NDC) with the view to build a full cell. Through the chemistry of Na₂-NDC it was possible to tune the crystalline structure and morphology of the particles to maximize their electrochemical properties which reach maximum value using aqueous preparation (208 mAh g⁻¹ of reversible capacity in the first cycle and 185 mAh g⁻¹ after 20 cycles). Such aqueous formulated electrode was then integrated in a full cell in association with $Na_3V_2(PO_4)_2F_3$ (NVPF), an inorganic cathode well known in the sodium-ion battery field. Thanks to an electrolyte screening, the different full hybrid cells assembled showed remarkable electrochemical performance, with best performances obtained with a specific electrolyte named MAGIC (NP30 with four additives). In the first cycle at C/20, the full cell showed a reversible capacity of 88 mAh g⁻¹ (based on the cathode mass), corresponding to a 30% of irreversibility. After the capacity loss during the formation step (5 cycles), the remained stable for 75 cycles (specific capacity of 70 mAh g⁻¹). Furthermore, in the long cycling tests performed at C/5 rate, the hybrid cell with MAGIC electrolyte exhibited a capacity retention of 67% after 400 cycles. These performances represent a significant improvement over the previous full hybrid cells, based on aromatic dicarboxylates, reported in literature. Regarding the rate performance, the cell with the NP30 showed the best performances, with 58 mAh g⁻¹ and 27 mAh g⁻¹ (based on cathode mass) of reversible capacity at 1C and 5C, respectively. The results obtained in hybrid cells, in terms of capacity, cycling stability and rate performance, are interesting and make this material an excellent candidate to replace Hard Carbon in future. In order to understand the causes of capacity loss during long cycling tests, a series of *post-mortem* analysis were performed. Such experiments enabled the identification of the main cause of the loss of capacity in the delamination of the electrodes from the Al current collector. Preliminary tests on Na₂-NDC electrodes, fabricated with as copper current collector, showed improved performances and the absence of delamination phenomena. As a future perspective, the use of new types of current collector or modification on aluminum can enable the use of organic carboxylate-based electrode, to deliver maximum specific capacity and ensure stability over cycling.

Chapter VI. General Conclusions and Remarks

The work presented in this manuscript was conducted in the framework of CIFRE (Industrial Agreements for Training through Research) PhD thesis, financed by the Ministry of Higher Education, Research and Innovations (through ANRT) and Électricité de France S.A. (EDF), a French electric utility company. The research work was carried out in partnership between the Laboratoire de Réactivité et Chimie des Solides (LRCS) and the EDF R&D research center "Les Renardières".

In the first part of the thesis, the research work focused on the design and development of new positive organic materials for Lithium-ion batteries.

The first strategy was to modify the benzoquinone electroactive group, in order to improve its electrochemical performance, but preserving its advantages in terms of high specific capacity and chemical flexibility of the structure. The choice fell on the use of oxime as an electroactive group, not yet reported in literature for energy storage applications at the beginning of this thesis. Galvanostatic tests showed an average redox potential of 3.0 V vs. Li⁺/Li, with an excellent specific capacity in the first cycle, measured in 277 mAh g⁻¹; however, the electrode exhibited low capacity retention after 100 cycles, around 10-20%. Furthermore, TEM/EELS analysis was coupled with *exsitu* XRD to experimentally validate the hypothesized redox process. The results confirmed the complete reversibility of the lithium de-/insertion process the active materials and elucidate the role of microstructure to tune the electrochemical properties. This work has paved the way for future development of benzoquinone dioxime as new eco-sustainable positive materials for lithium batteries: however, it requires a rational design of the molecular structure to increase the redox potential and the capacity retention, both too low for full-cell applications.

In order to obtain higher redox potentials and superior rate performances, the research work focused on *p*-type materials, in which the redox mechanism is based on the de-/insertion of anions in the active material. In this case, a different strategy was pursued: two electroactive molecules already reported in the literature, Carbazole and Thianthrene, were selected and the molecular structure was engineered to improve their electrochemical properties.

Concerning the Carbazole, the molecular structure was modified *via* N-substitution, to reduce the solubility of the active material in the electrolyte and to improve its electrochemical properties. Three different derivatives were synthesized, one with an electron-donor substituent, one with an electron-withdrawing substituent and a carbazole phenylene dimer. The comparison of the

first two showed better performances for the carbazole with the electron-withdrawing group as N-substituent; however, both molecules were characterized by low specific capacity. The dimer exhibited the highest redox potential, around 4.0 V *vs.* Li, with a good specific capacity after 50 cycles (100 mAh g⁻¹). However, all three derivatives showed an electro polymerization phenomenon, confirmed by both ex-situ FTIR and *operando* XRD, which lead to low coulombic efficiency in the first cycle.

The research work has therefore moved to Thianthrene, an electroactive material already studied in polymeric form. As in the case of Carbazole, the applied strategy consists in the design of substituted thianthrene in the single molecule form. Specifically, the synthetic approach focused on the development of 2,7-disubstituted derivates of Thianthrene. Two different substituent groups were employed, having different electrochemical characteristics: methyl group (electron donor) and fluorine (electron withdrawing). Galvanostatic tests showed an improvement in performance thanks to disubstitution, both in terms of specific capacity and capacity retention. The best results were obtained with 2,7-difluorothianhtrene (DFTNT), which exhibited a redox potential of 4.1V vs. Li⁺/Li, a specific capacity of 90 mAh g⁻¹ in the first cycle and an outstanding capacity retention, 83% of retention after 500 cycles at 2C.

Considering the excellent results shown, DFTNT was chosen as the cathode material for an allorganic full-cell. Dilithium Naphthalene Dicarboxylate (Li₂-NDC), a well-known *n*-type negate materials, was chosen as anode thanks to its excellent electrochemical performance reported in literature. The all-organic full-cell, based on the dual-ion mechanism, showed an outstanding output voltage of 3.4 V, one of the highest reported for an all-organic full-cell. Moreover, at C/5 the DFTNT//Li₂-NDC exhibited a reversible capacity of 80 mAh g⁻¹ and 65 mAh g⁻¹ with 1 M LP30 and 2 M LP30, respectively. Thanks to the low quantity of conductive carbon in the electrode and the high output voltage of the cell, the dual-ion DFTNT//Li₂-NDC cell showed an energy density in the range 190 Wh kg⁻¹ in the first cycle, based on the mass of the entire electrode: this is an encouraging result for a future industrialization of this materials.

In the last part of the thesis manuscript, a study was reported on Disodium Naphthalene Dicarboxylate (Na₂-NDC) as a negative organic material for Sodium ion batteries. Different synthesis strategies have been employed to modify the morphology and crystal structure of the active material particles, in order to improve the electrochemical performance. Thus, a hybrid
inorganic/organic full-cell was assembled coupling the Na₂-NDC electrode with Na₃V₂(PO₄)₂F₃ (NVPF), an inorganic cathode. An in-depth electrochemical study of the full cell was performed to evaluate the stability over cycling using different electrolyte additives. The Na-ion hybrid cell NVPF//Na₂-NDC showed outstanding electrochemical performances, in terms of reversible capacity, stability over cycling and rate performances.

The main perspective enabled by this thesis work include the following:

- the proof-of concept of dioxime electrochemistry opens the way to a molecular engineering study, using substituents that can increase electrochemical performance.
- The investigation of different thianthrene derivates, electrode engineering (morphology and particle size of active material) and electrolyte optimization (salts, solvents and concentration) for high performance Dual-ion cell.
- The results obtained in hybrid cells, in terms of capacity, cycling stability and rate performance, are interesting and make this material an excellent candidate to replace Hard Carbon in future.

Besides the work presented in this manuscript, the author has been involved in other project, in collaborations with researchers in the LRCS:

- Preparation of 3D-printed electrode using organic material to prevent the corrosion of the current collector.
- Development of an environmentally-friendly lithium-terephthalate/polylactic acid (Li2-TP/PLA) composite filament, for its use, once 3D-printed *via* Fused Deposition Modeling (FDM), as negative electrode of a lithium-ion battery.
- Simulation of manufacturing of sodium-ion battery electrode, using an organic-based active material. This three-dimensional computational workflow accounts for the slurry preparation, drying process and electrode calendaring steps.

Chapter VII. Experimental part

Experimental protocols

Chapter II.

Computational detail. Dilithium benzoquinone dioxime and dinitrosobenzene were studied using DFT calculations performed with Gaussian 09 code. M062X functional with 6-311+G (2d,2p) level of theory was employed to calculate molecular and electronic structure of both molecules, with very tight criterion of convergence and with the vibrational frequency analyses, to confirm the true local minima (carried out at the same computational level to evaluate the Gibbs free energy at 298K). For all the calculations, the solvent effects were considered using a polarizable continuum model (PCM), particularly through the solvation model based on density (SMD); the simulations were performed with acetonitrile as solvent (ϵ =37.5).



Figure VII.1 Liquid ¹H NMR spectra of BQD in DMSO- d_6

Synthesis of p-Benzoquinone dioxime lithium salt (Li₂-BQD) synthesis. The synthesis of Li₂BQD was performed in inert atmosphere, to avoid the oxidation from air. 100,0 mg of p-benzoquinone dioxime (0,72 mmol) were transferred in a glovebox under argon (O₂ content < 0.1 ppm) and added in a round flask containing 10 mL of methanol, resulting insoluble. 60,81 mg of LiOH·H₂O (1,44 mmol, 2 eq.) were added to the solution and mixed overnight at room temperature. After the reaction time, the solution appears clear dark brown, without any precipitate. The product was precipitated using acetone as antisolvent; then the precipitate was retrieved by filtration and washed three times with acetone. The greenish solid was dried under vacuum overnight at 110°C. Yield: 90%. IR (cm⁻¹) selected bands: 1448 (m), 1348 (m, C-N), 1128 (v_s), 970 (v_s), 834 (v_s), 792 (v_s). ¹H NMR (D₂O, 400 MHz, δ ppm): 7.00 (d, 1H), 6.88 (dd, 2H), 6.69 (dd, 2H), 6.58 (d, 1H).



Figure VII.2 Liquid 1H NMR spectra of Li₂-BQD in H₂O

Synthesis of dinitrosobenzoquinone (DNB): The synthesis of DNB was adapted from the procedure reported by Muller et al[189]. 1 g of BQD (7,2 mmol) was added in 100 ml of water and stirred at 80 °C, to form of a homogenous suspension. 5.84 g of FeCl·6H₂O (21.6 mmol, 3 eq.) were dissolved in 20 ml of water and the resulting solution was added warm to the BQD/water suspension over a period of 5 minutes under stirring. The green-brown suspension was then stirred for 5 minutes at 80 °C. The precipitate obtained was filtered off under vacuum while still hot, washed with hot water (60°C.) and then washed with acetone. The solid was dried at under vacuum at 100° C. The yield of DNB was 95%. IR (cm⁻¹) selected bands: 1485(s), 1306 (m, C-N), 1251 (v_s, trans N-O), 1102 (v_s, -N-N-), 995 (v_s, -N-N-), 858 (v_s, C-H), 775 (v_s) and 570. ¹H NMR (DMSO-d₆, 400 MHz, δ ppm): 7.23 (s, 1H), 7.13 (d, 2H), 6.74 (d, 2H), 6.65 (s, 1H).

Experimental part



Figure VII.3 Liquid 1H NMR spectra of DNB in DMSO-d6

Formula	$C_6H_4N_2O_2$
MW (g/mol)	136.11
Crystal system	Monoclinic
Space group	P21/n
a (Å)	6.3913(3)
b (Å)	11.29544(11)
c (Å)	3.71269(5)
lpha (deg)	<i>90</i> °
eta (deg)	<i>90</i> °
γ (deg)	92.523(4)°
V (ų)	267.770(14)
l (Å)	1.54056
D (g/cm ³)	1.70
Т (К)	298

Table VII.1 PDNN Crystal structure parameters.



Figure VII.4 TEM investigation of Li2-BQD at 0.5 cycle (a to c) and 1 cycle (d to f) with a) and d) general bright field images, b) and e) associated SAED pattern and c) and f) associated dark field image according to the direction circle in red. The arrows indicate the crystalline area.

Chapter III.

Synthesis of Lithium 2-(9H-Carbazol-9-yl)acetate (LiCZA): The synthesis of 2-(9H-Carbazol-9-yl)acetic acid (CZA) was adapted from the procedure reported by Zhang et al[201]. 501.6 mg of Carbazole (3 mmol) and 3 equivalent of sodium hydride (216,0 mg, 9 mmol) was dissolved in 20 mL of DMSO and heated to 85°C and stirred for 30 min. A dark-brown solution appears and 500.22 mg of bromoacetic acid (1.2 equiv., 3.6 mmol) was added over a 30 min time span; the solution was stirred overnight. The reaction mixture was then, poured into 100 ml cold water and filtrated to remove the insolubilities. After filtration under vacuum, HCl 36% was added until a pH of 0.5 was reached, during which time a white precipitate appeared. The precipitate was retrieved by centrifugation and washed with water three times. The white solid was dried under vacuum at 100°C for one night. Yield: 54%. IR (cm⁻¹) selected bands: 3051 (m, O-H), 1720 (v₅, C=O), 1705 (v₅), 1485 (v₅), 1459 (v₅, C-H), 1325 (v₅, C-N), 753 (v₅, C-H), 723. ¹H NMR (CDCl₃, 400 MHz, d ppm): 12.99 (s, 1H), 8.16 (d, 2H), 7.55 (d, 2H), 7.44 (t, 2H), 7.22 (t, 2H), 5.23 (s, 2H).



Figure VII.5 Liquid ¹H NMR spectra of CZA in CDCl₃

LiCZA was synthesized starting from intermediate **CZA**. 100 mg of CZA (0.44 mmol) were added in 10 mL of water, resulting insoluble. 18.48 mg of LiOH×H₂O (0.44 mmol, 1 eq.) were added to the solution and mixed for 5 hours at 60°C. After the reaction time, the solution appears clear and without precipitate. The solvent was evaporated under vacuum and a white powder was retrieved. The product was dried under vacuum overnight at 110°C. Yield: 89%. IR (cm⁻¹) selected bands: 3429 (m, O-Li), (v_s, C=O), 1485, 1460, (v_s, C-H), 1325 (v_s, C-N), 749 (v_s, C-H), 721 (v_s, C-H). ¹H NMR (D₂O, 400 MHz, d ppm): 8.11 (d, 2H), 7.46 (t, 2H), 7.36 (t, 2H), 7.22 (t, 2H), 4.78 (s, 2H).



Figure VII.6 Liquid ¹H NMR spectra of LiCZA in D₂O

Synthesis of Lithium 4-(9H-carbazol-9-yl)benzoate (Li-4-BACZ): The synthesis of Methyl *4-(9H-carbazol-9-yl)benzoate* (**4-MBACZ**) was using the procedure reported by Wan et al[261]. 501.6 mg of Carbazole (3 mmol), 904 mg of methyl 4-iodobenzoate (3.45 mmol) and 1.036g of potassium carbonate (7.5 mmol) and 15 mL of toluene (5 mL) were added into a two necked flask; the flask was previously flushed with argon three times. Then, 11.5 mg of (PPH₃)₄Pd⁰ (0.023 mmol) were added and the mixture was refluxed (110°C) for three days; the reaction was confirmed to have ended through thin-layer chromatography (TLC). The solution was then poured into cold H₂O and the product was extracted using toluene (3 times with 20mL). Organic phases were washed with brine. The solvent was evaporated under vacuum and the crude product was purified through column chromatography using Ethyl acetate/Cyclohexane 1/10 as eluent. A white solid was obtained in 63% yield. IR (cm⁻¹) selected bands: 1689 (v₅, C=O), 1601, 1516 (v₅, C-C), 1450, 1425, 1317 (v₅, C-N), 1169, 772, 747 (v₅, C-H), 723 (v₅, C-H). ¹H NMR (400 MHz, CDCl₃, d ppm): 8.33 (s, 1H), 8.30 (s, 1H), 8.16 (s, 1H), 8.14 (s, 1H), 7.70 (s, 1H), 7.68 (s, 1H), 7.49–7.41(m, 4H), 7.34–7.34 (m, 2H), 4.00 (m, 3H).



Figure VII.7 Liquid ¹H NMR spectra of 4-MBACZ in CDCl₃

4-BACZ was synthesized starting from **4-MBACZ**. 100 mg of 4-MBACZ (0.33 mmol) were dissolved in 10 mL of dioxane, then 13.95 mg of LiOH×H₂O in 10 mL of water were added to the solution and refluxed overnight under stirring. Afterwards, the solution was filtrated to remove insolubilities and the dioxane was evaporated under vacuum. The pH value was adjusted to 1-2 by adding HCl conc. (36%) and the solution was stirred for 3 hours. Acidification provokes the precipitation of a white powder. The precipitate was collected by centrifugation and washed three times with H₂O. The white solid was dried under vacuum overnight at 95°C. Yield: 91%. IR (cm⁻¹) selected bands: 3026 (v_s, O-H), 1698 (v_s, C=O), 1605, 1515 (v_s, C-C), 1450, 1220 (v_s, C-N), 1168, 740 (v_s, C-H), 723 (v_s, C-H). ¹H NMR (400 MHz, DMSO-d₆, δ, ppm) of 4-BACZ: 13.17 (s, 1H), 8.26-8.22 (m, 4H), 7.79-7.77 (m, 2H), 7.50-7.45 (m, 4H), 7.33-7.30 (m, 2H).

Experimental part



Figure VII.8 Liquid ¹H NMR spectra of 4-BACZ in DMSO-d₆

Li-4-BACZ was synthesized starting from **4-BACZ** intermediate. 100 mg of 4-BACZ (0.348 mmol) were added in 10 mL of water. Then 14.61 mg of LiOH×H₂O (0.348 mmol) were added to the reaction mixture and stirred for 5 hours at 60°C. Then, a clear solution without insolubilities appears. The solvent was evaporated under vacuum and a white powder was recovered and dried overnight under vacuum at 100°C. Yield: 97%. IR (cm⁻¹) selected bands: 3420 (m, O-Li), 1602 (v_s, C=O), 1545 (v_s, C-C), 1452, 1404, 1227 (v_s, C-N), 1015, 790, 746 (v_s, C-H). ¹H NMR (400 MHz, D₂O, δ , ppm): 8.26 (d, 4H), 8.17 (m, 2H), 7.51 (d, 2H), 7.45-7.40 (m, 4H), 7.30-7.28 (t, 2H).



Figure VII.9 Liquid ¹H NMR spectra of Li-4-BACZ in D₂O

Synthesis of di(carbazole-9-yl)phenylene (DCZP): DCZP was synthesized using an adapted procedure for Ulmann coupling[202,262]. The N-arylation reaction was conducted with 1,4-dibromo benzene (0.52 g, 3.0 mmol), carbazole (1.50 g, 9.0 mmol), K₂CO₃ (1.47 g, 3.5 mmol), Cul (0.45 g, 2.4 mmol), and 1,10-phenanthroline (45 mg, 0.24 mmol) under argon. Anhydrous dimethylformamide (DMF) (40 mL) was injected into the reaction flask, and the resulting solution was degassed for 15 min under stirring. The mixture was heated at 160 °C for 18 h. After that, the solution was poured into cold H₂O and the product was extracted using toluene (20mL x 3); the organic phase was then washed with brine. The solvent was evaporated under vacuum and the crude product was purified through column chromatography using DCM/Cyclohexane 1/10 as eluent. A white solid was obtained in 55% yield. IR (cm⁻¹) selected bands: 1515 (n_s, C-C), 1478, 1446 (n_s, C=C), 1350, 1229 (n_s, C-N), 1177, 750 (n_s, C-H), 723 (n_s, C-H). ¹H NMR (400 MHz, CDCl₃, δ , ppm): 8.23 (d, 4H), 7.86 (s, 4H), 7.62 (d, 4H), 7.51 (t, 4H), 7.37 (t, 4H).



Figure VII.10 Liquid ¹H NMR spectra of DCZP in CDCl₃

Single crystal X-ray Diffraction analysis

A specimen of $C_{30}H_{20}N_2$, approximate dimensions 0.030 mm x 0.060 mm x 0.180 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å). A total of 1040 frames were collected. The total exposure time was 5.77 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 55985 reflections to a maximum θ angle of 22.75° (0.92 Å resolution), of which 2794 were independent (average redundancy 20.038, completeness = 97.7%, R_{int} = 11.76%, R_{sig} = 3.81%) and 2128 (76.16%) were

Experimental part

greater than $2\sigma(F^2)$. The final cell constants of <u>a</u> = 8.2206(14) Å, <u>b</u> = 16.372(3) Å, <u>c</u> = 31.591(6) Å, volume = 4251.8(14) Å³, are based upon the refinement of the XYZ-centroids of 431reflections above 20 $\sigma(I)$ with 5.155° < 20 < 37.62°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.808. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P b c a, with Z = 8 for the formula unit, C₃₀H₂₀N₂. The final anisotropic full-matrix least-squares refinement on F² with 289 variables converged at R1 = 4.29%, for the observed data and wR2 = 10.23% for all data. The goodness-of-fit was 1.058. The largest peak in the final difference electron density synthesis was 0.163 e⁻/Å³ and the largest hole was -0.221 e⁻/Å³ with an RMS deviation of 0.051 e⁻/Å³. On the basis of the final model, the calculated density was 1.276 g/cm³ and F(000), 1712 e⁻.

Formula	C30H20N2
MW (g/mol)	408.48
Crystal system	Orthorhombic
Space group	Pbca
a (Å) b (Å) c (Å)	8.2206 (14) 16.372 (3) 31.591(6)
α (deg)	90
β (deg)	90
γ (deg)	90
V (ų)	4251.8
z	8
λ (Å)	0.71073
δ (g/cm³)	1.276
т (К)	120
Reflection collected	55985

Table VII.2 DCZP Crystal structure parameters.

Atom	х	У	Z	Ueq
N1	0.89021(19)	0.46320(10)	0.65693(6)	0.0249(5)
N2	0.3587(2)	0.32176(11)	0.57174(6)	0.0282(5)
C1	0.9379(3)	0.69334(14)	0.71007(8)	0.0393(7)
C2	0.8149(3)	0.68285(14)	0.68029(8)	0.0404(7)
C3	0.7886(3)	0.60862(13)	0.66082(8)	0.0336(6)
C4	0.8902(2)	0.54421(12)	0.67172(7)	0.0249(5)
C5	0.7570(2)	0.42542(12)	0.63543(7)	0.0232(5)
C6	0.6010(2)	0.43451(13)	0.65139(7)	0.0278(6)

Experimental part						
C7	0.4709(3)	0.39987(13)	0.63040(7)	0.0286(6)		
C8	0.4961(2)	0.35407(13)	0.59423(7)	0.0248(5)		
С9	0.2742(2)	0.25029(13)	0.58118(7)	0.0276(6)		
C10	0.1388(2)	0.24447(14)	0.55395(7)	0.0285(6)		
C11	0.0360(3)	0.17715(15)	0.55732(8)	0.0365(6)		
C12	0.0711(3)	0.11727(15)	0.58647(8)	0.0393(7)		
C13	0.2654(3)	0.36490(14)	0.72763(7)	0.0345(6)		
C14	0.1846(3)	0.31186(14)	0.70021(7)	0.0316(6)		
C15	0.0587(2)	0.33897(13)	0.67460(7)	0.0256(5)		
C16	0.0156(2)	0.42084(13)	0.67753(6)	0.0226(5)		
C17	0.0969(2)	0.47494(13)	0.70500(7)	0.0230(5)		
C18	0.2240(3)	0.44624(14)	0.72999(7)	0.0312(6)		
C19	0.0172(2)	0.55382(13)	0.70123(7)	0.0256(6)		
C20	0.0403(3)	0.62956(13)	0.72080(7)	0.0329(6)		
C21	0.7828(3)	0.37921(14)	0.59933(7)	0.0326(6)		
C22	0.6516(3)	0.34299(14)	0.57879(7)	0.0336(6)		
C23	0.2778(2)	0.36252(13)	0.53919(7)	0.0270(6)		
C24	0.1418(3)	0.31579(14)	0.52689(7)	0.0292(6)		
C25	0.0458(3)	0.34360(16)	0.49319(8)	0.0389(6)		
C26	0.0863(3)	0.41557(16)	0.47326(8)	0.0446(7)		
C27	0.2195(3)	0.46174(15)	0.48676(8)	0.0408(7)		
C28	0.3164(3)	0.43611(14)	0.51984(7)	0.0344(6)		
C29	0.2067(3)	0.12344(14)	0.61307(8)	0.0386(6)		
C30	0.3097(3)	0.18985(14)	0.61083(7)	0.0335(6)		

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Table VII.3 Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for DCZP at 125 K.



Figure VII.11 Powder X-rays diffraction patterns collected operando during the first cycle of DCZP vs Li metal within a voltage window of 2.7-4.2V at C/10 rate using 1M LiPF6 in PC electrolyte.

Chapter IV.



Figure VII.12 Liquid ¹H NMR spectra of Thianthrene in DMSO-d₆

Synthesis of 2,7-dimethylthianthrene (DMTNT): The synthesis of 2,7-dimethyl thianthrene was synthesized using the procedure reported by Edson et *al.* [220] 4-Methylbenzenethiol (3.35 g, 27 mol) was weighted and transferred 100 ml round-bottom flask. Fuming sulfuric acid (70 mL, 20-30% oleum) was slowly added form a blue solution that gradually turned purple. The solution was stirred with a magnetic bar for 22 hours at room temperature. Then, 200 mL of ice water were added to the solution, forming a brown precipitate. The product was filtrated under vacuum; the precipitate was washed with water, acetone and diethyl ether. The crude product was dissolved in 100 mL of boiling acetic acid and 2.68 g (41 mmol) of zinc dust were transferred into the solution. The solution was refluxed for 18 h and then the excess zinc was removed by filtration. Finally, the solution was poured in 200 mL of water and filtrate under vacuum to retrieve the product. The precipitate was washed with water, acetone and diethyl ether. Then, the solid was dried under vacuum 8 hours at 80° C to give a yellow, crystalline solid. Yield: 41%. IR (cm⁻¹) selected bands: 1697 (C-C stretch), 1584 (C-C stretch), (n₅, C-H), 1456 (n₅, C-H bend), 1378, 1110, 952, 805. ¹H NMR (DMSO-d6, 400 MHz, δ ppm): 7.33 (d, 2H), 7.27 (d, 2H), 6.98 (dd, 2H), 2.11 (s, 3H).



Figure VII.13 Liquid ¹H NMR spectra of DMTNT in DMSO-d₆

Synthesis of 2,7-difluorothianthrene (DFTNT): The synthesis of 2,7-difluoro thianthrene was synthesized using the procedure reported by Edson et *al.* [220] 4-Fluorobenzenethiol (5.06 mL, 6.09 g, 27 mmol) was weighted and transferred 100 ml round-bottom flask. Fuming sulfuric acid (70 mL, 20-30% oleum) was slowly added form a blue solution that gradually turned purple. The solution was stirred with a magnetic bar for 22 hours at room temperature. Then, 200 mL of ice water were added to the solution, forming a brown precipitate. The product was filtrated under vacuum; the precipitate was washed with water, acetone and diethyl ether. The crude product was dissolved in 100 mL of boiling acetic acid and 2.68 g (41 mmol) of zinc dust were transferred into the solution. The solution was refluxed for 18 h and then the excess zinc was removed by filtration. Finally, the solution was poured in 200 mL of water and filtrate under vacuum to retrieve the product. The precipitate was washed with water and dried under vacuum 8 hours at 80° C to give a light brown crystalline solid. Yield: 68%. IR (cm⁻¹) selected bands: 1594 (v_s), 1456 (v_s), 1255 (v_s, C-F), 1209 (C-F), 855 (v_s, C-H), 801 (v_s, C-H). ¹H NMR (DMSO-d₆, 400 MHz, d ppm): 7.62 (dd, 2H), 7.54 (dd, 2H), 7.27–7.22 (td, 2H).



Figure VII.14 Liquid ¹H NMR spectra of DFTNT in DMSO-d₆



Figure VII.15 XRD powder patterns of DFTNT recorder for the two first two cycles in half-cell vs. Li.

Single crystal X-ray Diffraction analysis of DFTNT: A specimen of C₁₂H₆F₂S₂ was used for the X-ray crystallographic analysis. The X-ray intensity data were measured ($\lambda = 0.71073$ Å). A total of 2865 frames were collected. The total exposure time was 15.92 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 15064 reflections to a maximum θ angle of 19.66° (1.06 Å resolution), of which 470 were independent (average redundancy 32.051, completeness = 100.0%, R_{int} = 10.97%, R_{sig} = 2.16%) and 435 (92.55%) were greater than $2\sigma(F^2)$. The final cell of a = 21.602(3) Å, b = 3.9479(6) Å, q = 14.051(2) Å, в $= 119.310(7)^{\circ},$ constants volume = 1044.9(3) Å³, are based upon the refinement of the XYZ-centroids of 7389 reflections above 20 $\sigma(I)$ with 4.324° < 2 θ < 38.96°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.854. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group C 1 2/c 1, with Z = 4 for the formula unit, $C_{12}H_6F_2S_2$. The final anisotropic full-matrix leastsquares refinement on F² with 73 variables converged at R1 = 8.57%, for the observed data and wR2 = 27.76% for all data. The goodness-of-fit was 1.266. The largest peak in the final difference electron density synthesis was 0.407 $e^{-}/Å^{3}$ and the largest hole was -0.352 $e^{-}/Å^{3}$ with an RMS deviation of 0.108 e⁻/Å³. Based on the final model, the calculated density was 1.604 g/cm³ and $F(000), 512 e^{-}$.

Formula	$C_{12}H_6F_2S_2$
MW (g/mol)	252.29
Crystal system	Monoclinc
Space group	C2/c
a (Å)	21.602 (3) Å
b (Å)	3.9479 (6) Å
<i>c</i> (Å)	14.051 (2) Å
lpha (deg)	90
eta (deg)	119.310 (7)°
$\gamma(deg)$	90
<i>V</i> (Å ³)	1044.9 (3) Å3
Ζ	4
λ (Å)	0.71073 Å
d (g/cm ³)	1.604
T (K)	298
Reflec. collec.	15064
R _{int}	0.11
S	1.27

Table VII.4 DFTNT Crystal structure parameters

		Ехреппенан ре			
Atom	Х	У	Z	Ueq	
S	0.53541 (16)	0.8943 (8)	0.3803 (2)	0.0543 (17)	
F	0.7546 (4)	0.390 (3)	0.3925 (8)	0.104 (4)	
C1	0.5808 (6)	0.729 (3)	0.3184 (9)	0.044 (3)	
C2	0.5501 (6)	0.730 (3)	0.2023 (10)	0.048 (3)	
C3	0.6491 (7)	0.610 (3)	0.3804 (10)	0.062 (4)	
C4	0.6860 (6)	0.500 (4)	0.3267 (11)	0.052 (3)	
C5	0.6584 (7)	0.495 (3)	0.2210 (13)	0.062 (4)	
C6	0.5886 (7)	0.606 (3)	0.1552 (12)	0.059 (4)	
H1	0.684917	0.419209	0.189443	0.074*	
H2	0.670361	0.602700	0.456121	0.074*	
H3	0.568023	0.596669	0.079619	0.071*	

Table VII.5 Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for DFTNT at 298 K.

	U ¹¹	U ²²	U ³³	U ¹²	U ¹³	U ²³
S	0.061 (3)	0.059 (3)	0.047 (2)	-0.0064 (17)	0.0296 (19)	-0.0179 (16)
F	0.065 (6)	0.130 (9)	0.119 (8)	0.021 (5)	0.047 (6)	0.015 (6)
C1	0.040 (8)	0.045 (8)	0.035 (7)	-0.006 (6)	0.010 (6)	-0.001 (6)
C2	0.050 (8)	0.024 (7)	0.079 (10)	-0.003 (6)	0.038 (8)	0.001 (6)
C3	0.066 (10)	0.068 (10)	0.042 (8)	-0.013 (8)	0.019 (8)	-0.009 (7)
C4	0.045 (8)	0.066 (9)	0.050 (9)	-0.001 (7)	0.027 (7)	-0.001 (7)
C5	0.062 (10)	0.058 (9)	0.091 (12)	-0.008 (8)	0.057 (9)	-0.007 (8)
C6	0.056 (10)	0.058 (9)	0.069 (9)	-0.005 (7)	0.034 (8)	0.001 (7)

Table VII.6 Atomic displacement parameters $(Å^2)$ for DFTNT at 298 K.

Synthesis of Naphthalene Dicarboxylate Lithium salt (Li₂-NDC): The synthesis of dilithium naphthalene dicarboxylate was adapted from the procedure reported by Fedele and coworkers[134,218]. 5.0 g of Naphthalene dicarboxylic acid (23.13 mmol) and 3 equivalent of lithium hydroxide (1.66 g, 69.38 mmol) were added in 50 mL of methanol and then the solution was stirred at reflux overnight. After that, the precipitate was retrieved by centrifugation and washed with methanol, acetone, and diethyl ether. The white solid was dried under vacuum at 120°C for 18 hours. Yield: 94%. IR (cm⁻¹) selected bands: 1716, 1703, 1560, 1486, 1459, 1406, 1326, 755, 723. ¹H NMR (H₂O, 400 MHz, δ ppm): 8.36 (s, 2H), 7.98 (d, 2H), 7.92 (d, 2H).



12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 fl (ppm)

Figure VII.16 Liquid 1 H NMR spectra of Li₂-NDC in D₂O



Figure VII.17 FTIR spectra of Li₂-NDC

Chapter V.

Synthesis of naphthalene dicarboxylate sodium salt (Na₂-NDC): 5.0 g of Naphthalene dicarboxylic acid (23.13 mmol) and 3 equivalent of sodium hydroxide (2.78 g, 69.38 mmol) were dissolved in 50 mL of methanol and heated to 75°C and stirred for 30 min; then, the solution was stirred at reflux overnight. After 24 hours, the precipitate was retrieved by centrifugation and washed with methanol, acetone, and diethyl ether. The white solid was dried under vacuum at 100°C for one night. Yield: 96%. IR (cm⁻¹) selected bands: 3049 (m), 1716 (v_s), 1703 (v_s), 1486 (v_s), 1459 (v_s), 1406 (v_s), 1326 (v_s), 755 (v_s), 723. ¹H NMR (CDCl₃, 400 MHz, δ ppm): 8.36 (s, 2H), 7.98 (d, 2H), 7.92 (d, 2H).



Figure VII.18 Liquid 1H NMR spectra of Na₂-NDC in D₂O

NVPF synthesis

Synthesis of vanadium phosphate fluorine sodium salt (NVPF): **NVPF** was synthesized from procedure reported by Tarascon. 4.44 g of H_3PO_4 (45.30 mmol) were weighted, added in a 250 mL round flask with 120 mL of water and stirred for 20 min; then, 3.5 g of V_2O_5 (19.24 mmol) and 1.75 g of agar-agar rubber (5.20 mmol) were added in the round flask and heat up to 85°C. After the water was evaporated, the solid was annealed for 2 hours under oxygen and then grounded. After that, the powder was annealed for the second time at 890 °C for 2 hours, to obtain VPO₄ carbon coated (C-VPO₄) at 5%. 2 equivalents of VPO₄ and 3 equivalents of NaF were grounded together and then annealed for 90 minutes at 700 °C, to obtain a carbon coated NVPF.



Figure VII.19 Comparison of X-rays diffraction powder patterns of recrystallized Na₂-NDC_{H2O} (red line) and Na₂-NDC_{insitu} (blue line). The marked difference in the background due to the presence of carbon and binder in the case of Na2-NDCinsitu, as it is a composite electrode.



Figure VII.20 Thermogravimetric analysis (TGA) of Na2-NDC electrode formulated in aqueous solvent.

Electrode preparation for coincell

The composite slurries reported in Chapter V were prepared by mixing the active material with conductive carbon (Carbon Super C45) and binder (CMC or PVDF) in a mortar and then for 30 minutes using an Ultra-Turrax® tube drive (IKA, Germany) at 6000 rpm. The mass fraction of AM, carbon, and binder was 60 wt.%, 25 wt.%, and 15 wt.%, respectively. After that, water was added as a solvent (solid content of 24.5 %) and mixed for 90 minutes at 4000 rpm. The slurry was casted into aluminum foil (20 µm thickness) and the coating process was performed using a doctorblade, with a comma gap of 350 μ m and line speed of 0.3 m min⁻¹. Then, the solvent evaporated using a hot plate with a temperature of 60 °C. After the drying process, the electrode was calendered to reduce the thickness and reach the optimum value of porosity. The calendering was performed through a prototype-grade lap press calender (BPN250, People & Technology, Korea), consisting of a two-roll compactor of 25 cm of diameter in which the gap between the rolls controls the pressure applied to the electrodes. The calendering was performed at various applied pressures, and at constant line speed (ca. 0.5 m min⁻¹) and roll temperature (60 °C). Finally, the electrodes were punched to 13 mm in diameter and dried overnight at 100° C under vacuum. The final electrodes exhibited a mass loading of 3.5-4.5 mg/cm², for an active material mass of 4.5-5.5 mg for each punched electrode. The electrode final thickness was 70-75 mm, with 30%-35% of porosity.

Electrolyte preparation for coincell

In Chpater V, the first electrolye was 1 M NaPF₆ solution in EC/DMC 50:50 vol.% (NP30). The second electrolyte was prepared by adding 3 wt.% of fluoroethylene carbonate (FEC) in 1 M NaPF₆ in EC/DMC 50:50 vol.% solution, henceforth called NP30+3%FEC. The last electrolyte was proposed in 2021 by Tarascon and coworkers.[254] The electrolyte was prepared with 1 M of NaPF₆ dissolved in mixed organic carbonates ethylene carbonate (EC)/ propylene carbonate (PC)/ dimethyl carbonate (DMC), with 4 additives: 0.5 wt.% sodium oxalato(difluoro) borate (NaODFB)[263], 3 wt.% vinylene carbonate (VC)[264], 3 wt.% succinonitrile (SN)[265], and 0.2 wt.% tris-trimethylsilylphosphite (TMSPi)[266]. This electrolyte, henceforward called MAGIC, showed optimal electrochemical performance when the formation step is carried out at a temperature of 55 °C. In the present work, the battery formation cycles (5 cycles) with MAGIC electrolyte were carried out at 55 °C.

Computational details

Dilithium benzoquinone dioxime and dinitrosobenzene were studied using DFT calculations performed with Gaussian 09 code. M062X functional with 6-311+G (2d,2p) level of theory was employed to calculate molecular and electronic structure of both molecules, with very tight criterion of convergence and with the vibrational frequency analyses, to confirm the true local minima (carried out at the same computational level to evaluate the Gibbs free energy at 298K). For all the calculations, the solvent effects were considered using a polarizable continuum model (PCM), particularly through the solvent (ϵ =37.5).

Material characterization

Infrared spectroscopy

The Fourier transformed infrared (FTIR) spectra were recorded in transmission mode using a Nicolet Avatar 370DTGS spectrometer in the range of 400-4000 cm⁻¹ with a resolution of 2 cm⁻¹. IR pellets were prepared by mixing the target molecule and potassium bromide (spectroscopic grade) in a ratio 1:100, then the mixture was pressed using 13 mm evacuable die set (Specac Ltd, UK) for IR pellet.

NMR spectroscopy

NMR spectra were recorded at 298 K using a BRUKER 400 MHz Avance III HD spectrometer, equipped with a 5 mm nitrogen cryoprobe Prodigy BBO+F and an Ascend SB magnet equipped with a SampleXpress 60 sample changer. All the chemical shifts (δ) in this paper are reported in ppm relative to TMS. The samples were prepared by dissolving 5 to 10 mg of product in approximately 1 mL of deuterated solvent (Sigma Aldrich, >99.5% purity).

Atomic Absorption Spectroscopy

Atomic Absorption Spectroscopy (AAS) was used to determine the amount of sodium ions. The analysis was performed using an AAnalyst 300 spectrometer (Perkin-Elmer, USA) with a lithium hollow cathode lamp (wavelength: 670.8 nm). An air / acetylene mixture in the ratio 5.8:1 was used as the oxidizer / fuel mixture.

Thermogravimetric analyses

Netzsch thermal analyzer STA 449C Jupiter instrument was used to perform Thermogravimetric analyses (TGA), equipped with a differential analysis microbalance coupled with a mass spectrometer QMS 403 Aeolos (heating rate: 5 C min⁻¹ under argon flow).

BET surface area

Brunauer-Emmett-Teller (BET) specific surface area (S_{BET}) of the active materials was measured with a Micromeritics ASAP 2020 instrument using N2 gas as adsorbate (77 K). Before analysis, the samples were degassed for 12 hours at 120 °C, under vacuum in the degassing port and a further two hours in the analysis port.

Scanning electron microscopy

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were performed using a Quanta 200 SEM (FEI, USA) equipped with an EDS detector (X-Max 80, Oxford Instruments Co., UK) to characterize the size, morphology, and composition of the materials. The micrographs were obtained with a secondary electron detector at an accelerating voltage of 10 kV and saved as TIFF files. These surfaces were imaged and EDS was used to map the elemental distribution or determine the elemental composition of individual points in the imaged areas.

X-ray powder diffraction analysis

The X-ray powder diffraction patterns were collected on a Bruker D8 Advance diffractometer with a Cu K α_1 and K α_2 radiation and equipped with a Lynkeye detector operating at 40 kV and 40 mA in between 2 θ = 10-60° with a 2 θ step size of 0.019° in reflection geometry.

In-situ and operando X-ray diffraction analysis

The organic electrodes for XRD cell were composed of 70 wt% of active material (7–11 mg), ballmilled for 30 minutes with 30 wt% of carbon black (Ketjenblack EC-600JD from AkzoNobel). In a glove box under argon, a quantity of *ca*. 40 mg of active material and carbon additive mixture was introduced into a Swagelok-like cell equipped with a beryllium window, as described in ref [229].

Single crystal x-ray diffraction

Single crystal x-ray diffraction experiments were carried out with a Bruker SMART APEX II CCD diffractometer, using Mo K α radiation (0.71073 Å) at 125 K or 298 K. The resolution of the structure was obtained by the direct method using the SHELXS97 software followed by a refinement carried out with the SHELXLE software.

Gas chromatography-mass spectrometry analysis

For the Gas chromatography–mass spectrometry analysis, the separators were treated with 1 mL of dried acetonitrile ($H_2O < 0.001\%$) then filtered and diluted 100 times before injection into GC/MS spectrometer. The GC analysis were performed using a trace 1300 series GC ultra-gas chromatograph (Thermo Scientific). The chromatographic separation was performed on a "BPX70" cyanopropylpolysilene-siloxane basedcapillary column (30 m x 0.25 mm i.d., 0.25 mm) from SGE. The GC was interfaced with an ISQ Mass Spectrometer (Thermo Scientific).

Electrochemical characterization

Electrode preparation for Swagelok-type cell

The organic electrodes reported in Chapter II, Chapter III and Chapter IV were composed of 70 wt% of active material (7–11 mg), ball-milled for 30 minutes with 30 wt% of carbon black (Ketjenblack EC-600JD from AkzoNobel). This type of grinding is highly energetic and involves "shock" type interactions with a motor rotation speed of 1200 rpm. In a glove box, a quantity of 100 mg of active material and carbon additive mixture was introduced into a steel grinding cell of 25 cm⁻³ containing two steel balls of 4 g each with a diameter of 8 mm.

The final electrode composite showed an areal loading of active material is around 2.5-3.5 mg/cm² for each electrode (electrode surface of 1.1 cm^2).

Galvanostatic test for Swagelok-type cell

Electrochemical performances reported in Chapter II, Chapter III and Chapter IV were studied using Swagelok[®]-type cell, assembled in an argon-filled glovebox (H₂O<0.1 ppm, O₂<0.1 ppm). The tests were carried out in half-cell configuration versus metallic lithium or in full-cell configuration. The fiberglass separator (Whatman[®]) was soaked with 150 μ L of electrolyte. All cells were tested in a galvanostatic mode using a Biologic VMP-3 (Biologic SAS, France) instrument with different potential range and current density.

Galvanostatic test for coincell

Electrochemical performances reported in Chapter V were performed using Coin-cell configuration (CR2032 type, Innovmetor, France), assembled in an argon-filled glovebox (H₂O<0.1 ppm, O₂<0.1 ppm). The tests were carried out in half-cell configuration versus metallic Na or in full-cell configuration. The fiberglass separator (Whatman[®]) was soaked with 150 mL of electrolyte; in chapter V, three different electrolytes were employed. All cells were tested in a galvanostatic mode using a Biologic VMP-3 (Biologic SAS, France) instrument with a potential range of 2.0–0.05 V for half-cell and 4.10-0.0V for full-cell configuration. The cells were cycled at different C-rates, as C/10, C/5, C/2, and 1C (1C corresponds to 200 mA g⁻¹). The electrode surface was 1.3 cm², with an active material loading in the range of 3.6-3.9 mg cm⁻² for all the samples.

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 013485567%5Cnhttp://pubs.acs.org/doi/abs/10.1021/ja00164a033%5Cnhttp://doi.wiley.com/10.1002/c.
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Abstract:

Driven by the growing demand for electrochemical energy storage systems, the quest for new material for Lithiumion and Sodium-ion batteries has intensified in recent years. Nowadays, battery technologies are based on inorganic materials, which are mainly composed of transition metals, such as Cobalt, Manganese, Nickel and Iron. Due to the marked increase in battery production, transition metals have showed several issues, mainly related to supply, as the abundance of the most popular metals (Ni and Co) is limited and characterized by a constrained geo-localization, and environmental impact, as they require energy-intensive process and are characterized by poor recyclability. To overcome these limitations, research on battery materials has started to focus on alternative materials able to replace inorganic materials. The present thesis focuses on the study of new organic materials for the development of eco-compatible batteries, both on Lithium-ion and Sodium-ion technology. Organic molecules are promising candidates for the development of eco-friendly batteries, as these materials are characterized by high abundancy, low production cost and low environmental impact. In the first part of the thesis, three different classes of organic compounds were investigated as positive materials: Dioximate as *n*-type material, Carbazole and Thianthrenes as *p*type materials. The redox potentials of the materials spanned from a potential of 3 V for Dioxime up to 4.10 V for Thianthrene derivatives, while their specific capacities range from 300 mAh g⁻¹ to 90 mAh g⁻¹, respectively. Furthermore, an all-organic full-cell was assembled using 2,7-difluorothianhtrene as cathode material and dilithium naphthalene dicarboxylate as anode material: this cell displayed an output voltage of 3.4 V and a specific capacity of 80 mAh g⁻¹ after the first cycle, for an overall energy density of 190 Wh kg⁻¹. In the second part, Disodium Naphthalene Dicarboxylate (Na₂-NDC) was studied as negative organic material for Sodium-ion battery. Different synthesis strategies have been employed to modify the morphology and crystal structure of the active material particles, in order to improve the electrochemical performance. Thus, a hybrid inorganic/organic full-cell was assembled coupling the Na₂-NDC electrode with Na₃V₂(PO₄)₂F₃ (NVPF), an inorganic cathode. An in-depth electrochemical study of the full cell was performed to evaluate the stability over cycling using different electrolyte additives. The Na-ion hybrid cell NVPF/Na₂-NDC showed outstanding electrochemical performances, in terms of reversible capacity, stability over cycling and rate performance.

Résumé:

Poussée par la demande croissante de systèmes de stockage d'énergie électrochimique, la recherche de nouveaux matériaux pour les batteries Lithium-ion et Sodium-ion s'est intensifiée ces dernières années. Les technologies de batterie sont basées sur des matériaux inorganiques, qui sont principalement composés de métaux de transition, tels que le cobalt, le manganèse, le nickel et le fer. Cependant, les métaux de transition présentent différents problèmes liés à l'approvisionnement, parce que l'abondance des certains métaux (comme le Ni et Co) est limitée et caractérisée par une géolocalisation contrainte, et un impact environnemental, parce qu'ils nécessitent des processus énergivores et se caractérisent par mauvaise recyclabilité. Pour surmonter ces limitations, la recherche sur les matériaux de batterie a commencé à se concentrer sur des matériaux alternatifs capables de remplacer les matériaux inorganiques. La présente thèse est centrée sur l'étude de nouveaux matériaux organiques pour le développement de batteries éco-compatibles, à la fois sur la technologie Lithium-ion et Sodium-ion: les molécules organiques sont des candidats prometteurs pour le développement de batteries écologiques, parce que ces matériaux se caractérisent par une grande abondance, un faible coût de production et un faible impact environnemental.

Dans la première partie de la thèse, trois classes différentes de composés organiques ont été étudiées comme matériaux positifs : le dioximate comme matériau de type n, le carbazole et les thianthrènes comme matériaux de type p. Les potentiels redox des matériaux s'étendent d'un potentiel de 3.0 V pour la dioxime à 4.1 V pour les dérivés du thianthrène, tandis que leurs capacités spécifiques vont de 300 mAh g⁻¹ à 90 mAh g⁻¹, respectivement. De plus, une cellule complète entièrement organique a été assemblée en utilisant du 2,7-difluorothianhtrene comme matériau de cathode et du dicarboxylate de dilithium naphtalène comme matériau d'anode : cette cellule affiche une tension de sortie de 3.4 V et une capacité spécifique de 80 mAh g^{-1} après la première cycle, pour une densité énergétique globale de 190 Wh kg⁻¹. Dans la deuxième partie, le dicarboxylate de naphtalène disodique (Na₂-NDC) a été étudié en tant que matériau organique négatif pour la batterie sodium-ion. Différentes stratégies de synthèse ont été employées pour modifier la morphologie et la structure cristalline des particules de matière active, afin d'améliorer les performances électrochimiques. Une cellule complète hybride inorganique/organique a été assemblée couplant l'électrode Na₂-NDC avec Na₃V₂(PO_4)₂F₃ (NVPF), comme cathode à base inorganique. Une étude électrochimique approfondie de la cellule complète a été effectuée pour évaluer la stabilité au cours du cycle en utilisant différents additifs électrolytiques. La cellule hybride NVPF/Na2-NDC a montré des performances électrochimiques remarquables, en termes de capacité réversible, de stabilité au cours du cycle et de performance à des densités de courant élevées.