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Review Article

Electrochemical double layer capacitors: What is next beyond the corner?

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This review summarizes some recent developments achieved in the fundamental understanding of ion confinement in microporous carbon supercapacitor electrodes. Combined with computational simulations, these advanced techniques provided new insights into the charge storage mechanism, providing guidelines for designing improved porous carbon structures with high-energy density. Also, innovative electrolytes have recently been proposed by introducing some redox-active moieties into electrolyte anions/cations, called biredox electrolytes, that combines redox contribution to double capacitance. This approach opens up new opportunities to develop high-energy supercapacitors and a new field of biredox electrolytes.

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modules for braking energy recovery and short-distance electric drive (to pass crossings). Besides, they also can sometimes replace batteries in electric buses where the limited autonomy is balanced by the fast charging that can be achieved during the passenger exchange [2].

Today, most (not to say all) commercialized supercapacitors use porous carbons as active materials. These devices, called electrochemical double layer capacitors (EDLCs), store the charge at the electrolyte/carbon interface through reversible adsorption of ions from an electrolyte onto the carbon surface, by charging the electrochemical double layer capacitance, which can be described in a crude approach by (1):

$$C = \frac{\varepsilon_r \varepsilon_0 A}{d} \text{ or } C/A = \frac{\varepsilon_r \varepsilon_0}{d}, \quad (1)$$

where C is the double layer capacitance (in F), ε_r is the electrolyte dielectric constant, ε_0 the dielectric constant of the vacuum (in F m^{-1}), d the charge separation distance (in m), and A the electrode surface area (in m^2).

Increasing the capacitance of porous carbons is one way to improve the energy density of supercapacitors. Beyond this basic consideration, there are important scientific challenges to tackle dealing with the understanding of the ions fluxes and adsorption mechanisms inside the porous carbon structure.

Ion confinement in carbon nanopores

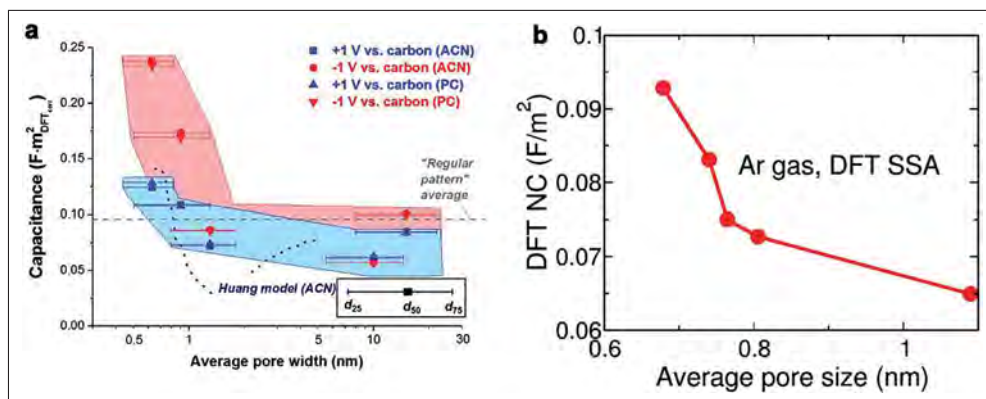
Following pioneer work from Aurbach [3], the discovery in 2006 of a different, more efficient storage mechanism in nanosized pores (less than one nm) led to a drastic change of view: not only the surface area but also the pore size was important to increase the charge capacity [4], also showing a maximum in capacitance when the ion size was similar to the carbon mean pore size [5]. Those results have also pointed out the importance of the measurements of the specific surface area and pore size distribution of microporous carbons from gas sorption technique [6]. As a result, the International Union of Pure and Applied Chemistry has recently confirmed that the Brunauer–Emmett–Teller (BET) analysis was not recommended for microporous carbons, as it over-estimates the surface of large micropores (>0.7 nm) [6]. Similarly, the use of N_2 gas for gas sorption measurement has to be discarded because of the existence of a quadrupole moment, which does not give accurate porosity for ultrami-

Introduction

In the past two decades, electrochemical capacitors, also known as supercapacitors, have received special attention since they are one of the most promising electrochemical energy storage devices for high power delivery or energy harvesting applications [1]. Originally developed for power electronics applications, they are facing increasing demand mainly driven by automotive and power electronics applications. Those include regenerative braking, voltage stabilization boost or start-stop systems. Numerous cities in Europe and around the world are developing tramways or buses with on-board supercapacitor

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Figure 1



A: specific capacitance (in $F \cdot cm^{-2}$) of porous carbons normalized to the accessible surface area for each ion in both solvents (acetonitrile AN and propylene carbonate PC). The regular pattern average of $0.095 F \cdot m^{-2}$ adapted from Ref. [7]. B: change of the specific capacitance normalized to the DFT-specific surface area versus the pore size of carbide-derived carbons (adapted from Ref. [4]). The trend is similar to that of Figure 1A.

ropores < 0.7 nm. The determination of the specific surface area for microporous carbons should then be done using Ar gas at 87 K and density functional theory (DFT) or non-linear DFT (NLDF) mathematical models should be used to calculate the pore size distribution and the mean pore size diameter. Also, the surface area accessible to the ions of the electrolyte (defined by considering the pore size larger than the neat ion size [7]) should be considered to calculate the specific capacity (in $F \cdot m^{-2}$) of the porous carbons. The specific surface area and pores size distributions of a series of porous carbons have been measured following the above recommendation [7]. Figure 1A shows the plot of the specific capacitance versus the carbon pore size measured in 1 M $(C_2H_5)_4N^+$, BF_4^- in acetonitrile or propylene carbonate electrolytes. The specific capacitance was obtained by dividing the gravimetric capacitance by the DFT accessible surface area measured using Ar gas that is the total surface of the pores larger than the neat ion size. The plot shows an increase of the capacitance in the small pore size region (less than 1 nm), such as originally proposed in 2006 (Figure 1B). For larger pore sizes (mesopores), the capacitance converges toward an average value below $0.1 F \cdot m^{-2}$, which aligns well with the “regular pattern” value reported by Centeno *et al.* [8] and with the calculated value limiting the double-layer capacitance at the planar carbon interface (or larger than the few-nm pores [9]).

However, the “real” structure of porous carbons being difficult to obtain from gas sorption measurements only, advanced experimental techniques have been recently proposed as tools to help in understanding the ion confinement and environment in carbon nanopores. In a recent paper, Prehal *et al.* [10•] studied the confinement and desolvation in nanometer sized carbon pores of 1 M CsCl in water electrolyte, by combining *in situ* small an-

gle X-ray scattering experiments (SAXS) together with Monte Carlo simulations. By modelling back the experimental SAXS data, they found that the average number of stripped-off water molecules increased for decreasing average pore size. Interestingly, the partial desolvation also occurred in carbon larger mesopores, although limited to about 1% water molecules removed from the solvation shell. These data thus show that ion desolvation seems to be a universal phenomenon for virtually all nanoporous carbons, because of the pore size dispersion and presence of ultranarrow (subnanometre) pores [10•].

Other *in situ* techniques have been recently developed the past years such as electrochemical quartz crystal microbalance (EQCM). EQCM in gravimetric mode, that tracks the weight change of an electrode during electrochemical polarization, has been successfully used to experimentally measure the extent of desolvation in carbon nanopores in non-aqueous electrolytes [11•–13]. EQCM results showed that EMI^+ cations lose half of their solvation shell in acetonitrile-based electrolyte while entering 1 nm pores in carbon electrodes [12]. Additionally, two different ion transfer mechanisms could be identified: counter ion (cation) adsorption at negative electrode and ion exchange mechanism at positive electrode. Recently, Levi *et al.* proposed the use of the EQCM-D technique (electrochemical QCM with dissipation monitoring), to perform a multiharmonic frequency analysis to assess the viscoelastic and hydrodynamic properties in porous active films [14]. Fitting the EQCM-D data with suitable hydrodynamic models allows tracking the change of the geometric parameters of porous electrodes in contact with an electrolyte. Such technique offers interesting opportunities to identify the impact of several parameters (nature of the electrolytes, ions, binder...) on the structure change of the electrodes.

Alternatively, not only the gravimetric or dissipation mode of EQCM offers opportunities to studying the ion fluxes in supercapacitor or energy storage electrodes. Perrot's group has developed the so-called AC-electrogravimetry technique [15]. It consists in running EQCM measurement in the gravimetric mode at a steady state (for instance constant potential) and, simultaneously, overimposing a sinusoidal perturbation to the steady-state and records the mass change Δm or the charge change ΔQ vs. the potential change ΔE [15]. These plots give access to the type of ions as well as the number of solvent molecules involved in the charge storage process depending on the potential range, as well as the ion dynamics inside the electrode depending on the frequency range explored [16•]. This technique seems promising for tracking the ion fluxes and could potentially push further our knowledge of ion transfer/adsorption in porous carbon electrodes, thus helping to designing the best porous carbon electrodes for the next generation of high-energy density supercapacitor electrodes.

Electrolytes for EDLCs

The energy density of supercapacitors changing with the voltage square ($1/2 \cdot C \cdot V^2$), there is a great interest in designing new electrolytes with improved voltage window stability, to go beyond 3 V. Today, conventional electrolytes for supercapacitors contain a salt dissolved in a solvent. Acetonitrile (CH_3CN , AN) is the solvent that leads to the highest conductivity when used in combination with an ammonium cation mixed with a fluorinated anion (such as $(\text{C}_2\text{H}_5)_4\text{N}^+$, BF_4^-). Although high cell voltage of 3 V can be obtained [17], AN-based electrolytes suffer from low flash point (5 °C) and high volatility. Alternatively, propylene carbonate-based electrolytes can be used but in that case, the power capability of the device is greatly affected (divided by three) as well as the low temperature applications. There is then an important need for alternative high voltage electrolytes [18].

However, it is well known that not only the electrochemical voltage window but also the conductivity, the viscosity, the boiling/melting points, the dielectric constant and salt chemistry deeply affects the electrochemical properties of the electrolyte [19]. As a result, it is really challenging to find a solvent/salt mixture that matches all the criteria at the same time. Also, research work developed in the Li-ion batteries field highlighted that the stability of the active materials at the positive electrode is an issue when operating at high potential (>4.5 V vs. Li, that is approximately >3.5 V cell voltage for a symmetric carbon/carbon device) [20,21]. However, Balducci and co-workers [22••] have proposed an interesting combinatory approach to select new solvent/salt couples and such efforts should be definitely pursued. Also, ionic liquids, which are solvent free electrolyte, are of particular interest to increase the cell voltage up to 3.5 V but the high viscosity and limited conductivity at room temperature

limits their interest. The use of eutectic ionic liquid mixtures can expand the temperature range, but the carbon structure must be specifically designed to ensure easy ion accessibility to the carbon surface [12,23].

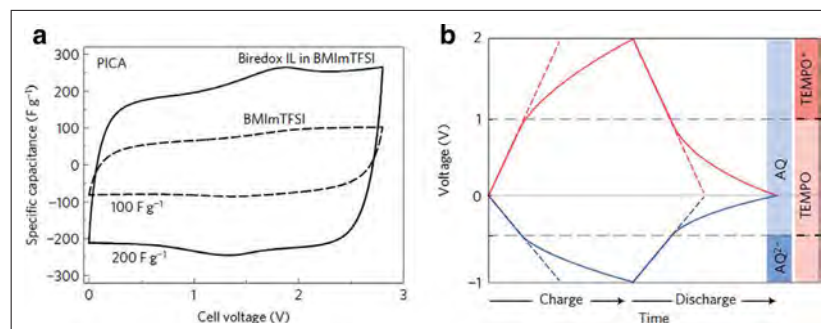
Another alternative approach has been recently proposed, which consists in using redox-active electrolyte [24•]. The idea is to modify ionic liquids electrolytes by grafting a redox-active groups onto the anions and/or cations, in the aim of playing with both the double layer charging process through basic ion adsorption and, at the same time, achieving an electron transfer through a redox reaction of the redox group at the operating potential of the carbon electrode.

This innovative concept has been reported in recent papers from two groups in France [24•] and Canada [25]. Fontaine and co-workers [24•], for instance, used a perfluorosulfonate anion (PFS^-) and a methyl imidazolium cation (MIm^+) ionic liquid, where anion and cation are functionalized with anthraquinone (AQ) and 2,2,6,6-tetramethylpiperidiny-1-oxyl (TEMPO) moieties, leading to the $(\text{AQ-PFS}^-)(\text{MIm}^+-\text{TEMPO})$ biredox electrolyte. These biredox were used as salt and dissolved at 0.5 M in BMIm^+ , TFSI^- neat ionic liquid. The resulting solution (ionic liquid plus the biredox salts) was used as electrolyte in supercapacitor cells in combination with activated porous carbon electrodes. As expected, these ionic liquids were able to increase the charge storage via both electrostatic—in the double layer—and redox reaction mechanisms. The obtained capacitance was twice larger in the biredox electrolyte compared to biredox-free solution (Figure 2a).

Figure 2b shows the schematic representation of a galvanostatic charge discharge cycle, with the respective potential stability domains of the reduced and oxidized forms of the biredox species. The figure shows that a Faradic contribution is added to the double layer contribution during charge by oxidation of the TEMPO moieties beyond 1 V vs. ref. In the same time, the reduction of the AQ groups on the anion at the negative electrode below -0.5 V vs. Ref. reduction reaction adds to the double layer contribution to increase the total capacitance. This example shows that the careful selection of the grafted moieties has the potential to greatly improve the capacitive performance of porous carbon electrodes. Moreover, the working voltage of the cell was kept as high as 2.7 V, which is typically the voltage AN-based electrolytes can achieve.

Capacitances up to 370 F g^{-1} were measured, depending on biredox ionic liquid concentrations and temperatures, stable for at least 2000 cycles with limited—if any—degradation. Another striking result was the evidence of the retention of the redox species into the porous electrode, as can be seen from both the low self-discharge

Figure 2



A: cyclic voltammetry at 5 mV s^{-1} with 0.5 M biredox IL in BMImTFSI (solid line) and pure BMImTFSI (dashed line), respectively. B: schematic representation of the galvanostatic voltage response of the electrostatic and Faradaic processes with the biredox IL and the stability regions for its oxidized/reduced species. The dashed lines illustrate the behavior if only electrostatic processes were to prevail. Adapted from Ref. [24^{*}].

and leakage currents measured. Although surprising, this still needs to be understood, but specific electrostatic interactions between ions and carbon pores (by creation of image charges for instance) could be possible [26]. This new electrolyte concept opens up new opportunities to develop high-energy supercapacitors and a wide new field in redox materials.

In this review, we summarized 1) recent development of fundamental understanding of porous carbon supercapacitors by using advanced experimental techniques and 2) electrolyte design strategy toward high-energy performance. Although the capacitance increase in sub-nanometer pores (less than 1 nm) in porous carbon electrode has been evidenced for a decade, the ion confinement effect in nanopores is still not completely understood. Theoretically and experimentally studies are needed to further unveil the charge storage mechanism. In that aim, advanced experimental techniques such as *in situ* NMR, *in situ* small angle X-Ray or neutrons scattering experiments (SAXS, SANS), *in situ* EQCM (in gravimetric or dissipation modes) techniques combined with computer modeling have been developed to probe deeply into the ion confinement in nanopores, thus guiding the design of better porous carbon electrodes with high-energy density. These efforts should be pursued during the next years and other tools such as electronic microscopy (*in situ* transmission electronic microscopy) or scanning electrochemical microscopy (SECM) could be of great help. Besides the strategy of electrode material design, developing advanced electrolytes with improved voltage window is as well important to enhance the energy density. Although interesting progresses have been made using a combinatory approach, the finding of high voltage electrolyte remains challenging. Alternatively, a recent approach has been developed by using active electrolyte ions functionalized together with redox moieties, offering real opportunities to increase the capacitance and voltage

window by introducing redox reaction in double layer capacitors. The abounding research works highlights the real interest for developing supercapacitor devices with improved performance for complementing—and sometimes replacing—conventional batteries in applications where high power, high cyclability and high charge/discharge rates are needed.

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