A study by electrochemical quartz crystal microbalance of charge storage mechanisms in materials for electrochemical energy storage applications

Yih-Chyng Wu

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A study by electrochemical quartz crystal microbalance of charge storage mechanisms in materials for electrochemical energy storage applications
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General Introduction
General introduction

The development of the modern society highly relies on energy. Among all the resources, natural gas, oil, and coal occupied most of the market. However, the depletion of natural resources and the pollution which comes along with industrialization has raised the alarm on the civilization. Finding alternative energy became a popular topic since the end of twenty centuries around the world. Renewable energy sources come mainly from natural resources, such as solar energy, wind energy, wave power, geothermal energy, bioenergy, tidal power, etc. However, the intermittent nature of the energy production from natural energy sources cannot always timely meet the demand. In order to use sustainable energy sources efficiently, compatible energy storage systems are certainly needed.

Ultracapacitors or electrochemical double layer capacitors (EDLCs), known as supercapacitors, ultracapacitors or electrochemical double layer capacitors (EDLCs) is one of the reliable energy storage devices. Because of their key features, they have had an important role to play by filling the gap in performance between batteries and capacitors. Compared with the high energy densities (up to 300 Wh·kg\(^{-1}\)) and low power densities (up to 1 kW·kg\(^{-1}\)) of batteries, electrochemical capacitors can deliver very high power densities (15 kW·kg\(^{-1}\)) with a lower stored energy (6 Wh·kg\(^{-1}\)). The difference of performance is based on their different charge storage mechanism. Due to the non-faradic, electrostatic storage by charge separation at the electrode / electrolyte interface in supercapacitors, the response time for storing and releasing the charges is much faster compared to batteries, in which faradic reactions are the main mechanisms. In addition, the electrical double layer set up by ions at the interface between a high-surface area carbon electrode and a liquid electrolyte results in a larger amount of energy storage compare to conventional electrostatic and electrolytic capacitors, which stored charges on low surface area plates. These fast and highly reversible storage mechanisms make supercapacitor a high power density and long cycling life ( > 10\(^6\) cycle) energy device. However, supercapacitors suffer from relatively low energy density, about 20 times less than batteries. As a result, the main challenge today for supercapacitors is to increase their energy density.

To improve the performance of supercapacitors, we need to develop our fundamental understanding of the charge storage mechanisms, as the building block for
novel electrode and electrolyte development. In this thesis, the main focus is to understand the charge storage mechanisms of EDLCs by using in situ electrochemical quartz crystal microbalance (EQCM) technique. Electrochemical quartz crystal microbalance (EQCM) has been used as an in situ gravimetric probe for the investigation ion dynamics in porous carbon-based electrode.\textsuperscript{5,6} The first chapter of the thesis includes a bibliographic study, which gives us a deep understanding regarding the recent theories and development of the charge mechanism of EDLCs. The charge storage mechanisms of EDLCs will be covered thoroughly, based on the up-to-date theoretical and experimental aspects. Chapter II of the thesis will go through the basic concepts of the experimental equipment and materials.

The first part of the results (chapter III) is an EQCM study of three-dimensional porous carbon electrode. The main charge carriers were identified by in situ EQCM from multi-ion aqueous electrolytes during ion transfer and adsorption in carbon micropores. The results will be discussed based on ion size, ion mobility and pH range. The following part of the results (chapter IV) aims to study the ion responses on two-dimensional carbon material. Single layer graphene (SLG) was used as a two-dimensional platform and model material for mimicking the interactions between ions from an electrolyte together with an ideal, flat sp\textsuperscript{2} carbon surface without the interference of the porosity. The SLG was successfully transferred onto the quartz electrode using a proprietary method, so that in situ EQCM enable to record the ion dynamics nearby the carbon/electrolyte interface in two different electrolytes: a neat ionic liquid and an ionic liquid used as a salt dissolved in a solvent. The last part (chapter V) is dedicated to the application of EQCM to track ion fluxes in different materials used for electrochemical energy storage applications. High rate performance materials, such as Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} MXene pseudocapacitive material and CaV\textsubscript{6}O\textsubscript{16} Ca-ion battery cathode material, were tested using EQCM technique. The charge storage mechanisms of each materials have been investigated in detail in this chapter.

The approach developed in this thesis demonstrates that EQCM is an efficient tool to provide a direct molecular-level insight into the charge storage process for different energy storage materials. It shows a great potential to be served as an electrogravimetric probe to monitor the ion and solvent molecule fluxes occurring at the electrode/electrolyte interface upon polarization.
References


Chapter I: Bibliography
1. Electrochemical double layer capacitors (EDLCs)

1.1 Why EDLCs?

Reducing the consumption of fossil fuels and developing renewable and sustainable energy sources have been considered to be effective strategies to tackle the climate change crisis. To efficiently use the energy harvested from natural energy sources, compatible electrical energy conversion and storage devices are developed.¹

![Figure I-1](image-url)

**Figure I-1:** The plot shows the trends towards greater specific power for batteries and specific energy for electrochemical capacitors (arrows), blurring the boundaries between the two as the trends approach the star. Dashed lines represent zones where the cyclability of the device is altered in the case of symmetric cycling (same charging and discharging rate at 100% depth of discharge). For Li-ion batteries, Li plating at the negative electrode is mainly responsible for the decrease in cycle life and the limitation of charging rate. All the data for generating Fig. I-1 come from commercial devices (datasheets or real tests). The data for solid state batteries come from industry roadmaps. The diagonal dotted lines and timescales represent characteristic operation timescales, obtained by dividing the energy by the power.²
Ragone plot is commonly used to display and compare the performance of the energy storage systems (Figure I-1). Among electrochemical energy storage systems, electrochemical double layer capacitors (EDLCs) and secondary batteries are the most used. Each system is characterized by its specific energy and power. Specific energy and specific power are relative to the amount of energy and power delivered by a device with respect to one unit of mass (kg) or volume (l). The dashed lines in Figure I-1 indicate the time needed to consume all the energy stored in the device. The green, red, and yellow colored regions correspond to high-performance Li-ion and other advanced secondary batteries. As shown in Ragone plot, battery systems can store much more energy than EDLCs; however, batteries suffer from poor power performance. In contrast, EDLCs (blue colored region in Figure I-1) can easily be charged and discharged in seconds, which meet the needs for applications requiring fast and high-power performance.

These performances lie on the origin of the charge storage mechanisms. Batteries store the energy through redox (faradaic) reactions at electrode materials, usually along with chemical conversions and phase changes, providing high energy supplement, such as Li-ion batteries (up to ~300 Wh·kg\(^{-1}\)). However, these battery-type faradaic reactions undergo sluggish kinetics and material irreversible processes, leading to limited power performance and lifetime. Even though, the discharge time of Li-ion batteries can be improved to a few minutes (see dashed line in Figure I-1), but the energy efficiency and cycle life will be affected significantly. By contrast, supercapacitors such as electrochemical double-layer capacitors (EDLCs) store the charge at the electrode/electrolyte interface, via a charge separation by physical ion adsorption/desorption process. These fast and highly reversible storage mechanisms make supercapacitor suitable for high power delivery/uptake, associated with high cycle life (few millions cycles). However, their low energy density - around 10 Wh·kg\(^{-1}\) for commercial devices - still limit their applications. To improve the energy density of EDLCs (the region marked by the star in Figure I-1), pseudocapacitive materials involving fast and non-diffusion limited surface faradaic reactions has been found to increase the capacitance and thus the energy density of supercapacitors. Figure I-2 shows a schematic presentation of the charge storage mechanisms of different electrochemical energy storage systems. These concepts will be detailed below.
1.2 Fundamentals of EDLC

1.2.1 Brief history

In the beginning of 18\textsuperscript{th} century, Ewald Georg von Kleist found that charge could be stored by connecting a high-voltage electrostatic generator by a wire in a glass jar full of water. Later, a Dutch physicist Pieter van Musschenbroek invented a similar device and named it the Leyden jar as shown in Figure I-3a.\textsuperscript{10} A brass rod is used as an electrode and connect to the tin foil at the inner surface of the jar. The jar is charged by connecting the brass rod to an electrostatic generator. The inner and outer surfaces of the jar store equal but opposite charges. The capacitance of the Leyden jar is about 1.1 nF. To increase the capacity, Daniel Gralath combined several jars in parallel as shown in Figure I-3b. In 19\textsuperscript{th} century, the design of capacitors has been improved by sandwiching a strip of impregnated paper between strips of metal and rolling into a cylinder cell. The capacitors were mainly used in telecommunications technology.\textsuperscript{11} However, the mechanism of electrical charge storage in capacitors was not clear until von Helmholtz proposed the first model of double layer capacitance in 1853.\textsuperscript{12}
EDLCs, known as supercapacitors, were developed in the early 1950s when an American company – Sohio - started to build capacitor with porous carbon materials. In 1957, when H. Becker developed a capacitor using porous carbon electrodes. The supercapacitor cells were designed by using two aluminum foils covered with porous carbon particles soaked in an electrolyte and separated by a thin, porous insulator. Under polarization, ions of the electrolyte where adsorbed at both carbon electrodes - cations balanced the charge at the negative electrode and anions at the positive – thus creating a capacitor. A large amount of charge could be stored at the porous carbon / electrolyte interface versus planar capacitor thanks to the use of high surface area, porous carbon. The first supercapacitors were marketed by Nippon Electric Company in 1978 mainly for computational devices, especially memory back-up applications which require low power and low voltage.

Until the end of 20th century, important improvements were achieved for supercapacitors regarding the electrolytes, electrode materials, and cell design. In 1982, the Pinnacle Research Institute successfully lowered the internal resistance of their supercapacitors by improving the conductivity of the electrolyte. This technology has then been further developed by Maxwell Technologies. From the fundamental point of view, B. E. Conway developed fundamental works on electrochemical capacitors. He further distinguished the difference between "electrochemical capacitors" and "batteries" behavior in electrochemical energy storage.

To date, supercapacitors are widely applied to various applications including electronics, transportation, and energy related products because of its high power and...
temperature stability. The market of supercapacitor was valued at USD 487.45 million in 2019, and it is expected to reach USD 1570.75 million by 2025.\textsuperscript{20} Commercial supercapacitors are mostly symmetric and incorporate porous activated carbons as electrode material. The electrodes are immersed in organic salt dissolved in either acetonitrile or propylene carbonate solvents. Table I-1 lists the properties of some of the commercial symmetric supercapacitors. Figure I-4 shows examples of the packaging of the commercial supercapacitors.

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>C(F)</th>
<th>Voltage max (V)</th>
<th>Energy (Wh·kg(^{-1}))</th>
<th>Power (kW·kg(^{-1}))</th>
<th>Cycle life</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maxwell</td>
<td>3400</td>
<td>2.85</td>
<td>7.6</td>
<td>18</td>
<td>&gt;1,000,000</td>
</tr>
<tr>
<td>Skeleton</td>
<td>3200</td>
<td>2.85</td>
<td>6.8</td>
<td>42</td>
<td>&gt;1,000,000</td>
</tr>
<tr>
<td>Nesscap Co., Ltd</td>
<td>3000</td>
<td>2.34</td>
<td>5.6</td>
<td>6.2</td>
<td>500,000</td>
</tr>
<tr>
<td>Samwha</td>
<td>3000</td>
<td>2.7</td>
<td>7.02</td>
<td>4.2</td>
<td>500,000</td>
</tr>
<tr>
<td>Ioxus Inc</td>
<td>3150</td>
<td>2.7</td>
<td>6.3</td>
<td>10.1</td>
<td>1,000,000</td>
</tr>
</tbody>
</table>

\textbf{Table I-1:} Characteristics of the commercial supercapacitors.\textsuperscript{21,22}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Schematic of a commercial spirally wound double layer capacitor (a) and a coin cell (b).}
\end{figure}

### 1.2.2 Operating principles

EDLCs are capacitive energy storage devices that store energy through a non-faradaic mechanism. An EDLC contains two parallel electrodes immersed in an electrolyte, with an ionically conducting but electrical insulating, porous separator placed in between to prevent electrical short circuits. When an external bias voltage is
applied, the electronic charges at the electrode surface are balanced by ions of opposite ionic charge from the electrolyte due to electrostatic attraction. A schematic of an EDLC is presented in Figure I-5.

![Schematic of EDLC](image)

**Figure I-5:** A schematic of a setup of EDLCs.

The total amount of charge $Q$ (Coulomb) can be stored in a supercapacitor is determined by capacitance $C$ (Farad) and the voltage difference $V$ (Volt) across the EDLC as shown in Equation I-1. The capacitance $C$ comes from the charge separation at the electrode/electrolyte interface (Equation I-2).

$$ Q = C \times V \quad \text{(Eq. I-1)} $$
$$ C = \frac{\varepsilon_0 \varepsilon_r A}{d} \quad \text{(Eq. I-2)} $$

where $\varepsilon_0$ ($8.85 \times 10^{-12}$ F·m$^{-1}$) is the permittivity of the vacuum, $\varepsilon_r$ is the relative dielectric constant of the electrolyte which is dimensionless, $d$ (m) is the average approaching distance of the ions to the electrode surface, and $A$ (m$^2$) is the accessible surface area of the electrode. The distance between the ions adsorbed onto the electrode surface and the electrode surface is in the order of molecular dimension. The chemical affinities of the ions and the field strength in the EDL are the factors which affect the adsorption process. Considering conventional values for the dielectric constant of the electrolyte (less than about 100) and the average approaching distance of the ions to the electrode surface $d$ (few $10^{-10}$ m), the double layer capacitance values is in the range of few tens $\mu$F cm$^{-2}$. To improve the total electrode capacitance, EDLC’s electrode materials are preferentially made with a porous carbon exhibiting high surface area (>
1,500 m²·g⁻¹). Besides, porous carbons have a good electrical conductivity, a decent electrochemical stability, and is low cost.²⁴-²⁶

1.2.3 Key characteristics of EDLCs

Based on the setup of EDLCs as mentioned earlier, the combination of negative and positive electrode is equivalent to two capacitors assembled in series; therefore, the capacitance C_{cell} of the device is expressed as:

$$C_{cell} = \frac{C_+ C_-}{C_+ + C_-} \quad \text{(Eq. I-3)}$$

where C_+ and C_- are capacitances of the positive and negative electrode, respectively. Similar to batteries, the two main performance metrics used to characterize EDLC devices are the energy and power density. For calculating energy (E, Wh) and maximum power (P, W) for supercapacitors,

$$E_{max} = \frac{1}{2} C_{cell} U_{max}^2 \frac{1}{3600} \quad \text{(Eq. I-4)}$$

$$P_{max} = \frac{U_{max}^2}{4R_s} \quad \text{(Eq. I-5)}$$

where U is the operating voltage window (V), R_s is the series resistance (Ω). The average power P_a (W) is associated with the energy delivered per unit time (s) and can be expressed as:

$$P_a = \frac{E}{t_D} \quad \text{(Eq. I-6)}$$

where t_D is the discharge time of the EDLCs.

To evaluate the performance of EDLCs, the energy and power can be presented and compared on gravimetric (per weight), volumetric (per volume), or areal (per area) basis. It is important to select suitable metrics for interpreting the performances of EDLCs.²⁷-³⁰ The energy and power density reported in Ragone plot are based on cell stack volume or total cell weight instead of the weight of active material alone.²⁷,²⁸ For microdevices and some flexible electronics which have a negligible mass loading (tens of μg) or an extremely thin film (hundreds of nm), volumetric and areal energy density is mostly used rather than gravimetric parameters.²⁷,³¹
1.3 **EDL capacitance at carbon/electrolyte interface**

1.3.1 **EDL models based on two-dimensional electrodes**

In EDLCs, the charge is stored at the electrode/electrolyte interface. Under polarization, the cations and anions are attracted to negative and positive electrodes, respectively, due to the electrostatic force. The charges are then separated and stored at the electrolyte/electrode surface, which is the so-called “electric double layer (EDL)”.

The first EDL model was proposed by Helmholtz and describes the charge separation at the electrode/electrolyte interface considering a planar electrode surface. In this model (Figure 1-6a), the charges accumulated at the electrode surface are balanced by a monolayer of counter-ions (ions that carry opposite charge of the electrode) from electrolyte by electrostatic adsorption, resulting in two compact layers of opposite charges at the electrode/electrolyte interface. This model is analogous to the conventional parallel-plate dielectric capacitors, and the Helmholtz layer capacitance can be therefore expressed as Equation 1-2.

Areal capacitance (per cm²) of the Helmholtz layer \( C_{H} \) can be normalized by \( \varepsilon_r \) the electrolyte dielectric constant and \( d \) the thickness of the Helmholtz layer, both of them depending on the selected electrolytes. The dielectric constant value of bulk water is around 78, and it falls in the range of 1 to 100 at room temperature for most of the solvents used in EDLC applications. It is worth noting that the Helmholtz model suggests a linear potential drop within the Helmholtz layer and the model does not take into account the ion movements.
Chapter 1: Bibliography

Figure I-6: Schematic diagram of EDL models based on the positive polarized ($\phi_E$) 2D electrodes in an electrolyte with solvent: (a) Helmholtz model (b) Gouy-Chapman model, and (c) Gouy-Chapman-Stern model. The dash lines indicate the potential drops ($\phi$) in each model. Bottom insets present the simplified equivalent circuits.\(^{35}\)

To tackle those limitations, Gouy in 1910 and Chapman in 1913 proposed a model where the ion movement in the electrolyte was taken into account.\(^{36, 37}\) Ions are transported not only by electrostatic forces originating from the charged electrode, but also by diffusion in the electrolyte, driven by the difference of ion concentration at the electrode surface and bulk electrolyte. The Gouy-Chapman model (Figure I-6b) includes a diffuse layer between the electrode and the electrolyte bulk to take into account the thermal fluctuation according to the Poisson-Boltzmann equation.\(^{10}\) The ion distribution of the diffuse layer highly depends on the distance since the electrostatic attractions decreases from the electrode surface to the electrolyte bulk. The average thickness of the diffuse layer (also called Debye length, $\lambda_D$) for monovalent electrolytes is defined as below:

$$\lambda_D = \sqrt{\frac{\varepsilon_0\varepsilon_r RT}{2(zF)^2C_o}}$$ \hspace{1cm} (Eq. I-7)

where $\varepsilon_0$ and $\varepsilon_r$ are respectively the vacuum dielectric constant (F·m\(^{-1}\)) and the relative constant of the electrolyte (dimensionless), $R$ is the ideal gas constant (J·mol\(^{-1}\)), $T$ is the absolute temperature (K), $F$ is the Faraday constant (C·mol\(^{-1}\)) and $C_o$ is the bulk electrolyte concentration (mol·m\(^{-3}\)). The capacitance $C_D$ of the diffuse layer can be
calculated from the Poisson-Boltzmann equation, leading to Equation I-8.

$$C_D = \frac{\varepsilon_r \varepsilon_0}{\lambda_D} \cosh \left(\frac{z F \phi}{2 R T}\right)$$  \hspace{1cm} (Eq. I-8)

$\phi$ is the electrical potential (Volt); $F$, the Faraday constant (C mol$^{-1}$); $R$, the ideal gas constant (J mol$^{-1}$); $T$, the temperature (K); $\varepsilon_0$ and $\varepsilon_r$, respectively the vacuum dielectric constant (F m$^{-1}$). According to Eq. I-8, the differential capacitance $C_D$ (F cm$^{-2}$) of the Gouy-Chapman model is then no longer constant. Instead, the model predicts a rapid increase of the capacitance at large potential resulting in a “U” shape of the differential capacitance with the electrode potential. Also, the capacitances experimentally measured (few tens of $\mu$F cm$^{-2}$ in aqueous electrolytes for instance) were far below than those predicted from the model (few hundreds of $\mu$F cm$^{-2}$). Indeed, the Gouy-Chapman model overestimates the double layer capacitance since it considers ions as point charges, which can almost approach the surface at zero distance leading to infinite capacitance.

In 1924, Stern proposed a new model considering both Helmholtz compact layer and the Gouy-Chapman diffuse layer (Figure I-6c). The resulting double layer capacitance ($C_{dl}$) can be seen as a capacitance conjugated of two capacitances generated from Helmholtz layer ($C_H$) and diffusion layer ($C_D$) as shown in Equation I-9.

$$\frac{1}{C_{dl}} = \frac{1}{C_H} + \frac{1}{C_D} = \frac{x_H}{\varepsilon_0 \varepsilon_r} + \frac{\lambda_D}{\varepsilon_0 \varepsilon_r \cosh \left(\frac{z F \phi}{2 R T}\right)}$$  \hspace{1cm} (Eq. I-9)

where $x_H$ (m) is the thickness of the Helmholtz layer, $C_H$ and $C_D$ are respectively the capacitance of Stern (Helmholtz) layer and of the diffuse layer, respectively (both in F m$^{-2}$). The potential decreases linearly within the compact layer, then decays quasi-exponentially in the diffuse layer. The total EDL capacitance is governed by the smallest capacitance between $C_H$ and $C_D$. For diluted electrolyte, at moderate potential range, the diffuse layer capacitance dominates the total capacitance; for large electrode polarization, $C_H$ will be considered as the total capacitance. The Gouy-Chapman-Stern model can be generally applied for diluted electrolyte, however, when the ion-ion correlation is strong, especially for solvent-free ionic liquid systems, the model cannot work properly.

For diluted concentration, at larger voltage, the electrochemical reactions (oxidation and/or reduction) of solvent or ions will occur without any ion crowding since in such electrolyte the ion-ion correlation is weak. However, for highly concentrated ionic systems as ionic liquids or in microfluidics, overscreening and
crowding (see Figure I-7 and below) was found by simulation techniques, which cannot be predicted by the Gouy-Chapman-Stern model. The details of electrolytes and their development will be discussed in the later section 2.3.

![Figure I-7: Schematic diagram of EDL models based on a polarized ($\phi_E$) 2D electrodes in an electrolyte without solvent: (a) Overscreening effect at a moderate voltage, $V = 10k_BT/e$ (-0.26 V) and (b) Crowding effect at a high voltage, $V = 100k_BT/e$ (-2.6 V). Reproduced from^41](image)

In the late 20th century, theoretical work suggested that, for highly-concentrated solution at planar electrode surface, an overscreening effect will occur.\textsuperscript{42-44} Overscreening, which consists in the formation of a condensed layer of counter-ions with an charge excess compared to the electrode, happens at small voltages polarization. The charge excess of the first layer is balanced by a second layer with opposite sign mainly populated by co-ions (ions having the same sign as the electrode). This phenomenon leads to an oscillatory radial distribution function of the charge density extending several layers from the electrode surface to the bulk electrolyte until electroneutrality is reached. As a result, the average counter charge distance is increased leading to a lower differential capacitance ($F \cdot m^{-2}$). The overscreening effect favors the crowding phenomenon at larger polarization: at high voltage, the layer of counter-ions extends across two monolayers resulting in an excess of co-ions at the third monolayer.

In 2007, Kornyshev et al. proposed an EDL model for a planar electrode in contact with ionic liquid electrolyte by using mean field theory. The model considers the concentration, volume, compacity, and special interactions between cations and anions. The capacitance simulated by mean-field theory is shown in Figure I-8. From high to low compacity of the electrolyte ($\gamma$), the capacitance versus potential has a transition
from bell-like to camel-like shape. When $\gamma$ is small, the empty space will be filled then a dense EDL is formed while the potential increases. This is closer to the Gouy–Chapman like behavior at moderate voltages (camel-like shape). In contrast, without voids or solvent molecules, the overscreening and crowding effect will result in a thicker EDL which the capacitance effectively decreases (bell-like shape). The model has been confirmed by experimental and simulation studies.\textsuperscript{45-49}

**Figure I-8:** Double-layer capacitance as a function of electrode potential for indicated values of the lattice-saturation parameter, $\gamma$.

### 1.3.2 EDL capacitance of porous carbon-based electrodes

Based on Equation I-2, by increasing the accessible surface area to ions of the electrode, the capacitance of EDLCs can be improved; this explains why porous carbon are commonly used as active materials. Indeed, porous carbons can achieve high SSA ($> 1500 \text{ m}^2\cdot\text{g}^{-1}$) together with a decent electrochemical stability, a high electrical conductivity, and a low cost.\textsuperscript{26, 50} Figure I-9a presents an EDLC using porous carbon electrode and the EDL formed at the negative electrode. The corresponding equivalent circuit of the EDLCs is shown in Figure I-9b, where $C_{\text{dl}}$ is the double layer capacitance, and $R_C$, $R_{Ely}$, and $R_L$ are the resistance of the contact between active material and current collector, bulk electrolyte, and leakage resistance, respectively. Figure I-9c is the simplified equivalent circuit of EDLCs, consisting in a parasitic inductance (L), an equivalent series resistance (R_S), a capacitance (C), and a Faradaic leakage resistance (R_F).
Figure I-9: Schematic of an EDLC: (a) configuration of an EDLC and the zoomed view at the negative electrode-electrolyte interface, (b) corresponding equivalent circuit, and (c) the simplified equivalent circuit.\(^{51}\)

However, for porous carbon-based EDLC electrodes, not only SSA, but also other parameters, such as, pore size and pore size distribution, the presence of surface groups, and the nature of the electrolytes influence the capacitance. Surface groups (such as -OH) are frequently present as impurities in activated carbons or rGO materials, coming from the synthesis and/or activated process. In addition, -N groups can be used as dopant to improve the electrochemical performance of carbons. These surface groups contribute to the capacitance in aqueous electrolytes by adding a pseudocapacitive contribution involving fast and non-diffusion limited surface faradaic reactions.\(^7,8\)

From the materials’ point of view, the capacitance of carbon-based materials is strongly correlated to the SSA and pore structures.

Initial research works on activated carbon were focused on increasing the pore volume by developing high SSA and refining the activation process. However, it was
quickly established that the gravimetric capacitance of activated carbons was limited even for porous carbon with high SSA.\textsuperscript{52-55} As pointed out by Ruoff \textit{et al.}, the area-normalized capacitance of various porous carbon-based electrodes decreased to 4-5 \( \mu \text{F} \cdot \text{cm}^{-2} \) when the SSA larger than 1500 \( \text{m}^2 \cdot \text{g}^{-1} \). Barbieri \textit{et al.} has attributed this capacitance saturation at ultrahigh SSA to a space charge capacitance, originating from a space charge gradient layer on the electrode side.\textsuperscript{55} Additionally, the presence of micropores was considered to be mainly at the origin of the capacitance limitation. Specifically, the narrow sub-nanometer size micropores in porous carbons were believed to be too small in size to accommodate the electrolyte ions, which excluded any EDL contribution from these non-accessible pores; such ion sieving effect was previously suggested as another explanation.\textsuperscript{57-59} As a result, no direct clear trend could be established between ultra-high SSA and capacitance.

It was known for a long time that carbon pore size larger than the solvated ion size was needed so that pores could be accessible to the electrolyte ions.\textsuperscript{53} In other word, porous carbon with a pore size smaller than the solvated electrolyte ions does not contribute to EDL capacitance and thus were considered useless. For the commonly used electrolytes, the sizes of bare ions and ions with solvation shells vary from few to tens of Å. For instance, the size of bare tetraethylammonium cation is around 0.68 nm, and its solvation shell in acetonitrile (ACN) increases the size of the solvated ion to 1.3 nm. Under this circumstance, larger pores seem the most suitable candidates for achieving high capacitance with porous carbons. However, several groups reported high capacitance by using microporous carbons with sub-nanometer pores in various electrolyte systems.\textsuperscript{60-63} Taking advantage of the tunable pore structure of CDCs, Chmiola \textit{et al.} reported an anomalous increase in gravimetric and volumetric capacitance for CDCs with controlled pore size below 1 nm.\textsuperscript{60} The specific gravimetric capacitance normalized by BET SSA (\( C/S_{\text{BET}} \)) obtained from Ar gas sorption (see Figure I-10a) revealed a capacitance increase for carbon pore size smaller than 1 nm. Same trend was found for microporous activated carbons in both aqueous and non-aqueous electrolytes.\textsuperscript{61} In addition, DFT SSA-normalized capacitance was also calculated and same capacitance increase was obtained, thus indicating that the underestimation of SSA of microporous carbons by BET model was not the cause of the increasing trend of \( C/S_{\text{BET}} \) (see Figure I-10b).\textsuperscript{60} Later on, by monitoring the potential change of each electrode by using a silver quasi-reference electrode, \textit{a different EDL}}}
capacitance behavior at negative and positive electrode was measured by Chimiola et al.,\textsuperscript{64} which confirmed partial desolvation during the charge/discharge process.

![Figure I-10: Plots of specific capacitance normalized by SSA vs. average pore size obtained from for various CDCs electrodes in 1.5 M TEABF$_4$ in ACN (a) and (b).\textsuperscript{60}](#)

However, because of the presence of the solvation shell that affects the effective ion size, it was not clear whether an optimum pore size could be achieved to maximize the capacitance. To this end, CDCs with various controlled pore sizes and PSD were characterized in solvent-free ionic liquid electrolyte, ethyl-methylimidazolium-bis(trifluoromethane-sulfonyl)imide (EMITFSI).\textsuperscript{65} Solvent-free ionic liquid electrolytes rule out the possibility for solvation effect, and EMIm$^+$ and TFSI$^-$ have similar ion sizes (0.79 and 0.76 nm in the longest dimension for TFSI and EMI ions, respectively).\textsuperscript{64, 65} Figure I-11 shows the change of the normalized capacitance of various CDC electrodes vs. pore size, in EMImTFSI electrolyte. The same trend was also reported for the change of the specific gravimetric and volumetric capacitance vs. the carbon pore size.\textsuperscript{60, 65} The capacitance reaches a maximum when the ion size is close to the carbon mean pore size. This result was a major finding since i) it shows that high capacitance could be achieved when ion was confined in pores of the same dimension, and ii) it evidences that the conventional way to describe the EDL formation using the Gouy-Chapman model in these confined nanopores was not anymore valid.
Figure I-11: Normalized capacitance change vs the pore size of the CDC samples.65

1.3.3 EDL models with surface curvature effects

The observed anomalous increase of specific capacitance in carbon nanopore has caught the interest of researchers to help in understanding the EDL formation in confined nanopores via advanced in situ techniques and simulation methods. Classical EDL models based on a 2-D planar electrode were insufficient to describe the EDL formation in carbon nanopores since of these 2-D models do not take into account curvature and porous effects. Nanoporous carbons have various shape of pores, including endohedral pores (cylindrical, slit, and spherical) and exohedral pores between the carbon nanoparticles (carbon nanotubes, onion-like carbons).32

Figure I-12: Schematic illustrations (top views) of (a) an electric double-cylinder capacitor based on mesopores and (b) an electric wire-in-cylinder capacitor based on micropores.66 (c) Schematic of a sandwich capacitor.67

Huang et al. proposed the first simple, heuristic models for nanoporous carbon-based supercapacitors which include endohedral pore curvatures.68, 69 They first
considered a cylindrical mesopore shape, where solvated ions could enter under polarization and approach the pore walls to form electric double-cylinder capacitors (EDCCs). Figure I-12a shows the schematic of the EDCC formed in a negatively charged mesopores, the corresponding double-cylinder capacitance being given by Equation I-10.

\[
C = \frac{2\pi \varepsilon_r \varepsilon_0 L}{\ln(b/a)} \quad \text{(Eq. I-10)}
\]

where \(L\) is the pore length, and \(b\) (nm) and \(a\) (nm) are the radii of the outer and inner cylinders, respectively.

The capacitance normalized by the surface area \(A\) is given as below:

\[
\frac{C}{A} = \frac{\varepsilon_r \varepsilon_0}{b \ln\left(\frac{b}{b-a}\right)} \quad \text{(Eq. I-11)}
\]

where \(d\) (nm) can be viewed as the distance between the center of counterions and the carbon walls. When the pore size was reduced from mesopores to micropores, the limited space inside of micropores does not allow to form a double cylinder; instead, the electric wire-in-cylinder-capacitors (EWCCs) was proposed by Huang et al. when assuming a cylindrical micropore filled with solvated (or desolvated) counterions (Figure I-12b). The corresponding capacitance is given as:

\[
\frac{C}{A} = \frac{\varepsilon_r \varepsilon_0}{b \ln\left(\frac{b}{a_0}\right)} \quad \text{(Eq. I-12)}
\]

where \(b\) (nm) is micropore radius, and \(a_0\) (nm) the radius of the inner cylinder. Both \(d\) and \(a_0\) are approximately independent of pore size, instead, their values are related to the effective size of the counterions. The EDCC/EWCC model can be further extended to porous carbons with bimodal porous distribution, which exhibit relatively narrow pore size distributions of micropores and mesopores (the contribution of macropores to the total SSA is neglected), the capacitance is given by Equation I-13.

\[
C = \frac{\varepsilon_r \varepsilon_0 A_{\text{mic}}}{b_{\text{micro}} \ln(b_{\text{micro}}/a_0)} + \frac{\varepsilon_r \varepsilon_0 A_{\text{meso}}}{b_{\text{meso}} \ln(b_{\text{meso}}/d)} \quad \text{(Eq. I-13)}
\]

The EDCC/EWCC model was based on two assumptions, that i) the total charges of the carbon wall can be screened by the counterions inside of the cylinder pore and ii) the space charge capacitance of the carbon walls can be neglected owing to the high conductivity of carbon materials. Equations I-11 and 12 indicate that the surface normalized capacitance depends on both the pore sizes of the nanoporous carbon and electrolyte ion size. The linear capacitance versus surface area relationship suggested
by the classical 2-D model is not expected in the present EDCC/EWCC model, because of the curvature effects. Besides, the change of the capacitance with the carbon pore size predicted by the EDCC/EWCC model for various porous carbons in both aqueous and organic electrolyte systems, well agrees with the experimental results.\textsuperscript{58, 69}

Another sandwich capacitor model was proposed by Feng \textit{et al.} by assuming the presence of slit-shaped pores.\textsuperscript{67} Using MD simulation, K\textsuperscript{+} ions distribution in the slit-shaped micropores was investigated by considering ion hydration and water-water interactions. As presented in Figure I-12c, the sandwich capacitor was formed by one layer of counterions located in the middle of two carbon walls with the same polarity, the corresponding capacitance is given by:

$$C/A = \frac{\varepsilon_r \varepsilon_0}{b-a_0}$$  \hspace{1cm} (Eq. I-14)

where $b$ (nm) is half of the slit-shaped pore width, and $a_0$ (nm) is the effective ion radius of the counterions which similar to the EDCC model.\textsuperscript{67}

\textbf{Figure I-13}: Schematic illustrations of (D) cross-section of an exohedral capacitor, and (E) steric views of 0D spheres (top) and 1D tubes (down) with counterions approaching the outer surface, respectively.\textsuperscript{70}

Exohedral capacitors can be formed on the outer surface of exohedral carbons. Figure I-13a gives the schematic illustration of a negatively charged exohedral capacitor, such as expected from the EDL charge of 0-D OLCs and 1-D CNTs (Figure I-13b).\textsuperscript{70} For 0-D OLCs, solvated counterions accumulate on the outer spherical surface under the polarization to form an exohedral electric double-sphere capacitor (xEDSC). In the case of 1-D CNTs, an exohedral electric double-cylinder capacitor (xEDCC) of solvated
counterions was formed between the solvated counterions and carbon walls. The surface-area normalized capacitance of xEDSC and xEDCC are given by Equation I-15 and 16:

\[
\frac{C}{A} = \frac{\varepsilon \varepsilon_0 (a + d)}{ad} \quad \text{(Eq. I-15)}
\]

\[
\frac{C}{A} = \frac{\varepsilon \varepsilon_0}{a \ln \left[ \frac{a + d}{a} \right]} \quad \text{(Eq. I-16)}
\]

where \(a\) (nm) is the radius of the inner sphere/cylinder charge layer, related to the carbon particle size, and \(b\) (nm) is the radius of outer sphere/cylinder charge layer, \(d\) (nm) is the effective double-layer thickness; \(d\) being the difference between the outer and the inner diameter.

Capacitance increase trend can be made using xEDSC and xEDCC models. The prediction made by these two models are in line with experimental results.\(^{70, 71}\) However, they consider the electrode charge to be entirely screened by a single layer of counterions on the carbon surface, so that the electrolyte contribution to the EDL beyond the counterion single layer is negligible. This situation is unlikely to occur in solvent-free ionic liquid electrolytes where an overscreening effect arises due to the strong ion-ion correlations in such concentrated electrolyte\(^{39}\) leading to the formation of extra layers of counterion/co-ions, and improved models were proposed.\(^{72}\)

In summary, although these models correctly depict the capacitance trend in carbon nanopores, the cylindrical and slit-shaped pores considered in these models are too simplistic to depict the electrode/electrolyte interface in amorphous, porous carbons. Understanding of the EDL charging can help us to optimize electrode materials for high performance EDLCs.

As a result, the core of this thesis is to utilize in-situ techniques to study the charge storage mechanisms of two- and three-dimensional carbon materials. The state-of-the-art of the experimental and modeling results will be discussed later in this chapter.

2. State of the art of the materials used for EDLCs

2.1 General material design concept

As mentioned before, according to Ragone plot, the main challenge for EDLCs is to improve the energy density without sacrificing their power performance. Based on
Equation I-4, the energy density can be enhanced by enlarge the operating voltage and the capacitance of the EDLCs. In general, the electrochemical window is determined by the nature of electrolytes. Increasing electrochemical window is an efficient way to enhance supercapacitor performance as it has a square relationship with both energy and power densities. Alternatively, by introducing a passive layer to the carbon surface, the oxidation/reduction potential of the electrolyte can be shifted to higher over-voltage.

On the other hand, the capacitance of EDLCs is proportional to the charge storage area ($A$) and the permittivity of the EDL, but inversely changes with the distance between ion center and carbon electrode surface ($d$). The specific surface area (SSA) of the carbon material is assumed to be the same as the surface area of electrode/electrolyte interface; hence the trend for designing supercapacitor electrode materials is to increase the SSA of the carbons, as previously mentioned. This is mainly done by creating micro and mesopores (e.g. CO$_2$ or KOH activation). However, as discussed in section 1.3.2, the SSA and capacitance does not have a straightforward correlation. The pore size, pore size distribution, porosity, pore shape and pore structure can be effetely changed while adjusting the SSA of carbon materials. It is difficult to modify solely one parameter without changing the others, and all of them play a different role in the charging process.

To play with the average approaching distance of the ions to the electrode surface parameter $d$, the charge storage mechanisms during the charging processes of EDLCs has to be understood. Although it was found that i) a drastic increase of capacitance can be achieved by creating micropores (pore size < 2 nm) and ii) the best pore size depends on the electrolyte ions, mesopores (2 – 50 nm) are also important for the ion transport (electrolyte tank) to improve power performance.\textsuperscript{73,74} The synthesis strategies of carbon materials becomes more crucial for EDLCs. With the development of the synthesis strategies for carbon materials, better control of the pore characteristics can help us to study both fundamental understanding of EDL charging mechanism and electrode design of better performance.

\section{2.2 Carbon electrode materials}

For EDLCs, high capacitance was believed to be reached by increasing the SSA of active materials for charging the double layer. Different forms of graphitic carbons have been developed for EDLCs application because of their characteristics: high
electronic conductivity, electrochemical stability, and open porosity. The moderate cost makes carbon materials more attracting for industrial used. It can be derived from natural resources like coconut shell, wood or coal which is not difficult to obtain. Also, synthetic materials like polymers can be used as precursors. Generally, a broad distribution of pore size is created in the bulk carbon grains, including mainly micropores and meso-pores. By adjusting the time and temperature at the activation step, the mean pore size can be tuned. The activation process is usually mixing carbon-contained precursor with chemical activation agent, then heat up to 400~700℃. Various kinds of carbon materials with several dimensionalities can be used for EDLC applications, from 0-dimensional (0-D) non-porous carbon onions, to 1-D (carbon nanotubes and carbon fibers), 2-D (graphene), and 3-D porous carbons (activated carbons, templated carbons, carbide-derived carbons). Table I-2 summarizes of the different categories of carbon materials used in supercapacitors.

<table>
<thead>
<tr>
<th>Material</th>
<th>Carbon onions</th>
<th>Carbon nanotubes</th>
<th>Graphene</th>
<th>Activated carbon</th>
<th>Carbide derived carbon</th>
<th>Templated carbon</th>
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<tbody>
<tr>
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<td>1-D</td>
<td>2-D</td>
<td>3-D</td>
<td>3-D</td>
<td>3-D</td>
</tr>
<tr>
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<td>Low</td>
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<tr>
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<td>Low</td>
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</tr>
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</tr>
</tbody>
</table>

Table I-2: Different carbon structures used in EDLCs with onion-like carbon (OLC), carbon nanotubes, graphene, activated carbons, and carbide-derived carbons.

**0-D: Onion-Like Carbons (OLCs)**

Carbon onions, also called onion-like carbons (OLCs), are spherical or polyhedral carbon nanoparticles, consisting of concentric defective sp²-hybridized carbon multiple
shells, with a small size around a few tens of nm. Among numbers of synthetic routes for preparing OLCs, thermal treatment of nanodiamond powders obtained by detonation is the most practical method. Since OLC particles are non-porous, they exhibit limited external SSA of 300-600 m²·g⁻¹, together with high interparticle pore volume around 1 cm³·g⁻¹. The pore structure of OLCs electrode consists predominantly in micro and mesopores existing between the OLC particles. However, being non-porous particles, the whole surface is highly accessible to electrolyte ions. As a result, OLCs-based electrodes can achieve limited capacitance of 50 F·g⁻¹, with an excellent power ability due to high accessible external surface area. In summary, OLCs are not good candidates to increase the capacitance of EDLC electrodes but can deliver high power. Besides, OLCs with a particle size around 10 nm are also employed as conductive additives for the EDLCs.

1-D Carbon nanotubes

Carbon nanotubes (CNTs) are large cylindrical carbon material consisting of a hexagonal arrangement of sp² hybridized carbon atoms, which are formed by rolling up a single sheet of graphene (single-walled carbon nanotubes, SWCNTs) or by rolling up multiple sheets of graphene (multiwalled carbon nanotubes, MWCNTs). To date, the commonly used synthesis techniques for CNTs are arc discharge, laser ablation, and chemical vapor deposition (CVD). SSA of CNTs ranges from 100 to 1000 m²·g⁻¹. CNTs can exhibit narrow pore size distribution, but the internal pores are unlikely to contribute to the EDL capacitance due to the ion transport limitation inside of the carbon walls and because of the absence of inner electric field in regular operating conditions. Instead, similar to OLCs, the external surface of CNTs can be used to form exohedral capacitors, leading to moderate capacitance below 100 F·g⁻¹. However, the highly accessible external surface and excellent electric conductivity make CNTs suitable candidates for high power devices, even under extreme climatic conditions. CNTs have been used as model material in simulation experiments to study the double layer formation in- or outside the tube.

2-D Graphene

Graphene, one of the most studied two-dimensional material in the early century, can be synthesized by (1) “bottom-up” approaches, such as CVD, epitaxial growth and
chemical synthesis, and (2) “top-down” methods, including the micromechanical and liquid-phase exfoliation of graphite and the reduction of graphene oxide (rGO).\textsuperscript{93} The bottom-up methodology is preparing graphene from smaller carbon precursors playing the role of building blocks; in contrast, top-down approaches are based on breaking down macro-compounds to basic elements. A single graphene sheet has a high theoretical SSA of 2630 m\textsuperscript{2}·g\textsuperscript{-1} and high intrinsic capacitance of about 21 μF·cm\textsuperscript{-2}.\textsuperscript{94,95} However, these excellent properties at single layer graphene scale do not translate at large macroscopic scale due to the restacking issue.\textsuperscript{93} In order to enhance the performance of graphene-based EDLCs, extensive efforts have been made to address such restacking issue.

One promising approach is to pre-insert molecules between the graphene layers or building 3D structures based on 2D rGO.\textsuperscript{96-99} For example, porous holey graphene (HGF) material showed an impressive capacitance beyond 200 F·g\textsuperscript{-1} and high gravimetric and volumetric stack energy densities\textsuperscript{100} thanks to the creation of 3D ionic pathways. However, the synthesis process has to be carefully controlled to prepare porous graphene with suitable structure and surface composition. In summary, graphene and graphene-based materials show some interesting performance at the lab level, but the cost issue and the lack of techniques for industrial-scale high-quality graphene electrode production still hamper their commercial development. However, as an ideal 2D carbon surface, graphene offers great opportunities as model surface materials to develop some fundamental studies on the understanding of EDL formation in real and simulation experiments. Figure 1-14 shows the morphology of graphene samples.

\textbf{Figure 1-14:} Structural model of pristine graphene, (b) TEM image of graphene, and (c) SEM image of graphene. Graphene in (b) and (c) are produced from chemical reduction of graphene oxide.\textsuperscript{101-103}
3-D Activated carbons (ACs), carbide derived carbons (CDCs), and templated carbons

Activated carbons (ACs) are amorphous porous carbons containing mainly sp² carbon atoms. They are prepared from physical (thermal) and/or chemical activation of various types of natural or synthetic organic precursors. In general, pre-carbonization is required before the activation process when natural precursors used as the carbon precursors. Physical activation takes place at high temperature range of 600-1200 °C under oxidizing atmospheres (such as steam and CO₂), while chemical activation requires a lower temperature range of 300-600 °C using chemical reagent (such as KOH, ZnCl₂, etc.). ACs are highly porous with a broad range of pore sizes from few tenths of nanometers to few nanometers, resulting in high SSA, mainly ranging from 1000-2000 m²·g⁻¹. The SSA and pore size distribution are predominantly determined by the carbon precursors and activation process. Thanks to their relatively good electrical properties and high SSA, and their low cost comparing to other carbon materials, ACs have been widely used as supercapacitors electrode materials. AC-based supercapacitors show a long cycle life span (>10⁶ cycles), making ACs the best option as supercapacitor electrodes in commercial devices. The electrochemical performances of ACs based electrodes have been significantly improved during past years, exceeding 200 F·g⁻¹ in nonaqueous based electrolytes. This has been mainly achieved by tuning the mean pore size and pore size distribution in the microporous range, below 1.5 nm (see below). In aqueous electrolytes, ACs electrodes enable to deliver capacitance ranging from 100 to 300 F·g⁻¹ depending on the pore size distribution and surface chemistry; but the penalty is the low energy density associated with the limited voltage window.

Carbide-derived carbons (CDCs) are made by extracting the atoms metal from metal carbides structure precursors. The most common CDC material for supercapacitor application is derived from titanium carbide. The chemical reaction is shown below:

\[ \text{TiC} + 2\text{Cl}_2 \rightarrow \text{C} + \text{TiCl}_4 \uparrow \]  

(Eq. I-17)

The synthesis time, temperature and the gas composition during chlorination process are the factors to modify the pore structure. CDC with enhanced pore volume could be produced using ternary carbides, such as Ti₂AlC, Ti₃AlC₂, and Ti₃SiC₂.
CDCs offer the key advantage to fine tune their pore size (below 2 nm) and pore size distribution by adjusting the synthesis parameters such as temperature and time; the carbon structures and particle size are defined by the carbide precursors. Generally, CDCs exhibit high BET SSA reach up to ~2000 m$^2$·g$^{-1}$ and with a narrow pore size distribution in the nanometer and sub-nanometer range. Taking TiC-CDCs as an example, their average pore sizes vary from 0.68 to 1.1 nm which can be tunable with 0.05 nm accuracy by changing the chlorination temperature in range of 500 to 1000 °C. The morphology of CDC samples are shown in Figure I-15. Thanks to their controlled, narrow pore size distribution in microporous range, CDCs have been extensively used as model materials to understand the fundamental EDL formation in porous materials and helped in identifying the capacitance increase in nanopores. TiC-CDCs show a specific capacitance value of 160 F·g$^{-1}$ was reported in ionic liquid, as well as a high volumetric capacitance of 85 F·cm$^{-3}$, higher than standard ACs at that time. Although pores below 1 nm size were proved to enhance the EDL capacitance efficiently, the relatively low ion transport rate in these small pores could affect their power performance. Several approaches have been proposed to design CDCs with high EDL capacitance without compromising of high-rate performance, including reducing the CDC particle size and adding mesopores. Interestingly, CDCs have moved into real products since they are now used in commercial EDLCs.

Figure I-15: (a) and (b) is the TEM images of CDC produced at 1200 and 400 °C, respectively. (c) is the SEM image of mesoporous silica-templated CDC.

Templated carbons (TCs) are obtained by templated-assisted carbonization of carbon precursors and subsequent removal of the templates. This approach leads to carbon materials with precise control of the pore size in the mesopore range, which is with great significance for electrode materials of supercapacitors. Pore structures of TCs can be controlled by using two kinds of templates, namely hard template (such as
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zeolites, mesoporous silicas, and metal oxides) and soft template (such as metal-organic frameworks and block copolymer surfactants). Numerous publications based on TCs have been published during the last decade, here we example a few. Zeolite templated carbons (ZTC) produced by acetylene CVD can achieve high capacitance of 140 to 190 F g\(^{-1}\) (70 to 85 F cm\(^{-3}\)) in the organic-based electrolytes. Such materials are interesting as well for conducting basic studies or ions transfer and adsorption in nanopores. However, the commercial development is limited by the cost of production.

2.3 Electrolytes

The electrolyte is one of the most critical factors that determine the performance of EDLCs. Equation I-4 and 5 indicate the two main properties of the electrolytes used for EDLCs: 1) electrochemical stability, defining the voltage window, which is essentials to both the energy and the power densities; 2) ionic conductivity related to the equivalent series resistance (ESR), which limits the power performance. In addition, the capacitance can be affected by the choice of solvents and ions (see Equation I-2). Electrolytes for supercapacitors can be classified into three main categories, depending on their nature: aqueous- and organic-based electrolyte and ionic liquids.

Aqueous electrolyte

For aqueous electrolytes, safety and low cost are key advantages from the industrial point of view. The electrolyte has higher ionic conductivity (few hundreds of mS cm\(^{-1}\)) comparing to organic electrolytes and ionic liquids. However, the operating voltage window for such electrolyte is limited by water electrolysis to 1~1.2 V. As a result, the energy density of aqueous-based EDLCs is still one order of magnitude smaller compared to devices operating with non-aqueous electrolytes. Acid-based (e.g., H\(_2\)SO\(_4\)) or alkali-based (e.g., KOH) electrolytes are commonly used.

To tackle the issue of the limited voltage window of aqueous electrolytes, several approaches have been developed over the years. Béguin’s group showed a great expansion of the voltage window in aqueous electrolyte using a porous carbon electrode. They discovered that the operating potential window for symmetric carbon-based supercapacitors could be expanded to almost 2 V in neutral aqueous electrolyte. The large overpotential is related to the hydrogen storage inside the
nanopores of AC electrode. When the water is reduced, then the produced hydrogen adsorbs onto carbon surface and/or recombine to form \( \text{H}_2 \) molecules. The electro-oxidation of the adsorbed hydrogen onto AC surface was observed on the anodic scan of the CV. With a high overpotential due to hydrogen storage in carbon nanopores, the energy density can then further be improved (see Equation I-4). Also, from the industrial point of view, the neutral aqueous electrolyte is less corrosive than acidic and alkaline aqueous electrolyte.

In 2015, Suo et al. introduced the concept of “water-in-salt” electrolytes (WIS) for lithium-ion batteries where cell voltage beyond 2 V could be reached thanks to the limited amount of free water molecules.\(^{125}\) As a result, the stability of water molecules toward oxidation is higher compared to conventional salt-in-water electrolytes. Using 31m LiTFSI electrolytes and activated carbon as electrodes, the operating voltage window broadens to 2.4 V.\(^{125}\) Although the existing LiTFSI shows decent performance, the cost, high viscosity and limiting operating temperature of this kind of electrolyte still need to be solved. Some alternative salts to LiTFSI have been reported in recent years, such as NaTFSI or NaClO\(_4\).\(^{126,127}\) In addition, an idea of introducing a co-solvent is shown to be effective for improving the power performance for such electrolytes.\(^{128}\) The ionic behaviors is similar to that of ionic liquid, instead of solvated aqueous or organic electrolytes, resulting in differences in the charging mechanisms such as mentioned in the previous part. Although the approach sounds interesting, the WIS concept did not yield into major breakthrough in the energy storage field due to poor power performance. Also, for supercapacitors, the porous structure of the electrode makes the ion exchange and transfer electrolyte/electrode interface even more complex compared to conventional battery materials.

**Organic electrolytes**

Generally speaking, organic-based electrolytes have a larger voltage window compared with aqueous electrolytes, which results in great improvement of the energy density. Most of the supercapacitors available on the market are using organic electrolytes, and their energy density can reach up to 10 Wh·kg\(^{-1}\).\(^{129}\) However, the drawbacks of these electrolytes are the flammable property, need for purification and lower conductivity compared to aqueous ones. For carbon-based supercapacitors, the most frequent formulation for commercial products is TEABF\(_4\) in PC or ACN.
Several works have focused on the degradation of organic electrolytes and the aging of carbon materials in such a system, for improving safety. Although the reactions are complex, an important knowledge has been acquired today about the degradation mechanisms and their impact on the supercapacitor performance. On the other hand, to enhance the performance of supercapacitors in such electrolyte system, the ionic dynamics and ion confinements in micropores have also been investigated, including the effect of solvent and the ion desolvation of ions while entering micropores.

Recently, a computational method approach was proposed to boost the process to discover new organic solvents in an efficient and systematic way. By screening the desirable properties of the solvent, such as voltage window, viscosity, and ion solubility, several combinations of new solvents (cyano esters-based and nitrile-based) and salts were proposed as alternative electrolytes. In combination with the conventional TEABF$_4$ salt, operating cell voltage up to 3.2 V was achieved.

**Room temperature ionic liquids (RTILs)**

Room temperature ionic liquids (RTILs), also referred as room temperature molten salts, only contain cations and anions. The general properties of ionic liquids are good chemical stability, wide electrochemical voltage window, but low to moderate ionic conductivity and limited low temperature operation. In the past decade, a lot of works have shown ionic liquids are safe and perform relatively well at a large range of temperatures (-50~80°C). Although the energy density has met the requirement for industrial used, however, because of their high viscosity (relatively lower ionic conductivity compared to other electrolytes), the improvement of power density for such system is a challenge. This work did not yet yield to a major breakthrough in terms of performance, but it has brought important advances in the scientific understanding of the ionic/carbon interaction in porous carbon electrodes. Recently, DFT calculation has been applied to predict the electrochemical potential windows for ionic liquids to accelerate the process for experimental selection.

A new concept proposed by Rochefort’s group uses a biredox ionic liquids as salt in an electrolyte to achieve bulk-like redox density with liquid-like fast kinetics. The cation and anion of these biredox ionic liquids bear moieties that undergo very fast reversible redox reactions. The capacitance in these biredox
electrolytes was twice as high as that of conventional ionic liquid electrolyte and remained stable for 2000 cycles.\textsuperscript{163} The power performance was similar in both electrolytes. Importantly, the leakage current measured for biredox IL was two to three times lower than that of the conventional ones, which means a decreased self-discharge. The biredox concept is certainly an interesting approach\textsuperscript{164-166,167}. These redox-active electrolytes offer opportunities for improving the energy density of EDLC devices.

3. Charge storage mechanisms and ion transport: from modeling to in situ techniques

3.1 Theoretical approaches

After the experimental discovery of the capacitance increase in carbon nanopores smaller than the solvated ion size, various nanoporous carbon structures and electrolytes have been used for modeling not only to improve the theoretical EDL models but also resolve the underlying theory and predict optimized carbon structures.\textsuperscript{39, 66, 91, 92, 168-171} In this section, the recent development of charge storage mechanisms and ion dynamics on planar and porous electrodes will be introduced first by simulation techniques.

3.1.1 Room temperature ionic liquids (RTILs)

In section 1.3, the EDL models of 2-D flat surface and 3-D ideal pores were described. The “superionic state” of ions confined in carbon nanopores can explain the increase of the normalized capacitance in neat ionic liquid electrolytes.\textsuperscript{172} A schematic overview of the overscreening effect is shown in Figure I-16A. Kornyshev \textit{et al.}\textsuperscript{172} applied mean field theory on a slit-pore model and reproduced the capacitance increase versus pore width. Afterwards, the results were confirmed by using Monte-Carlo stimulation for ionic liquid system\textsuperscript{60, 173} The comparison of the results is displayed in Figure I-16B. The superionic state is attributed to two effects. Firstly, the metallic properties of carbon materials weaken the electrostatic interactions of ions, resulting in breaking the Coulombic ordering of ions in the nanopores by the creation of image charges. Second, the negative free energy of ions entering the pores from bulk to the
pore favors the increase of ion density inside the pores. The transition from ion-rich to
ion-deficient nanopores was observed when reaching a threshold voltage $V_f$ as shown
in Figure I-16C.\textsuperscript{172} Futamura \textit{et al.} had proven the superionic state of ions in nanopores
experimentally.\textsuperscript{174} The structure of ILs confined in carbon nanopores was investigated
by simulation. Figure I-16D to F show different anion-anion pair ratios (R) at different
applied potentials. In the first coordination shell of TFSI$^-$ anion, there was also an
exitance of anions. The percentage of the anion and cation is calculated from Figure I-
16G to I.

\textbf{Figure I-16:} (A) A sketch presents a cross-section of a single, laterally infinite, slit-like
narrow pore as a part of a porous electrode. (L: pore width; V: the applied voltage; d:
the diameter of ions). (B) Differential capacitance per surface area versus the pore width.
Both approaches show the anomalous capacitance behavior. (C) The packing ratio at
different voltage. At $V_f$, the total ion density reaches its maximum. (D)-(F) are visual
views of co-ion pairs of anions of EMImTFSI (R is the anion-anion pair ratio) and (G)-
(I) concluded the population in the first coordination shell around a TFSI anion in the
0.7-nm pores under 2, 0 and -2V.\textsuperscript{172-174}

Differently from diluted solution, simulation of RTILs system needs considering
the uniformity of the molecular charge distribution and the short range ion-ion
interactions.\textsuperscript{175,176} As a result, simulating RTILs system is more time consuming and
costly.\textsuperscript{177} Two main categories of simulation methods can be classified into simple
models and molecular models. Simple models, also referred as coarse grain models, use
coarse-grain ion representation and solvent molecular structure. The overscreening
phenomenon discovered by mean-field theory mentioned before is an example of a key finding by using simple models.\textsuperscript{41} The bell-shape character as a function of the applied potential and the oscillation structure of the EDL have been confirmed based on simple model.\textsuperscript{47, 178-181} In addition, RTILs self-assembly in the EDL was predicted by using a simple model as well.\textsuperscript{182} When the chain of the cation increases, the alternating cation-anion monolayers change to tail-to-tail cation bilayers. The results are presented in Figure I-17.

![Figure I-17](image)

**Figure I-17:** Schematic presentation of ion orientations in (a) $[\text{C}_4\text{C}_1\text{im}]\text{[NTf}_2\text{]}$ at a film thickness of 2.3 nm showing alternating cation and anion monolayers for C(AC)$_2$; (b) $[\text{C}_6\text{C}_1\text{im}]\text{[NTf}_2\text{]}$ at 3.4 nm showing a single bilayer, (ACCA)$_1$.\textsuperscript{182}

To look into the effect of the molecular structure of RTILs in EDL, molecular models operate with sophisticated atomistic description of the molecular structure of the electrolyte components. Ion dynamics and some transport properties can be obtained from Molecular Dynamics (MD) and Monte Carlo (MC) simulations. MD simulations model the system by stimulating the ion movements according to the second Newton’s law.\textsuperscript{183, 184} With MD simulation, ion reorganization while increasing the applied potential was confirmed by using BMImPF$_6$ at graphite planar electrode due to the strong due to CH- $\pi$ intermolecular interactions between the alkyl side chain and the SLG surface and the $\pi$- $\pi$ stacking.\textsuperscript{185} For porous carbon electrode, simulation results proposed that the origin of the increase of capacitance in nanopores and further improvement (fast ion transport) is not only due to the structure and texture of the carbon but also to the combination of ion exchange and ion adsorption mechanisms during charging.\textsuperscript{186-188} The diffusion coefficients of the in-pore ions have also been correlated to the power performance of charging nanoporous carbon.\textsuperscript{189-191}

The working principle of MC is based on the statistic of the ion movements and sampling the probability of an organization based on anion and cation number, ion-pair number and potential energy of the system at molecular level.\textsuperscript{192-195} The superionic state
of ionic liquid have been studied by this method, which was also used to evidence the oscillation of charge and potential distribution in the ionic liquid system.\textsuperscript{196} Later on, Kornyshev’s group used MC to discuss the effect of ionphilicity and ionophobicity of slit-like nanopores on the improvement of the energy density for supercapacitors.\textsuperscript{197}

### 3.1.2 Solvent-containing electrolytes

The addition of acetonitrile (ACN) solvent molecules to salt has been studied at planar electrode by MD simulation, complemented by quantum DFT calculations.\textsuperscript{170} Near neutral electrode surface, the EDL structure is not homogeneous. The ions are mainly adsorbed on the electrode surface while the solvent molecules are orientated in order. Under polarization, alternating layers of counter-ion and co-ion were found losing their solvation shell in the directions parallel to the electrode. Interestingly, the capacitance of organic electrolyte is only slightly higher comparing to solvent-free electrolytes, although the dielectric constant off solvent is two times larger.\textsuperscript{198} This might due to the solvent screening effect which results in a weaker cation-anion correlation.

For porous carbon electrode, MD simulations were able to characterized different sites with various morphology of CDC materials (edge, plane, hollow and pocket) and calculate the degree of confinement of the adsorbed ions.\textsuperscript{199} The results showed that at the edge, plane, hollow and pocket sites (with the increased degree of confinement from edge to pocket sites) of CDC samples, the degree of desolvation of anion varies similarly to that of the electrolyte bulk. It was found that ions are mostly adsorbed on plane sites in ACN-based electrolytes. Electrowetting of the smallest pores at high potential was also observed, under polarization, the solvent molecules being expelled in less confined sites. This study not only raises the idea of a better way to confine ions in nanopores but also established the importance of how the carbon structure influences the ion organization, for further experimental and simulation works. Furthermore, the degree of desolvation increases as counter-ion access higher degree of confinement (Figure I-18a).\textsuperscript{200} The diffusion of ion in-pore is four magnitude slower than ion adsorption due to the confinement effect while a potential is applied (see Figure I-18b). Combining experiments and MD simulations, the pre-filled of pores was confirmed for various carbon and pore size.\textsuperscript{201}
Chapter 1: Bibliography

Figure I-18: (a) Average coordination number of the anions during typical events inside an electrode held at 1 V. (b) Summary of the various characteristic times extracted from the simulations for electrodes held at -1 V.²⁰⁰

The charging mechanisms in nanoporous carbon were studied in RTILs and organic electrolytes by MD simulation. For CDC samples with smaller anion with or without solvent molecules, under positive polarization, ion-exchange and counter-ion adsorption occurred together; during negative polarization, ion exchange mechanism was mainly observed, accompanied with a small amount of co-ion desorption.¹⁸⁶, ¹⁹⁹ However, when the size of cation and anion is similar, the charge mechanisms was reversed for positive and negative potentials.²⁰² This study indicated the importance of ion-ion interaction towards the charging mechanisms for porous carbon electrode.

3.2 In situ experimental approaches

3.2.1 Electrochemical quartz crystal microbalance (EQCM)

EQCM is a powerful in situ technique for monitoring the electrode/electrolyte interface and was developed by Sauerbrey in the 1950s.²⁰³ EQCM is composed of a thin piezoelectric quartz crystal sandwiched between two metal electrodes used to apply an alternating electric field across the crystal; as many oscillating system a resonance frequency can be defined. At this frequency, the impedance of the quartz is minimum. In gravimetric mode (linear assumption), the shift of the quartz resonance frequency (Δf) is assumed to be proportional to the mass change (Δm). Which is usually reached for a thin and rigid deposit on the quartz crystal. The Sauerbrey’s equation is defined as followed (more details in Chapter II):
\[ \Delta m = -C_f \Delta f \]  
(Eq. I-18)

It has been used in different research field due to its capability to finely track the ion fluxes at the electrode/electrolyte interface, such as the adsorption and detection of proteins for biology studies, the redox processes on electroactive polymer films, the electrochemical behaviors of electrolyte for Lithium-ion batteries, and the details of complex electrochemical reactions.\textsuperscript{204-208 139, 208-212}

EQCM has not been used much for two-dimensional planar electrode. Some of the work are dedicated to identify the conditions to utilize EQCM due to the sensitivity of the equipment.\textsuperscript{213-215} For EDL-related work, a study focusing on the diluted aqueous electrolyte on gold and iron electrodes deposited on AT cut quartz crystals has shown that the shift of the resonance frequency measured by EQCM charges with the concentration of the solution\textsuperscript{216}; this is attributed to the change of the thickness of the diffuse layer. In 2011, a Japanese group sputtered a thin amorphous carbon layer onto titanium electrode deposited on AT cut quartz crystal.\textsuperscript{217} The interface between carbon material and organic electrolytes was characterized by impedance measurements. Further on, the EQCM results confirms the adsorption of a monolayer of counter-ion and polarized solvent molecules to balance the electric charges on the carbon surface. Figure I-19 is the schematic presentation of the adsorption model in organic electrolyte which cation adsorption accompany with partial desolvation.

![Figure I-19: Schematic diagram for the electric double-layer structure in PC solutions containing LiBF\textsubscript{4}.\textsuperscript{217}](image)

For porous carbon material, the EQCM were used to study the EDL structure and charge storage mechanisms mainly for microporous carbon electrode. The primary experimental results observed that highly solvated Li\textsuperscript{+} in aprotic propylene carbonate electrolyte lost a part of its solvation shell while entering the micropores.\textsuperscript{209} Later on,
the solvation number of different cations and anions in aqueous environment confined in nanopores were calculated.\textsuperscript{208, 218} By comparing with the bulk hydration number of each ion, partial desolvation was proposed which well aligns with a previous study in organic systems.\textsuperscript{139} In addition, ion-sieving effect was overserved by playing with different ions sizes and the carbon perm-selectivity behavior was discussed by the same group.\textsuperscript{211} In 2014, EQCM was used to study the direct relationship between ion size and pore size by using solvent-free ionic liquid (EMim\textsuperscript{+},TFSI\textsuperscript{-}) and porous CDC, whose pore size and pore size distribution can be finely tuned by controlling the temperature such as mentioned before.\textsuperscript{139} Two sample with different pore sizes of 0.65 and 1 nm were selected. The results show that for 1 nm pore size carbon, that is when the pore size is close to both cation and anion size, cations are the only species involved in charge balance during negative polarization. Differently, under positive polarization, ions exchange mechanism (exchange between anions and cations) is dominant at low charge density, while counter ions (anions) adsorption only occurs at high charge density. The experimental results are shown in Figure I-20.

![Figure I-20](image)

**Figure I-20:** Scheme of neat ionic liquid EMI-TFSI transport in CDC-1nm pores during different charging states based on EQCM results. Blue solid lines are measured mass change (EQCM), red dashed lines are the theoretical mass change of neat ions calculated from Faraday’s law. The black dashed line shows the linear fitting of measured mass change.\textsuperscript{139}

Similar experiments were further conducted in the presence of solvent, using 2 M EMImTFSI in ACN electrolyte. Even in presence of solvent molecule, the same trend has been observed: counter ion (cations) adsorption at the negative electrode and mixed mechanism – so involving both co-ions (cations) and counter-ions (anions) – at the
positive electrode. This asymmetry in the adsorption process with the electrode polarity is still under investigation but this highlights the key role played by the ion-carbon interaction. Interestingly, the partial desolvation of ions was experimentally observed when entering carbon nanopores. EMIIm+ ions enter 1 nm pores together with 3 to 4 solvent molecules around, while they are surrounded by 8 solvent molecules in the electrolyte bulk. In 0.65 nm pore, the solvent number decreased down to 1-2.

Since the EQCM technique appeared to be a powerful tool to characterize the electrode/electrolyte interface during operation, several improvements have been made during the past years. As the main drawback of this technique is the drop of the quartz quality factor – because viscoelasticity – because of active material deposit, an important step is expected through the improvement of the deposition process. At this aim, it has been recently published a work dealing with the development of a deposition process of different active materials onto a quartz crystal resonators. Instead of typical drip coating or spray coating, a new method by using vacuum filtration has been developed to prepare homogeneous coatings on the Au coated quartz.219 The roughness and the homogeneity of the deposit being greatly improved, more accurate measurements are obtained with a lot less frequency noise.

Besides gravimetric EQCM, other advance EQCM modes have been developed over the years. One of them is called EQCM with dissipation monitoring (EQCM-D). EQCM-D takes into account the mechanical properties of the film present on the quartz surface.220-224 The use of EQCM-D to study the electrode/interface in the electrode for energy storage materials has been pioneered by Levi and Aurbach.206, 208-211, 218, 225 By analyzing the mechanical properties of the deposited materials, studies have shown that the selection of binder is crucial, which viscoelastic behavior can vary based on the electrolyte environment; affecting in turn the accuracy of the EQCM results.226-228 The analysis of EQCM-D signals and its subsequent modeling using complex equations and models allows for collecting textural, structural and mechanical data of the coating.224 Despite the additional mechanical information can be extracted by monitoring the dissipation, EQCM used in gravimetric and dissipation modes has still some limitations. For instance, since an electrolyte is a mixture, it is difficult to break down clearly the respective contribution of each single specie: individual ions, solvent molecules. For this aspect, ac-electrogravimetry (ac-EQCM) has shown up to be a great tool to help deconvoluting the role of each involved species in the charge exchange process;
interestingly such technique give access to rate constants.\textsuperscript{229-233} Escobar-Teran \textit{et al.} used ac-EQCM to study the electrochemical behavior of carbon nanotubes in complex aqueous electrolytes.\textsuperscript{230} They have shown that the relative concentration change of individual species can be estimated by ac-EQCM which allows distinguishing between the contributions of the different ionic species to the charge storage in nanoporous carbon. Although this technique is complex to set-up and use, the ionic fluxes in carbon nanopores during the charge/discharge process can be analyzed in detail.

\subsection{3.2.2 Other \textit{in situ} techniques}

\textit{Nuclear magnetic resonance spectroscopy (NMR)}

To observe and quantify the ion environments in porous carbons, nuclear magnetic resonance spectroscopy (NMR) is one of the promising techniques to work with.\textsuperscript{234-237} The working principle of NMR dedicated to the ion confinements in nanopores is based on the shift of resonance of the targeted atom from the electrolyte ions to lower frequency because of the sp\textsuperscript{2} delocalized electrons distribution present at the carbon surface that shields the signal when the ion get closer to the carbon surface in pores. The chemical shift difference between the resonances of ions confined inside nanopores and the neat electrolyte is defined as $\Delta \delta$. With the help of density functional theory (DFT) calculations, the $\Delta \delta$ is found to be related to the intrinsic electronic structures of carbon, carbon structure and pore size distribution.\textsuperscript{238-240} Studies show that this so-called nucleus-independent chemical shift (NICS) allows for distinguishing the ion confined within carbon pores, as well as the ion population.\textsuperscript{238, 239, 241-244}

In 2006, Lee \textit{at al.} used \textit{ex situ} magic angle spinning (MAS) NMR to study in adsorption in porous carbon in organic electrolyte.\textsuperscript{245} Solid state $^{11}$B NMR spectra could distinguish between the BF$_4^-$ anion located outside and inside the pores at the open-circuit voltage (OCP), charged, and discharged stages. The same technique was used to obtain the relative concentrations of cations, anions, and solvents inside or outside the carbon porosity. Moreover, the exchange of ions from the adsorption site to the free state of the electrolyte can be characterized using two-dimensional $^{13}$C and $^{11}$B NMR exchange spectra.\textsuperscript{246} To avoid cell dismantling needed for \textit{ex situ} NMR analysis, \textit{in situ} NMR has been developed by Grey’s group which allows to track the change of local environment in porous carbon in real-time as well as the charge storage mechanisms.
A detailed work aiming at understanding the electric double layer structure in microporous carbon YP50F in tetraethylphosphonium tetrafluoroborate (PEt$_4$BF$_4$) with acetonitrile has been published by combining in situ NMR and EQCM.\textsuperscript{244} In situ NMR results showed the evolution of the absolute ion population of cations and anions confined in carbon nanopores at various state of charge. Two charging mechanisms were identified, depending on the electrode polarity. During negative polarization, the charge is stored by counter-ion (cation) adsorption, while ion exchanged was the charge storage mechanism during positive polarization.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure_I-21.png}
\caption{(a) Calculated total in-pore ion populations of YP-50F electrode in 1.5M PEt$_4$BF$_4$ in ACN at different potentials. (b) Schematic of charge storage mechanism at positive, 0V and negatively charged. At 0V, there is an equal number of cations and anions in the pores of the carbon electrodes. (c) Correlation between $D_{\text{in-pore}}$ (cations) and total in-pore ion population.\textsuperscript{140}}
\end{figure}

Lately, in situ pulsed field gradient NMR has been introduced to explore the ionic transport in porous carbon electrode.\textsuperscript{140} As can be seen from Figure I-21a, the total in-pore ion population increase from 0 V to negative potential while the in-pore diffusion coefficients ($D_{\text{in-pore}}$) decreased significantly for both cation and anion (see Figure I-21b). In addition, the difference of electrolyte concentrations indicates that with less ions confined in nanopores, the $D_{\text{in-pore}}$ will increase because of the reduced ion-ion interactions (see Figure I-21c). This study emphasizes the strong correlation existing between the charging mechanisms and ion dynamics for microporous carbon electrode.
**Small angle scattering techniques (SAS)**

SAS techniques are well-known to be efficient techniques for characterizing three-dimensional structure at micro- and mesoscopic scale\textsuperscript{249-254}, using X-ray or thermal neutron. Small angle X-ray scattering (SAXS) has been widely used for porosity characterization for carbon materials.\textsuperscript{255-257} Iiyama et al. firstly operated advanced \textit{in situ} SAXS to study the formation of cluster-like water molecules adsorbed into activated carbon fibers micropores.\textsuperscript{258} Further on, SAXS also demonstrated its ability to study the adsorption of gas molecules into nanoporous carbon.\textsuperscript{259}

Since then, lots of studies based on \textit{in situ} SAXS revealed interesting facts during polarization of nanoporous carbon electrode. For instance, some inaccessible micropores at OCP can be filled with electrolyte under polarization, when the carbon electrode overpotential was large enough.\textsuperscript{255,260} This mechanism was proposed since the electron density contrast decreased greatly and barely reversible. Besides, ion confinement in carbon micropores also has been studied with SAXS.\textsuperscript{261} By combining \textit{in situ} SAXS and Monte Carlo simulation the degree of confinement (DoC) of ions in micropores has been reported for an aqueous-based electrolyte.\textsuperscript{138} For ionic liquid system, the \textit{in situ} SAXS and simulation also confirm the superionic state for EMImTFSI and EMImBF\textsubscript{4} ionic liquids confined in small 0.7 nm nanopores.\textsuperscript{174} The coulombic ordering was preserved in larger 1 nm nanopores under ion confinement. The partial breaking of the coulombic ordering – superionic state - was observed when monolayer confinement occurred due to the existence of image charges in the carbon walls that partially screen the repulsive electrostatic interaction between co-ions. In summary, the development of experimental \textit{in situ} SAS techniques has been a key for pushing further our basic understanding of the ion confinements in carbon nanopores and charging mechanisms of EDLCs.

**Atomic force microscopy (AFM)**

AFM is a type of scanning probe microscopy, with demonstrated resolution on the order of fractions of a nanometer. To study the EDL structure, the AFM is operated by measuring the forces between the probe and the sample. The force is called the rupture force which referred to the applied force by AFM probe to break through the solid-like layered structure. \textit{In situ} AFM was applied to planar gold and graphite electrodes reveling the structure of ions layering for ionic liquids. Figure I-22 shows an example
of RTIL layered structure on gold surface at OCP and positive polarization. The force-distance curve is consistent with the cation and anion diameter. The transition of layering of ionic liquids and the orientation of cations and anions from zero volt to the applied voltage on both electrodes.\textsuperscript{262-265} It was found that 4~7 layered structure of EDL is formed on Au surface for RTILs. During negative polarization, the layered structure is stabilized; on the positive polarization, the layering effect is weaker. The difference of layering effect might be due to the molecular structure of ions. By combining with STM and impedance spectroscopy, the structure of EDL for RTILs, especially the oscillating overscreening profile, and the electrolyte/electrode interface can be detailly characterized.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{Typical force versus distance profile for an AFM tip approaching from an Au (111) surface in [EMIm]FAP at OCP and 2 V vs Pt.}
\end{figure}

3.3 What do we know today about charging mechanisms?

After the discovery of a drastic capacitance increase when the ions were confined in sub-nanopores (<1 nm) of porous carbon materials\textsuperscript{60}, the elucidation of the charge storage mechanism became one of the main focus for EDLCs research. There are three charging mechanisms possible.\textsuperscript{243} First, the charges on the electrode surface is balanced by counter-ion adsorption only, aligning with the traditional point of view of charging. The second possibility is while counter-ion adsorption happens, the co-ion desorbed from the pores. The third possibility is that the co-ion desorption occurred solely. The drawing of the three charge storage mechanisms is presented in Figure I-23.\textsuperscript{201} Different charging mechanisms can take place simultaneously during polarization. On the other hand, the charge storage mechanisms of two-dimensional planar electrode can be much more complicated. Additionally, not only these three possibilities can be responsible for
charge storage, but also ion reorientation and/or redistribution is another possibility.

**Figure I-23:** Different possible charging mechanisms for carbon pores that are initially filled with electrolyte: counter-ion adsorption, ion exchange, and co-ion desorption.\textsuperscript{201}

The charging mechanisms depend on the electrode material and electrolyte that have been chosen to study. The factors which affect the EDL structures including molecular structure of ions, ion size, ion-ion correlation, ion-solvent interaction, ion-carbon interaction. The latter being influenced by the electrode pore structure, and the surface chemistry.\textsuperscript{65, 266, 267} As mentioned previously, the *in situ* techniques and simulation methods can probe the ion dynamics, further on, the charge storage mechanisms for various EDLCs systems. With the whole picture of the charging mechanisms, the design of high performance EDLCs can be achieved.

**4. Objectives of the thesis**

As mentioned above, several *in situ* techniques dedicated to probing the electrode/electrolyte interface and ion dynamics have shown their value by pushing further our basic understanding of the electrode/electrolyte interface under polarization. This thesis aims at studying the fundamentals of charge storage mechanisms in various energy storage materials by utilizing *in situ* EQCM in gravimetric mode. Chapters III and IV are dedicated to two- and three-dimensional carbon materials for EDLCs application, and chapter V focuses on 2-D metal carbides and 3-D metal oxides for
various energy storage devices.

### 4.1 EQCM study of charge storage mechanisms on carbon-based materials

For EDLCs applications, carbon-based materials are used as electrode materials due to their superior properties as mentioned in section 2.2. Three-dimensional nanoporous carbon exhibits high capacitance and its charge storage mechanisms has been studied thoroughly over the years by in situ techniques. To improve the performance with porous carbon electrode, studies have shown that the change of electrolyte composition can be an option.\(^\text{268, 269}\) However, the main charge carriers depend on the ion size, ion-ion correlation, and ion-solvent interaction.\(^\text{270, 271}\) In chapter III, TiC-CDC with specific micropore size and multi-ions aqueous electrolyte will be studied by EQCM to identify the main charge carrier in multi-ions containing electrolytes.

Chapter IV is focused on the study of electrode/electrolyte interface with two-dimensional carbon material (graphene). Although conventional EDL models were developed for planar electrode, there are only few experimental progresses - compared to simulation works - over the years to study the EDL formation at planar electrode, and single layer graphene (SLG)\(^\text{93}\) has been used as a model material in that aim. In this chapter, SLG has been transferred onto an EQCM quartz and served as a planar platform to study the ion fluxes during electrochemical polarization, in RTILs and organic electrolyte. The effect of additional solvent molecules and the nature of electrolytes towards the charge storage mechanisms on two-dimensional graphene platform are the main discussions in the chapter.

### 4.2 Application of EQCM on other energy storage systems

Besides supercapacitors, other energy storage systems have been developed for applications required high energy density. As mentioned in section 1.1, EDLCs based on pseudo-capacitive materials and battery can reach larger energy density due to different charge storage principle involving surface or bulk faradic reactions. Since chemical reactions occurred, the charge storage mechanisms are usually more complex.
As a result, in chapter V, pseudo-capacitive and battery materials are studied separately by EQCM. Combing EQCM and other in situ techniques and simulations, the charge storage mechanisms are discussed.

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Chapter II:

Materials Studied and Experimental Setups
1. Introduction

The aim of this chapter is to describe the different carbon-based materials and electrolytes which have been tested in this work. Following up, the electrochemical methods used to characterize the electrode material and electrode/electrolyte interface will be presented. Electrochemical Quartz Crystal Microbalance working principle, setups, and cell design will be introduced in this chapter as well. The working principle of the techniques for material characterization are also mentioned in the last part.

2. Carbon-based materials

2.1 Carbon-derived carbon (CDCs)

CDC is made by extracting metal layer-by-layer from carbides with a rigid metal lattice used as a template.\(^1\) The most common CDC material for supercapacitor application is derived from titanium carbide (TiC). The chemical reaction is shown below in Equation II-1:

\[
\text{TiC} + 2\text{Cl}_2 \rightarrow \text{C} + \text{TiCl}_4 \uparrow \quad \text{(Eq. II-1)}
\]

CDCs with enhanced pore volume could be produced using ternary carbides, such as Ti\(_2\)AlC, Ti\(_3\)AlC\(_2\), and Ti\(_3\)SiC\(_2\).\(^2\),\(^3\) The time, temperature and the gas composition during the chlorination process are the factors to modify the pore structure.\(^1\) Synthesis of TiC-CDCs with pore size from 0.5 to 3 nm with a 0.05-nm accuracy and SSA up to 2000 m\(^2\)g\(^{-1}\) have been reported.\(^1\) Because of their high surface area and tunable pore size in the micropore range, TiC-CDCs can achieve high specific capacitance up to 160 F g\(^{-1}\) in ionic liquid and conventional non aqueous electrolytes, as well as high volumetric capacitance of 85 F cm\(^3\), that positively compare with standard activated carbons.

CDCs has not only exhibit superior performance as supercapacitor material, they have been extensively used as model materials to understand the fundamental EDL formation in porous materials and helped in identifying the capacitance increase and the charging mechanisms in nanopores.\(^4\),\(^6\) In this thesis work, TiC-CDC from YCarbon Inc (USA) with a mean pore size of 0.67 nm has been selected as one model material. The Ar sorption isotherm (77K) and PSD obtained from QSDFT methods of the as-received CDC-0.67nm were shown in Figure II-1. The characteristics of the sample are
given in Table II-1.

**Figure II-1:** Porosity Characteristics of the as-received CDC-0.67 nm carbon: (a) Ar sorption isotherm collected at 77K and (b) pore size distribution calculated from QSDFT model.\(^7\)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BET SSA (m(^2)g(^{-1}))</strong></td>
<td>1822</td>
</tr>
<tr>
<td><strong>DFT SSA (m(^2)g(^{-1}))</strong></td>
<td>1767</td>
</tr>
<tr>
<td><strong>Pre-pore diameter (nm)</strong></td>
<td>0.67</td>
</tr>
<tr>
<td><strong>Pore volume (cm(^3)g(^{-1}))</strong></td>
<td>0.772</td>
</tr>
<tr>
<td><strong>Ash content (%)</strong></td>
<td>1.91</td>
</tr>
<tr>
<td><strong>Particle diameter (μm)</strong></td>
<td>75</td>
</tr>
</tbody>
</table>

**Table II-1:** Physical properties of the titanium carbide derived carbon (TiC-CDC) from YCarbon Inc.\(^8\)

### 2.2 Single layer graphene (SLG)

Graphene, one of the most studied two-dimensional material in the early century, can be synthesized by (1) “bottom-up” approaches, such as CVD, epitaxial growth and chemical synthesis, and (2) “top-down” methods, including the micromechanical and liquid-phase exfoliation of graphite and the reduction of graphene oxide (rGO).\(^9\) A single graphene sheet has a high theoretical SSA of 2630 m\(^2\) g\(^{-1}\) and theoretical capacity up to 550 F g\(^{-1}\) for macroscale EDLC applications.\(^10\)\(^-\)\(^12\)
The SLG samples were provided by our collaborators from University of Science and Technology of China (China). SLG films were obtained by chemical vapor deposition (CVD) on copper (Cu) substrate. After etching by 0.1 M of ammonium persulfate ((NH$_4$)$_2$S$_2$O$_8$), the transfer of CVD graphene from Cu to pressure sensitive adhesive (PSA) films coated polyethylene terephthalate (PET) substrate was carried out, as previously reported with further modification.$^{13,14}$ To characterize the SLG, Figure II-2 shows the Raman spectra of SLG film on SiO$_2$ which the $I_{2D}/I_G \sim 2$ and the full band width is less than 30 cm$^{-1}$. These results correspond to the features of SLG.$^{15}$

![Figure II-2: Raman spectra of single layer graphene on SiO$_2$ substrate.](image)

3. Electrolytes

Aqueous, organic, and ionic liquid-based solutions were used as electrolytes: potassium sulfate (K$_2$SO$_4$, CAS #7778-80-5) salt is bought from Acros. 1-ethyl-3-methylimidazolium hydrogensulfate (EMImHSO$_4$, CAS #412009-61-1) and 1-ethyl-3-methylimidazolium tetrafluoroborate (EMImBF$_4$, CAS #143314-16-3) are bought from Sigma-Aldrich. Ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMImTFSI, CAS #174899-82-2) is bought from Solvionic. The acetonitrile (ACN) (CAS #75-05-8, H$_2$O < 10 ppm) solvent was also obtained from Acros Organic.
4. Electrochemical characterization

4.1 Electrochemical characterization techniques

In this section, the working principles and the information can be obtained from several key characterization techniques used in this work are introduced.

4.1.1 Cyclic voltammetry (CV)

Cyclic Voltammetry (CV) is an electrochemical technique for fast screening and characterizing an electrochemical system. The electrochemical cell is controlled potentiodynamically, and the potential of the working electrode is measured and controlled against a reference electrode. The potential is swept between two pre-selected values with a fixed sweep rate and the current response is recorded. Some crucial information, including electrochemical window, capacitance, reactions kinetics and cyclability of the active materials or devices, can be obtained. The kinetics of the system are usually studied by varying the sweep rate.

For EDLCs, the CV profile corresponds to different equivalent circuit models as shown in Figure II-3. As an ideal double layer capacitor (C_{dl}), the CV profile exhibits a rectangular shape as in Figure II-3a. However, in reality, other processes can occur at the same time as double layer charging. The resistance from the separator, bulk electrolyte and the contact between electrodes and current collector will result in a CV profile shown in Figure II-2b, which the equivalent electric circuit has been added a series resistance R_s. Figure II-2c shows a distorted rectangular CV profile which is an example of involving faradic reactions which is the basis of self-discharge for EDLCs. R_{leakage}, called leakage resistance, is parallel to the C_{dl}. Although with the CV profile, one can have an idea of the system, other methods are required to examine the values of each element.
Figure II-3: Equivalent circuit models and corresponding cyclic voltammograms of (a) ideal double layer capacitor, (b) capacitor in parallel with leakage resistance, (c) and simplified supercapacitors model taking leakage resistance and equivalent series resistance into account.

The capacitance of the electrode can be calculated by integration of the CV which expressed as in the following equation:

\[
C_g = \frac{1}{v \cdot m} \int_{V_{\text{min}}}^{V_{\text{max}}} \frac{idV}{V_{\text{max}} - V_{\text{min}}}
\]  

(Eq. II-2)

where \( C \) is electrode capacitance in Farads per gram (F g\(^{-1}\)) in a non-symmetrical three-electrode cell, \( i \) is current in Ampere (A), \( V_{\text{max}} \) and \( V_{\text{min}} \) is the maximum and minimum voltage (V), \( v \) is the the voltage scan rate (V s\(^{-1}\)), \( m \) is the mass of active materials in gram (g). For symmetrical cell, since the calculated capacitance includes both electrodes, the values must be multiplied by two for the capacitance of a single electrode.

4.1.2 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance Spectroscopy (EIS) is one of the advanced techniques for electrochemical studies. The reason why EIS has gained a lot of attention over the years is that the technique allows or distinguishing the contributions of various
processes to the impedance. As we mentioned previously, different electrochemical systems correspond to an equivalent electric circuit. For electrochemical systems, EIS offers an analysis of the physical or chemical phenomenon happened at the electrode/electrolyte interface by separating the fast processes at high frequencies (electronic and ionic conductivity) from slow processes at low frequencies (mass transport by diffusion). Each physical/chemical phenomenon can then be separated by a large range of frequency since its relaxation time is unique.

The impedance of a system depends on the frequency. To obtain the electrochemical impedance, a small sinusoidal voltage signal at various frequencies is over-imposed to a steady-state (with or without bias voltage, to ensure the linearity of the system) over a wide range of frequency, and a sinusoidal current is recorded; the impedance is calculated by dividing the sinusoidal voltage signal by the current at various frequencies.

In this work, a low sinusoidal voltage amplitude (+/- 5 mV) was applied to a three-electrode cell. The excitation signal, expressed as a function of time, has the form of:

\[ V(\omega) = V_0 \sin(\omega t) \]  \hspace{1cm} \text{(Eq. II-3)}

where \( V_0 \) is the (RMS) amplitude of the alternating voltage signal in Volt, \( \omega \) is the angular frequency in radian per second, which is related to frequency \( (f, \text{ in Hertz}) \) by the equation \( \omega = 2\pi f \).

The current response to the sinusoidal voltage is measured and expressed as a sinusoidal function with the amplitude of \( I_0 \) and a phase shift \( \phi \):

\[ I(\omega) = I_0 \sin(\omega t + \phi) \]  \hspace{1cm} \text{(Eq. II-4)}

Applying Euler’s formula: \( e^{jx} = \cos x + j \sin x \), Equation II-3 and II-4 can be presented in complex and thus facilitate the mathematical calculation later:

\[ V(\omega) = V_0 e^{j\omega t} \]  \hspace{1cm} \text{(Eq. II-5)}
\[ I(\omega) = I_0 e^{j(\omega t + \phi)} \]  \hspace{1cm} \text{(Eq. II-6)}

An expression analogous to Ohm's Law allows us to calculate the admittance \( Z \) as the following equation:

\[ Z(\omega) = \frac{V_0}{I_0} e^{-j\phi} \]  \hspace{1cm} \text{(Eq. II-7)}

It can be presented as complex number as:

\[ Z(\omega) = |Z| e^{-j\phi} = Z' + jZ'' \]  \hspace{1cm} \text{(Eq. II-8)}

where \( Z' \) and \( Z'' \) are the real and imaginary parts of the complex impedance, respectively.

For an electrochemical system, the equivalent circuit model is usually described by
a combination of capacitances and resistances. They can be expressed as below:

\[ Z_C = \frac{1}{j\omega C} \quad \text{(Eq. II-9)} \]

\[ Z_R = R \quad \text{(Eq. II-10)} \]

where \( C \) is a capacitance associated with a capacitor, \( R \) is a resistance (resistor), and \( L \) is an inductance (inductor). Since there is not imaginary part in a resistance, the current through a resistor is always in phase with the voltage. A capacitance decreases as the frequency is raised and exhibits only an imaginary part. The current through a capacitor is phase shifted 90 degrees with respect to the voltage.

Nyquist plot is one of the most commonly used in EIS measurements. The X-axis is the real part \((Z')\) and the Y-axis is the imaginary part \((Z'')\). For example, for a pure capacitive behavior on a metal electrode is shown as Figure II-4a and corresponds to the equivalent circuit model in Figure II-4b. In an ideal case, the Nyquist plot should be a vertical line for pure capacitive metal electrode. From Figure II-4a, at high frequency, the impedance curve intercepts with x-axis can give the value of the series resistance. The double layer capacitance can be obtained by fitting the Nyquist plot by the equivalent electric circuit model.

**Figure II-4:** (a) Nyquist plot and (b) the equivalent circuit model of the capacitive behavior for a metal electrode. (c) Nyquist plot of a porous carbon-based EDLC from low frequency to high frequency.

For porous carbon electrode, the equivalent electric circuit model is more complex because the non-uniform charging rate between the inner - porous network - and outer surface. The Nyquist plot of using porous carbon electrode is shown in Figure II-4c. Three different frequency ranges can be identified on the Nyquist plot. At high frequencies (10 kHz), the system behaves as a resistance; at low frequencies (13 mHz),
the vertical line corresponds to the capacitive behavior. At the middle frequency range, a line with a slope of 45° was observed, which correspond to the electrolyte penetration inside the porous structure of the electrode. One model that can be used to fit the Nyquist plot was proposed by de Levie.\textsuperscript{17, 18} The model for porous carbon material has been established based on the different charging rates at the outer and inner – pores - surface of the carbon electrode. Compared with conventional planar electrode, the porosity of carbon material hinders/limits ion transport to reach the inner carbon surface. This results, in the medium frequency region, in a characteristics slope of 45° on the Nyquist plot.

A simplification of the de Levie model consists in using a constant phase element (CPE) to replace the capacitance when the measured data is deviated from the ideal capacitive behavior (imaginary part increasing with an angle < 90°), expressed as below:

\[ Z = \frac{1}{Y(j\omega)\alpha} \]  

(Eq. II-11)

where \( Y (F s^{(1-\alpha)}) \) and \( \alpha (0 < \alpha < 1) \) are both constant. When this equation describes a capacitor, the constant \( Y \) is the inverse of the capacitance and the exponent \( \alpha = 1 \). For a constant phase element, the exponent \( \alpha \) is less than one.

In this work, an alternative method is used to model the EIS spectra of porous carbon electrodes, proposed by Taberna \textit{et al}.\textsuperscript{19} This method aims to separate the real \( C'(\omega) \) and imaginary \( C''(\omega) \) part of the capacitance \( C(\omega) \). The \( C'(\omega) \) and \( C''(\omega) \) corresponds to the capacitance of the cell and an energy dissipation by an irreversible process, respectively. By combining Equation II-12 and II-13, the \( C(\omega) \) can be expressed as Equation II-14.

\[ Z(\omega) = \frac{1}{j\omega \times C(\omega)} \]  

(Eq. II-12)

\[ Z(\omega) = Z'(\omega) + jZ''(\omega) \]  

(Eq. II-13)

\[ C(\omega) = \frac{-Z''(\omega) + jZ'(\omega)}{\omega |Z(\omega)|^2} \]  

(Eq. II-14)

When we separate the real and imaginary part of \( C(\omega) \) as Equation II-15, the \( C'(\omega) \) and \( C''(\omega) \) can be expressed as Equation II-16 and II-17.

\[ C(\omega) = C'(\omega) - jC''(\omega) \]  

(Eq. II-15)

\[ C'(\omega) = \frac{-Z'(\omega)}{\omega |Z(\omega)|^2} \]  

(Eq. II-16)
\[ C''(\omega) = \frac{Z'(\omega)}{\omega Z(\omega)} \]  
(Eq. II-17)

The values of \( C'(\omega) \) and \( C''(\omega) \) can be calculated based on Equation II-16 and II-17; Figure II-5a and 5b show the change of \( C' \) and \( C'' \) versus frequency. From Figure II-5b, the capacitance is low in the high frequency range. When the frequency decreases, the capacitance increases until the capacitance becomes less dependent to frequency again, when the ions from the electrolyte have reached the whole porosity of the active material. The change of \( C' \) versus frequency depends on the material structure, electrode thickness, electrolyte, and weight loading, which are all related to the power performance of the cell. For the imaginary part versus frequency (Fig. II-4b), the maximum value for the imaginary part of the capacitance occurs at a frequency \( f_0 \) corresponding to a time constant \( \tau_0 \) (defined \( \tau_0 = 1/ f_0 \)). \( \tau_0 \) is called relaxation time which represents a transition for a supercapacitor from resistive behavior to capacitive behavior. From application aspect, the time constant also corresponds to the minimum time to charge a capacitor while still maintaining an energy efficiency more than 50%. At \( f_0 \), the \( C' \) is half of the \( C \) at lower frequency. In this thesis, this method is used to distinguish the electrochemical response from different materials by deconvolute the capacitance response with \( C'(\omega) \) and \( C''(\omega) \).

**Figure II-5:** (a) is the Nyquist plots of the system. (b) and (c) is the real and imaginary part versus frequency derived from the EIS data.

### 4.1.3 Electrochemical Quartz Crystal Microbalance (EQCM)

EQCM allows for tracking the mass variation of an electrode under polarization and its basic principle relies on the piezoelectric effect. As an alternating potential is
applied to a quartz crystal, a vibrational motion will be generated with amplitude parallel to the surface of the crystal, resulting in a transverse acoustic wave propagates along the direction perpendicular to the crystal surface.

**Resonance Frequency – Sauerbrey’s Equation**

Quartz crystal is a piezoelectric material. When a mechanical stress is applied on an acentric material across a proper direction, the distortion of lattice will result in a corresponding change in net dipole moment. A net change in electrical charge on the surface of the crystal will be generated by this action. This behavior is named as “piezoelectric effect”\(^{20}\). Conversely, application of a voltage across quartz crystal afforded a corresponding mechanical strain. This is called “converse piezoelectric effect” which is the foundation of QCM. For quartz, this deformation is elastic. The degree of deformation is proportional to the applied potential, and an identical strain in the opposite direction is produced by the opposite polarity. When an alternating potential is applied to quartz, a vibrational motion will be generated with amplitude parallel to the surface of the crystal, resulting in a transverse acoustic wave propagates along the direction perpendicular to the crystal surface.

The reflection of the transverse acoustic wave goes back into the crystal, and its antinode point is at the surface of quartz. When the wavelength equals to two times of the thickness of the quartz crystal \((2t_q)\), a standing wave condition is accomplished. The resonance frequency of the transverse acoustic wave \((f_0)\) is expressed below:

\[
f_0 = \frac{v_{tr}}{2t_q} = \sqrt{\frac{\mu_q/\rho_q}{2t_q}}, \quad \text{(Eq. II-18)}
\]

where \(v_{tr}\) is the transverse velocity in AT-cut quartz \((3.34 \times 10^4 \text{ m s}^{-1})\), \(\rho_q\) is the density of quartz \((2.648 \text{ g cm}^{-3})\), \(\mu_q\) is the shear modulus of quartz \((2.947 \times 10^{11} \text{ g cm}^{-1}\text{s}^{-2})\).

Accordingly, when a uniform layer of a foreign material is added to the surface of the quartz crystal, the acoustic wave can travel across the interface between the quartz and the layer and propagates through the foreign layer. This essentially assumes that particle displacement and shear stress are continuous across the interface (no viscoelastic loss). In addition, if the assumption of the acoustic properties of the foreign layer and quartz crystal are identical is established (which is assumed if foreign layer thickness a lot smaller than the one of the quartz), the addition of foreign layer can be
seemed as an increase of the quartz thickness. This is shown in Figure II-6, where \( t_f \) is the thickness of the additional film.

![Figure II-6: Scheme of the transverse wave in quartz crystal.](image)

As the additional film is assumed to be alike as the quartz crystal, the fractional change of thickness is proportional to the fractional change of frequency. The mathematical expression is shown in Equation II-20 which \( \Delta f \) is the measured frequency shift and \( \Delta t \) is the change of thickness. If the idea of the traverse wave velocity and the density of the material are identical as quartz crystal is assumed, \( \Delta t \) can be replaced by \( \Delta m/\rho_q A \) and combine with the substitution of \( v_tr \) from Equation II-20, the Sauerbrey equation can be derived shown in Equation II-21. From Eq. II.18, we got:

\[
\Delta f = -\frac{v_tr}{2} \cdot t^{-2} \Delta t \tag{Eq. II-19}
\]

It comes:

\[
\frac{\Delta f}{f_0} = -\frac{\Delta t}{t_q}
\]

Since we got:

\[
\Delta m = \rho_q A \Delta t \tag{Eq. II-20}
\]

\[
\Delta m = -\frac{A v_q \rho_q}{2f_0^2} \Delta f = -C_f \Delta f \tag{Eq. II-21}
\]

where \( \Delta m \) is the change of mass (ng), \( A \) is the piezoelectrically active area (cm\(^2\)) and \( C_f \) is the sensitivity factor of the crystal (ng Hz\(^{-1}\)) which is also called calibration factor. The other assumption for Sauerbrey equation is that the frequency shift because of the deposited mass is indifferent from various distance from the center of the crystal. The Sauerbrey’s equation is the fundamental equation to convert frequency change to mass change.
change during electrochemical process. Nevertheless, the Sauerbery’s equation is not applicable in non-ideal or unexpected situations, including the deposited film is not rigid, the mass loading exceeds 2% of the mass of the crystal, and the roughness of the electrode because of the trapped liquid in surface cavities will result in an additional mass component and/or dissipation: all those factors will lead to a dramatic drop of the quality factor of the QC compromising the linearity of its response and so its accuracy. Therefore, the condition of the QCM system is needed to be noted before applying the Sauerbery’s equation.

**Butterworth-Van Dyke (BVD) equivalent circuit - Motional resistance**

A convenient way for studying the electroacoustical/electromechanical behavior of a QCM is through its electrical equivalent circuit. The basic Butterworth-Van Dyke (BVD) model is based on two parallel branches: one for the electrical behavior and the other one is for the mechanical behavior. It is a typical model used to described quartz resonator without deposition or liquid loading. The equivalent circuit of the BVD model is shown in Figure III-7. On the electrical branch, $C_0$ represents the sum of the static capacitances of the crystal’s electrodes, holder, and connector capacitance. The mechanical behavior is presented as three elements at the motional branch. $L_1$ represents the inertial component related to the displaced mass during oscillation (analogous to a purely mechanical model of a mass attached to a spring of compliance). $C_1$ represents the energy stored during oscillation (elasticity of the quartz and surrounding medium), and $R_1$ represents the energy dissipated during oscillation (damping coming from viscosity and the mounting of the quartz).

![Butterworth-Van Dyke (BVD) equivalent circuit for an unperturbed quartz crystal microbalance.](image)

**Figure III-7**: Butterworth-Van Dyke (BVD) equivalent circuit for an unperturbed quartz crystal microbalance.22
For QCM application in gravimetric mode, the shift of the resonance frequency is only related to $L_1$ and $C_1$ components of the motional branch. But the phase of the complete resonator also depends on the specific values of the motional resistance $R_1$ and on the parallel capacitance $C_0$. In practice, the $C_0$ will be cancelled out by another capacitor. When a mass is added on the quartz electrode, the $L_1$ increased resulting in a shift of the resonance frequency which will then be detected by QCM.

To evaluate the surrounding of the quartz, $R_1$ is frequently analyzed because the nature of the surrounding can influence the internal frictions and mechanical losses of the resonator. For QCM with additional film added to the quartz, $R_1$ has been frequently used to provide information of the viscoelastic properties of the deposited film on the quartz electrode, such as the density and the viscosity of the liquids, the properties of the quartz, and the thickness and mass of the deposited film. In this work, it is important to track the motional resistance to ensure the quality of the deposited film.

Generally, the electrochemical instrument can be potentiostat or galvanostat operated from a computer (Figure II-8). The computer is interfaced to both the electrochemical instrumentation and the frequency instrumentation. The potentiostat drives the electrochemical tests while the frequency response of the quartz disk is recorded at the same time. By summarizing all data, information of redox or other chemical processes at electrode surfaces can be obtained, including film deposition and dissolution, surface morphology changes and mass changes in thin film.

**Figure II-8:** Scheme of an EQCM apparatus.
4.2 Setups

In this work, two electrochemical setups have been used. The first one is Swagelok cell, and the other one is for EQCM. After cell assembly, the electrochemical measurements of these cells were conducted using a VMP3 (Biologic, France) or Autolab PGSTAT101 (Metrohm Autolab B.V., The Netherlands) potentiostat.

4.2.1 Three-electrode Swagelok™ cell

![Diagram of three-electrode Swagelok™ cell](image)

**Figure II-9:** Scheme of three-electrode Swagelok™ cell setup.\(^{26}\)

For determination of potential of zero charge in each electrolyte (Chapter III), a three-electrode Swagelok™ cell was used. The cell is composed of a T-shaped stainless-steel body and three stamps that contact the electrodes. Electrical insulation is provided with a polypropylene tube inside the body. The presentation of the set-up of the cell is shown in Figure II-9. For the working electrode, the active material was deposited on the platinum foil which is the current collector then dry in the oven overnight. The loading of TiC-CDC is controlled around 0.8 to 1.7 mg·cm\(^{-2}\). The counter electrode is an overcapacitive loading YP-50F electrode film (23 mg·cm\(^{-2}\)). A separator is placed between the two electrodes to avoid short circuit. The separator is a 25 μm-thick porous cellulose. Before placing the reference electrode, the electrolyte is introduced into the cell by a pipette. The reference electrode is Hg/Hg\(_2\)SO\(_4\). When using non-aqueous electrolyte, all the cells were assembled in a glove box under Ar atm (< 1 ppm H\(_2\)O and O\(_2\) contents)
Electrode film preparation for Swagelok™ cells

The electrode films were prepared by mixing 95 wt.% active materials with 5 wt.% of polytetrafluoroethylene binder (PTFE; 60 wt.% dispersion in water) in ethanol (see Figure 9b). The slurry was uniformly stirred on a watch glass until it formed a paste-like material. The carbon film then was dried in the vacuum oven around 60 °C overnight. Afterwards, the carbon film will be cut into circles and served as the working or counter electrode with well controlled of the thickness and mass.

4.2.2 EQCM cell

The EQCM cell is shown in Figure II-10. Figure II-10a shows all the component of the cell. After assembling all the components as shown in Figure II-10b, a clip clamps all the components together tightly. With this cell setup, the electrolyte required to fill the glassware is around 7~10 ml. The quartz holder is then connected to the wire and fixed in the middle of a plastic sealed box (assembled in glove box under Ar atm). Figure II-10c shows the side view of the cell setup with the quasi-reference electrode and counter electrode that are Ag wire and Pt coil, respectively. After placing the EQCM cell and connect each electrode with wire in the plastic box in the glove box, the plastic box is sealed with four screws at the corners of the box as shown in Figure II-10d and II-10e. Then, the box is transferred outside the glove box and operated in air while the cell is still under Ar atm. For experiments carry out with organic and ionic liquid electrolyte, this EQCM cell operates perfectly. The length, width, and the height of the box is 12.8, 7.5, and 10 cm, respectively.

All the electrodes then are connected to potentiostat and EQCM. The EQCM electrochemical measurements were carried out by a Maxtek RQCM system combined with Autolab PGSTAT101 was used for simultaneous EQCM and electrochemical measurements.
Chapter 2: Material Studied and Experimental Setups

Electrode preparation for EQCM cell

For powder active materials, there are different ways to deposit the material onto quartz crystal. The amount and homogeneity of active material on the Au current collector is required to be controlled. If the material is too less, there will not be clear electrochemical signals from the active material. However, for too large weight loading, the top of the deposition may not be fully attached. When the quartz immersed in the electrolyte, the powder will fall out from the quartz. Also, a large weight loading leads to a poor-quality factor making the QC unsuitable for proper experiments under linear conditions (Sauerbrey); in some extreme cases, no relevant frequency resonance is present. The homogeneity of the deposition also affects the quality factor of the QC. With a thin and homogeneous deposition of the materials on the Au current collector, the recorded frequency signal should be smooth and accurate. There are some common ways to deposit materials onto Au current collector, which is drip coating or spray coating.

In this work, the powder active materials were deposit onto Au current collector by drip coating. The quartz is coated using a precise pipette (Gilson PIPETMAN Classic P20) with a slurry containing 80 wt.% of TiC-CDC powder and 20 wt.% of polyvinylidene fluoride (Arkema, CAS #24937-79-9) binder in N-Methyl-2-

Figure II-10: (a) The components for EQCM cell. (b) Schematic of the cell setup. (c) A side view of the cell setup. (d) and (e) is the overlook and the side view of the cell, respectively.
pyrrolidone (Sigma-Aldrich, CAS #872-50-4). "The suspension was stirred for xx minutes under ultrasonication. It is worth noting more even deposits were achieved after the suspension settled down for few minutes. The upper part of the suspension was then used for the drop casting which allowed for selecting the smallest, homogeneous in size, carbon particles. The coated quartz crystal was put into an oven at 60 °C for overnight.

For SLG film, another transferred process was carried out. The transferring process of SLG will detailed in Chapter IV. In short, a SGL layer is grown from CVD process onto a Cu foil. After Cu dissolution, the SGL is transferred onto a PET film, and further transferred onto the quartz.

In this work, to check the quality of the coated quartz, the frequencies and resistance in air and in electrolyte were monitored after solvent completely evaporated.

5. Materials characterization techniques

5.1 X-ray diffraction (XRD)

XRD is an analytical technique to obtain structural information of materials. For solid material, it is commonly used to study the crystalline phases present in a material and thereby reveal chemical composition information. In the early 20 centuries, Max von Laue found that the diffracted X-ray from a crystalline substance is similar to the spacing of planes in a crystal lattice.\textsuperscript{27} The working principle of XRD is based on detecting the diffracted X-ray which come from the constructive interference of monochromatic X-rays and a crystalline sample. The constructive interference is produced when the conditions satisfy Bragg’s law which is shown below:

\begin{equation}
    n \lambda = 2d \sin \theta
\end{equation}

which $d$ is the spacing between diffracting planes, $\theta$ the incident angle, $n$ is any integer, and $\lambda$ is the wavelength of the X-ray beam. Figure II-11 is a schematic presentation of the working principle of XRD.
X-ray diffractometers are composed of three basic elements: the X-ray tube, sample holder, and a X-ray detector. X-rays are generated in a cathode ray tube by heating a filament to produce electrons. The electrons will then accelerate toward the target material by applying a voltage. When the electron has sufficient energy to displace inner shell electrons of the target material, a characteristic X-ray spectrum is produced. The target material has a specific wavelength, for example the most common used target material is Cu which has a wavelength of 1.54 Å.

During XRD experiment, the sample and detector will rotate so that all possible diffraction directions of the lattice should be obtained due to the random orientation of the powdered material. When the geometry of the incident X-rays impinging the sample satisfies the Bragg’s law, constructive interference occurs and a peak in intensity occurs. The detector position is recorded as the angle $2\theta$. Figure II-12 shows the orientation of each components.

To analyze the XRD pattern, a full pattern fitting method is necessary to refine a model of the sample. The model is refined until the difference between the recorded and calculated patterns are minimized. The, the peak positions $2\theta$ can be converted into d.

**Figure II-11:** An illustration of the working principle of XRD.\(^{28}\)

**Figure II-12:** An illustration of the composition of a X-ray diffractometer.
spacing by using Bragg’s law (Eq. II-22). The Miller indices (hkl) can also be obtained, then further on the unit cell lattice parameters will be calculated. To sum up, XRD is a non-destructive and rapid analytical technique which is a widely used to characterize the atomic or molecular structure of materials.

5.2 Temperature programmed desorption coupled with mass spectroscopy (TPD-MS)

Temperature programmed desorption (TPD), also known as thermal desorption spectroscopy, is a dynamic measurement that monitors the evolution of a gas while heating. Gas evolution can be monitored by a pressure sensor, mass flow meter, or using a mass spectrometer (MS). TPD is commonly used to measure the gas storage capacity and the interaction between the reacted gases and the surface of the material.

The theory behind this technique is based on the energy of desorption. When gas molecules contact with the material surface, a physical adsorption will occur. The binding energy between adsorbate and surface varies with the combination of both. If the material surface is heated, the gas molecules will receive the energy, then desorb from the surface. The temperature of the desorption happen is called the desorption temperature. This technique is often used in the field of catalyst.

5.3 X-ray absorption near edge structure (XANES)

Different from X-ray scattering, XANES is based on the adsorption of one or part of the X-ray photon which results in the excitation of the core electron of an atom. When the electron is ejected to an excitonic state, the empty place left behind is called the core hole. The hole is electronegative and unstable. There are two ways to fill off the core hole which results in emitting a photon or Auger electron. When a higher-level electron decays into the core hole, a fluorescent photon will be emitted. Auger electron emission occurs when the transition energy from the relaxation process is adsorbed partially by another higher-level electron. An illustration of the two different relaxation process is shown in Figure II-13.
Figure II-13: The right and left scheme corresponds to via an Auger process or by capture of an electron from another shell followed by emission of a fluorescent photon, respectively.

The emitted photon or Auger electron will be detected, then be plotted in an energy spectrum. Each element has a characteristic set of excitation and fluorescence energies. Also, the absorption edge energy is sensitive to the oxidation state of the element. As a result, the valence state of the element can be found with XANES.

6. Reference

Chapter III:

EQCM Study of Ion Adsorption in Three-Dimensional Porous Carbon Electrode
1. Introduction

The main challenge in supercapacitor field today is to increase its energy density. One way to do it is to optimize pore structure of the activated carbon to increase the specific capacitance. This approach allows using the symmetric carbon-carbon EDLC systems which promises high power density and cyclability. This is usually a compromise between gaining in energy density over power density. As the energy density increases due to the use of porous carbon with high specific surface area, the time constant is locally increased because the accessibility of the carbon porous for the electrolyte ions is reduced.\(^1\) Such limitations could also be attributed to bottlenecks in the electrode materials that restrict the exit of adsorbed ions at fast rates for supercapacitor systems with high power. To increase the accessibility of electrolyte ions approaching to the surface of electrode material, tailor-made open structure carbons for less conductive non-aqueous electrolytes were introduced such as carbon onion; however, the capacitance is limited to a few tens of \(\text{F per g}\).\(^2\)

![Figure III-1](image)

**Figure III-1:** (A) A plot of specific normalized capacitance versus average pore size. (B–D) Drawings of solvated ions occupied in pores with various distance between the pore walls.\(^3\)

A breakthrough discovery of significant increase of capacitance was reported in 2006, which opposite the traditional belief in supercapacitors.\(^3\) The experiment was designed by using TiC-CDCs as active material which its pore size was controlled ranging from 0.6 nm to 1.2 nm in combination with AN-based electrolyte containing 1M \(\text{NEt}_4\text{BF}_4\) whose solvated ion size is 1.3 nm and 1.2 nm for \((\text{NEt}_4^+\text{-7ACN})\) and \((\text{BF}_4^-\text{-AN})\).
9ACN), respectively. From a traditional point of view, the pore size of active materials should be larger than the solvated electrolyte ions to reach a higher capacitance. The normalized capacitance (by BET SSA for the carbon) was believed to decrease with the decrease of the pore size as shown in region I in Figure III-1A. However, according to region III in Figure III-1A, the normalized capacitance drastically increased when the pore size is less than 1nm which is smaller than the solved cation and anion. Partial ion desolvation was then proposed to explain the enhanced capacitance in sub-nanometer pores: thanks to the distortion of the solvation when entering nanosized pores, the ion could get closer to the carbon wall so that the average approaching distance of the ions to the electrode surface decreases resulting in an increase of the capacitance.

After the significant research works have revealed that the capacitance increases dramatically when the carbon pore size is below the solvated ion size, the charge storage mechanisms of microporous carbon electrode and the relationship between ion size and pore size have been studied thoroughly in different electrolyte systems, aiming for improving the performance of supercapacitor electrode as discussed in Chapter I.

In order to understand about ion adsorption and transport in nanoporous materials for designing better supercapacitor electrodes and devices, in-situ electrochemical techniques are required to fulfill our knowledge and give a better insight of the ion adsorption in carbon nanopores. The last 10 years, a series of works have shown that EQCM can also be served as a useful and quantitative tool for studying the behavior of Electradsorbed ions and solvent molecules in porous carbon materials for supercapacitor applications. The ion desolvation, achieved by stripping-off the solvent molecules present around the ion, was studied with porous carbons containing micropores in various electrolyte systems. The primary experimental results observed that highly solvated Li+ in aprotic propylene carbonate electrolyte lost a part of its solvation shell while entering the micropores. Later on, the solvation number of different cations and anions in aqueous environment confined in nanopores was calculated. By comparing with the bulk hydration number of each ion, partial desolvation was observed, which aligns with the previous study in organic systems. In addition, ion-sieving effect was observed by playing with different ion sizes and the carbon perm-selectivity behavior was discussed by the same group. Figure III-2 is an example of the experimental results of NEt4BF4/PC in porous carbon observed by EQCM. Zone I from Figure III-2b represents
the ion-mixing zone at low charge density. While sweeping towards higher polarization, ion adsorption without solvation shell occurred (zone II). At high polarization, the ion absorbed into the pores with solvent molecules resulting in pore expansion (zone III). This zone allows calculating the number of solvent molecules of the solvation shell which is normally smaller quantity than bulk solvation number.

Figure III-2: CVs of a carbon-coated quartz crystal electrode in 0.1 and 0.025 M TEABF₄/PC solutions (a), and the related treated EQCM responses, Γ vs. Q (b). Three domains with the characteristic different Γ/Q slopes for the 0.025 M solution are indicated. The slope within domain II (the broken blue line) is equal to the theoretical slope of the broken red straight line calculated from the Faraday law.⁵

As mentioned above, EQCM has been applied to study the ion dynamics of porous carbon materials. However, none of the previous works extended the discussion to complex mixtures of ions in the electrolyte mixture despite it has been reported that the performance of supercapacitor electrodes can be improved by using a mix of ions and/or solvent molecules.¹²-¹⁵ For instance, for RTILs electrolytes, by playing with the size, molecular weight, and diffusion coefficients of cation and anion, the operating voltage window of symmetric carbon-based supercapacitor can be expended.¹² In addition, it was found by adding smaller size cation, the capacitance has been improved by almost 30% with mesoporous carbon due to a tighter packing of cations on the negatively charged surface.¹⁴ For organic electrolytes, the mixture of solvents can enhance the thermal stability, conductivity, and viscosity of the electrolytes which the safety of the supercapacitors is improved. Although the electrochemical performance has proven to be effectively improved by mixing electrolytes, the effect on the charge storage mechanisms have not yet been investigated. In this chapter, we will be focusing on EQCM study of microporous carbon electrode in multi-ion aqueous electrolytes. The ionic fluxes in porous carbon electrodes were monitored and further analyzed. The study of main charge carriers in multi-ion aqueous electrolytes during ion transfer and adsorption in carbon micropores have been achieved and explained in this study based
on ion size, ion mobility and pH range.

2. Experimental

2.1 Carbon-derived carbon (CDCs)

CDC is made by extracting metal layer-by-layer from carbides with a rigid metal lattice used as a template. TiC-CDCs has been reported to have the pore size from 0.5 to 3 nm with a 0.05 nm accuracy and the SSA up to 2000 m$^2$·g$^{-1}$. In this thesis work, TiC-CDC from YCarbon Inc (USA) with the pore size of 0.67 nm was chosen to be the model materials. PSD was obtained via a QSDFT model (SAIEUS from Micromeritics) from an Ar-isotherm at 77K. The as-recieved CDC-0.67nm isotherm and PSD can be found in Figure II-1; the related characteristic information, in Table II-1.

2.2 Electrolytes

To study the effect of ion size, ion mobility, and the pH of the electrolyte for porous carbon materials, a series of aqueous electrolytes were prepared. Table III-1 shows the composition of aqueous electrolytes used in this work. Table III-2 presents the chemical structure, maximum and minimum length of cations and anions. Table III-3 shows the bulk solution hydration number for aqueous-based cation and anion.

<table>
<thead>
<tr>
<th>Number</th>
<th>Composition</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1 M K$_2$SO$_4$</td>
<td>6.3</td>
</tr>
<tr>
<td>2</td>
<td>0.1 M EMIm$^+$-HSO$_4^-$</td>
<td>0.8</td>
</tr>
<tr>
<td>3</td>
<td>0.1 M K$_2$SO$_4$ + 0.1 M EMIm$^+$-HSO$_4^-$</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Table III-1: The list of aqueous electrolytes had been used in this chapter.

<table>
<thead>
<tr>
<th>Type of ions</th>
<th>Chemical structure</th>
<th>Max/min length (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMIm$^+$, 1-ethyl-3-methylimidazolium)</td>
<td><img src="image" alt="EMIm+ structure" /></td>
<td>0.76/0.43$^{18}$</td>
</tr>
<tr>
<td>K$^+$, Potassium</td>
<td>K$^+$</td>
<td>0.133/---$^{19}$</td>
</tr>
</tbody>
</table>
Chapter 3: EQCM Study of Ion Adsorption in Three-Dimensional Porous Carbon Electrode

<table>
<thead>
<tr>
<th>Type of ions</th>
<th>Bulk solution hydration number</th>
<th>Hydrated ion size</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSO₄⁻, Hydrogensulfate</td>
<td></td>
<td>0.44/---²⁰</td>
</tr>
<tr>
<td>SO₄²⁻, Sulfate</td>
<td></td>
<td>0.46/---²⁰</td>
</tr>
</tbody>
</table>

Table III-2: Chemical structure and size of the ions studied in this chapter.

<table>
<thead>
<tr>
<th>Type of ions</th>
<th>Bulk solution hydration number</th>
<th>Hydrated ion size</th>
</tr>
</thead>
<tbody>
<tr>
<td>K⁺, Potassium</td>
<td>7²¹</td>
<td>0.66²²</td>
</tr>
<tr>
<td>SO₄²⁻, Sulfate</td>
<td>13²³</td>
<td>0.76²⁴</td>
</tr>
</tbody>
</table>

Table III-3: The bulk solution hydration number and ion size for aqueous-based cation and anion studied in this chapter.

3. Results

3.1 The EQCM setup

AWSensors 1-in-diameter Au-coated quartz crystals (oscillating frequency, f₀, 5 MHz) were coated by drip-coating using a precise pipette with a slurry containing 80 wt.% of TiC-CDC mixed with 20 wt.% of polyvinylidene fluoride binder in N-Methyl-2-pyrrolidone. The coated quartz crystal was dried in an oven at 60 °C for overnight. The working electrode is the coated quartz crystal placed on a PTFE holder which the coated side is orientated toward the reference and counter electrode. The reference electrode in this experiment is mercury-mercurous sulfate (Hg/Hg₂SO₄) placed between the working electrode and counter electrode. Three electrodes were set in a glassware and immersed in electrolyte as in Figure III-3a.
The interfacial mass changes of the deposited carbon will result in frequency response directly from EQCM. To obtain the mass change, it is necessary to apply Sauerbrey’s equation (Eq. III-1) with frequency shift ($\Delta f$) under few assumptions: (1) the mass change is small relative to the total mass and (2) the surface is rigid.

$$\Delta m = -C_f \Delta f$$  \hspace{1cm} (Eq. III-1)

This suggests that the mass of carbon deposited on the quartz needed to be small enough to maintain the resonance of the quartz, but at the same time large enough to obtain a sufficiently strong signal for analysis. Therefore, the amount of carbon deposition needed to be optimized. According to literatures, the optimized commercial carbon powder (e.g., Kuraray YP-17) on Maxtek 1-in-diameter Au-coated AT-cut quartz crystal is 20-60 $\mu$g·cm$^{-2}$.\textsuperscript{25} However, the optimized mass of deposition varies with different quartz crystals and different systems, so the loading given by literatures was used as a starting reference. The amount of active materials (TiC-CDC) for this experiment was controlled between 40-60 $\mu$g·cm$^{-2}$. An example of a deposited quartz is shown in Figure III-3b.

All the EQCM electrochemical measurements were carried out by a Maxtek RQCM system combined with Autolab PGSTAT101 for simultaneously performing EQCM and electrochemical measurements. To obtain a smooth frequency response without too much noise, various scan rates (5 mV·s$^{-1}$, 10 mV·s$^{-1}$, 20 mV·s$^{-1}$) for cyclic voltammetry tests were run and the sampling rate for the RQCM system were adjusted. The experiments results shown in this report were done at scan rate of 10 mV·s$^{-1}$ and 120 points per minute of sampling rate. Moreover, to obtain consistent results, all the
experiments were run for a few cycles before stable signal were shown to make sure the electrode materials had completely soaked in electrolyte.

3.2 Calibration (sensitivity constant, \( C_f \))

As mentioned in above, the mass change (\( \Delta m, \text{ng} \)) can be obtained indirectly from the frequency shift (\( \Delta f, \text{Hz} \)) by applying Sauerbrey’s equation (Eq. III-1). By further mathematical treatments of the cyclic voltammogram and simultaneous frequency response, other missing information on ion adsorption can be retrieved. To use Sauerbrey’s equation (Eq. III-1), the calibration constant (\( C_f, \text{ng} \cdot \text{Hz}^{-1} \) or \( \text{ng} \cdot \text{Hz}^{-1} \cdot \text{cm}^{-2} \)) of the carbon-coated quartz is needed. The calibration test of the coated crystal was a copper deposition experiment conducted in 0.1 M CuSO\(_4\) mixed with 1 M H\(_2\)SO\(_4\) by applying a constant current of 5 mA for 120 seconds. At the same time, the frequency response was recorded which is shown in Figure III-4a.

\[ m = \frac{Q \cdot M_w}{\pi F} = \frac{I \cdot t \cdot M_w}{\pi F} \]  

(Eq. III-2)

where \( m \) is the mass of deposited film in gram, \( Q \) is the charge in Coulomb, \( I \) is the

Figure III-4: (a) and (b) is the recorded frequency shift versus time and mass during calibration, respectively.

According to Sauerbrey’s equation (Eq. III-1) the increase of mass because of the copper deposition will result in a decrease of frequency shift. To collect the calibration constant, Figure III-4a should be replotted into frequency change versus mass change. For calculating the mass of copper deposited on the quartz, Faraday’s law shown below can be applied assuming a 100 % faradic efficiency (Eq. III-2).
current in Ampere, t is the time in second, Mw is the molecular weight, F is the Faraday constant (96485 C·mol$^{-1}$), and n is the valence number of the ion (in this case it is two for copper ion). The replotted graph is shown in Figure III-4b. The calibration constant $C_f$ was then determined from the slope of $\Delta f$ vs. $\Delta m$ curve. The value of calibration constant used in this work is 14.598 ng·Hz$^{-1}$ which is close to the theoretical value (17.86 ng·Hz$^{-1}$).

### 3.3 Determination of Potential of Zero Charge (pzc)

Potential of zero charge is an interfacial phenomenon for EDLCs, defined as the potential at which the electrode does not exhibit any excess charge. When an electrode (or a solid) is immersed in an electrolyte, the electron density distribution on the solid electrode surface is balanced by attracting counter-ions of the electrolyte at the interface. So, depending on the electrode polarization, counter-ion charges accumulate at the surface of the electrode leading to an increase of the charge density. The pzc refers to the potential the net electrode charge is zero; the potential where no interactions with the electrolyte ions presents anymore. The pzc is obviously dependent on the presence of any surface groups (chemisorption, impurities...). According to the Gouy–Chapman theory, the minimum of the differential capacitance corresponds to the potential of zero charge. In other words, the pzc can be found where the capacitance is the minimum. As a consequence, for porous carbon the pzc corresponds to the potential where the cationic and anionic fluxes into carbon micropores are separated. The experiments have been carried out in different aqueous electrolytes by using three-electrode Swagelok cells. The first step was the determination of the pzc, which can be measured at the minimum of the capacitance in a capacitive voltammogram. For instance, the cyclic voltammogram (at 5 mV·s$^{-1}$) of the full window scan in 0.1 M EMIm$^+$-HSO$_4^-$ is shown in Figure III-5a. The red box indicates the minimum capacitance region. For accuracy, a second order polynomial fitting was done, as shown in Figure III-5b.
Chapter 3: EQCM Study of Ion Adsorption in Three-Dimensional Porous Carbon Electrode

Figure III-5: (a) CVs of CDC-0.67nm in 0.1 M EMI$^+$-HSO$_4^-$ at 5 mV·s$^{-1}$ (3-electrode Swagelok cell); (b) shows the zoomed zone highlighted in (a).

The value of pzc in 0.1 M EMI$^+$-HSO$_4^-$ is calculated at +0.13 V versus Hg/Hg$_2$SO$_4$. To make sure the value of pzc obtained from three-electrode Swagelok cell is consistent, another series of experiments were done with EQCM setup.$^9,^{30}$ Table III-4 shows all the results from different experiment setups. The difference of pzc from different experimental setups is around ±50 mV on average which is acceptable. The difference is probably due to the difference in material loading and electrode surface area which result in dissimilar potential distribution on the active material.

<table>
<thead>
<tr>
<th>Number</th>
<th>Composition</th>
<th>3-electrode Swagelok (mV vs. Hg/Hg$_2$SO$_4$)</th>
<th>EQCM (mV vs. Hg/Hg$_2$SO$_4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1 M K$_2$SO$_4$</td>
<td>17±2</td>
<td>3±1</td>
</tr>
<tr>
<td>2</td>
<td>0.1 M EMI$^+$-HSO$_4^-$</td>
<td>130±5</td>
<td>74.1±4</td>
</tr>
<tr>
<td>3</td>
<td>0.1 M K$_2$SO$_4$ + 0.1 M EMI$^+$-HSO$_4^-$</td>
<td>89±2</td>
<td>120±2</td>
</tr>
</tbody>
</table>

Table III-4: Calculated pzc vs. reference for a series of aqueous electrolytes with CDC-0.67nm as active material.

After determining the calibration factor and pzc, the following sections present the EQCM results of porous carbon in several aqueous electrolytes. The objective of this chapter is to distinguish the main charge carriers in a mixture of aqueous electrolytes.
by using EQCM. Using CDC microporous carbon material with fixed pore size, some key parameters such as ion size, mobility, and the pH of aqueous electrolytes, were adjusted to observe the difference in ionic fluxes, and the results will be discussed.

3.4 Ion fluxes in 0.1 M K$_2$SO$_4$ Aqueous Electrolyte (pH = 6.3)

3.4.1 With/Without deposition

To confirm that CDC-0.67nm powder was deposited onto the quartz crystal, an experiment was performed for a comparison between bare quartz and deposited quartz. The CVs are shown in Figure III-6. Both electrodes were scanned from 0-0.5 V and the scan rate was fixed at 5 mV·s$^{-1}$. As shown in Figure III-6, the current density is way much higher for the quartz with the CDC carbon deposit. The calculated discharged capacitance for deposited quartz was 2.02*10$^{-3}$ F and for the bare quartz was 3.6*10$^{-5}$ F. According to the significant difference of the capacitance and current density for both samples, it was sure that the TiC-CDC active material had been deposited on the quartz.

![Figure III-6: CVs for the comparison of with and without CDC-0.67nm deposited quartz crystal.](image-url)
3.4.2 Cyclic Voltammogram and Frequency Response

![Figure III-7](image)

Figure III-7: (a) Cyclic voltammogram and frequency response at 10 mV·s⁻¹ and (b) CVs at different scan rates (5, 10 and 20 mV·s⁻¹) obtained from EQCM with CDC-0.67nm carbon electrode in 0.1 M K₂SO₄.

Figure III-7 shows the cyclic voltammogram recorded at a scan rate of 10 mV·s⁻¹ from -0.3 to 0.2V vs. Hg/Hg₂SO₄ using CDC-0.67nm carbon electrode in 0.1 M K₂SO₄ electrolyte, and the simultaneous frequency response (Δf vs. E) measured by EQCM. The frequency response was smoothed by Savitzky-Golay filter method which is shown as red dash line (polynomial order is 2). Cyclic voltammetry can provide valuable sample information on the capacitive behavior of a cell. The distortion of a cyclic voltammogram can be symmetric simply due to a resistive material or electrolyte, or asymmetric owing to sieving effect due to limitation of pore size for the adsorption of larger electrolyte ions.

In addition, since the amount of CDC-0.67nm on the quartz was limited to obtain resonance within the detection range of the EQCM setup, the contact resistance was greatly increased with the high contact area to deposited ratio. According to Figure III-7b, there is no further major distortion as the scan rate increased which indicates that
the accessibility of electrolyte ions to the pore surface remains more or less similar within the potential scan rate studied.

### 3.4.3 Motional resistance

The motional resistance (see chapter II) has been tracked during cycling the CDC-0.67nm carbon electrode in 0.1 M K₂SO₄.

![Figure III-8](image)

**Figure III-8**: Motional resistance response of CDC-0.67nm carbon electrode in 0.1 M K₂SO₄ at 10 mV·s⁻¹.

The measured motional resistance was stable around 1060 Ohm and only exhibits a change less than 5 Ω during cycling. This indicates that the carbon electrode was stable on the quartz in the electrolyte and that the frequency change only originated from gravimetric events (ion adsorption/desorption); hence the use of Sauerbrey’s equation to convert frequency change into mass change is valid.31

### 3.4.4 Calculation

Combining Sauerbrey’s equation (Eq. III-1) and the frequency response from EQCM, the mass change on the quartz can be calculated. The change of mass corresponds to the adsorption and desorption of ions with their solvation shell (solvent molecules, in this experiment is water) in the carbon nanopores. Figure III-9 shows the electrochemical results and the mass change of CDC-0.67nm carbon electrode in 0.1 M
K$_2$SO$_4$ at 10 mV·s$^{-1}$. Potential of zero mass change (pzmc) is the potential at the minimum mass change in Δm vs. E plot.

According to section 3.3, it is assumed that the electrode surface was negatively charged at a potential below pzmc (Q < 0), and the current measured in cyclic voltammogram and the mass changed derived from EQCM below pzmc were mainly ascribed to cations; above pzmc (Q > 0), the anions were the main contributor to the charge compensation. Since the pzmc separated the fluxes into carbon micropores due to adsorption cations and anions on the negatively and positively charged surface (Q < 0 and Q > 0) respectively, the cyclic voltammogram can be divided into four various parts, corresponding to adsorption and desorption of cations and anions as illustrated in Figure III-10a. The four parts include: (I) SO$_4^{2-}$ anion adsorption from pzmc to 0.2 V vs. Hg/Hg$_2$SO$_4$; (II) SO$_4^{2-}$ anion desorption from 0.2 V vs. Hg/Hg$_2$SO$_4$ to pzmc; (III) K$^+$ cation adsorption from pzmc to -0.3 V vs. Hg/Hg$_2$SO$_4$ and (IV) K$^+$ cation desorption from pzmc to -0.3 V vs. Hg/Hg$_2$SO$_4$. These areas are also shown in the Δm vs. E curve as shown in Figure III-9b.

**Figure III-9:** (a) Cyclic voltammogram obtained from EQCM with CDC-0.67nm carbon electrode in 0.1 M K$_2$SO$_4$ at 10 mV·s$^{-1}$ (b) Mass change on the quartz versus potential.

From Figure III-9b, the mass first decreases and then increases during positive scan owing to cations desorption and anion adsorption in the carbon nanopores due to the electrode polarization. Then, the mass decreases and increases again during negative sweep since anions desorbed and cations adsorbed. The vertex of the mass change curve has a rounded minimum instead of sharp V-shape due to mixed cation–anion fluxes of the adsorbed ions directed oppositely, which means the adsorption of counter-ions
(SO₄²⁻ anions) was accompanied by the desorption of co-ions (K⁺ cation) at the same time. The higher the charge density, the more the co-ions were electrostatically expelled from carbon pores. This behavior is called perm-selectivity for carbon materials. Furthermore, the difference of mass changes comparing the positive and negative sweep can be observed from Figure III-9b. When the potential shifted from pzc to the positive, the adsorption of anion dominated (Δm increases). However, when the potential swept negatively back to pzc, an unexpected smaller mass change was observed which demonstrates the company of cation adsorption into carbon micropores as anodic polarization of the electrode decreased. This indicates a competition of anion desorption and cation adsorption in carbon micropores.

**Figure III-10:** Electrode mass change vs. charge during polarization (sweep from negative to positive potential) of CDC-0.67nm in 0.1 M K₂SO₄ at various scan rates (5, 10 and 20 mV·s⁻¹)

The information on extent of solvation can be obtained from Δm versus ΔQ plot (Figure III-10). The charge was calculated from different parts of cyclic voltammogram. The part derived from the potential smaller than pzc was assigned to have negative Q value since the electrode surface is negatively charged; while the part derived from potential larger than pzc was assigned to have positive Q value. The theoretical line from Figure III-10 represents bare cations and anions adsorbed and desorbed on the carbon nanopores. It was calculated with the help of Faraday’s law (Eq. III-2).

For Q > 0 form Figure III-10, the mass change of experimental lines at each scan rate are lower the theoretical one. The difference indicates the anion probably did not
enter the carbon micropores or ions exchange happened. However, further confirmation will be done by calculating the experimental molecular weight at high polarization with the slope of each experimental lines and Faraday’s law. For \( Q < 0 \), the mass change of experimental lines at each scan rate are larger than the theoretical one which mark the existence of solvated cations at the negative polarization in carbon micropores. From Figure III-10, at the potential between pzc and pzmc, a decrease of electrode mass due to the desorption of anions is observed instead of the expected increase in electrode mass due to the adsorption of cations. This is the result of the cation-anion mixing which is mentioned before because of the different combinability of cation and anion.\(^{32}\)

Moreover, for 20 and 10 mV·s\(^{-1}\) scan rate experiments, the pzmc - which is around -0.1 V vs. Ref – is roughly constant. However, the pzmc has shifted to more negative potential, being for instance -0.16 V vs. Ref, at 5 mV·s\(^{-1}\) scan rate. This shows that, during positive scan at low scan rate, there is a huge difference in the kinetics of cation desorption and anion adsorption which result in a larger deviation between pzc and pzmc. Levi \textit{et al.}\(^{32}\) showed that the pzmc was shifted to negative potential comparing to pzc at all scan rates with bulky cations which the ion size is close to the pore size. They claimed that the slow adsorption kinetic of the bulky cation was the cause of the results. In our case, although the pzmc has also been shifted to negative potential, the difference between the adsorption/desorption kinetics of anion and cation seem not proportional to the ion size. In addition, the size of hydrated potassium cation and sulfate anion are both close to the pore size (see Table III-3). To study the difference of adsorption/desorption kinetics of anion and cation, additional EQCM experiments were performed at one scan rate.

Those evidence help in further understanding the ion dynamics/adsorption in carbon nanopores. With the calculation of molecular weight, more information can be found. However, ion-mixing should be avoided for the calculation of the exact molecular weight for cation and anion in carbon micropores. As a result, the experiments of separation scans from pzc to cathodic and anodic vertex potential with CDC-0.67nm electrode material in 0.1 M K\(_2\)SO\(_4\) were performed and are shown in Figure III-11 below.
Figure III-11: Electrode mass change versus charge during the polarization of CDC-0.67nm in 0.1 M K₂SO₄ aqueous electrolyte, with a potential scan starting from pzc to positive and negative directions. Black solid marks are measured mass change (EQCM), green dashed lines are the theoretical mass change of neat ions. The red solid line shows the linear fitting of measured mass change.

<table>
<thead>
<tr>
<th></th>
<th>Mₜheo (g·mol⁻¹)</th>
<th>Mₑxp (g·mol⁻¹)</th>
<th>Calculated hydration number</th>
<th>Bulk solution hydration number²¹, ²³, ³³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cation</td>
<td>39.1</td>
<td>134</td>
<td>5.3</td>
<td>7</td>
</tr>
<tr>
<td>Anion</td>
<td>96.1</td>
<td>115</td>
<td>0.9</td>
<td>13</td>
</tr>
</tbody>
</table>

Table III-5: Average molecular weight calculated from slope of ∆m-∆Q plot, the estimated hydration number, and the reported bulk solution hydration number.

Figure III-11 shows the results illustrated in ∆m versus ∆Q. The EQCM experiments were operated with CDC-0.67nm electrode material in 0.1 M K₂SO₄ at 10 mV·s⁻¹ sweeping from pzc to cathodic and anodic vertex potential, separately. By using Equation III-1, the average molecular weight of the species that enters or exits carbon nanopores can be inversely extracted from the slope of ∆m versus ∆Q plot. Since the theoretical curve was originally derived from Faraday’s law, the molecular weight calculated back from slope in Q < 0 and Q > 0 should be, in a first approach, equal to
the molecular weight of bare $K^+$ ($= 39.1 \text{ g mol}^{-1}$) and $SO_4^{2-}$ ($= 96.1 \text{ g mol}^{-1}$), respectively. Considering the slopes of experimental curve in the appropriate range (as indicated in red lines in Figure III-11) and using Faraday’s equation, average molecular weights of cations or anions with solvent molecules, $M_{\text{Exp}}$, were calculated. We assumed that the difference between average molecular weights and bare ion molecular weight was attributed solely to water molecules, the hydration number of each ion could be estimated. The result and the comparison with bulk solution hydration number were shown in Table III-5.

The estimated hydration numbers of potassium ions ($K^+$) and sulfate ion ($SO_4^{2-}$) in carbon micropores are 5.3 and 0.9, respectively. By comparing the values of bulk solution hydration number and calculated hydration number, it is shown that for both cation and anion, the desolvation of solvent ions occurred. For $K^+$ ions, the calculated hydration number is not very different from the bulk solution hydration number. This might due to the size of the hydrated potassium ion which its diameter was reported as 0.662 nm. The pore size of TiC-CDC is 0.67 nm is very similar to the size of the fully hydrated potassium ion (diameter = 0.66 nm). As a result, the degree of desolvation was lower than bulkier $SO_4^{2-}$ sulfate ions. For bulkier $SO_4^{2-}$ sulfate ions, the value of calculated hydration number is between 0 and 1 which indicates most of the water molecules were removed while anions entered in carbon micropores. According to literature, the size of bare $SO_4^{2-}$ sulfate ion is 0.46 nm and the mean ion-water inter-nuclear distance of sulfate is 0.381 nm. Based on those information, the desolvation of sulfate ions can be explained since the hydrated ion size of sulfate (diameter = 0.76 nm) is way much larger than the pore size of TiC-CDC (pore size = 0.67 nm). However, one must notice that the ion-mixing phenomena should still be considered because a rounded minimum of the concave curve from Figure III-13 are still shown. Thus, further experiments are suggested to be done to exclude the ion-mixing phenomena.

3.5 0.1 M EMIm$^+$-$HSO_4^-$ Aqueous Electrolyte (pH = 0.8)

The preliminary EQCM study using common $K_2SO_4$ electrolyte and the corresponding mathematical methodology was demonstrated in previous section. To further understand the relationship between electrolyte ion size and the pore size of TiC-CDC nanoporous carbon material, another aqueous electrolyte with bulky cation was chosen for studying ion dynamics in this section, where $K^+$ cations were replaced
with larger EMIm$^+$ cations by using a solution of 0.1 M EMIm-HSO$_4$ (pH = 0.8). Figure III-12a and b show the cyclic voltammogram and simultaneous frequency response recorded by EQCM at scan rate of 10 mV·s$^{-1}$ from pzc to -0.3 V vs. Hg/Hg$_2$SO$_4$ and pzc to 0.5 V vs. Hg/Hg$_2$SO$_4$, respectively. Both III-12a and b exhibit a characteristic capacitive behavior with rectangular CV profiles showing that there is no limitation for cations and anions to access the carbon nanopores.

![Figure III-12](image)

**Figure III-12**: CVs obtained from EQCM with CDC-0.67nm carbon electrode in 0.1 M EMIm$^+$-HSO$_4^-$ at 10 mV·s$^{-1}$ (a) is scanned from pzc to -0.3 V vs. Hg/Hg$_2$SO$_4$ and (b) is scanned from pzc to 0.5 V vs. Hg/Hg$_2$SO$_4$.

As mention in the previous section, to minimize the effect of ion-mixing, the experiments from EQCM were performed separately from pzc to cathodic and anodic vertex potential. Figure III-13 shows a combined Δm versus ΔQ plot from pzc to cathodic and anodic vertex potential with CDC-0.67nm electrode material in 0.1 M EMIm$^+$-HSO$_4^-$. Although individual experiments were operated to avoid ion-mixing behavior, from Figure III-13 within the range of 0.3 to -0.9 mC·cm$^{-2}$, the ion-mixing zone was still observed. The calculated equivalent molar weights in the appropriate range (as indicated in red lines in Figure III-13) for cation and anion are shown in Table III-6. For cation, the data with negative sweep was used; for anion, the data with positive sweep was used.
Figure III-13: Electrode mass change versus charge during the polarization of CDC-0.67nm in 0.1 M EMIm\(^+\)-HSO\(_4^-\) aqueous electrolyte (pH = 0.8).

<table>
<thead>
<tr>
<th>Cation</th>
<th>M(_\text{Theo}) (g·mol(^{-1}) per charge)</th>
<th>M(_\text{Exp}) (g·mol(^{-1}) per charge)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anion</td>
<td>48 (SO(_4^{2-}))/ 97 (HSO(_4^-))</td>
<td>31</td>
</tr>
</tbody>
</table>

Table III-6: Molecular weight of the bare EMIm\(^+\) cation and HSO\(_4^-\) anion and the average molecular weight calculated from slope of Δm-ΔQ plot

The calculated average molecular weight for anion and cation is 31 and 1.3 g·mol\(^{-1}\) per charge, respectively. For positive charge (Q > 0), Figure III-13 shows an increase of mass change in carbon micropores. The calculated molecular weight per charge (31 g·mol\(^{-1}\)) is less than that of bare HSO\(_4^-\) anion (97 g·mol\(^{-1}\)). It is also smaller than that of SO\(_4^{2-}\) anion (48 g·mol\(^{-1}\)), even though SO\(_4^{2-}\) anion adsorption should not be predominant because of the low pH value of the electrolyte. This indicates that not only adsorption of solvated anion occurred in carbon pores, but also desorption of cations. Unfortunately, without other supplement methods, the hydration number of HSO\(_4^-\) anion could not be obtained since the exchanged of cations and anions occurred.

Some interesting results were observed for Q < 0 mC·cm\(^{-2}\). According to Figure III-13, no (or only slight) mass change was observed from Q < -0.9 mC·cm\(^{-2}\). This can be explained by two possibilities: (1) Only protons adsorbed and desorbed in carbon
nanopores; (2) At high charge densities, small adsorption of the bulky cations was counterbalanced by desorption of the anions. The first possibility can be explained by the fact that adsorption or desorption of proton will not show frequency change in EQCM because of its molecular weight. Under the assumption that only proton accessed into carbon micropores, the reason to exclude the probability of adsorption/desorption of EMIm$^+$ cation is needed to discuss, which is the relationship between the pore size and size of EMIm$^+$ cations. The longest dimension of EMIm$^+$ cation was calculated to be 0.76 nm which is larger than the pore size of CDC-0.67nm. It is expected that the ions have limited access to the pores. Moreover, on top of the large excess of proton in such acidic electrolyte, the mobility of proton is higher than bulkier EMIm$^+$ cation. In this scenario, protons (M = 1 g·mol$^{-1}$) should be the main charge carriers during cation adsorption via Grotthuss mechanism.

The second scenario is assumed that solvated EMIm$^+$ cation could squeeze into carbon micropores. It was reported that in the solvated environment, solvated EMIm$^+$ cation (effective ion size in acetonitrile = 0.7 nm) was able to access into confined carbon micropores (pore size = 0.65 nm) with partial removal of its solvation shell. Nevertheless, the EMIm$^+$ cations in our experiments were surrounded by water molecules instead of acetonitrile which the effective ion size may vary. Based on the improbable assumption that solvated EMIm$^+$ cation could access carbon micropore, the change of mass from Q = -0.9 to 0 mC·cm$^{-2}$ could be attributed to the dominance of anions in the ion-mixing in carbon micropores through their adsorption at Q > 0 and continuing desorption at Q < 0. Still in this scenario of EMIm$^+$ adsorption, for Q < -0.9 mC·cm$^{-2}$, almost no change of mass could refer to the adsorption of a small amount of EMIm$^+$ cations were coupled with the desorption of anions which were previously stayed in the carbon micropores. This scenario will be discussed in the next section.

3.6 Mixture of 0.1 M K$_2$SO$_4$ and EMIm$^+$-HSO$_4^-$ Aqueous Electrolyte

(pH = 1.2)

The previous study of ion dynamics with 0.1 M EMIm$^+$-HSO$_4^-$ electrolyte in CDC-0.67nm carbon micropores the relationship between the pore size and electrolyte ion size and the difference in size/mobility of various electrolyte ions have been discussed. To further study how the electrolyte environment influenced the adsorption of ions in
microporous carbon, a mixed of 0.1 M $\text{K}_2\text{SO}_4$ and 0.1 M EMIm$^+$-HSO$_4^-$ electrolyte with bulky cation was used in this section. The pH of the solution was measured to be 1.2.

Figure III-14a and b shows the cyclic voltammogram and simultaneous frequency response recorded by EQCM at scan rate of 10 mV·s$^{-1}$ from pzc (0.12V vs. Hg/Hg$_2$SO$_4$) to -0.45 V vs. Hg/Hg$_2$SO$_4$ and pzc to 0.4 V vs. Hg/Hg$_2$SO$_4$, respectively.

![Figure III-14](image)

**Figure III-14:** Cyclic voltammogram obtained from EQCM with CDC-0.67nm carbon electrode in mixed electrolyte at 10 mV·s$^{-1}$ (a) is scanned from pzc to -0.45V vs. Hg/Hg$_2$SO$_4$ and (b) is scanned from pzc to 0.4V vs. Hg/Hg$_2$SO$_4$.

The CVs in Figure III-14 show a rectangular shape which referred to capacitive behaviors. However, with the same amount of active material deposited on the quartz, the current for cation adsorption/desorption is higher than anion adsorption/desorption. The frequency change of Figure III-14a is smaller than Figure III-14b. The hysteresis in the frequency response of the electrode was observed especially in Figure III-14b, which might relate to the kinetic difference between ion adsorption and desorption.$^{36, 37}$ In mixed electrolyte, the composition of cations ($\text{K}^+$, EMIm$^+$, H$^+$, H$_3\text{O}^+$) and anions ($\text{SO}_4^{2-}$, HSO$_4^-$) are more complex. Therefore, for more information, the mass change versus charge density plots are needed which are shown below in Figure III-15.

The $\Delta m$ versus $\Delta Q$ plot is shown in Figure III-15. For positive polarization, the charge of mass versus charge is a straight line. However, for the negative polarization, the failure of perm-selectivity can still be observed closed to $Q = 0$ mC·cm$^{-2}$. From the selected range (as indicated in red lines in Figure III-15), the average molecular weight in microporous carbon can be calculated. In this section, since the valence state of anions varies, the calculated results will be shown in molecular weight per charge for better comparison.
Figure III-15: Electrode mass change versus charge during the polarization of CDC-0.67nm in mixture of 0.1 M K$_2$SO$_4$ and EMIm$^+$-HSO$_4^-$ aqueous electrolyte (pH = 1.2).

<table>
<thead>
<tr>
<th>Cations</th>
<th>Anions</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$^+$</td>
<td>EMIm$^+$</td>
</tr>
<tr>
<td>$M_{\text{Theo}}$ (g/mol·charge)</td>
<td>30.01</td>
</tr>
<tr>
<td>$M_{\text{Exp}}$ (g/mol·charge)</td>
<td>17</td>
</tr>
</tbody>
</table>

Table III-7: Average molecular weight per charge calculated from slope of $\Delta m$-$\Delta Q$ plot.

The calculated experimental average molecular weight per charge for cation and anion is 17 and 58 g·mol$^{-1}$, respectively. For $Q > 0$ mC·cm$^{-2}$ since no ion-mixing phenomena was observed, only anion adsorption was considered. According to previous results obtained in K$_2$SO$_4$ electrolyte, the calculated hydration number for sulfate anion is between 0 to 1, which indicates that almost bare sulfate ions adsorbed into carbon micropores. Due to a higher valence state of sulfate anion than HSO$_4^-$ bisulfate ion, more energy will be needed for desolvation of water molecules while entering carbon micropores. As a result, bare bisulfate anion accessing to TiC-CDC micropores can be expected. This supports the existence of a mix of sulfate and bisulfate anions adsorbed into TiC-CDC carbon micropores from pzc to positive charge density. From direct calculation, the contribution of sulfate anion and bisulfate anion can be estimated to 80 % and 20 %, respectively, during the anion adsorption process.

For high negative charge ($Q < 0$), the calculated average molecular weight per
charge (17 g·mol⁻¹) is much smaller than K⁺ and EMIm⁺ cations. To understand the EQCM result in the mixed electrolyte at negative polarization, the next section will summarize and discuss all the results obtained in different electrolytes with CDC-0.67nm electrode material scanned at the same scan rate in the negative charge range.

4. Discussions

In this chapter, in situ EQCM has been operated to track the ionic fluxes in CDC-0.67nm micropores. Three electrolytes have been chosen to be tested which are: 0.1 M K₂SO₄ (pH = 6.3), 0.1 M EMIm⁺-HSO₄⁻ (pH = 0.8), and Mixture of 0.1 M K₂SO₄ and EMIm⁺-HSO₄⁻ (pH = 1.2). Table III-8 is a summary of the calculated average molecular weight and the molecular weight of bare cations and anions.

<table>
<thead>
<tr>
<th></th>
<th>Cations (Q-)</th>
<th>Anions (Q⁺)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K⁺</td>
<td>EMIm⁺</td>
</tr>
<tr>
<td><strong>M_{Theo} (g·mol⁻¹ per charge)</strong></td>
<td>30</td>
<td>111</td>
</tr>
<tr>
<td>0.1 M K₂SO₄ (pH = 6.3)</td>
<td>134</td>
<td>115</td>
</tr>
<tr>
<td>0.1 M EMIm⁺-HSO₄⁻ (pH = 0.8)</td>
<td>1.3</td>
<td>31</td>
</tr>
<tr>
<td>Mixture of 0.1 M K₂SO₄ and EMIm⁺-HSO₄⁻ (pH = 1.2)</td>
<td>17</td>
<td>58</td>
</tr>
</tbody>
</table>

Table III-8: The experimental molecular weights calculated from the experimental Δm vs. ΔQ curves.

For positive polarization, a relatively larger increase of mass (comparing with Q⁻) has been observed in all aqueous electrolytes from neutral to acidic aqueous solution. From the experiment in 0.1 M K₂SO₄ aqueous electrolyte, a high degree of desolvation of sulfate anion is observed, in agreement with previous reports from the literature dealing with ion confinement in carbon micropores. In 0.1M EMIm⁺-HSO₄⁻ acidic aqueous electrolyte, anion adsorption occurs simultaneously with cation desorption. However, EQCM is not able to discriminate between cationic and anionic fluxes in the ion mixing zone and the exact contribution of HSO₄⁻ and SO₄²⁻ anions remains unknown for 0.1 M EMIm⁺-HSO₄⁻ acidic aqueous electrolyte. For the mixed 0.1 M K₂SO₄ +
EMIm$^+$-HSO$_4^-$ aqueous electrolyte, anion adsorption involved desolvated HSO$_4^-$ and SO$_4^{2-}$ as we discussed previously.

**Figure III-16:** Comparison of electrode mass change versus charge density for different electrolytes with CDC-0.67nm electrode material from $Q = 0$ mC·cm$^{-2}$ to negative charge density.

In the negative charge density range, as shown in Figure III-16, both electrolytes containing K$^+$ cations show an increase of mass change (green and blue line in Figure III-16). However, the weight change of mixed electrolyte (blue) is smaller than in neutral K$_2$SO$_4$ electrolyte, that is without the presence of bulky EMIm$^+$ cation. For neutral K$_2$SO$_4$ electrolyte (pH = 6.3), the desolvation of K$^+$ has been confirmed. For the EMIm$^+$-HSO$_4^-$ acidic electrolyte, as we mentioned in section 3.4, the second scenario of EMIm$^+$ adsorption can now be eliminated since the mobility of proton is ten times higher than EMIm$^+$ cation which is not comparable.$^{38,39}$ The main charge carrier should be proton, considering the ion size and mobility for EMIm$^+$-HSO$_4^-$ acidic electrolyte. The last is the mixed electrolyte, where at low negative charge density ($Q = 0$ to -0.6 mC·cm$^{-2}$) the slow increase of electrode mass is caused by ion-mixing. Then, at high negative charge density ($Q < -0.6$ mC·cm$^{-2}$), based on the calculated experimental molecular weight (17 g·mol$^{-1}$), it is confirmed that K$^+$ (39 g·mol$^{-1}$) is not the only cation involved in the charge process. In the electrolyte mixture at pH = 1.2, the potassium molar ionic conductivity is in the range of proton’s one (which is not the case for EMIm$^+$). This explains that the calculated average molecular mass per charge is found between the theoretical molecular weight of proton and potassium at pH equals to 1.2.
From direct calculation, the contribution of proton and potassium cation is 44% and 56%, respectively, during the cation adsorption process. Although the experimental molecular weight is very close to the molecular weight of hydronium, according to the Grotthuss mechanism (conductivity via proton hopping), H$_3$O$^+$ adsorption is not likely to be the dominant process in acidic electrolyte versus proton adsorption. Based on the discussion above, it is confirmed that during charge/discharge process in multi-ion aqueous solution at low pH, both cations (H$^+$ and K$^+$) and anions (HSO$_4^-$ and SO$_4^{2-}$) contribute to the adsorption/desorption process.

Speaking about the presence of bulkier EMIm$^+$ cation in aqueous solution, in this work, the desolvation of EMIm$^+$ cation has not been observed. However, its larger diameter and its higher form factor resulting in the lowest ionic mobility has an impact to its contribution to the adsorption process at negative polarization, especially in acidic environment. Another observation is that the ion mixing zone enlarged by the presence of bulky EMIm$^+$ cation, especially at the negative charge region (red and blue line in Figure III-16). One possibility is that the bulky cation slows down the access of water or hydronium to the electrode surface during charging. The origin of the enlarged ion mixing zone needs extended experiments to confirm the origin.

5. Conclusions

In this study, cyclic voltammetry with in situ EQCM measurement has been used to study the ion dynamic in porous carbon electrodes from different aqueous electrolytes. In binary aqueous electrolytes 0.1 M K$_2$SO$_4$ and 0.1 M EMIm$^+$-HSO$_4^-$, protons were found to be the main charge carriers during negative polarization in EMIm$^+$-HSO$_4^-$ electrolyte. In mixed 0.1 M K$_2$SO$_4$ and EMIm$^+$-HSO$_4^-$ electrolyte, the main charge carriers have been identified to be H$^+$, K$^+$, HSO$_4^-$ and SO$_4^{2-}$ during cycling. Moreover, these results show that the change of electrolyte pH changes the main charge carrier during cycling. In addition, the ion size and mobility have been discussed and shown that to be effective to the contribution of ions during cycling.

Overall, the profile of ionic fluxes was revealed by EQCM in simple and mixed electrolyte environment. This approach demonstrates that EQCM served as an advanced analytical method extends our understanding for ion adsorption/desorption in porous carbon material, which is of high importance for designing porous carbon electrodes for supercapacitor applications. To extend the knowledge of the charge
mechanisms of EDLCs in depth, the next chapter will demonstrate the setup of a 2D carbon-based platform and the analysis of the electrode/electrolyte interface.
6. References


Chapter 3: EQCM Study of Ion Adsorption in Three-Dimensional Porous Carbon Electrode

theoretical and general crystallography, 1976, 32, 751-767.


Chapter IV:

EQCM Study on Charge Storage

Mechanisms of Two-dimensional Single Layer Graphene
1. Introduction

Electrochemical double layer capacitors (EDLCs), also known as supercapacitors, store energy by reversible electrostatic attraction of electrolyte ions onto high surface area carbon electrodes. Since the limitation of battery-like charge transfer kinetics is not involved in the charge storage mechanism, supercapacitors can operate at very high charge and discharge rates within a few seconds and can have excellent cyclability of over a million cycles, which make them useful in a broad range of applications such as high power delivery and energy harvesting.\(^1, \, 2\)

As an excellent building block for three dimensions (3-D) porous carbons electrode, graphene with its high theoretical specific surface area of 2630 m\(^2\)·g\(^{-1}\) and capacity of 550 F·g\(^{-1}\) (21 uF·cm\(^{-2}\)), has already attracted great attention for supercapacitor.\(^3, \, 4\)

Graphene and their derivatives have been reported to boost the capacitance of such devices over 200 F·g\(^{-1}\).\(^5-7\) Multilayer stacked graphene film electrodes, on the other hand, show great results in small-scale supply source required to power the next generation of micro-electronic devices.\(^8, \, 9\) Furthermore, as typical two-dimensional (2-D) carbon nanosheet has been demonstrated both theoretically and experimentally to resolve the peculiar interfacial capacitance of some certain carbon.\(^10,11\)

Despite all efforts mentioned above, the intrinsic capacitances of graphene-based devices are still far from theoretical value.\(^10\) In reality, the capacitance of carbon is governed significantly by the properties of the electrode/electrolyte structure.\(^11\) For very high surface area materials such as graphene or highly porous carbons, it is critical to understand the charge storage mechanism in the double layer from the electrolyte side, in addition to the space charge or quantum capacitance related to the electronic properties of the carbon. To some extent, how to ensure ion adsorption sites and capacitance related ion fluxes/adsorption among graphene/electrolyte interface still remain an unresolved puzzle, hampering the development of high-performance 2- and 3-D carbon materials.

**Figure IV-1:** A schematic of CVD graphene grown on Cu foil.
Single layer graphene (SLG) exhibits superior thermal and electrical conductivities.\textsuperscript{12, 13} It has been used as sensors for gas, tactile, and temperature detection for a wide range of applications.\textsuperscript{14-16} In addition, the physics of SLG has attracted great attention due to special phenomena: for example, the magnitude driven metal-insulator transition,\textsuperscript{17} the quantum Hall effect,\textsuperscript{18} and the 2-D Dirac fermions.\textsuperscript{19} The synthesis of SLG has been reported by mechanical exfoliation of graphite,\textsuperscript{13} reduction of graphene oxide,\textsuperscript{20} and chemical vapor deposition (CVD).\textsuperscript{21} Large surface area of SLG is possible to be synthesized on Cu foil. SLG was prepared on Cu substrate for 30 minutes at temperatures up to 1000 °C by CVD using a mixture of methane and hydrogen. The copper foil is acting as the catalyst and substrate. The growth mechanism on Cu surface is a surface adsorption process owing to the low solubility of C atoms in Cu, offering a path to grow monolayer graphene based on self-limiting process as shown in Figure IV-1.

\textbf{Figure IV-2:} Total capacitance (blue line) and quantum capacitance (red line) of graphene measured in ionic liquid BMImPF$_6$.

SLG with low defects may provide a model platform for developing fundamental understanding of ionic adsorption and transport at graphene/electrolyte interface. Several works have reported a unique U-shaped capacitance versus a wide-range of applied potential (C-V) for SGL, where the minimum capacitance is located around the Dirac point and the total capacitance increase linearly with gate potential (see Figure IV-2).\textsuperscript{22, 23} The total capacitance of the SGL/electrolyte interface ($C_{int}$) has several contributions\textsuperscript{24}: the double layer capacitance ($C_{EDL}$) and the quantum capacitance ($C_Q$), as presented in Equation IV-1. The existence of a quantum capacitance, related to the
number of available charge carriers on the graphene side\textsuperscript{22, 25}, has been proposed to explain such V-shape signature where $C_Q$ controls the total capacitance of single layer graphene and leads to a stronger ion-carbon correlation. As reported by the authors, as the number of graphene layers increases, the quantum capacitance increases, so the total capacitance levels off as it is driven by the EDL capacitance.\textsuperscript{26, 27}

\[ \frac{1}{C_{int}} = \frac{1}{C_Q} + \frac{1}{C_{EDL}} \]  \hspace{1cm} (Eq. IV-1)

On the other hand, the nature and concentration of electrolytes are critical aspects in determining the EDL at the electrode surface.\textsuperscript{27} Experiments have shown that the shape of $C-V$ plots has a transition from camel-like to U-like one when moving from pure ionic liquid to dilute electrolyte ($< 2$ molarity) using Ag electrode, in agreement with the mean-field model where short-range ion-ion correlations need to be taken into consideration.\textsuperscript{28-30} Simulation based on the mean-field theory has also been used to stimulate the contribution of $C_Q$ capacitance from Helmholtz layer and diffusion layer ($C_H$ and $C_{DL}$) in various electrolytes. A series of works from Mišković’s group established the models which include the contribution of $C_H$ and $C_{DL}$ to describe the experimental results of SLG in aqueous electrolytes.\textsuperscript{31-33} For ionic liquids at charged metal electrode, simulations demonstrate that the differential capacitance can be influenced by the degree of cation-anion interactions and volume ratio between cation and anion, especially near potential of zero charge (pzc).\textsuperscript{34, 35} Further on, with polarized SLG electrode, the differential capacitance changed with the degree of ion packing (the total number of moles in the electrolyte bulk respects to total ion number of moles on available sites), ion correlation and the size of cation and anion in neat ionic liquids.\textsuperscript{36} However, the simulation work has not yet been verified by experiments.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{FIGURE_IV_3.png}
\caption{A schematic of the difference between 2-D and 3-D platforms.}
\end{figure}

SLG allows running experimental mimicking the behaviors of ions from an electrolyte in contact with an ultrahigh specific surface area carbon surface, in the
absence of complex porosity or presence of defects such as observed in porous materials. A schematic comparison is shown in Figure IV-3. In this chapter, we analyzed using electrochemical impedance spectroscopy (EIS) technique the effect of the nature of electrolytes on SLG, such as neat ionic liquid and solvated ionic liquid electrolytes. Further on, we demonstrate for the first time in-operando probing of ion fluxes at the SLG electrode surface using an electrochemical quartz crystal microbalance (EQCM), allowing to get further understanding of the charge storage mechanisms at the SLG electrode in different electrolytes. This work has been made in collaboration with Jianglin YE from Hefei National Research Center for Physical Sciences at the Microscale & CAS Key Laboratory of Materials for Energy Conversion (China), who achieved the SGL synthesis and transfer onto EQCM quartz.

2. Experimental

2.1 Materials

2.1.1 SLG preparation

First, monolayer graphene (G) films were obtained by chemical vapor deposition (CVD) by flowing 3 sccm H₂ (70 mTorr) and 30 sccm CH₄ (340 mTorr) gases at 1000 °C on copper (Cu) substrate (Wuxi Graphene Film Co., Ltd). After etching copper by 0.1 M of ammonium persulfate ((NH₄)₂S₂O₈), the transfer of CVD graphene from Cu to pressure sensitive adhesive (PSA) films coated polyethylene terephthalate (PET) substrate was carried out, as previously reported with further modification (see Figure IV-4).⁹,⁴⁷

![Figure IV-4: Schematic illustration of the synthesis procedures.](image-url)
2.1.2 Electrolytes

The ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMImTFSI, CAS #174899-82-2) is bought from Solvionic. The acetonitrile (ACN) (CAS #75-05-8, H₂O < 10 ppm) solvent was obtained from Acros Organics. The detailed information is shown in Table IV-1.

<table>
<thead>
<tr>
<th>Type of ions</th>
<th>Chemical structure</th>
<th>Max/min length (nm)</th>
<th>Molecular weight (g mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMIm⁺</td>
<td><img src="EMIm.png" alt="Chemical structure" /></td>
<td>0.76/0.43³⁸</td>
<td>111</td>
</tr>
<tr>
<td>1-ethyl-3-methylimidazolium</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TFSI⁻</td>
<td><img src="TFSI.png" alt="Chemical structure" /></td>
<td>0.79/0.37³⁸</td>
<td>280</td>
</tr>
<tr>
<td>Bis(trifluoromethanesulfonyl)imide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ACN</td>
<td><img src="ACN.png" alt="Chemical structure" /></td>
<td>0.58/0.4³⁹</td>
<td>41</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table IV-1: Chemical structure, size, and molecular weight of the ions studied in this chapter.

2.2 Electrochemical cell setup

2.2.1 Quartz crystal electrode preparation

BioLogic 1-in.-diameter Au-coated quartz crystal (oscillating frequency, f₀, 5 MHz) was coated by SLG. The transferring process of SLG is shown in Figure IV-5.

Figure IV-5: Transfer process of single layer graphene on Au-coated quartz substrate.
The obtained large area of PET-graphene films (PET-G) were used to further assist the transfer of graphene to quartz at around 85°C for 30 min. The SLG-coated quartz was dried in an oven at 60°C for overnight after peeling the PET films.

2.2.2 EQCM cell configuration

The SLG coated quartz crystal working electrode was placed on a PTFE holder, in which the coated side was orientated toward the reference and counter electrode in a 3-electrode electrochemical cell. The counter electrode was a platinum wire. The silver wire was used as quasi-reference electrode placed between working and counter electrodes. Three electrodes were set in a glassware and immersed in electrolyte.

2.3 Experiment settings and data processing

2.3.1 EIS experiments

Electrochemical impedance spectroscopy (EIS) measurements were carried out with a VMP3 electrochemical working station (Biologic, S.A.). The frequency range studied was 100 kHz to 50 mHz, and the measurements were made at different potentials in the range of −0.7 to 0.9 V versus an Ag reference electrode. The DV signal amplitude applied was 10 mV.

In this chapter, an alternative EIS method was used to characterize the electrode/electrolyte interface. This method aims to separate the real \(C'(\omega)\) and imaginary \(C''(\omega)\) part of the capacitance \(C(\omega)\). The \(C'(\omega)\) and \(C''(\omega)\) corresponds to the capacitance of the cell and an energy dissipation by an irreversible process, respectively. By combining Equation IV-2 and IV-3, the \(C(\omega)\) can be expressed as Equation IV-4.

\[
Z(\omega) = \frac{1}{j\omega \times C(\omega)} \quad (\text{Eq. IV-2})
\]
\[
Z(\omega) = Z'(\omega) + jZ''(\omega) \quad (\text{Eq. IV-3})
\]
\[
C(\omega) = \frac{-(Z''(\omega) + jZ'(\omega))}{\omega |Z(\omega)|^2} \quad (\text{Eq. IV-4})
\]

When we separate the real and imaginary part of \(C(\omega)\) as Equation IV-5, the \(C'(\omega)\) and \(C''(\omega)\) can be expressed as Equation IV-6 and IV-7.

\[
C(\omega) = C'(\omega) - jC''(\omega) \quad (\text{Eq. IV-5})
\]
Chapter IV: EQCM Study on Charge Storage Mechanisms of Two-dimensional Single Layer Graphene

\begin{align*}
C'(\omega) &= \frac{-Z''(\omega)}{2\pi f |Z(\omega)|^2} \quad \text{(Eq. IV-6)} \\
C''(\omega) &= \frac{Z'(\omega)}{2\pi f |Z(\omega)|^2} \quad \text{(Eq. IV-7)}
\end{align*}

2.3.2 EQCM experiments

All the EQCM electrochemical measurements were carried out by a Maxtek RQCM system combined with Autolab PGSTAT101 was used for simultaneous EQCM and electrochemical measurements.

For the EQCM results, the electrode mass change was calculated using Sauerbrey equation: \( \Delta m = -C_T \cdot \Delta f \), where \( \Delta m \) is the change of mass of the coating and \( C_T \) is the sensitivity factor of the crystal. The sensitivity factor of the coated quartz was obtained by performing a copper deposition experiment conducted in 0.1 M \( \text{CuSO}_4 \) mixed with 1 M \( \text{H}_2\text{SO}_4 \) by applying a constant current of 5 mA for 120 seconds. In this experiment, the \( C_T \) was calculated to be 27.7 ng·Hz\(^{-1}\) (or 21.8 ng·Hz\(^{-1}\)·cm\(^{-2}\) taking into account the Au crystal electrode surface of 1.27 cm\(^2\)). For consistent results, few cycles were run before starting EQCM measurements, to start from stable, reproducible electrochemical signatures.

Furthermore, the molecular weight of charged ion species \( (M_w) \) involved in positive charging was calculated by using Faraday’s law, assuming a 100% faradic efficiency:

\[ \frac{M_w}{nF} = \frac{m}{Q} \quad \text{(Eq. IV-8)} \]

where \( Q \) is the charge passed in the electrode, \( m \) is the corresponding weight change of the electrode during charging process (\( \Delta m-\Delta Q \) curve), \( n \) is the valence number of the ion species, and \( F \) is the Faraday constant (96485 C·mol\(^{-1}\)).

3. Results

3.1 SLG material characterization

Raman spectroscopy (Figure IV-6a) reveals a typical signal of single-layered graphene with distinct G- and 2D-bands.\(^{40}\) The G-band is shifted to higher wavenumbers (~1597 cm\(^{-1}\)) compared to that of charge-neutral graphene (1581 cm\(^{-1}\)),

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and the intensity ratio of 2D-band and G-band is around 1 with negligible defect (D) peak, indicating that the graphene sample used in this study was $p$ type doped.\textsuperscript{41}

**Figure IV-6:** Characterization of graphene transferred onto Au coated quartz substrate. (a) Raman spectra of single layer graphene film. (b) and (c) Optical images of transferred graphene film on quartz substrate. The arrows in (c) show the distinct uncovered Au surface. d) AFM image of the surface of graphene film.

In addition, optical microscopy study (Figure IV-6c) revealed that over 90\% of the Au quarts surface was covered with SLG. These cracks are unavoidable due to the intrinsic mechanical properties on SLG and the method of transfer initially used.\textsuperscript{42} Nanometer-high ripples of the graphene films were also observed from the atomic force microscopy (AFM) image (shown in Figure IV-6d), due to the wrinkles of CVD graphene.

### 3.2 EIS analysis

To examine the electrochemical properties of SLG, electrochemical impedance spectroscopy (EIS) measurements in neat EMImTFSI and 2 M EMImTFSI in acetonitrile were carried out at different constant potentials. The Nyquist plots measured at various potentials have shown a capacitive behavior (Figure IV-7).
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**Figure IV-7:** (a) and (b) are typical Nyquist plots of SLG measured at different potentials versus Ag reference electrode in neat EMImTFSI and 2 M EMImTFSI/ACN. The real $C'(\omega)$ and imaginary $C''(\omega)$ parts of the capacitance were extracted from the Nyquist plots, in which $C'(\omega)$ corresponds to the total interfacial capacitance ($C_{\text{int}}$) while $C''(\omega)$ accounts for dissipative processes.

The real $C'(\omega)$ and imaginary $C''(\omega)$ parts of the capacitance were extracted from the Nyquist plots, in which $C'(\omega)$ corresponds to the total interfacial capacitance ($C_{\text{int}}$) while $C''(\omega)$ accounts for dissipative processes. Figure IV-8 shows the typical change of the SLG double layer capacitance $C'(\omega)$ with the frequency at a bias potential of 0.2 V vs. Ref. As expected, $C'(\omega)$ increased when the frequency decreases, then became less frequency dependent below the knee frequency at around 200 Hz and 1 Hz, meaning the ions from the electrolyte reached the whole SLG. However, capacitance saturation was not observed even at 0.1 Hz, especially for negative polarization partially because of leakage current from some side reactions. The change of $C'$ versus frequency can vary from the material structure, electrode thickness, electrolyte, and weight loading, which are all related to the power performance of the cell. For the imaginary part versus frequency, the maximum value for the imaginary part of the capacitance occurred at a frequency $f_0$ corresponding to a time constant $\tau_0$ (defined $\tau_0 = 1/f_0$). $\tau_0$ is called relaxation time, which represents a transition for a supercapacitor from resistive behavior to capacitive behavior. In addition, at $f_0$, the $C'$ is half of the low frequency capacitance. Using this peculiar frequency point allows for calculating the capacitance without taking into account the stray capacitance adding up at low frequency (see ellipse in figure IV-8), which is responsible to the continuous increase of the capacitance at low frequency. From Figure IV-8, $C''(\omega)$ goes through two maxima at characteristic frequencies $f_0$ of 610 Hz and 2.5 Hz, corresponding to a time constant
(τ₀= 1/ω₀) of 1.6 ms and 395 ms, respectively. To obtain the signal from the SLG only, measurements were also performed on a bare gold quartz sample in the same experimental conditions; the results are shown as blue scatters in Figure IV-8. The Au quartz substrate without SLG coating only shows one C"(ω) peak at around 413 Hz, corresponding to τ₀ of 2.4 ms. As a result, the SLG and exposed Au current collector can be seen as two parallel branches in an equivalent electrical circuit, to contribute to the total capacitance in our system. The relaxation response at low frequencies (2.5 Hz) for the SLG-coated quartz is assumed to correspond to the double layer charging process on SLG alone.

![Graph](image.png)

**Figure IV-8:** The real part C'(ω) and imaginary part C"(ω) of the capacitance on electrodes with or without SLG coated in neat EMI-TFSI electrolyte recorded at 0.2 V vs Ref, Inset shows the equivalent circuit model.

The normalized real C'(ω) and imaginary C"(ω) parts of the capacitance C(ω) in the 2M EMImTFSI in acetonitrile shows two peaks for C"(ω) as neat EMImTFSI (Figure IV-9). Two maxima peaks were observed for C"(ω), at characteristic frequencies (ω₀) of 2479 Hz and 2.7 Hz corresponding to time constants (τ₀= 1/ω₀) of 0.4 ms and 370 ms, respectively. The characteristic frequency measured at 2.7 Hz is comparable to the one found for a SLG electrode in neat EMImTFSI which corresponds to some uncovered Au substrate.
Chapter IV: EQCM Study on Charge Storage Mechanisms of Two-dimensional Single Layer Graphene

Figure IV-9: Electrochemical capacitance (C’ and C”) with respect to frequency of SLG measured at different potentials in 2 M EMImTFSI/ACN

For each time constant (τ), the capacitance response C(ω) can be described using a Debye model through the following the equation:

\[ C(ω) = \frac{C_{EDL}}{1 + jωτ} \]  

(Eq. IV-9)

At the peak of C”(ω), corresponding to the characteristic frequency \( f_0 \), \( ωτ \) is 1 and the total \( C_{int} \) can be calculated as \( C_{int} = 2C' \). By removing the capacitance contribution from Au, the change of area-normalized EDL capacitance versus potential was plotted as in Figure IV-10.

Figure IV-10: The \( C_{int} \)-E curve of SLG in neat ionic liquid and ionic dissolved in acetonitrile electrolytes.
The $C_{int-SLG}$-$E_{we}$ curve shows a dependence on the electrode potential with distinct V shape for both electrolytes. However, the $C_{EDL}$ in solvated IL is higher than pure IL. In addition, the pzc of neat IL is lower than solvated IL. Detailed discussion of the effect of solvent will be presented in the section 4.

3.3 EQCM analysis

EQCM technique was used to track ion fluxes and adsorption (interaction) on (with) SLG electrode during polarization, which can help to distinguish the EDL response from the electronic properties of graphene. To ensure the electrochemical signals are from SLG, CVs of bare Au and SLG are shown in Figure 11a. By comparing the different CVs, it is clear that the SLG exhibits different electrochemical signature compared to bare Au. In addition, the EQCM result of bare Au in EMImTFSI was performed for comparison with SLG sample (see Figure IV-11b).

**Figure IV-11:** (a) Comparison of CV response of bare gold electrode and single layer graphene in EMImTFSI at 20 mV·s$^{-1}$. (b) EQCM frequency response ($\Delta f$) of quartz substrate vs potential of Au substrate during polarization in neat EMImTFSI, recorded at 50 mV·s$^{-1}$.

The cyclic voltammogram (CV) of SLG in neat EMImTFSI (Figure IV-12a, blue line) shows a typical capacitive behavior. No hysteric behavior was observed since the associated electrode frequency changes ($\Delta f$ vs $E_{we}$) shown in black circles in Figure IV-12a overlaps. The change of motional resistance was just around ± 2 Ω, which had no influence on the observed mass change during polarization (see Figure IV-12b).
Figure IV-12: (a) CV and EQCM frequency response and (b) Change of the motional resistance response during the polarization of SLG on gold substrate in neat EMImTFSI recorded at 50 mV·s⁻¹.

Figure IV-13 shows the experimental change of the electrode weight (Δm) vs the charge (ΔQ) passed in the electrode, where Δm was calculated from the frequency change by Sauerbrey’s equation. The pzc was determined by EIS experiments which is -0.2 V vs. Ref. The Δm-ΔQ plot shows two different ionic behaviors: in the grey area (for Q ≥ 0), the electrode weight decreases linearly with the increasing charge while, differently, the electrode mass has no significant change from pzc to more negative charge.

Figure IV-13: Electrode mass change vs charge during the polarization of SLG on gold substrate in neat EMImTFSI recorded at 50 mV·s⁻¹.
From pzc to positive polarization, the decrease of mass corresponds to ions expelled from SLG. By using Faraday’s law, the calculated average molecular weight in the grey area is $M/z = 338 \text{ g}\cdot\text{mol}^{-1}$. Considering the molecular weight of EMIm$^+$ cation (111 g\cdot mol$^{-1}$) and TFSI$^-$ anion (280 g\cdot mol$^{-1}$), it turns out that charged species, which can be statistically expressed as $[\text{EMIm}_{1.58}\text{TFSI}_{0.58}]^+$ with a net charge of +1, were involved in the charge screening from the electrolyte side. From pzc to negative polarization, no significant mass change is observed while a capacitive charge storage signature is still observed in this potential range below -0.2 V vs. Ref, as shown in CV (Figure IV-12a). The absence of significant mass change implies that the applied potential cannot bring additional cations or charged ion species near to the surface. Instead, since there is still capacitive behavior observed below pzc, the negative charge storage can be understood as an ion reorganization phenomenon at the electrode surface. The strong electron-ion correlation between the imidazolium ring plane and alkyl chain of EMIm$^+$ and the graphene surface (sp$^3$ carbons) may force parallel alignment, brought them in closer contact, resulting in a closer ion packing ($\sim 0.025 \text{ mC}\cdot\text{cm}^{-2}$) on SLG.

**Figure IV-14:** (a) CV and EQCM frequency response and (b) Change of the motional resistance response during the polarization of SLG on gold substrate in 2 M EMImTFSI/ACN recorded at 30 mV\cdot s$^{-1}$.

On the other hand, when acetonitrile solvent molecules were added into EMImTFSI, EQCM detected different trends of signals comparing to neat EMImTFSI (Figure IV-14a). The frequency response recorded by EQCM appears as black scatters in Figure IV-14a. For positive and negative scans, the frequency decreased at higher
positive and lower negative potentials; a hysteresis was also observed between the positive and negative scans during one cycle. Since there is no irreversible mass loss or gain after a full cycle as can be seen from the similar starting and ending points of the $f$ vs $E$ plot, the hysteresis is assumed to origin from the difference of adsorption kinetics between cations and anions, especially near pzc charge where ion exchange occurred as previously reported.\textsuperscript{44, 45} The motional resistance was stable during polarization as shown in Figure IV-14b.

To minimize the hysteresis in the ion-mixing zone, cycling experiments were done separately from pzc to both negative and positive potentials. The pzc for 2 M EMImTFSI/ACN was measured to be 0.1 V vs. Ref by EIS experiments. Figure IV-15 shows the change of the electrode weight ($\Delta m$) vs the charge ($\Delta Q$) recorded at a potential scan rate of 10 mV·s$^{-1}$ where the weight change is calculated from the Sauerbrey’s equation.

![Graph showing electrode mass change vs charge at 10 mV·s$^{-1}$ of SLG on gold electrode in 2 M EMImTFSI/ACN organic electrolyte during pzc to positive and negative polarization separately.](image)

**Figure IV-15:** Electrode mass change vs charge at 10 mV·s$^{-1}$ of SLG on gold electrode in 2 M EMImTFSI/ACN organic electrolyte during pzc to positive and negative polarization separately.

Figure IV-15 shows an increase of mass from pzc to positive and negative charges. The yellow-shaded areas appear constant mass change while the increasing of charge. Using Faraday’s law, the calculated molecular weight of the yellow areas is 152 and 325 g·mol$^{-1}$ during negative and positive polarization, respectively. With the theoretical
molecular weight of EMIm$^+$ cation (111 g·mol$^{-1}$), TFSI$^-$ anion (280 g·mol$^{-1}$) and acetonitrile solvent molecule (41 g·mol$^{-1}$), the calculations show that, from pzc to negative charge, the solvated EMIm$^+$ cation which contains in average 1 acetonitrile molecule adsorbed onto single layer graphene; from pzc to positive charge, the TFSI$^-$ anion was solvated in average 1.3 acetonitrile molecule responded to the positive polarization. Counter-ion adsorption onto single layer graphene at high charge region are observed during negative and positive polarization in the presence of solvent molecules.

4. Discussions

Two key results were obtained from the EIS analysis of SLG in neat EMImTFSI and 2 M EMImTFSI/ACN electrolytes: i) the $C_{\text{EDL}}$ in solvated IL is higher than that of pure IL and ii) the pzc of SGL electrode in neat IL electrolyte is lower than the one in solvated IL. The larger capacitance in solvated IL compared to neat IL electrolyte is assumed to be due to an overscreening effect and ion crowding at electrified interface occurring in neat IL electrolytes, such as proposed by Kornyschev et al$^{46,47}$, leading to a thicker double layer and a decrease of capacitance (longer Debye length). Also, the dielectric constant of acetonitrile-based electrolyte is higher - from calculation - than that of neat IL, which increase the capacitance.$^{48}$ From this phenomena, the screening effect from solvent reduced the double layer thickness, thus improving the overall capacitance for ILs plus solvent.

The increase of the pzc when moving from neat to solvated IL is likely to be explained by the specific interactions between SGL and EMIm$^+$ cations. From simulation approaches, the interaction between EMIm$^+$ cation and SLG was proven to be stronger due to CH-π intermolecular interactions between the alkyl side chain and the SLG surface and the π-π stacking, which result in a preferable orientation of EMIm$^+$ cation on negative charged SLG.$^{49-51}$ With the presence of solvent molecules, the screening effect diminished the affinity between the solvated EMIm$^+$ cations and SLG, which accounts for the observed more positive pzc. From the calculated values of differential capacitance from pzc to negative and positive potentials in neat EMImTFSI and 2 M EMImTFSI/ACN (see Table IV-2), an obvious effect of the strong interaction of EMIm$^+$ and SLG was observed as well. From pzc to positive polarization, the differential capacitance almost remains constant with the addition of solvent.
However, from $pzc$ to negative polarization, the differential capacitances were strongly affected with the presence of solvent. The differential capacitance is known to be related to the change of charge carriers of the materials while applying potential. Some experimental and simulation works have discussed about the effect from the electrolyte on the differential capacitance.\textsuperscript{25, 34, 36, 52}

<table>
<thead>
<tr>
<th>Slope $[\mu F/cm^2 \cdot V]$</th>
<th>EMImTFSI</th>
<th>2 M EMImTFSI in ACN</th>
</tr>
</thead>
<tbody>
<tr>
<td>From $pzc$ to positive potentials</td>
<td>8.3</td>
<td>9.6</td>
</tr>
<tr>
<td>From $pzc$ to negative potentials</td>
<td>-6.1</td>
<td>-2.9</td>
</tr>
</tbody>
</table>

**Table IV-2.** The calculated differential capacitance for neat IL and solvated IL electrolytes.

Mott-Schottky method is frequently employed to characterize semiconductor material/electrolyte interface.\textsuperscript{53} It can determine the flat-band potential, and estimate charge carrier density of the material.\textsuperscript{54, 55} To have a deeper understanding of what happen to the SLG in different electrolyte, Mott-Schottky analysis was used.

**Figure IV-16:** The Mott-Schottky plots of SLG supported on gold coated quartz in ionic liquid electrolyte EMImTFSI and organic based electrolyte 2 M EMImTFSI/ACN.
Chapter IV: EQCM Study on Charge Storage Mechanisms of Two-dimensional Single Layer Graphene

Figure IV-16 shows the Mott-Schottky plot \( \frac{1}{C^2} - E \)\(^{56}\) of neat IL and solvated IL from pzc to negative and positive potentials. By comparing with the result from bare Au in neat IL (see the inset: showing that \( C_{EDL} \) is essentially a Helmholtz capacitance), SLG material in both electrolyte systems exhibit n-type and p-type semiconductor characteristic during negative and positive polarizations, respectively.\(^{54,56}\) According to Raman measurement, the SLG used in the study is p-type\(^{57}\) which correspond to the slope of the Mott-Schottky analysis from pzc to positive polarization. After polarized the SLG from pzc to negative potential, slightly carrier doping resulting in a change of the sign of the slope of the Mott-Schottky analysis.\(^{27,58}\) The doping might due to the strong interaction of EMIm\(^+\) and SLG.\(^{59}\) On the other hand, the change of \( 1/C^2 \) respective to the potential was different depending on the electrolyte, that is neat EMImTFSI or 2 M EMImTFSI/ACN solution. The change of \( 1/C^2 \) versus potential allows for distinguishing between the contribution of capacitance from semiconductor material for instance (called space charge capacitance, \( C_{SC} \) and \( C_{EDL} \) based on Eq. IV-10.\(^{55}\)

\[
\frac{1}{C_{int}} = \frac{1}{C_{SC}} + \frac{1}{C_{EDL}} \quad \text{(Eq. IV-10)}
\]

\[
\frac{1}{C_{SC}^2} = \frac{2}{\varepsilon \varepsilon_0 A^2 e N_D} (V - V_{FB} - \frac{k_B T}{e}) \quad \text{(Eq. IV-11)}
\]

where \( A \) is the area, \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon \) is the dielectric constant of the semiconductor, \( N_D \) is the charge carriers density, \( e \) is the electronic charge, \( V \) is the applied voltage, \( k_B \) is the Boltzmann’s constant, \( T \) the absolute temperature, and \( V_{FB} \) is the flat band potential.

<table>
<thead>
<tr>
<th>Slope</th>
<th>EMImTFSI</th>
<th>2 M EMImTFSI/ACN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pzc to positive potential</td>
<td>-31.3</td>
<td>-29.1</td>
</tr>
<tr>
<td>Pzc to negative potential</td>
<td>45.1</td>
<td>7.62</td>
</tr>
</tbody>
</table>

Table IV-3: The calculated slope from Mott-Schottky for various electrolytes.
According to Eq. IV-10, the $C_{SC}$ and $C_{EDL}$ both dominate to the total capacitance. As noticed in Figure IV-16 (insert), within this potential range with a pure Au electrode, the interfacial capacitance is only ascribed to $C_{EDL}$, which in such electrolyte concentration is essentially constant and can be assigned to a simple Helmholtz capacitance. On the other hand, $C_{SC}$ gradually decreases with increasing applied potential, resulting in an interfacial capacitance governed by $C_{SC}$ (see Eq. IV-11). Also, when the number of charge carriers (donors or acceptors, $N_D$) is high enough, the effect of $C_{SC}$ is suppressed and the interfacial capacitance is dominated by $C_{EDL}$, which offer opportunities to examine the difference of charge carriers in different electrolytes. This phenomenon is not observed with a pure Au electrode, where the differential capacitance remains constant throughout the whole range polarization. As shown in Figure IV-16 and Table IV-3, the evolution of the slope of $1/C^2$-$E$ curves evidence that the nature of electrolytes used impacts the charge carrier density at the SLG/ILs interface, on the SLG surface. The charge carrier density $N_D$ was calculated in the range of $10^{23}$ cm$^{-3}$ for a SLG electrode immersed in neat IL electrolyte, from pzc to positive and negative polarizations. We assume the calculated change of $N_D$ should be associated with the charged species from the electrolyte side at the graphene/IL interface, and the doping density of the SLG material solely measured by Raman spectroscopy ($\sim10^{12}$-$10^{14}$ cm$^{-3}$). More importantly, the slopes of EMImTFSI with (-29.1) and without (-31.3) solvent slightly change, indicating a close $N_D$ level (little higher $N_D$ in solvated electrolyte). However, from pzc to negative polarization, the slope of $1/C^2$-$E$ in EMImTFSI is five times higher than in 2 M EMImTFSI/ACN. As a result, the calculated charge carrier in 2 M EMImTFSI/ACN is one magnitude larger than neat ionic liquid from pzc to negative polarization. The higher charge density observed for solvated electrolyte, especially from pzc to negative polarization, indicates that ACN solvent molecules buffer the interaction between charged ions and polarized SLG electrode, resulting in more mobile charged ions on the SLG surface. Our results suggest the charge carrier density on SLG/IL interface during polarization was introduced and modified by the long-range Coulombic force from the electrolyte side.

Apart from the analysis of the interface between SLG and different electrolytes at
Chapter IV: EQCM Study on Charge Storage Mechanisms of Two-dimensional Single Layer Graphene

the static mode, the dynamic behaviors of ions during polarization has shown significantly difference with and without solvent molecules. Table IV-4 shows the comparison of the calculated average molecular weight for different electrolytes.

<table>
<thead>
<tr>
<th>m/z [ g·mol⁻¹]</th>
<th>SLG</th>
<th>CDC-1nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>From pzc to positive potentials</td>
<td>-338</td>
<td>+325</td>
</tr>
<tr>
<td>From pzc to negative potentials</td>
<td>0</td>
<td>+153</td>
</tr>
</tbody>
</table>

Table IV-4: The calculated molecular weight per charge for neat IL and solvated IL electrolytes.

As previously mentioned, the charge storage mechanism of EMImTFSI ionic liquid on SLG at the positive and negative charge region are different. Based on calculation, under positive polarization, a cluster which is mixed of cation and anion expressed as [EMIm₁.₅₈, TFSI₀.₅₈]⁺ with a net charge of 1, desorbed from single layer graphene; from pzc to negative charge, the ion rearrangement is responsible for the charge storage of SLG. This result is consistent with the EIS analysis of the more negative pzc of SLG in EMImTFSI due to the strong correlation between EMIm⁺ cation and SLG. The change of preferred orientation of EMIm⁺ cation by applying a negative potential is aligned with simulation work. As the solvent molecules were added, counter-ion adsorption was observed on negative and positive polarization. Differently from IL electrolyte, the solvent partially screens the ion electrostatic interactions between cations and anions, resulting in less number of ion pairs and more mobile ions. In addition, the long range electrostatic force between charged electrode surface and ionic liquids has been found to create thicker double layer which can limit the ion movements at the interface in neat IL electrolyte.

Since SLG has been served as a 2-D carbon-based platform to study the ion response during polarization, the comparison of the EQCM results with 3-D porous carbon also shown in Table IV-3. For microporous carbon which has a pore size slightly
bigger than the ion size, it has been discovered by EQCM that counter-ion adsorption at high positive and negative charge density in ionic liquid with and without solvent molecules. For ionic liquid electrolyte, the ion responses of microporous carbon and SLG during polarization are different. Ions in confined or open space seems to have an impact on the charge storage mechanisms during polarization for ionic liquid electrolyte. On the other hand, for solvated ionic liquid, the ion dynamics in microporous carbon aligns with the SLG one with electrode mass increased at both positive and negative charge density. However, at negative charge density, cation adsorption occurred with up to almost 4 solvent molecules in microporous carbon. Instead, for SLG, the EMIm$^+$ adsorbed only with 1 solvent molecule. The difference of the ion responds is possibly due to the specific strong CH-$\pi$ intermolecular interactions and $\pi-\pi$ interaction of EMIm$^+$ and SLG,$^{49-51}$ which has not yet been found for amorphous carbons. Thanks to solvent molecules, this effect has been diminished by screening out the charges of ions. By using the two-dimensional SLG platform, the effect of solvent molecules has demonstrated without the limitation by the structure and morphology of porous carbon.

5. Conclusion

Following up the last study of ionic liquid on SLG, in this work, the effect of solvent toward SLG has been analyzed from static and dynamic aspects. The interface of SLG and solvated ionic liquid was characterized by EIS, then further investigated by Mott-Schottky method. The screening effect due to the solvent molecules increased the charged species in the electrolyte which significantly alter the capacitance of the SLG material. Particularly, the strong interactions between EMIm$^+$ cation and SLG was diminished. On the other hand, the charge storage mechanisms of SLG in solvated ionic liquid electrolyte exhibits different ion responses comparing to neat ionic liquid. Counter-ion adsorption was observed on both positive and negative polarization. The experimental results aligned with the classic electrical double layer theory based on planar electrode.

We believe the knowledge obtained from the experimental approach developed here will be help in designing carbon-based materials for various applications including energy storage (supercapacitors) but also capacitive deionization cell for water desalination, where counter-ion adsorption mechanism has to be favored to improve the desalination efficiency.$^{64,65}$
6. References

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34. Y. Han, S. Huang and T. Yan, J Phys Condens Matter, 2014, 26, 284103.


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Chapter V:
Use of EQCM Technique to Other Energy Storage Systems
Part 1: Unraveling the charge storage mechanism of Ti$_3$C$_2$Tx MXene electrode in acidic electrolyte

1. Introduction

Due to the crisis of climate change, more efficient energy conversion and storage devices are developed to meet the need in modern society. In addition to EDLCs, another category of materials that also exhibit higher power density compared with batteries is called pseudocapacitive materials. Different from EDLCs, pseudocapacitive materials store charges through surface confined, non-diffusion limited faradic reactions, resulting in higher energy densities than EDLCs. One interesting pseudocapacitive material family includes two-dimensional (2D) transition metal carbides, carbonitrides and nitrides called MXenes, discovered in 2011. During the past decade, MXenes have been identified as promising materials for pseudocapacitive energy storage applications due to their unique properties including high intrinsic electronic and ionic conductivity, highly accessible surface area and the presence of redox-active sites. 2D MXenes are commonly prepared by chemical etching of the A element of the MAX phases used as precursors, where M is an early transition metal, A represents elements from group 13 and 14 of the periodic table, and X is carbon and/or nitrogen. The general formula of MXenes is $M_{n+1}AX_nT_x$ ($n= 1$-$4$), where $T_x$ represents the termination groups originating from the synthesis process.

The most studied MXene material to date is Ti$_3$C$_2$Tx ($T_x= -F, -O, -OH$). Studies have shown that high volumetric capacitance can be achieved in aqueous electrolytes by cation-ion intercalation in between the MXene layers. In particular, Ti$_3$C$_2$Tx hydrogel films in H$_2$SO$_4$ electrolyte demonstrated a record volumetric capacitance of 1,500 F cm$^{-3}$, still delivering 800 F cm$^{-3}$ at a scan rate of 1 V s$^{-1}$. Following these exciting performances, numerous experimental and computational approaches were combined to study the charge storage mechanisms of a Ti$_3$C$_2$Tx electrode in the H$_2$SO$_4$ electrolyte. \textit{In situ} X-ray absorption spectroscopy (XAS) measurements have shown a change in the oxidation state of Ti during the electrochemical reactions in H$_2$SO$_4$ electrolyte, evidencing a pseudocapacitive charge storage mechanism based on the change of the
redox state of Ti as a result of proton intercalation. Protonation of oxygen functional groups was suggested by in situ Raman spectroscopy via reversible bonding/debonding reactions between hydronium ions and oxygen functional groups during the reduction/oxidation process. Ex and in situ XRD technique was frequently used to track the change of the interlayer distance in Ti₃C₂Tx layers upon cations and H⁺ intercalation. The results showed an expansion/shrinkage of MXene interlayer spacing during charge/discharge, which explained the diffusion-limitation behavior observed with a stacked Ti₃C₂Tx electrode. Figure V-1-1 is an example of Na⁺ ions intercalated/deintercalated in-between MXene layers resulting in a change of interlayer spacing with the help of ex situ XRD. In addition, molecular dynamics (MD) simulations proposed a rapid surface redox reaction in acidic electrolyte at the Ti₃C₂O₂/water interface between oxygen functional group and proton and a fast proton transfer process via water confined in-between the MXene layers. However, the main charge carrier responsible for the superior performance in acidic aqueous electrolytes has yet been experimentally identified.

![Figure V-1-1](image)

**Figure V-1-1:** (a) CVs for Ti₃CTₓ in a 1 M NaPF₆/EC-DEC electrolyte at a scan rate of 0.2 mV·s⁻¹. (b) Ex situ XRD patterns during the CV cycles. (c) Schematic illustration of the reaction mechanism of Ti₃CTₓ by electrochemical activation.

Furthermore, three possible EDL charging mechanisms have been proposed in the literature, namely counter-ion adsorption, co-ion desorption, and ion exchange. Thus, during negative polarization of MXene materials, an additional charging mechanism beyond the redox reaction of Ti could be either intercalation of cations (H⁺ and/or H₃O⁺), de-intercalation of anions (HSO₄⁻ and/or SO₄²⁻), or ion exchange. In this
work, EQCM will be used to identify the main charge carrier responsible of the charge storage mechanism of a Ti$_3$C$_2$T$_x$ MXene electrode in H$_2$SO$_4$ electrolyte, in combination with Molecular Dynamics simulations, in and ex situ XRD, and in situ XANES. This work has been done in collaboration with Antonella Iadecola (in situ XANES).

2. Materials and techniques

2.1 Materials

2.1.1 Ti$_3$C$_2$T$_x$ MXene preparation

Ti$_3$C$_2$T$_x$ was prepared by removing the Al atom layers from Ti$_3$AlC$_2$ (400 mesh, purchased from Carbon-Ukraine Ltd.) in an etching solution of HCl and LiF, similar to a previously reported process. Specifically, 2 g LiF salt (Fisher, Technical) dissolved in 40 ml of 9 M HCl (Fisher, Technical) served as the etchant, and 2 g of Ti$_3$AlC$_2$ powder was slowly added into the etching solution. After stirring for 48 h in a 35 °C water bath, the obtained multiple-layer Ti$_3$C$_2$T$_x$ suspension was centrifuged and washed with deionized water for several times until the suspension pH reached 6. Then, delamination of Ti$_3$C$_2$T$_x$ was achieved by sonication for 1 h in an ice bath under N$_2$ gas bubbling. Afterwards, the obtained mixture was centrifuged for 1 h at 3500 r.p.m. The dark supernatant was collected and dried via a freeze-drying method. The obtained Ti$_3$C$_2$T$_x$ powder was mixed with deionized water and used for preparing freestanding Ti$_3$C$_2$T$_x$ electrode by using a vacuum-filtering process. The thermal treatment used for 500-MXene and 600-MXene film was performed under Ar atmosphere with a rate of 10 °C min$^{-1}$. After reaching 500 and 600 °C, the samples were rapidly cooled down by using a high-power fan. After the samples being cooled off to room temperature, they were directly used for testing or stored in a glove box.

2.2 Characterization techniques

2.2.1 X-ray diffraction (XRD)

XRD and in situ high temperature (HT) XRD patterns of Ti$_3$C$_2$T$_x$ films were
recorded by a D4 and D8 diffractometer (Bruker, Germany), respectively, using a Cu Kα radiation. *In situ* HT XRD measurements were performed under N₂ atmosphere (100 ml·min⁻¹), with an annealing treatment up to 600 °C at a rate of 10 °C·min⁻¹. At each step, the temperature was held at certain values (e.g., 100 °C, 200 °C, etc.) for recording the XRD patterns. SEM images were made using a FEG-SEM (Jeol JSM 6700F, Japan). Raman spectra were collected on a LabRAM HR Evolution (HORIBA Jobin Yvon, France) Raman microscope with a 532 nm laser.

2.2.2 Temperature programmed desorption coupled with mass spectroscopy (TPD-MS)

The surface groups on the MXene material was characterized by this instrument. TPD-MS measurement was conducted under Ar atmosphere (100 ml·min⁻¹). Ti₃C₂Tx film was placed in a thermo-balance and heat up to 1200 °C at a rate of 10 °C·min⁻¹. The resulted decomposition products were monitored by online mass spectrometry (Skimmer, Netzsch, Germany).

2.2.3 X-ray absorption near edge structure (XANES)

*In situ* Ti K-edge (4790 to 5260 eV) XAS measurement was performed in the fluorescence mode with a passivated implanted planar silicon detector at the ROCK beamline at synchrotron SOLEIL (France) with the help of Antonella Iadocella. 3-electrodes set-up was used for the test, a Kapton tape with deposited Ti₃C₂Tx MXene served as the working electrode, an over-capacitive YP50F film and a Hg/Hg₂SO₄ as the counter and reference electrode, respectively. MXene electrode was held on each of the selected potentials controlled by a VMP3 potentiostat (Biologic) for 40 mins to collect *in situ* XAS spectroscopic data. The Ti K-edge energy was calibrated using Ti foil before and after measurement.

2.2.4 Electrochemical quartz crystal microbalance (EQCM)

The working principle of EQCM can be found in Chapter II. In this part a, BioLogic 1-in.-diameter Au-coated quartz crystal (oscillating frequency, f₀, 5 MHz)
was coated using a precise pipette (Gilson PIPETMAN Classic P20) with a slurry containing 80 wt.% of active material MXene powder, 20 wt.% of polyvinylidene fluoride (Arkema) binder in N-Methyl-2-pyrrolidone (Sigma-Aldrich). The coated quartz crystal was placed on a PTFE holder in which the coated side was orientated toward the reference, and the counter electrode served as the working electrode in a 3-electrode set-up. The counter electrode was a platinum wire. The Hg/Hg$_2$SO$_4$ was used as a reference electrode placed between working and counter electrodes. Three electrodes were set in a glassware and immersed in 3 M H$_2$SO$_4$ aqueous electrolytes. All the EQCM electrochemical measurements were carried out by a Maxtek RQCM system combined with Autolab PGSTAT101. The EQCM data were treated based on the Sauerbrey’s equation.

2.3 Molecular dynamics (MD) simulation

Molecular dynamics is a computational method which is meant to simulate the movement state of molecules and atoms across a time period. The behavior of the system's evolution over time is investigated from a dynamic perspective. Generally, the tracks of molecules and atoms are obtained by numerically solving the second Newton's law of motions for molecules experiencing a Lennard-Jones potential. In the energy storage field, MD simulation has opened up new insights regarding the charging dynamics of ions nearby the electrode surface. For instance, it is useful to calculate the transport properties of molecules and ions. A study has shown that the volumetric changes of the electrode materials and the ion arrangement inside the electrode materials during charging/discharging can be observed by MD simulation. As a result, in this work, MD simulation is used to give a comprehensive insight of the charge storage mechanisms of Ti$_3$C$_2$T$_x$ MXene.

The simulation system is constituted by MXene electrode layers and 3 M H$_2$SO$_4$ aqueous electrolyte. The dynamic and structural properties of two kinds of MXene (P-MXene and 500-MXene) electrode and aqueous electrolytes were detailed studied. Four layers of MXene layer were constructed and immersed in a 3 M H$_2$SO$_4$ electrolyte, as schematically shown in in Figure V-1-2. The size of the simulation cell was $12.0 \times 4.0 \times 10.0$ nm$^3$ and the periodic boundary condition (PBC) was set in all three directions. Different initial c-LPs were set at the initial state, and the MXene electrode layer were all kept free during the simulation.
Figure V-1-2. Schematic representation of the simulation model, inner four layers were Pristine-MXene.

The simulations were performed with LAMMPS molecular dynamics code package\(^{21}\) and the ClayFF force field was employed to determine the interaction between the atoms\(^{22}\). The relevant force field parameters could be found in a previous work.\(^{23-25}\) Canonical ensemble (NVT) with 300 K target temperature was utilized. The particle-particle particle-mesh scheme in k-space was utilized to calculate the long-range electrostatic interactions. All simulations were performed with a long enough time period of 3 ns to ensure that the structure adequately converged.

### 2.4 Electrochemical measurements

The electrochemical performances of MXene electrodes were conducted using 3-electrodes Swagelok cell, where 10 mm-diameter disks of freestanding Ti\(_3\)C\(_2\)T\(_x\) films (mass-loadings around 1.9 to 2.1 mg·cm\(^{-2}\)) were used as the working electrodes, Hg/Hg\(_2\)SO\(_4\) as the reference electrode, and over-capacitive YP50F film as the counter electrode. 3 M H\(_2\)SO\(_4\) was used as the electrolyte. Electrochemical tests were recorded by a VMP3 potentiostat (Biologic). After pre-cycling at 50 mV·s\(^{-1}\) for 50 cycles, the cells were tested at the scan rates ranging from 50 to 1000 mV·s\(^{-1}\). EIS measurement was recorded with the 10 mHz – 100 kHz frequency range with a potential amplitude of 10 mV.
3. Results

3.1 MXene material characterization

As mentioned in the experimental part, pristine Ti$_3$C$_2$Tx MXenes (termed as P-MXene) used in this study were prepared by etching Ti$_3$AlC$_2$ precursor in a mixed LiF/HCl solution (details can be found in section 2.1.1). X-ray diffraction (XRD) patterns (Figure V-1-3a) show the disappearance of the characteristic peaks of the Ti$_3$AlC$_2$ MAX phase after etching, together with the addition of new sets of (00l) peaks, evidencing the formation of Ti$_3$C$_2$T$_x$ MXene.\textsuperscript{26} It is worth noting that the (002) peak position of P-MXene is at 6.94°, corresponding to a c lattice parameter (c-LP) of 25.5 Å. SEM analysis (Figure V-1-3b) shows that the layered structure of Ti$_3$C$_2$T$_x$ MXene is preserved.

![Figure V-1-3: (a) XRD patterns of Ti$_3$AlC$_2$ MAX phase and Ti$_3$C$_2$T$_x$ MXene. (b) Cross-section SEM image of MXene film of P-MXene.](image)

As previously reported, the surface termination groups of MXene materials depend on the synthesis conditions.\textsuperscript{27, 28} Therefore, the surface termination groups of MXene films were analyzed by TPD-MS. TPD-MS analysis was conducted not only to analyze the surface chemistry, but also to characterize the thermal stability of the Ti$_3$C$_2$T$_x$ MXene film in the 25-1200 °C temperature range. From Figure V-1-4a, two substantial weight losses were observed in the temperature ranges of 100-600 °C and 800-1000 °C, respectively. The first weight loss corresponds to the removal of intercalated water and -OH termination groups, while the second one is mainly due to the irreversible structural transformation of Ti$_3$C$_2$T$_x$, such as reported in previous
The total weight loss of P-MXene at 600 °C was around 7.1 wt.%, including 3.9 wt.% of H₂O and 2.8 wt.% of -OH termination groups. In other words, the weight loss of H₂O and -OH accounted for 94% for the total weight loss up to 600 °C. As observed, water was almost fully removed at 300°C while -OH groups at 600°C. A weight-loss peak was observed at about 120°C for water and at 350°C for -OH groups.

To examine the relationship between the surface termination groups and the interlayer spacing of MXene material, in situ XRD studies were achieved during heating of the P-MXene sample. From Figure V-1-4b, the (004) peak positions of MXene film shifted significantly to higher degrees when the annealing temperature was increased up to 300 °C, which indicated a dramatic decrease of c-LP. Further annealing from 300 to 600 °C had less impact on reducing c-LP. Combining the XRD and TPD-MS results, one can conclude that the rapid decrease of c-LP on heating below 300 °C is associated with the removal of pre-intercalated H₂O.

**Figure V-1-4:** (a) TPD-MS measurements at temperature range up to 1200 °C. (b) *In situ* XRD patterns during heating of Ti₃C₂Tx MXene film.

To study the roles of H₂O and -OH termination groups on the charge storage mechanism in an acidic electrolyte, two different samples annealed at 500 °C (noted as 500-MXene) and 600 °C (noted as 600-MXene) were prepared and characterized by XRD, Raman and SEM. As shown in Figure V-1-5a and 5b, the layered morphology was well maintained for both samples. Moreover, the typical set of (00l) peaks characteristics of 2D MXenes were still observed (Figure V-1-5c) and no noticeable changes were evidenced from Raman spectra (Figure V-1-5d). It can be assumed that the annealing treatment under the inert atmosphere (Ar) up to 600 °C did not degrade the 2D structure and the chemical composition of titanium carbide; instead, the amount
of pre-intercalated H$_2$O and -OH termination groups were modified, as reflected on the enhanced peak intensity of the XRD peaks. This is in line with the previous results that the 2D nature and composition of titanium carbide were not affected by annealing treatment up to 600 °C.$^{29-31}$ Based on the XRD patterns, the c-LP of the P-MXene, which contains H$_2$O molecules and -OH termination groups in-between MXene layers, is 25.5 Å. On the other hand, c-LP is 21.2 Å and 20.7 Å for 500-MXene and 600-MXene, respectively. As previously mentioned, after annealing at 300 °C, the H$_2$O molecules were removed from MXene layers (see Figure V-1-4a). For 500-MXene sample, the H$_2$O molecules in between the MXene layers were completely removed with 5% of -OH termination groups remaining. For the 600-MXene, as shown by TPD-MS, both H$_2$O and -OH were removed.

![Figure V-1-5](image)

**Figure V-1-5:** (a) and (b) is cross-section SEM image of MXene film of 500-MXene and 600-MXene sample, respectively. XRD patterns (c) and Raman tests (d) of P-MXene, 500-MXene, and 600-MXene.

### 3.2 Electrochemical study

All the samples were pre-cycled for 50 cycles at 50 mV·s$^{-1}$. The cyclic voltammetry (CV) profiles are presented in Figure V-1-6a at a scan rate of 50 mV·s$^{-1}$ after pre-cycling (the reason why the samples were pre-cycled will be explained later). A set of redox peaks is visible at around -0.75 V (vs. Hg/Hg$_2$SO$_4$) for P-MXene and 500-MXene such as expected in such electrolyte,$^{32}$ while these redox peaks vanished for 600-MXene.
The gravimetric specific capacitance was calculated from CV profiles where 325 F·g⁻¹, 343 F·g⁻¹, and 127 F·g⁻¹ for P-MXene, 500-MXene, and 600-MXene, respectively. While both P-MXene and 500-MXene exhibited the expected electrochemical signature in the H₂SO₄ electrolyte, the capacitive signature of the 600-MXene sample was strongly affected, as can be seen from the disappearance of the redox peaks around -0.75 V (vs. Hg/Hg₂SO₄). From this result, we can suspect the presence of -OH termination groups - with have been removed from the 600-MXene sample - has an impact on the pseudocapacitive behavior of MXene materials in acidic electrolytes.

Figure V-1-6: (a) CV profiles of three MXenes at a scan rate of 50 mV·s⁻¹ after 50 cycles. (b) and (c) are the initial first 50 cycles of P-MXene and 500-MXene at a scan rate of 50 mV·s⁻¹, respectively. Furthermore, we observed a difference between P-MXene and 500-MXene in the first 50 cycles. Figure V-1-6b and 6c show that the electrochemical capacitance of 500-MXene sample gradually increased and stabilized after 10 cycles to reach similar values as P-MXene. However, the P-MXene did not have obvious changes in the capacitive signature even during the first 10 cycles. To investigate the difference between the electrochemical behaviors of P-MXene and 500-MXene, electrochemical impedance spectroscopy (EIS) experiments had been made. Figure V-1-7a and 7b show the Nyquist plots recorded at the open-circuit potential (OCP) before and after cycling for P-MXene and 500-MXene.

The EIS results were treaded by separating the real and imaginary parts of the capacitance. The real and imaginary part were calculated by using equation V-1-1 and 2.

\[
C'(\omega) = \frac{-Z''(\omega)}{2\pi f|Z(\omega)|^2}
\]  
(Eq. V-1-1)
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\[ C''(\omega) = \frac{Z'(\omega)}{2\pi f|Z(\omega)|^2} \]

(Eq. V-1-2)

where \( Z'(\omega) \) and \( Z''(\omega) \) are the real part and imaginary part of the electrochemical impedance \( (Z(\omega)) \), respectively. Both the real and imaginary parts of the impedance of the 500-MXene sample decreased significantly after cycling comparing with P-MXene sample. Also, the real part of capacitance increased for 500-MXene, while almost no changes were observed after electrochemical cycling for P-MXene. The difference between P-MXene and 500-MXene being the presence of \( \text{H}_2\text{O} \) molecules between the MXene layers, one can assume that during the first 10 cycles for 500-MXene, \( \text{H}_2\text{O} \) molecules intercalated back between the MXene layers, leading to the recovery of the capacitive signature. Such intercalation of water molecule after removal by thermal heating could be ensured by the presence of \( {-\text{OH}} \) groups in the 500-MXene sample. Such intercalation of water molecule also coincides with the EIS results showing that both the ionic conductivity and capacitance have been improved after the \( \text{H}_2\text{O} \) molecules intercalated during cycling the 500-MXene sample. This further indicates the key role of the \( \text{H}_2\text{O} \) in-between MXene layers for the electrochemical storage of MXene in acidic electrolyte.

**Figure V-1-7:** (a) and (b) is the Nyquist plot at OCP before (black) and after (red) electrochemical cycling of P-MXene and 500-MXene, respectively. (c) and (d) The real part of the capacitance calculated from EIS data for P-MXene and 500-MXene, respectively.
3.3 Determination of charge storage mechanisms of MXene materials

For MXene materials, the total capacitance comes from different charge storage mechanisms which we called pseudocapacitive and EDL behaviors. To better distinguish between these two contributions, several analysis techniques were used.

3.3.1 In situ XANES analysis

To characterize the redox-based pseudocapacitive behavior of Ti$_3$C$_2$, we conducted in situ XANES at the Ti K-edge of P-MXene within the full potential range (~1 V). Spectra were recorded at various potential versus Hg/Hg$_2$SO$_4$ electrode using chronoamperometry technique. The valance state of Ti was calculated from the position of Ti edge energy at the half-height of normalized XANES spectra.

Figure V-1-8: (a) In situ XANES analysis of P-MXene electrode in 1 M H$_2$SO$_4$ electrolyte. The reference electrode using in the setup is Hg/Hg$_2$SO$_4$. (b) CV profile of P-MXenes at a scan rate of 50 mV·s$^{-1}$ in 3 M H$_2$SO$_4$. The shaded part indicates the estimated proportion of charge stored by EDL-like mechanisms.

From Figure V-1-8a, the Ti K-edge shifted to lower energy during negative polarization, indicating a decrease of Ti oxidation state. The maximum energy shift is 0.58 eV. Based on the linear dependence between Ti average oxidation state and the edge energy position$^{33,34}$, the change of average oxidation state of Ti was estimated to be about 0.134 electron per Ti atom over a 0.9 V potential window, corresponding to a specific capacitance value of 213 F·g$^{-1}$. Given that the specific capacitance of P-MXene measured in Swagelok cell is 325 F·g$^{-1}$, the stored charge involving pseudocapacitive behavior (change of the oxidation state of Ti) accounts for about 65% of the total charge.
This result is similar as the estimation from the CV profile as shown in Figure V-1-8b, where the EDL contribution can be estimated to 43% of the total charge, leaving 57% to the pseudocapacitive behavior. Also, the Ti oxidation state barely changed when the MXene electrode negatively polarized from -0.2 to -0.5 V (vs. Hg/HgSO₄). These suggest that the charge storage of P-MXene in H₂SO₄ aqueous electrolyte was partially achieved by a pseudocapacitive mechanism.

### 3.3.2 EQCM analysis

During negative polarization, the possible ion fluxes to balance the charge due to the redox reaction of Ti could be intercalation of cations (H⁺ and/or H₃O⁺) or de-intercalation of anions (HSO₄⁻ and/or SO₄²⁻), or ion exchange. To get a better insight about the ions involved in the charge storage mechanism, electrochemical quartz crystal microbalance (EQCM) study was performed on a Ti₃C₂Tx MXene-coated golden quartz crystal in a 3 M H₂SO₄ electrolyte. For consistent results, few cycles were run before starting EQCM measurements, to start from stable, reproducible electrochemical signatures.

![Figure V-1-9: The recorded frequency shift versus mass.](image)

The calibration test was performed in 0.1 M CuSO₄ mixed with 1 M H₂SO₄ by applying a constant current of 5 mA for 120 seconds. The result of the recorded frequency shift versus the calculated mass based on Faraday’s law is shown in Figure V-1-9. According to Sauerbrey’s equation, the calibration factor is calculated to be 14 ng·Hz⁻¹ or 11.02 ng·Hz⁻¹·cm⁻² (for bare Au, it is calculated to be around 16 ng·Hz⁻¹·cm⁻²) taking into account the Au crystal electrode surface of 1.27 cm².
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Figure V-1-10: (a) CV profile and EQCM frequency response and (b) motional resistance charge during the polarization of P-MXene on a gold substrate in 3 M H$_2$SO$_4$ recorded at 10 mV·s$^{-1}$.

For the EQCM measurement for P-MXene sample, a narrow potential window of -0.25 to -0.55 V (vs. Hg/Hg$_2$SO$_4$) was selected to avoid any H$_2$ evolution during cycling. Figure V-1-10a shows the CV and the frequency response of MXene at 10 mV·s$^{-1}$, where the red arrows indicate the direction of the scan. The start and end point of the frequency scan loop overlapped together, which means no overall mass loss or gain within a full cycle occurred (reversible process from the mass change point of view) such as expected for an active material under steady-state condition. Therefore, the hysteresis observed between positive and negative scans is likely due to the different kinetics of ion adsorption and desorption processes.$^{35,36}$ On the other hand, during the polarization, the maximum change of the motional resistance was 15 Ω (Figure V-1-10b) which is less than 0.7 %. This result validates the gravimetric approach during the test. Since the Sauerbrey’s equation can be applied, the calculated mass change versus charge is plotted in Figure V-1-11.

A previous EIS study demonstrated that the potential of zero charge (pzc) of similar Ti$_3$C$_2$T$_x$ MXene in H$_2$SO$_4$ electrolyte is around -0.2 V vs. Hg/Hg$_2$SO$_4$ reference electrode.$^{37}$ The OCV we used in this study is -0.25 V vs. Hg/Hg$_2$SO$_4$. To identify the species of the ion adsorbed on the electrode surface, then intercalated in-between MXene layers, the negative scan was chosen to be processed. From the potential range of -0.25 to -0.55 V (vs. Hg/Hg$_2$SO$_4$), where a nearly linear increase of mass versus accumulated charge was observed. This corresponds to a change in the oxidation state of Ti, as shown in Figure V-1-8a, as a result of the pseudocapacitive mechanism.
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Figure V-1-11: Electrode mass change versus charge during the polarization of P-MXene on a gold substrate in 3 M H₂SO₄ recorded at 10 mV·s⁻¹.

According to Faraday’s law, the average molecular weight per charge was calculated to be 13±3 g·mol⁻¹, which is a bit lower than the molecular weight of hydronium H₃O⁺ (19 g·mol⁻¹). Based on literatures, proton is suspected to be the main charge carriers for charging MXene materials. As a result, based on EQCM results, while charging the P-MXene material from OCV to negative potential in acidic aqueous electrolyte, the main charge carrier responsible for the pseudocapacitive behavior is assumed to be a mixture of H₃O⁺ hydronium and proton. Based on their respective molar weights, the contribution of proton and hydronium during charging negatively MXene materials can be estimated to 35 % and 65 %, respectively. As a result, a mixture of hydronium ions intercalated into MXene layers together with protons transported via a Grotthuss mechanism, suspected to occur in-between MXene layers during negative polarization.

<table>
<thead>
<tr>
<th>C-lattice parameter (Å)</th>
<th>Before cycling in H₂SO₄</th>
<th>After cycling in H₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine-MXene</td>
<td>25.5</td>
<td>27.5</td>
</tr>
<tr>
<td>500-MXene</td>
<td>21.2</td>
<td>27.5</td>
</tr>
<tr>
<td>600-MXene</td>
<td>20.7</td>
<td>20.7</td>
</tr>
</tbody>
</table>

Table V-1-1: Calculated c-lattice parameter based on in situ XRD patterns for pristine-MXene, 500-MXene, and 600-MXene samples before and after cycling in 3 M H₂SO₄.

The EQCM result is aligned with the in situ XRD result (Table V-1-1). The
calculated c-LP of P-MXene and 500-MXene increased after cycling which corresponds to not only protons intercalated into MXene layers, but also hydronium ions.

### 3.3.3 MD simulation

MD simulations were carried out to get a further understanding of the charge storage mechanism in P-MXene and 500-MXene samples. Ti$_3$C$_2$O$_{0.9}$F$_{0.8}$(OH)$_{0.3}$ and Ti$_3$C$_2$O$_{1.185}$F$_{0.8}$(OH)$_{0.015}$ materials were used as P-MXene and 500-MXene samples, respectively. The stoichiometric proportion of the -F, =O, -OH functional groups were estimated according to our TPD-MS results (Figure V-1-4a) and previous reports.$^{27}$ Knowing that both P-MXene and 500-MXene have pre-intercalated H$_2$O molecules in-between MXene layers, the equilibrium c-LPs are calculated to be 26.7 Å for the P-MXene and 26.0 Å for the 500-MXene, closed to the one obtained from XRD.

**Figure V-1-12:** Side view of (a) P-MXene and (b) 500-MXene layers with surrounding electrolytes. Top view of the water molecules in-between the (c) P-MXene and (d) 500-MXene layers, MXene atoms are not shown here. (e) and (g) Close-up top view and side view of water molecules distribution in-between the p-MXene and 500-MXene layers. (f) Comparison of probability profiles of dipole orientation of water molecules inside p-MXene and 500-MXene layers, $\theta$ gives the angle between water molecular dipole moment and electrode surface normal.

Figures V-1-12a and 12b show the side view of the two MXene layers for P-
MXene and 500-MXene samples, respectively. For the P-MXene, the higher content of -OH existing on the outermost surface significantly disturbs the hydrogen bond network of the interlayer molecules (Figure V-1-12c and 12e). In the case of 500-MXene, water molecules and hydronium ions form a compact and well-organized layer (Figure V-1-12d and 12g) between MXene layers. The hydrogen-bonded water network provides a rapid proton transfer, possibly via a Grotthuss mechanism, during the electrochemical process. The probability profiles P(θ) of the dipole orientation of the interlayer water molecules for the P-MXene and 500-MXene samples are shown in Figure V-1-12f. It shows that the dipole orientation was more concentrated around 90° for the case of 500-MXene, suggesting a flat orientation (nearly parallel to the MXene layers). Differently, a more disorder distribution of H₂O was found for P-MXene. These results suggest that the formation of a hydrogen bond network containing well-organized H₂O layers in-between the MXene layers for 500-MXene, thus giving further evidence to the intercalation of water molecules for P-MXene and 500-MXene samples.

4. Discussions

Figure V-1-13: Gravimetric specific capacitances and capacities vs. various scan rates.

Regarding the role of -OH termination group, 600-MXene which has none -OH termination groups show poor electrochemical performance comparing with P-MXene and 500-MXene sample (Figure V-1-6a and V-1-13). The absence of -OH termination group seems to be related to the intercalation of H₂O molecules which result in much less charges stored in-between MXene layers. From Table V-1-1, the calculated c-LP of
600-MXene remains the same before and after cycling proves that no H$_2$O molecules intercalated into MXene layers. From MD simulation work, we observed a well-organized network of H$_2$O molecules in between MXene layers were formed after cycling for 500-MXene sample. However, for the P-MXene, the pre-intercalated H$_2$O molecules in-between MXene layers did not orientate in orders. The difference between the structures of the H$_2$O network in-between MXene layers could be the key factor for the power performance of MXene materials. Based on Figure V-1-13, the power performance of P-MXene has been improved by constructing an organized H$_2$O network as 500-MXene sample. Thanks to the H$_2$O network in-between MXene layers, better proton transportation, possibly via a Grotthuss mechanism, can be achieved.

5. Conclusions

In this study, a combination of experimental (electrochemical measurements, \textit{ex situ} and \textit{in situ} techniques) and molecular dynamics simulation works was conducted to understand the charge storage mechanisms of Ti$_3$C$_2$Tx MXene in acidic aqueous electrolyte. Pristine and heat-treated MXene have been prepared and characterized by XRD and Raman confirming the 2D morphology. TPD-MS was used to analyze the remaining surface termination groups of the heat treated MXene samples. The surface termination groups have further shown a great impact on the electrochemical performance of MXene materials due to the lack of H$_2$O pre-intercalation in-between MXene layers. For the charge storage mechanisms, \textit{in situ} XANES confirms the charge of valance state of Ti which corresponds to the pseudocapacitive behavior of MXene materials. EQCM has shown that the responsible ionic species to store charges in-between MXene layers are H$_3$O$^+$ hydronium ions and protons. The results from \textit{in situ} XRD and MD simulation confirm with the EQCM result as well. While this work focuses on Ti$_3$C$_2$Tx MXene in the H$_2$SO$_4$ electrolyte, it should apply to other kinds of MXenes, such as Ti$_2$CT$_x$, Nb$_2$C$_3$T$_x$, V$_2$C$_2$T$_x$, etc. The present work offers an opportunity to push further the high-rate performance of MXenes electrodes in aqueous electrolytes.
6. References

Chapter V: Use of EQCM Technique to Other Energy Storage Systems- Part 1


37. Z. Lin, Université de Toulouse, Université Toulouse III-Paul Sabatier, 2017.

Part 2: The Charge Storage Mechanisms of Cathode Material for Aqueous Calcium-Ion Battery Application

1. Introduction

To satisfy the demand for portable electronics and the electric vehicle market, the development of rechargeable batteries technique plays a significant role. Unlike EDLCs, batteries store the energy through faradaic reactions in the bulk of electrode materials in contact with electrolytes, usually along with chemical interconversions and phase changes, providing high energy densities up to 300 Wh·kg⁻¹ for the best Li-ion batteries. In the past decades, considerable efforts have been devoted to monovalent-ion batteries beside Li⁺ such as Na⁺, and K⁺ intercalation materials. Recently, researchers have started to pay more attention to multivalent charge carriers. Among them, various divalent metal ions have been proposed as alternatives to monovalent ions, including Ca²⁺, Mg²⁺, or Zn²⁺. The adoption of divalent ions results in a potential improvement in the specific capacity and hence to a significant boost in the energy density of cells compared to monovalent ion cells since divalent metal ion can double the charge exchanged per mole during intercalation/deintercalation. Furthermore, the abundance of these divalent elements largely reduces the cost of storage systems and relieves the stress of the lack of lithium resources.

Nevertheless, multivalent-ion electrodes suffer from slow cation diffusion because of the strong interactions between the multivalent-ions and the negatively charged active materials. Thanks to the low charge density of Ca-ion (see Table V-2-1), this problem has been effectively alleviated in Ca-ion intercalation electrodes compared to the other multivalent-ion materials.

<table>
<thead>
<tr>
<th>Ionic Radius, Å</th>
<th>Li⁺</th>
<th>Na⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Al³⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrated Ionic Radius, Å</td>
<td>1.58</td>
<td>1.83</td>
<td>2.6</td>
<td>3.0</td>
<td>3.37</td>
</tr>
<tr>
<td>Polarization Strength** (10⁴ pm⁻²)</td>
<td>2.16</td>
<td>1.11</td>
<td>1.92</td>
<td>4.73</td>
<td>5.66</td>
</tr>
<tr>
<td>Charge density, e Å⁻³</td>
<td>0.54</td>
<td>0.23</td>
<td>0.49</td>
<td>1.28</td>
<td>4.55</td>
</tr>
</tbody>
</table>

Table V-2-1: Comparison of different characteristics of monovalent and multivalent ions. The polarization strength \(P\) is calculated as \(P = q \cdot r^{-2}\), where \(q\) is the charge...
number of the cation and \( r \) is the ion radius.\(^\text{10}\)

Differently from non-aqueous systems, the charge storage mechanism in aqueous electrolyte is more complex because of the possible contribution of proton or hydronium ions together with the alkali cation. For instance, Sun \textit{et al.} reported the simultaneous insertion/de-insertion reactions of H\(^+\) and Zn\(^{2+}\) at the positive MnO\(_2\) electrode of aqueous Zn-MnO\(_2\) battery.\(^\text{13}\) Hyoung \textit{et al.} studied K\(_{0.31}\)MnO\(_2\)·0.25H\(_2\)O as cathode material in aqueous Ca-ion batteries.\(^\text{14}\) They confirmed that Ca\(^{2+}\) was the main contributor to the electrochemical reaction while hydronium ions were also proposed to co-intercalate during the reaction.

In this work, EQCM has been used to investigate the charging/discharge process of the cathode material for Ca-ion battery. Ca\(_{6}\)V\(_{16}\)O\(_{16}\)·7H\(_2\)O (CVO) positive electrode material is prepared using a molten salt synthesis route (MSM). Such MSM synthesis method can be extended to the preparation of a large variety (Li\(^+\), Na\(^+\) besides Ca\(^{2+}\)) of ion intercalated vanadium oxides all with large interlayer distance in a very short time with high yield.\(^\text{15, 16}\) The experiments were conducted in 4.5 M Ca(NO\(_3\))\(_2\) aqueous electrolyte but different pH. This work has been made in collaboration with Liyuan Liu.

2. Experimental

2.1 Materials

2.1.1 Ca\(_{6}\)V\(_{16}\)O\(_{16}\)·7H\(_2\)O (CVO) synthesis

The sample was prepared by a molten salt method (MSM). The MSM synthesis method uses, chlorides- and sulfates-based molten salt served as a solvent for preparing complex oxides. Typically, a mixture of the reactants and salt is heated above the melting temperature of the salt which the salt will start melting. When the salt melts, the product forms in particles. The characteristics of the product powder are controlled by selecting the temperature and duration of the heating. Then, the reacted mass is cooled to room temperature and washed with an appropriate solvent to remove the salt. The complex oxide powder is obtained after drying.
Chapter V: Use of EQCM Technique to Other Energy Storage Systems - Part 2

Figure V-2-1: Realistic and schematic representation of the molten salt method synthesis process. (a) The precursor was added when salts were heated to the molten state. (b) The sample was removed from the furnace after reacting for a few minutes. (c) The samples were obtained after washing with DI water.

In this work, 6 g of nitrate powder (Ca(NO$_3$)$_2$·4H$_2$O:NaNO$_3$ = 1:1 in weight ratio) mixed in a quartz crucible were transferred into the furnace at a temperature of 450°C in the air to get colorless molten salt. 0.2 g of V$_2$O$_5$ powder was then added to the molten salt. After 3.5 minutes of hold time, the product inside the crucible was quenched in the air. The as-synthesized product was thoroughly washed with distilled water to remove nitrate powder in excess and finally freeze-dried. Figure V-2-1 depicts the realistic and schematic representation of the synthesis route.

The chemicals including Ca(NO$_3$)$_2$·4H$_2$O (99 %), LiNO$_3$ (99 %), NaNO$_3$ (99 %), and KNO$_3$(99 %) are obtained from Sigma Aldrich. V$_2$O$_5$ (99.6 %) is from Aldrich, and VCl$_3$(97 %) is from Alfa Aesar.

2.2 Physical characterization

In this work, X-ray diffraction (XRD) pattern was collected using a D4 ENDEAVOR diffractometer (Bruker, Germany) equipped with Cu Kα radiation (λ = 0.154 nm). Data were collected in the 5 to 50 2θ angle range using 0.0099° steps in 1
hour. The patterns were refined using the Profile matching method implemented in the Jana2006 software.

The morphology and composition of the sample were observed with a Scanning Electron Microscope (SEM) JSM 7100F (JEOL, Japan) at an accelerating voltage of 20 kV with energy-dispersive X-ray spectroscopy (EDX) capabilities. Thermo Gravimetric analysis (TGA) was performed in an alumina crucible using an ATG-ATD Setaram TGDTA 92 in Nitrogen using a ramping rate of 10 °C·min⁻¹.

2.3 Electrochemical measurement

For the electrochemical performance evaluation, 3-electrode Swagelok® cells were assembled in ambient conditions. In this setup, the counter electrode was YP-50 (Kuraray, Japan) and the reference electrode was a saturated calomel electrode (SCE). To prepare electrolyte, 4.5 M Ca(NO₃)₂ was dissolved in deionized water firstly and then saturated Ca(OH)₂ was added inside to increase the pH to 10. Finally, additional Ca(NO₃)₂·4H₂O was added to ensure the concentration of Ca(NO₃)₂ still keep 4.5 M. The electrolyte was then purged with argon gas before using. The separator was two layers of 260 μm-thick porous borosilicate glass fibers (Whatman GF/A). To prepare the working electrode, 70 wt.% active material and 20 wt.% conductive carbon (Super-P) were mixed homogeneously first and then added inside a bottle containing 10 wt.% of polyvinylidene fluoride (PVDF) binder in N-Methyl-2-pyrrolidone. The active material mass loading is around 2–4 mg·cm⁻². Multichannel VMP3 electrochemical working station (Biologic, S.A.) has been used for all the electrochemical tests. (see Chapter II) The Electrochemical impedance spectroscopy measurement was scanned from 1 MHz to 0.01 Hz.

For sample preparation for EQCM measurements, conducting carbon (Super-P) was added to the slurry to improve the electrical conductivity of the tested electrode. The EQCM data were treated with Sauerbrey’s equation. Similarly, to previous chapters, the sensitivity factor of the coated quartz was obtained by performing a Cu deposition experiment. Few cycles were run before starting EQCM measurements, to start from stable, reproducible electrochemical signatures.
3. Results

3.1 CVO material characterization

1D CVO compounds were prepared in a mixture of calcium nitrate and sodium nitrate used as molten salt. SEM images from Figure V-2-2a show the 1D nano-ribbon morphology of the prepared CVO sample with lengths from 2 to 10 μm. These nano-ribbon structures are highly ordered with uniform shapes and flat surfaces. The ribbonlike morphology of CVO was confirmed by TEM (Figure V-2-2a) with diameters of 50–200 nm. The morphology of particles is directly related to the atomic structure itself. With MSM synthesis, the short reaction time is emphasized, and V$_4$O$_{11}$ and V$_2$O$_6$ strings grow rapidly along [010] direction. The thickness of the ribbon corresponds to the [001] direction grow relatively slow. As a result, 1D nano-ribbon morphology was formed.

Figure V-2-2b shows the X-Ray diffraction pattern, where the pattern was refined, and all peaks are well indexed with the CaV$_6$O$_{16}$·7H$_2$O (JCPDS card number: 01-084-2134). Additionally, it is found that the peaks are broadening, and the intensity is relatively weak. This corresponds to a typical nanocrystalline structure for the prepared CVO. The refinement of lattice parameters (a = 11.96 Å, b = 3.56 Å, c = 10.47 Å) leads to an interlayer spacing of 10.4 Å, which is larger than that of LiV$_3$O$_8$ (6.36 Å) and V$_2$O$_5$ (4.37 Å) and some other vanadium bronzes incorporating alkali metals.$^{17}$

To confirm the water content in our CVO material, TGA experiments were achieved under argon atmosphere. The hydrated calcium vanadate mineral CaV$_6$O$_{16}$·nH$_2$O has three distinct phases containing 9, 7 and 3 water molecules, respectively.$^{18}$ The result reveals a total weight loss of 20.5 % from room temperature to 400 °C. Two peaks can be clearly observed in the derivative thermogravimetric curve (DTG) shown in Figure V-2-2c. The first part which is from room temperature to 100 °C, a smaller weight variation 3.7 % weight loss corresponds to physisorbed water on the CVO material. The second weight loss from 100 to 200 °C is calculated to be 16.8 % of weight loss which is due to the crystal water in CVO sample. This value matches well with the theoretical content in the formula CaV$_6$O$_{16}$·7H$_2$O (17 wt.%).
Figure V-2-2: Characterization of CaV$_6$O$_{16}$·7H$_2$O (CVO) nanomaterial. (a) SEM image and TEM image, (b) X-ray diffraction pattern, (c) TGA result (d) EDX image and atom ration of calcium and vanadium element.

EDX analysis was also achieved to confirm the composition of the CVO particles (see Figure V-2-2d). Therefore, the final product can be written as CaV$_6$O$_{16}$·7H$_2$O. The presence of crystal water might due to the washing process at the end of the MSM synthesis process. This high content of crystal water might explain the large interlayer spacing of CVO sample since the interlayer distance of CaV$_6$O$_{16}$·7H$_2$O (10.4 Å) is larger than the partial dehydrated CaV$_6$O$_{16}$·3H$_2$O (8.08 Å) as reported.$^{19}$

3.2 Electrochemical characterizations

The prepared CVO samples were electrochemically tested in three-electrode Swagelok cells, where an over-capacitive activated carbon electrode was used as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode. The electrolyte was 4.5 M aqueous Ca(NO$_3$)$_2$ with pH equals to 2.3. Another alkaline aqueous electrolyte (pH = 10) with the same concentration of Ca(NO$_3$)$_2$ was prepared to tackle the problem of partial dissolution of CVO reported by literature.$^{20}$ A working potential window of ~ 1.3 V (from -0.7 V to 0.6 V vs. SCE, also 2.44 to 3.74 V vs. Ca$^{2+}$/Ca) which falls within the H$_2$O stability potential window) was obtained during
cyclic voltammetry (CV) experiments, achieved at 0.2 mV·s⁻¹ (Figure V-2-3a). A set of redox peaks is observed at -0.48 and -0.25 V vs. Ref, as the result of cation (Ca²⁺ in a first approach) intercalation/intercalation in the host structure. The initial three charge/discharge galvanostatic results are shown in Figure V-2-3b. The initial charge and discharge specific capacities are 203 mAh·g⁻¹ and 208 mAh·g⁻¹ respectively, at a current density of 0.3 C, corresponding to a 5.5 electrons redox process per Ca₆V₆O₁₆·7H₂O unit. The first three cycles are almost totally overlapped which indicate the high reversibility of the Ca²⁺ insertion/extraction process. A potential plateau is observed at -0.48 V vs. Ref during discharge, shifted down to -0.25 V vs. Ref during charge, resulting in a voltage hysteresis of about -0.23 V, consistent with the CV curves shown in Figure V-2-3a.

**Figure V-2-3:** (a) Initial five first CV cycles of Ca₆V₆O₁₆·7H₂O (CVO) recorded at 0.2 mV·s⁻¹, and (b) galvanostatic charge–discharge profiles at a current density of 0.3 C in 4.5 M Ca(NO₃)₂ aqueous electrolyte with Ca(OH)₂ to adjust the pH at 10.

To distinguish between Ca²⁺ and H⁺ intercalation, a comparison between the CV profiles of CVO samples in 4.5 M Ca(NO₃)₂ aqueous electrolytes at different pH (adjusted by addition of Ca(OH)₂) is shown in Figure V-2-4a. A similar electrochemical signature is observed whatever the electrolyte pH. However, the capacity of CVO in pH = 10 electrolyte was found to be slightly higher at various current densities (Figure V-2-4b). The lower capacity of CVO in acidic aqueous electrolyte might come from the replacement of part of the Ca²⁺ ion intercalation by proton or hydronium ion intercalation. EQCM measurements were further performed to study the ion fluxes and state about the charge storage mechanisms of CVO electrode in acidic and alkaline
aqueous electrolytes.

![Graphs](image)

**Figure V-2-4:** Electrochemical behavior of a CaV$_6$O$_{16}$·7H$_2$O (CVO) electrode in pH = 2.3 (4.5 M Ca(NO$_3$)$_2$) and pH = 10 (4.5 M Ca(NO$_3$)$_2$ + Ca(OH)$_2$) electrolytes. (a) CV plots recorded at a potential scan rate of 2 mV·s$^{-1}$ and (b) comparison of the discharged (reduction process) specific capacity versus various current density of the CVO electrode.

### 3.3 EQCM analysis

EQCM study was achieved using CVO electrode in the two electrolytes (pH = 2.3 and pH = 10), to get further information on the charge storage mechanism. The CVO material coated quartz was first used to obtain the calibration factor by conducting Cu deposition experiment. Based on Sauerbrey’s equation, the $C_f$ was calculated to be 5.08 ng·Hz$^{-1}$ (or 4.05 ng·Hz$^{-1}$ cm$^{-2}$ considering the electrode surface of 1.27 cm$^2$).

![Graphs](image)

**Figure V-2-5:** CV and EQCM frequency response (a) in pH = 2.3 aqueous electrolyte at 20 mV·s$^{-1}$ (b) in pH = 10 aqueous electrolyte at 10 mV·s$^{-1}$. 
Few cycles were run before starting EQCM measurements to start from the steady state. EQCM measurement of CVO sample in pH = 2.3 and 10 are shown in Figures V-2-5a and 5b, respectively. The red point indicates the starting point of the cycle. The starting and ending point of the cycle almost overlapped, indicating the absence of material dissolution occurred during cycling. The blue line represents the current response during charging/discharging. The CV profiles from EQCM measurements in pH = 2.3 and 10 aqueous electrolytes are similar to those recorded in Swagelok cells. More pronounce of redox peaks are observed around -0.43 and -0.25 V vs. Ref for CVO sample in alkaline aqueous electrolyte. The black and orange marks correspond to the associated frequency response measured by EQCM during positive and negative sweep, respectively. Both figures show a frequency raise from negative to positive potential (black lines) and the other way around for negative sweep (orange lines). In addition, there are almost no hysteresis observed between the positive and negative sweep for both EQCM results.

![Figure V-2-6](image_url)

**Figure V-2-6:** (a) and (b) is the change of motional resistance versus potential during polarization of a CVO electrode in pH = 2.3 and 10 aqueous electrolytes, respectively.

To examine the quality of the EQCM data, the motional resistance was tracked during the experiments. The recorded motional resistance results are shown in Figure V-2-6. For both acidic and alkaline aqueous electrolyte, the motional resistance is stable from 0 to -0.5 V (green shaded area), which is the potential range corresponding to redox peaks in CVs. This means the Sauerbrey’s equation is applicable in this potential range. However, the motional resistance is less stable on the positive potential (note: the Y-axis is zoomed). This might be due to the electrolysis of electrolyte at the small
amount of uncovered Au current collector of the quartz since Au is known for its high catalytic activity versus H₂O oxidation.²¹, ²² The oxygen bubbles due to the water electrolysis can affect the motional resistance. Also, the potential of water oxidation for pH = 10 alkaline aqueous electrolyte is around 0.64 V vs SCE which is close to our operating potential range. There might be small bubbles generated during cycling, which causes an unstable motional resistance at the positive potential. Nevertheless, the change of the motional resistance is relatively small (2 %), and the potential range which the redox reactions occurred is stable. As a result, the further calculation of the main charge carriers proceeds.

**Figure V-2-7:** Polarization of CVO electrode in pH = 10 aqueous electrolyte: (a) and (b) is the change of mass and current response versus potential and time, respectively. Black and orange lines show the weight change during positive and negative polarizations.

Figure V-2-7a shows the electrode mass change during polarization in pH = 10 aqueous electrolyte, calculated from Sauerbrey’s equation. During positive sweep corresponding to the oxidation of CVO, the mass decreased evidencing an ion deintercalation from the electrode (black line). Note that the weight increase at low potential is due to the cathodic current upon potential reversal which is indicated in the orange area in Figure Vb-7b. On the other hand, from positive to negative potential, ions intercalated into CaV₆O₁₆·7H₂O resulting in an increase in mass (orange line).

4. **Discussions**

To identify the main charge carrier involved in the charge/discharge of the CaV₆O₁₆·7H₂O material, a summary of the EQCM results is shown in Figure V-2-8.
The results obtained in the acidic and alkaline electrolytes are plotted as the change of the electrode weight versus the charge passed in the electrode during the reduction process at 10 mV·s⁻¹ (negative charges). Shaded areas represent the potential regions where the redox reactions occur (from -0.2 to -0.45 V vs. Ref in acidic electrolyte and from -0.2 to -0.6 V vs. Ref for alkaline electrolyte). The calculated molecular weight based on Faraday’s law is 40 g·mol⁻¹ and 11 g·mol⁻¹ where obtained in the pH = 10 and pH = 2.3 electrolytes, respectively.

**Figure V-2-8:** Electrode mass change vs charge during the polarization of CaV₆O₁₆·7H₂O (CVO) in pH = 2.3 (4.5 M Ca(NO₃)₂) and pH = 10 (4.5 M Ca(NO₃)₂ + Ca(OH)₂) electrolytes at 10 mV·s⁻¹.

In pH = 10 electrolyte (4.5 M Ca(NO₃)₂ + Ca(OH)₂), the calculated molecular weight is equivalent to the intercalation of Ca²⁺ ion (M/z = 20 g·mol⁻¹) solvated with about one water molecule (M/z = 18 g·mol⁻¹). On the other hand, in pH = 2.3 acidic electrolyte (4.5 M Ca(NO₃)₂), the calculated molecular weight is in between Ca²⁺ ion, hydronium H₃O⁺ (M/z = 19 g·mol⁻¹), and proton (M/z = 1 g·mol⁻¹).

The EQCM analysis thus supports the Ca²⁺ ion intercalation during charging/discharging of CaV₆O₁₆·7H₂O electrode in pH = 10 alkaline 4.5 M Ca(NO₃)₂ + Ca(OH)₂ electrolyte, which result in the highest capacity. As for acidic aqueous electrolyte, not only Ca²⁺ ion, but also hydroniums and protons also involving in charging CVO which could explain the decrease of total capacity. Based on the same amount of active material, by exchanging higher number of electrons, the capacity
should be improved which align with the results. However, the kinetics between \( \text{Ca}^{2+} \) ion and hydronium or proton intercalation can influence the power performance.

5. Conclusions

In this part of the work, EQCM is utilized to understand the charge storage mechanisms of a positive electrode for Ca-ion battery applications. \( \text{CaV}_6\text{O}_{16} \cdot 7\text{H}_2\text{O} \) was synthesized by the MSM method with 1D nano-ribbons like morphology. The difference in capacity of \( \text{CaV}_6\text{O}_{16} \cdot 7\text{H}_2\text{O} \) material in acidic (pH = 2.3) and alkaline (pH = 10) aqueous electrolytes is assumed to originate from the nature of the cation involved in the charging/discharging process. Moving from acidic to alkaline aqueous electrolyte, the charging mechanisms involving \( \text{Ca}^{2+} \) ion, hydronium and proton have been replaced with only solvated \( \text{Ca}^{2+} \) ion, resulting in a higher gravimetric capacity of \( \text{CaV}_6\text{O}_{16} \cdot 7\text{H}_2\text{O} \) material. With the help of EQCM, the understanding of the charge storage mechanisms for energy storage materials can further promote the development of energy storage applications.
6. Reference

General conclusions and perspectives
General conclusions and perspectives

General conclusions

This thesis aimed to utilize in situ technique, such as EQCM, to develop our fundamental knowledge about the charge storage mechanisms in energy storage electrode materials. For EDLCs (supercapacitors), the double layer charging at the electrode/electrolyte interface of three- and two-dimensional carbon-based materials were monitored by EQCM. The same methodology was applied to study other electrode materials involving faradic reactions. The charge storage mechanisms were revealed by combining EQCM, other in situ techniques, and simulation.

Charge storage mechanisms of carbon-based materials

For three-dimensional carbon-based materials, nanoporous carbon material with high SSA has been studied deeply since high capacitance was found to be achieved using microporous carbons. TiC-CDC microporous carbon with 0.67 nm pore size was studied in two aqueous electrolytes: K₂SO₄, EMImHSO₄, and a mixture of them. Results presented in Chapter III have demonstrated that the ion size, mobility, and the electrolyte pH are important factors to define the main charge carriers involved in the charging mechanisms. In all aqueous electrolytes, counter-ion adsorption was observed for highly positive and negative charges. Although the experimental methods had been changed from full scan to separated scan from OCV to positive and negative potentials to minimize the ion mixing effect, at low charge density near pzc, ion mixing zone still occurred. For negative polarization, anion adsorption with a high degree of desolvation was observed. In acidic environment (pH = 1), a mixture of SO₄²⁻ and HSO₄⁻ was found to be adsorbed into the micropores, which was explained by the similar ion size and mobility for these two species. During positive polarization, in neutral aqueous electrolyte (pH = 7), potassium ion adsorption occurred while in acidic aqueous electrolyte containing EMIm⁺ cation (EMImHSO₄ electrolyte, pH = 1), protons were responsible of the charging in micropores due fast ionic transport base on Grotthuss mechanism. When the pH increased to 4 by mixing K₂SO₄ and EMImHSO₄, the ionic flux was a mixture of potassium ion and protons during negative polarization.

Graphene is one of the most interested two-dimensional materials for EDLC
application. In chapter IV, a planar platform was set up by attaching single layer graphene (SLG) on gold current collector. Without the interference of carbon porosity, SGL electrode was used as a model material to study the effect of solvent towards the formation of the double layer at graphene electrode. The study was carried out in neat ionic liquid EMImTFSI and organic electrolyte that is EMImTFSI in acetonitrile. The graphene/electrolyte interface was analyzed by electrochemical impedance spectroscopy. The SLG and uncovered Au current collector were both detected. The change of differential capacitance versus potential and the shift of pzc were observed and discussed with/without the presence of solvent molecules. The existence of strong interactions between EMIm$^+$ and graphene material was not only reflected from the shift of pzc, but also from the EQCM results. In neat ionic liquid EMImTFSI electrolyte, the desorption of a positive charged cluster [EMIm$_{1.58}$TFSI$_{0.58}$]$^+$ was observed from pzc to positive polarization. From pzc to negative polarization, EMIm$^+$ cation was found to reorganize at the electrode surface, imidazolium ring being parallel to the graphene surface. Also, the ion-ion and ion-graphene correlation were found to decrease with the addition of solvent molecules. In 2 M EMImTFSI/ACN electrolyte, counter-ion adsorption was detected during positive and negative polarization with very little solvent molecules. Besides, the results with solvent molecules aligned with the experimental results based on microporous carbon material, that is counter-ion adsorption. The difference in ion dynamics for neat ionic liquid is likely due to the specific interaction between EMIm$^+$ cation and SLG which has not yet been found for amorphous carbons. Thanks to the 2D SLG platform, the effect of solvent molecules and the real-time ion responses toward charged SLG have been demonstrated without the limitation by the structure and morphology of porous carbon.

**Application of EQCM on other energy storage systems**

The charge storage mechanisms in 2-D MXene material in acidic electrolyte were not yet very clear. In this work, other techniques and molecular dynamics simulation were carried out combined together with EQCM to get a better view of the whole picture of the charging mechanisms. *In situ* XANES detected the change of valence state of titanium, which confirms its pseudocapacitive origin. EQCM identified the main charge carrier as H$_3$O$^+$ hydronium ion and protons, which were stored in-between MXene layers. The results from *in situ* XRD and MD simulation agreed with the EQCM.
results.

Additionally, CaV$_6$O$_{16}$$\cdot$7H$_2$O (CVO) battery material with ribbon-like morphology was studied to understand the charging mechanisms in acidic and alkaline (pH= 1 and 10) aqueous electrolyte. CVO electrode was tested in 4.5 M Ca(NO$_3$)$_2$ and 4.5 M Ca(NO$_3$)$_2$ + Ca(OH)$_2$ alkaline (pH = 1 and 10) aqueous electrolytes. CV profiles exhibited different intensity of current at the redox potentials. EQCM experiments were performed in these two aqueous electrolytes as well. In acidic electrolyte, the main charge carrier was found to be a mixture of hydronium ion and proton while, for the alkaline electrolyte, solvated calcium ion was the main charge carrier.

These results bring important insights at the molecular level of the charge storage process which can be used further for material design, to improve the performance of energy storage devices. In solvated electrolyte, counter-ion adsorbs into pores or onto electrode surface with a certain degree of desolvation during polarization. On the other hand, in RTIL electrolyte with strong ion-ion interaction, ion desorption and local reorganization and reorientation of the electrolytic species are found at planar electrode surface, which confirm previous results using porous carbon.\textsuperscript{1} Although the charge storage mechanisms has not been fully understood, these works provide analysis of the electrode/electrolyte interface with the help of EQCM. Four papers have been published from these results.\textsuperscript{2-5} One paper is still in preparation.

\textbf{Perspectives}

Over the years, different studies had confirmed that the optimization of the electrode/electrolyte interface holds the key for the future of supercapacitors. Great potential has been demonstrated by coupling \textit{in situ} techniques and simulations to get information about the ion environment in confined micropores or at planar electrode. Although simulation works have been dedicated to understanding the EDL, especially based on planar electrode, their results need to be confirmed by experimental approach. As this thesis is dedicated to study EDLCs from the fundamental point of view, the following questions are concerned in this aspect.

Because of the development of advanced electrolytes, such as for example new organic solvent and water-in-salt, the full picture of the EDL structure and charging mechanisms still need to be clarified. To improve the EDL models, simulation works have been done with planar electrode by changing the properties of electrolytes,
General Conclusions and Perspectives

including ion size of cation and anion, ion-ion interaction, and specific interaction between ions and electrode materials. The EDL model is refined over the years, thanks to the advanced simulation methods. However, there is lack of experimental approaches to confirm with the modeling results. Other questions still need to be addressed, such as: how molecular structures and interactions between molecules affect the charging mechanisms? How/why does the charging mechanisms move from counter-ion adsorption to ion exchange or co-ion desorption? Does the surface modification or the doping of the carbon material has an impact on the charge storage mechanisms? By combing the advantages of complementary techniques, different aspects could be covered, resulting in a more complete scenario of the EDL charge storage can be achieved.

From the performance point of view, porous carbon materials have been studied widely. Still, the optimum pore volume within different pore sizes needed to reach a higher energy density without sacrificing the power performance must be identified. Other questions on that topic deal with the suitable proportion of different pore sizes corresponding to various types of electrolyte. To improve energy density, replacing porous carbon with pseudocapacitive material is also an option. For pseudocapacitive materials, the main challenge will be maintaining the same level of power performance as carbon-based supercapacitors, as well as cyclability. In addition, the definition and how to classify such materials are debatable due to the lack of fundamental understanding of the charge storage mechanisms. With the additional development of the in situ techniques and computational simulation, important fundamental insights can be acquired for building better energy storage devices.
General Conclusions and Perspectives

References
Résumé de Thèse
Introduction

Le développement de notre société moderne dépend fortement de l'énergie. Parmi toutes les ressources, le gaz naturel, le pétrole et le charbon occupent la plus grande partie du marché. Cependant, l'épuisement des ressources naturelles étant de plus en plus préoccupante, il est urgent de trouver des solutions d'énergies alternatives. Les sources d'énergie renouvelables proviennent principalement de ressources naturelles, telles que l'énergie solaire, l'énergie éolienne, l'énergie des vagues, l'énergie géothermique, la bioénergie, l'énergie marémotrice, etc. Toutefois, le caractère intermittent de la production d'énergie à partir de sources naturelles ne permet pas toujours de répondre à la demande en temps voulu. Afin d'utiliser efficacement ces sources d'énergie durables, il devient important de mettre au point des systèmes de stockage d'énergie adaptés.

Figure 1-1: Le graphique montre les tendances vers une plus grande puissance spécifique pour les batteries et une énergie spécifique plus élevée pour les condensateurs électrochimiques (flèches). Les lignes pointillées représentent les zones où la cyclicité de la cellule est modifiée dans le cas d'un cyclage symétrique (même courant de charge et de décharge, à une profondeur de décharge de 100 %).

Le diagramme de Ragone est couramment utilisé pour comparer les performances des systèmes de stockage d'énergie (Figure 1-1). Parmi les systèmes de stockage d'énergie électrochimique, les condensateurs électrochimiques à double couche (EDLC) et les batteries secondaires sont les plus utilisés. Chaque système est caractérisé par son
énergie et sa puissance spécifiques. L'énergie spécifique et la puissance spécifique sont relatives à la quantité d'énergie et de puissance fournie par un dispositif par rapport à une unité de masse (kg) ou de volume (L). Comme le montre le graphique de Ragone, les systèmes de batteries peuvent stocker beaucoup plus d'énergie que les EDLC; cependant, les batteries ont des densités de puissance limitées. Au contraire, les EDLC (région colorée en bleu dans la Figure I-1) peuvent être facilement chargées et déchargées en quelques secondes, ce qui répond aux besoins des applications nécessitant des performances rapides et de haute puissance.

Ces performances reposent sur l'origine des mécanismes de stockage de la charge. Les batteries stockent l'énergie par des réactions d'oxydoréduction (faradique) au niveau des matériaux des électrodes, généralement entraînant des réactions de conversions chimiques et des changements de phase, fournissant un supplément d'énergie élevé, comme les batteries Li-ion (jusqu'à ~300 Wh kg⁻¹). Toutefois, ces réactions faradiques sont limitées par une cinétique lente et des processus irréversibles au niveau des matériaux, ce qui limite la puissance et la durée de vie. En revanche, les supercondensateurs, tels que les condensateurs électrochimiques à double couche (EDLC), stockent la charge à l'interface électrode/électrolyte, via une séparation de charge par un processus physique d'adsorption/désorption d'ions. Ces mécanismes de stockage rapides et hautement réversibles font que les supercondensateurs sont adaptés pour délivrer/récupérer des puissances élevées, ainsi que des durées de vie élevées (quelques millions de cycles). Toutefois, leur faible densité énergétique - environ 10 Wh kg⁻¹ pour les appareils commerciaux - limite encore leurs applications. Par conséquent, le principal défi aujourd'hui pour les supercondensateurs est d'augmenter leur densité énergétique.

Pour améliorer les performances des supercondensateurs, nous devons approfondir notre connaissance des mécanismes de stockage de charge, pour développer de nouvelles électrodes et de nouveaux électrolytes. Dans cette thèse, l'objectif principal est de comprendre les mécanismes de stockage de charge des EDLC en utilisant une technique de microbalance électrochimique in situ à cristal de quartz (EQCM). La microbalance électrochimique des cristal de quartz (EQCM) a été utilisée comme une sonde gravimétrique in situ pour l'étude de la dynamique des ions dans une électrode poreuse à base de carbone.
Chapitre 1

Le premier chapitre de cette thèse comprend une étude bibliographique, qui présente les aspects théoriques et expérimentaux les plus récents du stockage de charge dans les supercondensateurs de type EDLC. Les mécanismes de stockage de charge sont plus particulièrement détaillés.

À ce jour, les supercondensateurs sont largement utilisés dans diverses applications, notamment l'électronique, les transports et les produits liés à l'énergie, en raison de leur grande stabilité en termes de puissance et de température. Le marché des supercondensateurs était évalué à 487,45 millions de dollars en 2019, et il devrait atteindre 1570,75 millions de dollars d'ici 2025.⁹ Les supercondensateurs commerciaux sont pour la plupart symétriques et incorporent des charbons actifs poreux comme matériau d'électrode. Les électrodes sont immergées dans un sel organique dissous dans des solvants à base d'acétonitrile ou de carbonate de propylène. Compte tenu des valeurs conventionnelles des constantes diélectriques des électrolytes utilisés (moins de 100 environ) et de la distance d'approche des ions à l'électrode (quelques 10⁻¹⁰ m), les valeurs de la capacité de la double couche se situent dans la plage de quelques dizaines de µF cm⁻². Pour améliorer la capacité totale de l'électrode, les matériaux des électrodes EDLC sont de préférence fabriqués avec un carbone poreux présentant une surface élevée (> 1 500 m² g⁻¹). En outre, les carbones poreux ont une bonne conductivité électrique, une excellente stabilité électrochimique et sont peu coûteux (quelques euros par kW).¹⁰⁻¹² L'état de l'art des matériaux carbonés est discuté, couvrant les oignons de carbone 0D, les nanotubes de carbone 1D, le graphène 2D et le carbone activé 3D et également les carbones dérivés de carbone. En outre, le développement avancé d'électrolytes tels que les liquides ioniques (LI), aqueux et organiques est présenté.

Dans les EDLCs, la charge est stockée à l'interface électrode/electrolyte. Sous polarisation, les cations et les anions sont attirés respectivement vers les électrodes négatives et positives, en raison de la force électrostatique. Les charges sont ensuite séparées et stockées à la surface de l'électrolyte/electrode, ce qu'on appelle la "double couche électrochimique (EDL)". Les modèles EDL de surface plane en 2D et de pores en 3D développés sont décrits dans ce chapitre I, du plus ancien de Helmholtz au plus récent, où les phénomènes liés à l'augmentation de densité ionique dans les liquides ioniques ont été introduits (voir les figures 2a et 2b). Dans les électrodes poreuses, depuis la découverte expérimentale de l'augmentation de la capacité normalisée dans
Les nanopores de carbone de taille inférieure à celle des ions solvatés, les effets de courbure et de porosité ont été pris en compte pour décrire la formation d'EDL dans les nanopores de carbone. Dans les liquides ioniques, à température ambiante, un état “superionique” des ions confinés dans des nanopores de carbone explique l’augmentation de la capacité normalisée.\textsuperscript{13}

Figure 2: Schéma des modèles EDL basés sur les électrodes 2D sous polarisation (\(\phi E\)) dans un électrolyte de type liquide ionique pur (sans solvant) : (a) Effet de sur-écrantage à une tension modérée, \(V = 10k_BT/e\) (-0.26 V) et (b) Effet d'encombrement, à une tension élevée, \(V = 100k_BT/e\) (-2.6 V). Reproduit de\textsuperscript{14}. (c) Un schéma de "l'état superionique" des ions confinés dans les nanopores de carbone (L : la largeur des pores ; V : la tension appliquée ; d : le diamètre des ions). Reproduit d’après\textsuperscript{13}.

Les travaux théoriques et expérimentaux visant à étudier la formation de la double couche électrochimique sont présentés et discutés. D'un point de vue théorique, les résultats obtenus en utilisant la théorie de la fonctionnelle de la densité (DFT), la dynamique moléculaire (DM) et les simulations Monte Carlo (MC) ont été passés en revue sur la base des différents systèmes d'électrolyte. Les mécanismes de stockage de charges dans les électrodes poreuses ont également été étudiés par simulations. A ce jour, les résultats montrent que la diffusion des ions dans les nanopores sous potentiel est quatre fois plus lente que l'adsorption des ions en raison de l'effet de confinement. Comme le transport des ions conditionne la puissance des supercondensateurs, des méthodes expérimentales ont également été utilisées pour comprendre la dynamique des ions dans le réseau poreux des électrodes par modélisation. Du point de vue expérimental, plusieurs techniques expérimentales \textit{in situ} ont été présentées comme la microbalance électrochimique à quartz (EQCM), la spectroscopie de résonance
magnétique nucléaire (RMN) in situ, les techniques de diffusion des rayons X à petits angles in situ (SAXS) et la microscopie à force atomique (AFM). Les résultats expérimentaux couvrent plusieurs sujets, notamment la caractérisation de l'interface électrode/électrolyte, la dynamique des ions, l'environnement ionique à l'intérieur des pores et la structure de l'EDL.

L'objectif de cette thèse est d'étudier les mécanismes fondamentaux du stockage de charges dans divers matériaux en utilisant l'EQCM in situ en mode gravimétrique, afin d'approfondir notre connaissance de l'interface électrode/électrolyte sous polarisation. Des matériaux carbonés à deux et trois dimensions ont d’abord été étudiés pour des applications dans les EDLCs. D’autres matériaux tels que les carbures métalliques 2D et les oxydes métalliques 3D fonctionnant mettant en jeu des réactions faradiques, ont été ensuite été étudiés par EQCM pour comprendre les mécanismes de stockage de charge.

Chapitre 2

Le chapitre II présente les différents matériaux et électrolytes qui ont été testés dans le cadre de cette thèse. Les méthodes électrochimiques utilisées pour caractériser le matériau des électrodes et l'interface électrode/électrolyte ainsi que les techniques de caractérisation des matériaux sont ensuite présentées, et leur principe de fonctionnement brièvement expliqué. Le principe de fonctionnement de la microbalance électrochimique à quartz est plus particulièrement détaillé. Les configurations et la conception de cellules à trois électrodes Swagelok™ cell et EQCM cell sont également montrées.

Chapitre 3

Suite aux travaux montrant une augmentation spectaculaire de la capacité lorsque la taille des pores du carbone est inférieure à la taille des ions solvatés, les mécanismes de stockage de la charge de l'électrode en carbone microporeux et la relation entre la taille des ions et la taille des pores ont été étudiés en détail.

Ces dix dernières années, une série de travaux a montré que l'EQCM pouvait être un outil quantitatif pour étudier le transport et l’adsorption des ions et des molécules de solvant dans les électrodes poreuses de supercondensateurs. Bien que l’EQCM
ait été utilisée pour étudier les flux ioniques dans les matériaux carbonés poreux, aucun des travaux précédents n'a étendu la discussion à des électrolytes comprenant un mélange complexe d'ions, et ce bien qu'il ait été signalé que les performances des électrodes de supercondensateurs peut être améliorées en utilisant un mélange d'ions et/ou de molécules de solvants.\textsuperscript{18-21} Par exemple, pour les électrolytes de type liquides ioniques pur (RTILs), en jouant sur la taille, la masse moléculaire et les coefficients de diffusion des cations et des anions, la fenêtre de tension de fonctionnement d'un supercondensateur symétrique à base de carbone peut être élargie.\textsuperscript{18} Dans ce chapitre, nous nous concentrerons sur l'étude par EQCM d'une électrode en carbone microporeux, dans les électrolytes aqueux contenant des mélanges de cations et d'anions.

\textbf{Partie Expérimentale}

Des carbones dérivés de carbure (CDC) ont été utilisés comme matériau d'électrode. Les CDC dérivés du carbure de titane (TiC) présentent une taille de pores contrôlée entre 0.5 et 3 nm avec et une surface spécifique (SSA) jusqu'à 1800 m\textsuperscript{2}·g\textsuperscript{-1}.\textsuperscript{22} Les CDC n'ont pas seulement montré des performances supérieures en tant que matériau de supercondensateur, ils ont été largement utilisés comme matériaux modèles pour comprendre la formation de la double couche dans les matériaux poreux. Ils ont aidé à identifier l'origine de l'augmentation de capacité dans les nanopores et les mécanismes de stockage de charges associé.\textsuperscript{8, 15, 23} Dans ce travail de thèse, un TiC-CDC de YCarbon Inc (USA) avec une taille de pores de 0,67 nm a été choisi comme matériau modèle. A partir de l'isotherme d'adsorption d’Ar (77K), le calcul de la distribution en tailles de pores (PSD) par les méthodes QSDFT ont permis de mesurer une taille moyenne de pores de 0,67 nm (Tableau 1).

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</tr>
<tr>
<td>DFT SSA (m\textsuperscript{2}·g\textsuperscript{-1})</td>
<td>1767</td>
</tr>
<tr>
<td>Pre-pore diameter (nm)</td>
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<tr>
<td>Pore volume (cm\textsuperscript{3}·g\textsuperscript{-1})</td>
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</tr>
<tr>
<td>Ash content (%)</td>
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</tr>
<tr>
<td>Particle diameter (μm)</td>
<td>75</td>
</tr>
</tbody>
</table>

\textbf{Tableau 1} : Propriétés physiques du carbone dérivé du carbure de titane (TiC-CDC) de YCarbon Inc.\textsuperscript{24}
Résultats

Une première étude de l’électrode de carbone CDC-0,67nm a été faite dans un électrolyte aqueux K₂SO₄ 0,1 M (pH = 6,3) à 10 mV·s⁻¹. Le voltampérogramme cyclique montre un comportement capacitif et peut être divisé en quatre parties différentes, correspondant à l'adsorption et à la désorption des cations et des anions comme l’illustre la Figure 3a. D'après la Figure 3b, la variation de masse avec la densité de charge de l’électrode (obtenue par EQCM) est convexe : elle diminue puis augmente ensuite pendant le balayage positif en raison de la désorption des cations et de l'adsorption des anions dans les nanopores de carbone. Ensuite, la masse diminue et augmente à nouveau pendant le balayage négatif car les anions sont désorbés et les cations adsorbés. Le variation de masse en fonction de la densité de charge présente un minimum en ligne courbe et non brisée en raison de la non sélectivité des flux ioniques : une zone de densité de charge mixte où les cations et les anion interviennent dans le processus de compensation de charge de l’électrode. Ainsi, lors de la polarisation positive, l'adsorption des contre-ions (anions SO₄²⁻) est simultanément accompagnée de la désorption des co-ions (cation K⁺). Plus la densité de charge est élevée, plus les co-ions seront électrostatiquement expulsés des pores du carbone.

Figure 3: (a) Voltampérogramme cyclique obtenu par EQCM avec une électrode en carbone CDC-0,67nm dans du K₂SO₄ 0,1 M à 10 mV s⁻¹ (b) Changement de masse de l’électrode en fonction de la densité de charge (obtenus à partir de (a)), avec un balayage de potentiel partant du pzc vers les directions positive et négative. La courbe en trait plein noir montre le changement de masse mesuré (EQCM), les lignes pointillées vertes sont relatives au changement de masse théorique obtenus en considérant l’adsorption des contre-ions seuls, sans molécule de solvant. La ligne rouge pleine montre une variation linéaire de la masse mesurée en fonction de la charge.
En considérant les pentes de la courbe expérimentale dans la gamme appropriée (comme indiqué dans les lignes rouges de la Figure 3b) et en utilisant l'équation de Faraday, les masses molaires moyens des cations ou des anions avec des molécules de solvant, $M_{Exp}$, ont été calculées. En supposant que la différence entre les masses molaires moyennes et la masse molaire des ions nus est attribuée uniquement aux molécules d'eau, le nombre d'hydratation de chaque ion peut être estimé. Les nombres d'hydratation des ions potassium ($\text{K}^+$) et de l'ion sulfate ($\text{SO}_4^{2-}$) dans les micropores de carbone sont respectivement de 5,3 et 0,9. Pour les ions $\text{K}^+$, l'indice d'hydratation calculé n'est pas très différent de l'indice d'hydratation dans le volume de la solution (7). Cela pourrait être dû à la taille de l'ion potassium hydraté, dont le diamètre est estimé à 0,662 nm.\textsuperscript{25} La taille des pores du TiC-CDC est de 0,67 nm, ce qui est très similaire à la taille de l'ion potassium entièrement hydraté (diamètre = 0,66 nm). Pour les ions sulfate $\text{SO}_4^{2-}$ plus volumineux, la valeur de l'indice d'hydratation calculée est comprise entre 0 et 1, ce qui indique que la plupart des molécules d'eau ont été éliminées lorsque les anions accèdent aux micropores de carbone. La taille de l'ion sulfate $\text{SO}_4^{2-}$ nu est de 0,242 nm et la distance moyenne entre l'ion et l'eau du sulfate est de 0,381 nm.\textsuperscript{26} Sur la base de ces informations, la désolvatation des ions sulfate peut être proposée puisque la taille de l'ion hydraté du sulfate (diamètre = 0,76 nm) est beaucoup plus grande que la taille des pores du TiC-CDC (taille des pores = 0,67 nm).

**Figure 4:** Changement de masse de l'électrode en fonction de la charge pendant la polarisation du CDC-0,67nm dans (a) un électrolyte aqueux EMIm-\text{HSO}_4 de 0,1 M (pH = 0,8) et (2) un mélange de $\text{K}_2\text{SO}_4$ de 0,1 M et d'électrolyte aqueux EMIm-\text{HSO}_4 (pH = 1,2).
La CV du CDC-0,67nm dans un électrolyte aqueux 0,1 M EMIm⁺-HSO₄⁻ (pH = 0,8) montre un comportement capacitif. La figure 4a montre la courbe Δm en fonction de ΔQ, du pzc vers les potentiels cathodique puis pzc vers anodique. Pour des charges positives (Q > 0), la figure 4a montre une augmentation du changement de masse dans les micropores de carbone. La masse molaire par charge calculée (31 g mol⁻¹) est inférieure à celle de l'anion HSO₄⁻ nu (97 g mol⁻¹). Elle est également inférieure à celle de l'anion SO₄²⁻ (48 g mol⁻¹), même si l'adsorption de l'anion SO₄²⁻ ne devrait pas être prédominante en raison de la faible valeur du pH de l'électrolyte. Cela indique que non seulement l'adsorption de l'anion solvaté s'est produite dans les pores du carbone, mais aussi la désorption des cations. Pour Q < 0 mC cm⁻², aucun (ou un très léger) changement de masse n'a été observé. Étant donné que la dimension la plus longue du cation EMIm⁺ est de 0,76 nm, ce qui est plus grand que la taille des pores du CDC-0,67 nm, on s'attend à ce que les ions aient un accès limité aux pores. En outre, vu le grand excès de proton dans un tel électrolyte acide et la grande mobilité du proton - plus élevée que celle du cation EMIm⁺, plus volumineux, les protons (M = 1 g mol⁻¹) devraient être les principaux porteurs de charge pendant l'adsorption des cations par le mécanisme de Grotthuss.²⁷ Dans un mélange de 0,1 M de K₂SO₄ + EMIm-HSO₄ (à pH = 1,2), la CV montre également un comportement capacitif. Dans cet électrolyte mixte, la présence de différents cations (K⁺, EMIm⁺, H⁺, H₃O⁺) et anions (SO₄²⁻, HSO₄⁻) rend les choses plus complexes. Pour Q > 0 mC cm⁻², la variation de la masse par rapport à la charge est linéaire, ce qui signifie qu'aucun phénomène d'échange ionique ne se produit ; seule l'adsorption d'anions semble se dérouler. La masse moléculaire moyenne expérimentale calculée par charge pour l'anion est de 58 g mol⁻¹. Selon les résultats obtenus précédemment dans l'électrolyte K₂SO₄, les ions sulfates, pratiquement entièrement désolvatés, sont adsorbés dans les micropores de carbone. En raison de l'état de valence plus élevé pour l'anion sulfate que pour l'ion bisulfate HSO₄⁻, on s'attend à ce qu'un mélange d'anions sulfate et bisulfate soit adsorbé dans les micropores du carbone pour les polarisations positives. Un calcul direct donne des contributions de 80% et 20%, respectivement pour l'anion sulfate et l'anion bisulfate. Pour une charge négative élevée (Q < 0), la masse molaire moyenne calculée par charge (17 g mol⁻¹) est beaucoup plus faible que celui des cations K⁺ et EMIm⁺. D'après les résultats obtenus dans l'électrolyte acide, on s'attend à ce que les protons soient impliqués dans le processus d'adsorption
des cations. En outre, la conductivité ionique molaire du potassium est de l'ordre de celle du proton, ce qui n'est pas le cas pour l'EMIm\(^+\). Cela explique que la masse moléculaire moyenne calculée par charge se situe entre la masse moléculaire théorique du proton et du potassium dans cet électrolyte de faible pH (1,2). La contribution du proton et du cation de potassium sont estimées à 44% et 56% d'après les courbes de variation de masse, respectivement, pendant le processus d'adsorption du cation. Ces résultats confirment donc que pendant le processus de charge/décharge dans une solution aqueuse multi-ionique à faible pH, les cations (H\(^+\) et K\(^+\)) et les anions (HSO\(_4\)\(^-\) et SO\(_4\)\(^{2-}\)) contribuent tous au processus d'adsorption/désorption.

En résumé, le profil des flux ioniques dans les nanopores a été révélé par EQCM dans un électrolyte constitué d'un mélange de plusieurs cations et anions. Les résultats obtenus montrent que la modification du pH de l'électrolyte modifie la nature des ions impliqués dans le stockage de la charge.

**Chapitre IV**

Le graphène, avec sa surface spécifique théorique élevée de 2630 m\(^2\) g\(^{-1}\) et sa capacité théorique de 550 F g\(^{-1}\) (21 uF cm\(^{-2}\)), a déjà fait l'objet de nombreuses études pour des applications dans les supercondensateurs.\(^{28,29}\) Il a été montré que le graphène et ses dérivés peuvent atteindre des capacités expérimentales de de plus de 200 F g\(^{-1}\).\(^{30-32}\) Le graphène monocouche (SLG), qui présente une conductivité thermique et électrique supérieure, peut être utilisé comme un matériau modèle pour étudier l'adsorption et le transport des ions à l'interface graphène/électrolyte.

Dans ce chapitre, nous avons analysé, à l'aide de la technique de spectroscopie d'impédance électrochimique (SIE), l'effet de la nature des électrolytes sur la capacité de double couche du SLG, en utilisant des électrolytes liquides ioniques purs et des électrolytes liquides ioniques solvatés. Nous proposons pour la première fois l'étude des flux d'ions à la surface de l'électrode de SLG en utilisant une microbalance électrochimique à cristal de quartz (EQCM), ce qui permet de mieux comprendre les mécanismes de stockage de charges à l'électrode de SLG dans différents électrolytes.

**Partie Expérimentale**

Des films monocouches de graphène (G) ont été préparés par dépôt chimique en
phases vapeur (CVD) en faisant circuler 3 cm$^3$ min$^{-1}$ de H$_2$ (70 mTorr) et 30 cm$^3$ min$^{-1}$ de CH$_4$ (340 mTorr) à 1000 °C sur un substrat de cuivre (Cu) (Wuxi Graphene Film Co., Ltd). Après avoir gravé le cuivre avec 0,1 M de persulfate d'ammonium ((NH$_4$)$_2$S$_2$O$_8$), le graphène est transféré du Cu vers des films adhésifs sensibles à la pression (PSA) revêtus d'un substrat en polyéthylène téréphtalate (PET), utilisés ensuite pour transférer le SLG sur le quartz de la microbalance EQCM.

La spectroscopie Raman du film SGL (figure 5) montre un signal typique de graphène monocouche avec des bandes G et 2D distinctes. La bande G est décalée vers des nombres d'ondes plus élevés (~1597 cm$^{-1}$) par rapport à celle du graphène (1581 cm$^{-1}$); le rapport d'intensité de la bande 2D sur la bande G est d'environ 1 avec un pic de défaut (D) négligeable, ce qui indique que l'échantillon de graphène utilisé dans cette étude est dopé de type p.

Figure 5: Spectres Raman de graphène monocouche sur substrat de quartz revêtu d'Au.

Résultats

Des mesures par spectroscopie d'impédance électrochimique (SIE) dans l'EMImTFSI pur et 2 M EMImTFSI dans l'acétonitrile ont été effectuées à différents potentiels constants. Les tracés dans le plan de Nyquist de l'impédance à différents potentiels ont montré un comportement de type capacitif.
Figura 7: La parte réelle $C'(\omega)$ y la parte imaginaria $C''(\omega)$ de la capacidad en las
electrodes en (a) EMImTFSI pur y (b) 2M EMImTFSI en el electrolito
d'acetonitrile registrado a diferentes potenciales.

La figura 7a muestra la variación de la capacidad de la electrode ($C'(\omega)$) de SLG con
la frecuencia, a diferentes potenciales. $C'(\omega)$ aumenta cuando la frecuencia disminuye, y
deviene menos dependiente de la frecuencia en el rango de frecuencia de onda situada a
alrededor de 200 Hz y 1 Hz$^{37}$, frecuencia para la cual la capacidad máxima del SLG es
alcanzada. Ciertamente, la capacidad continúa aumentando hasta 0,1 Hz, incluyendo
particularmente durante las polarizaciones negativas: la presencia de un corriente de fuga due a
la existencia de reacciones secundarias parasitas puede explicar esto. La parte imaginaria de la capacidad
$C''(\omega)$ pasa por dos máximos a dos frecuencias características $f_0$ de 610 Hz y 2,5
Hz, correspondiendo a dos constantes de tiempo ($\tau_0 = 1/f_0$) de 1,6 ms y 395 ms,
respectivamente.$^{37}$ En base a las mediciones efectuadas en una electrode Au en las
mismas condiciones experimentales, se atribuye la relajación a baja frecuencia (2,5 Hz)
a quartz revestido de SLG, correspondiendo al proceso de carga de la double couche
electroquímica sobre el SLG solo.

La figura 8 muestra la variación de la capacidad EDL normalizada en función de la
superficie por rapport au potentiel de l’électrode de SGL, obtenue en soustrayant la
capacitance de la electrode liée à l’Au. Cette courbe muestra una dependencia de la
capacitance de double couche de l’électrode de SGL avec le potentiel de l’électrode avec
una forma en V similar para los dos electrolitos. Ciertamente, la $C_{EDL}$ en el IL
solvatado es más elevado que en el IL pur. En outre, le pzc de l’électrode dans el
IL pur es inferior a celui l’IL solvatada. On suppose que la capacitance plus importante
en l’electrolyte IL solvatado por rapport a l’électrolyte IL sans addition de solvant est
due à un effet de sur-écrantage à l'interface électrifiée au contact de l’électrolyte IL pur, ce qui entraîne une double couche plus épaisse et une diminution de la capacité (longueur de Debye plus importante). En outre, la constante diélectrique de l’électrolyte à base d’acétonitrile est plus élevée - d'après les calculs - que celle de l’IL pur, ce qui augmente la capacité. L’effet d’écrantage des charges ioniques liée à la présence du solvant réduit également l'épaisseur de la double couche, contribuant aussi à améliorer la capacité globale dans l’électrolyte solvaté. L'augmentation du pzc lors du passage du IL pur au IL solvaté s'explique probablement par les interactions spécifiques entre les cations SGL et EMIm\(^+\) plus prononcées en l’absence de solvant. Cette forte interaction entre le cation EMIm\(^+\) et le SLG affecte également la dynamique des ions.

**Figure 8:** Courbe de la variation de la capacité $C_{\text{EDL}}$ d’une électrode de SGL en fonction du potentiel $E$ dans un électrolyte liquide ionique pur (points noirs) et liquide ionique dissous dans de l’acétonitrile (points rouges).

La figure 9a montre la variation expérimentale de la masse de l’électrode SLG ($\Delta m$) par rapport à la charge ($\Delta Q$) passée dans un électrolyte EMImTFSI pur. En partant du pzc vers les polarisations positives, la diminution de la masse correspond à des ions expulsés de la surface du SLG. En utilisant la loi de Faraday, le poids moléculaire moyen calculé dans la zone grise est $M/z = 338 \text{ g mol}^{-1}$. D’après le signe de la pente (négatif), il s’agit d’un flux d’espèce chargées positivement, en considérant le poids moléculaire du cation EMIm\(^+\) (111 g mol\(^{-1}\)) et de l’anion TFSI\(^-\) (280 g mol\(^{-1}\)), cela peut être exprimé statistiquement par l’implication d’un « cluster » $[\text{EMIm}_{1.58}\_\text{TFSI}_{0.58}]^+$ dans la charge de la double couche électrochimique côté électrolyte. Du pzc vers les polarisations négatives, aucun changement de masse significatif n'est observé, alors
qu'une signature de stockage de charge capacitive est toujours observée dans cette plage de potentiel en dessous de -0,2 V par rapport à Ref. Le stockage de charge négative peut être interprété comme un phénomène de réorganisation des ions à la surface de l'électrode. La forte corrélation électron-ion entre le plan du cycle imidazolium et la chaîne alkyle de l'EMIm\(^+\) et la surface du graphène (carbones sp\(^2\)) peut venir forcer un alignement parallèle des cations à la surface de l’électrode de SGL, les rapprochant l’un de l’autre, ce qui se traduit par une augmentation de la densité d’ions et donc de charge plus proche de la surface (~0,025 mC cm\(^{-2}\)) sur le SLG.

![Figure 9](image)

**Figure 9:** Changement de masse de l'électrode en fonction de la charge pendant la polarisation du SLG sur un substrat en or à l'état pur (a) EMImTFSI et (b) 2M EMImTFSI/ACN.

D'autre part, lorsque des molécules de solvant d'acétonitrile sont ajoutées dans l'EMImTFSI, la figure 9b montre une augmentation de la masse du pzc vers les charges positives et négatives. La masse moléculaire calculée dans les zones jaunes est de 152 et 325 g mol\(^{-1}\), respectivement durant la polarisation négative et positive. Le calcul montre que, du pzc vers les charges négatives, l’adsorption du cation EMIm\(^+\) sur le SG se fait en moyenne avec 1 molécule d'acétonitrile; du pzc vers les charges positives, l’anion TFSI\(^-\) est solvaté en moyenne par 1,3 molécule d’acétonitrile durant son adsorption. Un mécanisme de stockage de charge contrôlé par l’adsorption des contre-ions sur une électrode de graphène monocouche est donc mis en évidence en présence de molécules de solvant.
Tableau 2: Masses molaires calculée par charge pour dans des électrolytes IL pur et IL solvaté dans l’acétonitrile (ACN).

<table>
<thead>
<tr>
<th>M/z [ g mol⁻¹]</th>
<th>SLG</th>
<th>CDC-1nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EMImTFSI</td>
<td>EMImTFSI</td>
</tr>
<tr>
<td>Du pzc vers les potentiels &gt; 0</td>
<td>-338</td>
<td>+325</td>
</tr>
<tr>
<td>Du pzc vers les potentiels &lt; 0</td>
<td>0</td>
<td>+153</td>
</tr>
</tbody>
</table>

La dynamique ionique dans des matériaux carbonés à 2- (SGL) et 3-Dimensions (CDC) est comparée dans le Tableau 2. Pour le carbone microporeux de type CDC, il a été montré par EQCM dans un travail précédent de notre groupe que l'adsorption des ions dans un électrolyte liquide ionique avec et sans molécules de solvant était gournée par l’adsorption du contre ion (polarisations négatives) et un mécanisme d’échange ionique (polarisations positives). Les réponses du carbone microporeux et du SLG sous polarisation sont donc différentes. Plus particulièrement, dans un électrolyte de type liquide ionique solvaté, durant la polarisation négative, l'adsorption des cations se fait avec 3 à 4 molécules de solvant dans le carbone microporeux. Sur une électrode de SLG, dans le même électrolyte, les cations EMIm⁺ s’adsorbent avec une seule molécule de solvant. Si ce résultat peut être surprenant au premier abord, cette différence de réponse ionique peut s’expliquer par la forte interaction entre les cations EMIm⁺ et la surface du SLG (interaction π−π), ce qui n'est pas le cas dans les carbones amorphes (pas d’ordre sp² à longue distance). Il a été démontré d’autre part qu’une monocouche de graphène engendre une plus forte interaction ion-carbone. Lors de polarisation positive, l’absence de mécanisme d’échange ionique avec l’électrode de SGL peut être due à la plus grande mobilité des anions, les cations étant plus liés à la surface du SGL du fait de ces interactions π−π. La différence de stockage de charges dans un électrolyte EMIM,TFSI sans solvant peut également s’expliquer par ces interactions cation-SLG fortes. En résumé, l'effet de la présence de molécules de solvant a été étudié en utilisant une électrode de SGL comme matériau modèle, et les différences significatives de comportement lors de la charge de la double couche électrochimique i) en l’absence ou présence de solvant et ii) par rapport à un carbone...
poreux de type CDC ont été mises en évidence et expliquées.

**Chapitre V**

Le dernier chapitre est consacré à l'utilisation de l'EQCM pour suivre les flux d'ions dans différents matériaux utilisés pour des applications de stockage d'énergie. Des matériaux fonctionnant sur la base de réactions faradiques comme les Ti$_3$C$_2$Tx MXene de type pseudocapacitif ou encore des oxydes de type CaV$_6$O$_{16}$ pour des applications de type batteries Ca-ion ont été caractérisés à l'aide de l'EQCM et les mécanismes de stockage des charges étudiés en détail dans ce chapitre.

**Première partie: Comprendre le mécanisme de stockage de charge dans les MXenes (électrode Ti$_3$C$_2$Tx) en électrolyte acide**

Les MXènes sont des carbures, carbonitrures ou nitrures de métaux de transition bidimensionnels (2D). Le MXne Ti$_3$C$_2$Tx (Tx= -F, -O, -OH), matériau MXène le plus étudié à ce jour, atteint des capacités volumétriques élevées dans des électrolytes aqueux acides de type H$_2$SO$_4$, par un mécanisme mettant l’intercalation de cations entre les feuillets de MXène et le changement de degré d’oxydation du cation métallique M. De nombreux travaux ont porté sur l’étude des mécanismes de stockage de charge dans le Ti$_3$C$_2$Tx en milieu H$_2$SO$_4$. Cependant, le mécanisme n'a pas encore été complètement identifié expérimentalement dans les électrolytes aqueux acides. Dans ce travail, l'EQCM sera utilisée pour étudier le mécanisme de stockage de charge dans une électrode Ti$_3$C$_2$Tx MXene dans un électrolyte H$_2$SO$_4$. Ce travail a été réalisé en collaboration avec Antonella Iadecola (pour les expériences de XANES in-situ).

Les MXènes Ti$_3$C$_2$Tx purs (appelés P-MXène) utilisés dans cette étude ont été préparés par dissolution de la phase A d’un précurseur Ti$_3$AlC$_2$ dans une solution mixte LiF/HCl. la caractérisation par diffraction des rayons X (XRD) (figure 10a) montre la disparition des pics caractéristiques de la phase Ti$_3$C$_2$Tx MAX après dissolution, ainsi que l'apparition de nouveaux pics (00l), mettant en évidence la formation de Ti$_3$C$_2$Tx MXene 2-D. La structure en feuillets du P-Mxène a été également observée par MEB (figure 10b).
Figure 10: (a) Diffractogrammes (XRD) de la phase Ti$_3$C$_2$Tx MAX et du Ti$_3$C$_2$Tx MXene. (b) Image MEB en coupe transversale du film de MXène (Pristine-MXène).

La CV du P-Mxène est présenté sur la figure 11b à une vitesse de balayage de 50 mV s$^{-1}$, après un précyclage. Un ensemble de pics d'oxydoréduction est visible à environ -0,75 V (vs. Hg/Hg$_2$SO$_4$), correspondant l’activité rédoc du couple Ti$^{2+}$/Ti$^{3+}$, comme attendu dans ce type d'électrolyte.$^{38}$ La capacité spécifique gravimétrique calculée à partir des profils CV est de 325 F g$^{-1}$ pour le P-MXène.

Figure 11: (a) CV d’une électrode P-MXène à une vitesse de balayage de 50 mV s$^{-1}$ dans H$_2$SO$_4$ 3 M. La partie ombrée indique la proportion estimée de la charge stockée par des mécanismes de type double couche (EDL). (b) Analyse XANES in-situ de l'électrode P-MXene dans un électrolyte H$_2$SO$_4$ de 1 M, à différents potentiels. L'électrode de référence utilisée dans la configuration est Hg/Hg$_2$SO$_4$.

Pour les matériaux à base de MXène, la capacité totale provient de différents mécanismes de stockage de charge : pseudocapacitifs (d’origine faradique) et ED
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Pour caractériser le comportement pseudocapacitif du Ti\textsubscript{3}C\textsubscript{2}, nous avons réalisé une étude par XANES in-situ au seuil Ti K du P-MXène dans toute la gamme de potentiel (~1 V). Sur la figure 11b, on observe un déplacement du seuil du pic K du Ti vers une énergie plus faible lors de la polarisation cathodique (de 0,2 à -0,7 V par rapport à Hg/Hg\textsubscript{2}SO\textsubscript{4}), ce qui indique une diminution de l'état d'oxydation du Ti. L'état d'oxydation du Ti est quasiment inchangé lorsque l'électrode de MXene est polarisée négativement de +0,2 à -0,1 V (par rapport à Hg/Hg\textsubscript{2}SO\textsubscript{4}). Ces résultats suggèrent que le stockage de la charge du P-MXene dans l'électrolyte aqueux Hg\textsubscript{2}SO\textsubscript{4} est en partie (principalement) réalisé par un mécanisme de type pseudocapacitif. Le changement de l'état d'oxydation moyen du Ti est estimé à environ 0,134 électron par atome de Ti sur une fenêtre de potentiel de 0,9 V, ce qui correspond à une valeur de capacité spécifique de 213 F g\textsuperscript{-1}. Étant donné que la capacité spécifique du P-MXène mesurée dans la cellule Swagelok est de 325 F g\textsuperscript{-1}, la charge stockée impliquant un comportement pseudo-capacitif (changement de l'état d'oxydation du Ti) représente environ 65 % de la charge totale. Ce résultat est similaire à l'estimation du profil CV comme le montre la figure 11a, où la contribution de l'EDL peut être estimée à 43% de la charge totale.

Figure 12: (a) Profil CV et réponse en fréquence EQCM et (b) changement de masse de l'électrode en fonction de la charge pendant la polarisation du P-MXène sur un substrat d'or dans du H\textsubscript{2}SO\textsubscript{4} 3 M enregistré à 10 mV s\textsuperscript{-1}.

Pour obtenir un meilleur analyse de la nature des ions impliqués dans le mécanisme de stockage des charges, une étude par microbalance électrochimique à quartz (EQCM) a été réalisée avec un quartz doré revêtu de Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} MXène dans un électrolyte H\textsubscript{2}SO\textsubscript{4} 3 M. La figure 12a montre la CV et la réponse en fréquence du
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MXene à 10 mV s⁻¹, qui est similaire au profil obtenu en configuration Swagelok. La variation de masse en fonction de la charge est représentée sur la figure 12b. Selon la loi de Faraday, la masse moléculaire moyenne par charge est calculée à 13±3 g mol⁻¹. La masse molérale moyenne par charge se situe entre celle de l’ion hydronium H₃O⁺ (19 g mol⁻¹) et du proton (1 g mol⁻¹). En conséquence, sur la base des résultats de l’EQCM, P-MXene est chargé de OCV à un potentiel négatif dans un électrolyte aqueux acide, les espèces impliquées dans le comportement pseudocapacitif du P-MXène en polarisation cathodique sont un mélange de hydronium (H₃O⁺) et de proton. Sur la base de leur masse molérale respective, la contribution du proton et de l'hydronium peut être estimée respectivement à 35% et 65%. En conséquence, un mélange d'ions d'hydronium s'insère dans les couches de MXène pendant la charge, et des protons sont transportés par un mécanisme de type Grotthuss dans le volume inter-feuillets.

Partie 2: Etude du mécanisme de stockage de charge dans l’oxyde CaV₆O₁₆, pour application dans les batteries aqueuses Calcium-ion.

Dans ce travail, l’EQCM a été utilisée pour étudier les processus de charge/décharge d’une cathode CaV₆O₁₆·pour batterie Ca-ion. Le matériau d’électrode positive CaV₆O₁₆·7H₂O (CVO) est préparé en utilisant une voie de synthèse de sel fondu (MSM). Les expériences ont été menées dans un électrolyte aqueux de Ca(NO₃)₂ de 4,5 M mais à des pH différents. Ce travail a été réalisé en collaboration avec Liyuan Liu.

**Figure 13:** Caractérisation du nanomatériau CaV₆O₁₆·7H₂O (CVO). (a) Image MEB et image MET, (b) Modèle de diffraction des rayons X.

Les composés 1D CVO ont été préparés dans un mélange de nitrate de calcium et de nitrate de sodium utilisé comme sel fondu. L’image MEB de la figure 13a montre une morphologie en nanorubans 1D pour l’échantillon de CVO préparé, avec des longueurs de 2 à 10 μm. La figure 13b montre le diffractogramme de diffraction des
rayons X ; tous les pics sont bien indexés avec la phase CaV₆O₁₆·7H₂O (numéro de carte JCPDS : 01-084-2134).

Figure 14: (a) CV de CaV₆O₁₆, 7H₂O enregistrées à 2 mV s⁻¹ en cellules Swagelok et (b) réponse en fréquence des CV et EQCM, à 20 mV s⁻¹ en électrolyte Ca(NO₃)₂ 4,5 M aqueux à pH = 2 et (c) en électrolyte en électrolyte aqueux Ca(NO₃)₂ 4,5 M + Ca(OH)₂ à pH = 10 à 10 mV s⁻¹..

Un premier électrolyte est le Ca(NO₃)₂ aqueux 4,5 M, avec un pH de 2,3. Un autre électrolyte aqueux alcalin (pH = 10) avec la même concentration de Ca(NO₃)₂ a été préparé en ajustant le pH avec Ca(OH)₂. Une signature électrochimique similaire est observée quel que soit le pH de l’électrolyte. Cependant, la capacité de CVO dans l’électrolyte à pH = 10 est légèrement supérieure. Les profils CV de la mesure EQCM à pH = 2,3 et 10 sont similaires à ceux enregistrés en cellules Swagelok (figure 14b et 14c), confirmant la qualité des mesures.

Figure 15: Variation de la de masse des électrodes en fonction de la charge pendant la polarisation de CaV₆O₁₆-7H₂O (CVO) dans un électrolyte à pH = 2,3 (4,5 M Ca(NO₃)₂) et dans un électrolyte à pH = 10 (4,5 M Ca(NO₃)₂ + Ca(OH)₂), à 10 mV s⁻¹.
Un résumé des résultats de l'EQCM est présenté en figure 15, qui montre la variation de la masse de l'électrode en fonction de la charge passée dans l'électrode pendant le processus de réduction à 10 mV s\(^{-1}\) (charge négative) dans les électrolytes acide et alcalin. La masse molaire calculée selon la loi de Faraday est de 40 g mol\(^{-1}\) et de 11 g mol\(^{-1}\) respectivement pour des pH de 10 et 2,3. À pH = 10, dans l'électrolyte (4,5 M Ca(NO\(_3\))\(_2\) + Ca(OH)\(_2\)), la masse molaire calculée équivaut à l'intercalation de l'ion Ca\(^{2+}\) (M/z = 20 g mol\(^{-1}\)) solvétée avec environ une molécule d'eau (M/z = 18 g mol\(^{-1}\)). D'autre part, dans l'électrolyte acide (4,5 M Ca(NO\(_3\))\(_2\)) à pH= 2,3, la masse molaire calculée se situe entre celle de l'ion Ca\(^{2+}\), l'hydronium H\(_3\)O\(^+\) (M/z = 19 g mol\(^{-1}\)) et le proton (M/z = 1 g mol\(^{-1}\)). L'analyse EQCM est donc en faveur de l'intercalation d'ions Ca\(^{2+}\) pendant la charge/décharge de l'électrode CaV\(_6\)O\(_{16}\)-7H\(_2\)O en électrolyte 4,5 M Ca(NO\(_3\))\(_2\) + Ca(OH)\(_2\) à pH = 10, ce qui donne une capacité la plus élevée. En électrolyte aqueux acide, l'ion Ca\(^{2+}\), mais aussi les ions hydroniums et les protons participent à la charge de la CVO, ce qui pourrait expliquer la plus faible capacité observée (intercalation d'ions monovalent versus divalent).

**Conclusions**

Le but de cette thèse était d'utiliser une technique in situ, l'EQCM, pour approfondir nos connaissances fondamentales sur les mécanismes de stockage de charge dans les matériaux d'électrodes pour le stockage d'énergie (supercondensateurs, batteries). Pour les supercondensateurs, la charge de la double couche électrochimique a été étudiée avec des matériaux carbonés tri- (CDC) et bi-dimensionnels (SGL) par l'EQCM. La même méthodologie a été appliquée à l'étude d'autres matériaux d'électrode impliquant des réactions faradiques. Les mécanismes de stockage de charge ont été révélés dans les différents systèmes, en combinant l'EQCM, avec d'autres techniques de caractérisations in-situ, ainsi qu'avec des résultats de simulation.

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