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# Future Directions for Electrochemical Capacitors

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## Abstract

Recently, extensive research efforts on electrochemical energy storage materials have been developed, motivated by the urgent need for efficient energy storage devices for the automotive market. Electrochemical capacitors (ECs) bridge the gap between batteries and solid-state and electrolytic capacitors. While the high power density of these devices is attractive, greater energy density is required for the future. To address this need, both experimental approaches that modify the electrolyte-electrode interface and the use of analytical methods to characterize these interfaces are being actively pursued. The development of advanced *in-situ* analytical techniques to understand fundamental electrochemical processes and structural effects (pores, surface groups) down to the nanoscale level are expected to play a key role in developing the next-generation of ECs with high energy and high power performance.

Electrochemical energy storage systems (EES) are currently at the core of major societal and economic challenges, providing a key technology for addressing greenhouse gas emission and global warming <sup>1</sup>. A prominent component of this energy storage portfolio is the R&D efforts directed towards realizing high energy density batteries which satisfy the requirements for long-range battery electric vehicles (BEV). As the energy density increases to appropriate levels, the Achilles' heel of Li-ion batteries remains their limited power delivery and fast charging capabilities, which may be even more pronounced with the future development of solid-state battery technology. Electrochemical capacitors (ECs), also termed as supercapacitors, are another major family of EES whose electrical performance complements that of batteries <sup>2</sup>. They can harvest / deliver higher power than batteries but contain lower energy density, resulting in an operation time of only tens of seconds to minutes. Nonetheless, the number of technologies which benefit from these characteristics is quite extensive as applications of ECs range from power electronics, to automotive (power

delivery and regenerative braking) and grid energy storage (power quality and smoothing, frequency regulation). Supercapacitors are also used in the control systems of wind turbines. Although applications will continue to emerge, the need for increasing the energy density of these high power devices is expected to become even more apparent in the near future. In this perspective, we highlight the significant role that electrolyte-electrode interfaces can play in increasing the energy density of ECs.

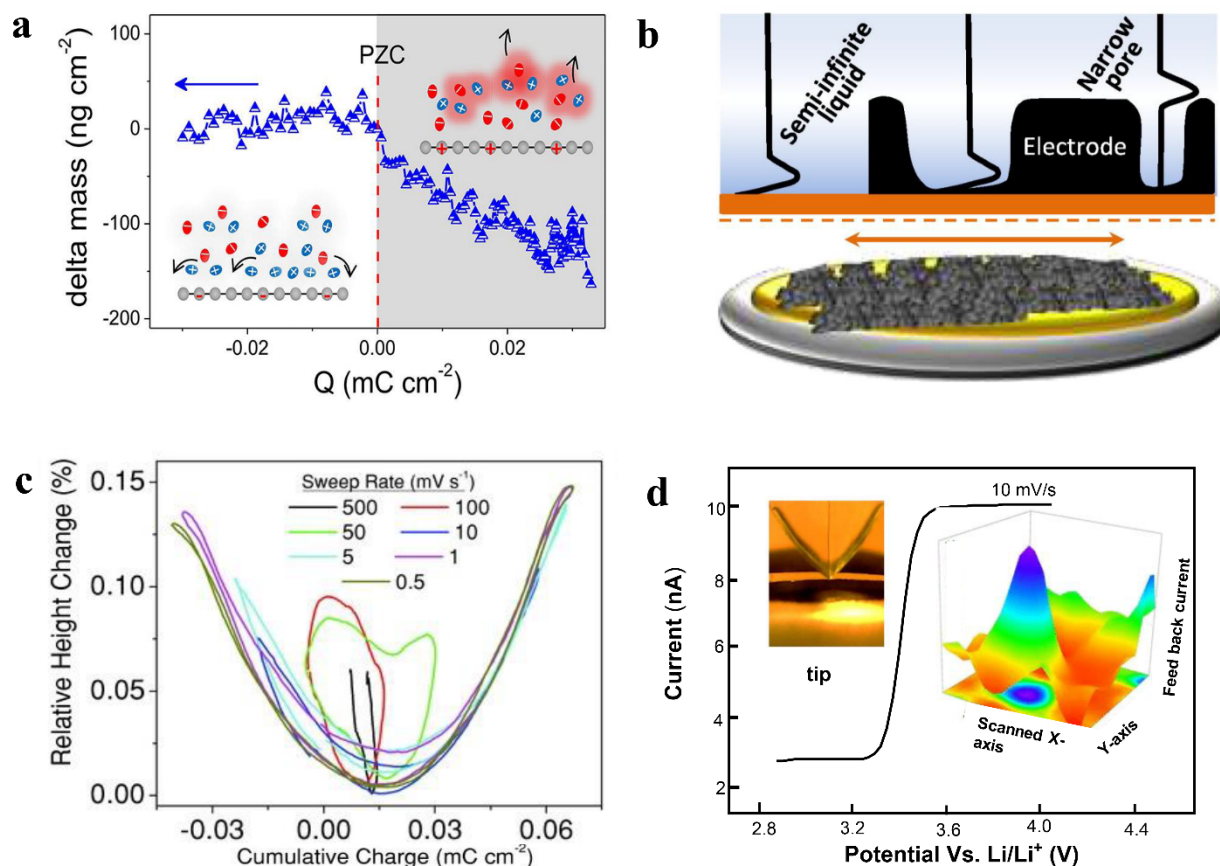
### ***Electrochemical Double Layer Capacitors***

Electrochemical Double Layer Capacitors (EDLCs) store charge via ion adsorption onto high surface area porous carbons, without any redox reactions. There has been significant progress in the past 10 years in understanding ion adsorption in carbon nanopores <sup>2</sup> and it is now well established that the confinement of ions in nanopores results in increased charge storage due to the partial desolvation of ions <sup>3,4</sup>. Because of these and other discoveries, the energy density of commercial EDLC devices has doubled over the past decade, reaching values close to 10 Wh kg<sup>-1</sup>, while still delivering extremely high peak power density (~30 kW kg<sup>-1</sup>) <sup>2</sup>.

In the research efforts directed towards improved energy density of supercapacitors, experimental approaches which modify the electrolyte-electrode interface as well as the use of analytical methods to characterize these interfaces are being actively pursued. Recent examples of the former include attempts at increasing cell voltage above the 1.0 V range that limits aqueous electrolyte systems. The design of new electrolytes with large voltage window stability, including ionic liquid electrolytes <sup>2</sup>, is of great importance, but remains a challenge. One alternative route is based on cleaning the porous carbon surface from surface groups present at carbon edge and basal planes <sup>5</sup>, while a second scheme involves preparing ionically conducting hydrophobic passive layers onto porous carbon particles for operation in the aqueous electrolyte <sup>6</sup>.

The utilization of analytical tools which characterize the electrolyte-electrode interface is becoming increasingly important. To some degree, the approach towards achieving higher energy density supercapacitors is generic as one starts by designing porous carbon structures with controlled pore size and texture <sup>5</sup>. Where the characterization tools become important is in analyzing ion and electron transfer at the nanoscale (< 1 nm). In recent years, the use of electrochemical quartz crystal microbalance (EQCM) has gained renewed interest. This technique allows for measuring the electrode weight change under polarization <sup>7,8</sup>. The latest results have shown that local carbon ordering was

important as charge storage was enhanced as a result of increased carbon-ion interaction simply by having cation reorganization at the electrode surface.<sup>9,10</sup> (Fig. 1a). Electrochemical QCM with Dissipation Monitoring (EQCM-D) analyzes the change of the resonance frequency over multiple overtones to track the change of the visco-elastic properties of the electrode / electrolyte interface and the modification of the mechanical properties<sup>11,12</sup> (see Fig. 1b).



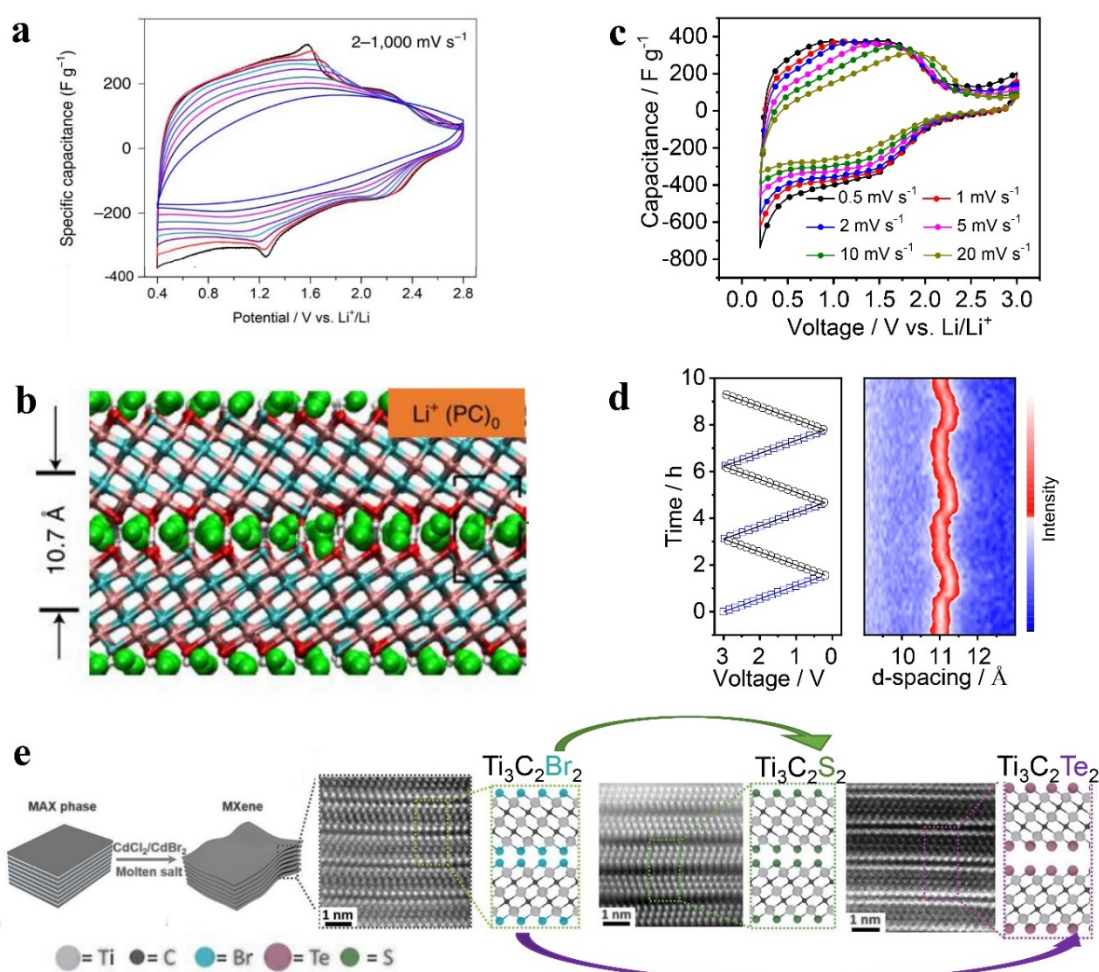
**Figure 1:** In-situ and in-operando advanced electrochemical and analytical techniques (EQCM, in-situ AFM, and SECM) for carbon-based electrical double-layer capacitors. (a) Mass change as a function of charge during the polarization of a single layer graphene coated on a quartz crystal resonator in EMI,TFSI electrolyte. (b) Sketch of a quartz crystal coated with a uniform porous layer with an in-situ hydrodynamic probe of rough/porous electrode structure. (c) In-situ AFM test result of EMI,TFSI ionic liquid electrolyte between two porous carbon electrodes with relative height change of inactivated carbon membrane plotted as a function of applied charge for various potential sweep rates. (d) CV of the microprobe cycled between 2.8 V and 3.8 V vs. Li<sup>+</sup>/Li in 1 M LiPF<sub>6</sub>/EC:DEC:EMC electrolyte (inset: Photo of the microprobe and SECM feedback area scan). Reproduced with permission from: a, ref.<sup>9</sup>; b, ref.<sup>11</sup>; c, ref.<sup>13</sup>; d, ref.<sup>14</sup>.

In contrast to conventional gravimetric EQCM, AC-electrogravimetry is an alternative and complementary characterization tool which couples fast electrochemical quartz crystal microbalance (EQCM) with electrochemical impedance spectroscopy (EIS). AC-electrogravimetry allows for accessing the gravimetric EQCM response of individual cations, anions and solvent molecules even in complex electrolyte mixtures <sup>15</sup>. This enables the double-layer formation mechanism to be refined. Another recent development has been the use of Atomic Force Microscopy (AFM) with an *in-situ* electrochemical cell. The advantage here is the ability to determine the electrode volume change at the nanometer level as a function of applied potential <sup>16</sup> (Fig. 1c). The development of scanning electrochemical microscopy (SECM) is certain to have an impact on understanding the electrode-electrolyte interface as it enables one to determine local electrode reactivity and kinetic parameters of the electrochemical processes by recording the current flowing through an ultra-microprobe electrode (the tip), while controlling the tip-electrode distance <sup>17</sup> (Fig. 1d). While there is the expectation that these electrochemical tools will provide a new understanding which, in turn, can be expected to lead to advances in energy density, the energy density values for EDLCs will always be lower than batteries because of the electrostatic charge storage mechanism. For this reason, there has been significant interest in pseudocapacitive materials.

### ***From double layer to high-rate (pseudocapacitive) redox materials***

Significant improvements in energy density can be achieved in certain materials where charge storage occurs via redox reactions. Because the reactions are not limited by semi-infinite diffusion, the materials maintain high power performance <sup>18</sup>. While pseudocapacitive materials were once restricted to largely RuO<sub>2</sub> and MnO<sub>2</sub>, research efforts during the past decade have resulted in the discovery of new materials as well as developing our basic knowledge regarding the charge transfer process under confinement <sup>2,19</sup>. In particular, the design and use of mesoporous architectures, where the electrolyte accesses the redox-active walls through nanoscale porosity, was instrumental in recognizing the pseudocapacitive behavior of various transition metal oxides <sup>20,21</sup>. MXene materials complement this work as they provide interesting opportunities as model 2-dimensional (2D) materials systems <sup>18</sup>. MXenes are prepared by selective etching of atomically thin A layer elements from MAX phase precursors, where M is an early transition metal, A is an element from group 13 or 14 of the periodic table and X is C and/or N <sup>18</sup>. The 2D Ti<sub>3</sub>C<sub>2</sub> material, the most popular member of the MXene family, achieves high capacitance and fast charge storage in aqueous sulfuric acid electrolyte <sup>18,22</sup> as the Ti<sup>3+/2+</sup> redox couple is activated following H<sup>+</sup> intercalation in the interlayer gap between Ti<sub>3</sub>C<sub>2</sub>

sheets <sup>23,24</sup>. In this material, fast H<sup>+</sup> transport is achieved from the presence of interstitial H<sub>2</sub>O molecules between the MXene layers. This pathway for fast proton transport effectively activates the redox reaction of the Ti atoms <sup>24</sup>. A similar mechanism is at work in other materials such as tungsten oxide WO<sub>3</sub>, where structural water molecules in crystalline tungsten oxide hydrates WO<sub>3</sub>·nH<sub>2</sub>O, enables highly reversible proton intercalation at subsecond time scales <sup>25,26</sup>. These results highlight the importance of the confined, interlayer H<sub>2</sub>O solvent molecules and their influence on the charge storage mechanism. It is not surprising that upon thermal annealing of Ti<sub>3</sub>C<sub>2</sub> MXene samples, a drastic decrease in charge storage occurs, suggesting that the surface termination groups control the presence of the confined H<sub>2</sub>O molecules <sup>24</sup>. Although charge storage in MXenes arises from redox reactions, it is evident that electrolyte-electrode interactions are of central importance as the solvent molecules are confined within the MXene layers. For this reason, electrochemical characterization of the electrolyte-electrode interface at the nanoscale by using advanced techniques such as EQCM and SECM may help in clarifying the fast charge storage mechanism in these layered materials <sup>24,27</sup>.



**Figure 2:** The electrochemical performance and charge storage mechanism of MXene electrodes in non-aqueous electrolyte. (a) CV of a  $\text{Ti}_3\text{C}_2\text{T}_x$  electrode in 1 M LiTFSI in PC electrolyte, showing intercalation pseudocapacitive behavior. (b) Structure of  $\text{Ti}_3\text{C}_2\text{T}_x$  showing intercalated and desolvated Li-ions. (c) CV of a  $\text{Ti}_3\text{C}_2\text{T}_x$  electrode prepared from the molten salt method in LP30. (d) In situ XRD maps of the (002) peak shows the peak position shift is less than  $0.25\text{\AA}$  during cycling. (e) Tuning surface groups of MXene by performing substitution and elimination reactions in molten inorganic salts. Reproduced with permission from: a,b, ref.<sup>28</sup>; c,d, ref.<sup>29</sup>; e, ref.<sup>30</sup>.

While aqueous electrolytes allow for high capacity and fast redox reaction rates, a significant challenge for pseudocapacitive materials is to achieve similar performance in non-aqueous electrolytes which can increase the energy density due to an extended voltage window. Li-ion intercalation in host materials is governed by desolvation and charge transfer kinetics at the material / electrolyte interface, as well as by Li-ion diffusion in the material host structure. Thus, one approach for preparing materials with high-rate Li-ion intercalation redox reactions is to design specific material structures which allow for fast Li ion diffusion. A good example of this strategy is mesoporous orthorhombic  $\text{Nb}_2\text{O}_5$ <sup>31</sup> where the mostly empty octahedral sites between (001) planes provides natural tunnels for lithium-ion transport throughout the a-b plane. Tuning the surface group and/or widening the interlayer gaps in 2D materials stacked by van der Waals (vdW) interaction is another promising research direction to follow. In the case of  $\text{MoS}_2$ , (002) oriented planes lead to a high degree of edge sites and extremely fast kinetics with 80% of the theoretical capacity for Li achieved in only 20 seconds<sup>32</sup>. The creation of oxygen vacancies in  $\text{MoO}_3$  is another route for improved electrochemical properties. In this case, a larger *b*-axis lattice spacing promotes faster kinetics without altering the  $\alpha$ - $\text{MoO}_3$  phase upon Li-ions insertion and de-insertion<sup>33</sup>. These approaches also apply for multi-ion batteries. For example, a highly defective iron phosphate-carbon composite was reported to enhance magnesium-ion diffusion in the solid phase, leading to fast, reversible ion intercalation reactions and stable cycling<sup>34</sup>.

The study of MXenes in non-aqueous electrolytes has led to an interesting series of results in which pseudocapacitive charge storage is influenced by surface groups<sup>29,30</sup>. In particular, F- and O-rich surface terminated  $\text{Ti}_3\text{C}_2$  MXene showed high capacity with fast ion transport in an electrolyte of 1M LiTFSI in propylene carbonate due to intercalation of partially desolvated Li-ions between the MXene layers<sup>28</sup> (Fig. 2a). This behavior was the result of specific interactions between the  $\text{Ti}_3\text{C}_2$  MXene surface groups and solvent molecules (Fig. 2b). It is interesting to note that the

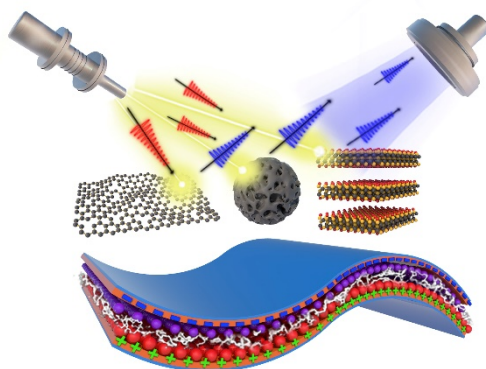
desolvation effects leading to increased capacitance in nanoporous carbons also influence pseudocapacitive charge storage. In addition, the modification of the MXene surface groups has a profound effect on the electrochemical properties. In O- and Cl-terminated  $\text{Ti}_3\text{C}_2$  MXene prepared by molten salt synthesis<sup>29</sup>, the cyclic voltammetry sweeps resembled the characteristic 'box' of a capacitive material in which a constant current is obtained as a function of potential, similar to what is observed in a pseudocapacitive material (Fig. 2c). In this study, the intercalation of desolvated  $\text{Li}^+$  between the MXene layers (see Fig. 2d) was deemed responsible for high capacity ( $200 \text{ mAh.g}^{-1}$ ) and high-rate performance ( $75 \text{ mAh g}^{-1}$  at 128C rate), as a result of the absence of hydrophilic -OH surface groups. It is evident that the use of non-aqueous electrolytes with MXene is at an early stage where the relationships between surface chemistry and electrochemical properties are still being identified. (Fig. 2e). In general, the development of oxide and non-oxide pseudocapacitive materials which exhibit high rate redox properties associated with Li-ion insertion and de-insertion is providing the basis for a new generation of fast charging Li-ion batteries<sup>19</sup> or hybrid capacitors that combine a capacitive electrode with a battery electrode<sup>2</sup>.

## **Summary**

This perspective has emphasized the role of electrode-electrolyte interfaces in electrochemical capacitors. In the case of supercapacitors, it is evident that techniques dedicated to characterizing surface structure and chemistry are bringing new insights to this field with the likely result being increased energy density. The pseudocapacitive materials field is still emerging as design rules for identifying this promising group of materials are still being established. It is interesting that both types of ECs are linked by the importance of solvation/de-solvation and confinement. The latter topic seems to be especially important. Finally, the search for new pseudocapacitive or redox capacitive materials that store the charge by fast, non-diffusion limited redox reaction will also benefit the entire battery field and it is a safe bet that such materials will emerge in the next few years.



## **TOC Graphics**



## **Biographies**

Liyuan Liu received her PhD degree from the Université Paul Sabatier (Toulouse, France) in 2020 and she continued her research as a post doc under the supervision of Prof. Patrice Simon and Dr. Pierre-Louis Taberna. Her research mainly focuses on 2D materials for energy storage devices including electrochemical capacitors and metal ion batteries.

Pierre-Louis Taberna received his PhD in Electrochemistry Science from Pierre et Marie Curie University (Paris, France) and he is currently CNRS research director at CIRIMAT institute, Université Paul Sabatier (Toulouse, France). His research activities have been devoted for more than twenty years to electrochemical characterization and modification of interfaces for electrochemical energy storage and conversion applications.

Bruce Dunn is Associate Dean for Research and Physical Resources and the Nippon Sheet Glass Professor of Materials Science and Engineering at UCLA. His research interests concern the synthesis of organic–inorganic materials and characterization of their electrical, optical, biological, and electrochemical properties. His current programs in electrochemistry include creating pseudocapacitive materials and the fabrication of three-dimensional batteries.

Patrice Simon is currently a distinguished professor of Materials Sciences at Université Paul Sabatier (Toulouse, France) and serves as Deputy director of the French network on electrochemical energy storage (RS2E), Member of the French Academy of Sciences. His research activities are focused on the modification of material/electrolyte interfaces in electrodes for electrochemical energy storage devices, including electrochemical capacitors and batteries.

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## **Quotes**

The development of advanced in-situ analytical techniques to understand fundamental electrochemical processes and structural effects (pores, surface groups) down to the nanoscale level will help in better understanding the ion adsorption and electron transfer in (pseudo)capacitive materials.

The emergence of new pseudocapacitive materials offers opportunities for developing the next-generation of ECs combining high power performance together with improved energy density.

The effect of electrolyte confinement in host materials and the associated ion solvation/de-solvation on electrochemical performance should be further explored.

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