

Capacitive Energy Storage in Nanostructured Carbon – Electrolyte Systems

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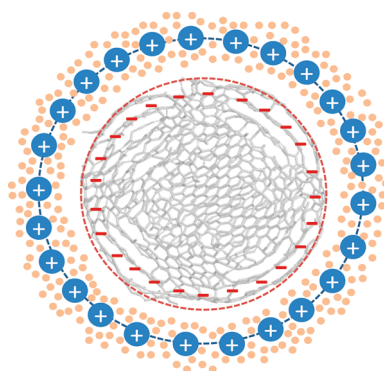
CONSPECTUS

Securing our energy future is the most important problem that humanity faces in this century. Burning fossil fuels is not sustainable, and wide use of renewable energy sources will require a drastically increased ability to store electrical energy. In the move toward an electrical economy, chemical (batteries) and capacitive energy storage (electrochemical capacitors or supercapacitors) devices are expected to play an important role. This Account summarizes research in the field of electrochemical capacitors conducted over the past decade.

Overall, the combination of the right electrode materials with a proper electrolyte can successfully increase both the energy stored by the device and its power, but no perfect active material exists and no electrolyte suits every material and every performance goal. However, today, many materials are available, including porous activated, carbide-derived, and templated carbons with high surface areas and porosities that range from subnanometer to just a few nanometers. If the pore size is matched with the electrolyte ion size, those materials can provide high energy density. Exohedral nanoparticles, such as carbon nanotubes and onion-like carbon, can provide high power due to fast ion sorption/desorption on their outer surfaces. Because of its higher charge–discharge rates compared with activated carbons, graphene has attracted increasing attention, but graphene had not yet shown a higher volumetric capacitance than porous carbons.

Although aqueous electrolytes, such as sodium sulfate, are the safest and least expensive, they have a limited voltage window. Organic electrolytes, such as solutions of $[\text{N}(\text{C}_2\text{H}_5)_4]\text{BF}_4$ in acetonitrile or propylene carbonate, are the most common in commercial devices. Researchers are increasingly interested in nonflammable ionic liquids. These liquids have low vapor pressures, which allow them to be used safely over a temperature range from $-50\text{ }^\circ\text{C}$ to at least $100\text{ }^\circ\text{C}$ and over a larger voltage window, which results in a higher energy density than other electrolytes.

In situ characterization techniques, such as nuclear magnetic resonance (NMR), small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS), and electrochemical quartz crystal microbalance (EQCM) have improved our understanding of the electrical double layer in confinement and desolvation of ions in narrow pores. Atomistic and continuum modeling have verified and guided these experimental studies. The further development of materials and better understanding of charged solid–electrolyte interfaces should lead to wider use of capacitive energy storage at scales ranging from microelectronics to transportation and the electrical grid. Even with the many exciting results obtained using newer materials, such as graphene and nanotubes, the promising properties reported for new electrode materials do not directly extrapolate to improved device performance. Although thin films of nanoparticles may show a very high gravimetric power density and discharge rate, those characteristics will not scale up linearly with the thickness of the electrode.



1. Introduction

Energy storage systems (ESSs), such as batteries and electrochemical capacitors (ECs), play a large role in our lives.

Li-ion batteries are the best performers, with energy densities reaching 200 W h/kg due to major efforts dedicated to their development. ECs were attracting less attention until

very recently.¹ Because Li-ion batteries suffer from a sluggish charge/discharge and a limited lifetime, faster and higher power ESSs are needed in a number of applications. ECs also known as supercapacitors or ultracapacitors, are power devices that can be fully charged/discharged in seconds; consequently, their energy density (about 5 W h/kg) is lower than that in batteries, but a much higher power delivery or uptake (>10 kW/kg) can be achieved for shorter times (few seconds). While small-size ECs (few farad cells) have been used in electronic devices since the mid-1990s, their implementation in the Airbus A380 jumbo-jet for emergency door opening has placed ECs as the most reliable ESS device.² Then, the combination of Li-ion batteries (energy) with supercapacitors (power) in hybrid and electric vehicles and trams has proven to increase the battery life and the energy recovery efficiency in braking.² Automotive use of supercapacitors for power applications includes board-net stabilization, electric braking assistance, and starter–generators recently introduced by Citroën and Peugeot.

Using carbon as the active material, electrochemical double layer capacitors (EDLCs) represent today more than 80% of the commercially manufactured ECs. The energy is stored at the electrolyte/carbon interface by charging the “double-layer capacitance” through reversible ion adsorption on the carbon surface:

$$C = \frac{\epsilon_r \epsilon_0 A}{d} \text{ or } C/A = \frac{\epsilon_r \epsilon_0}{d} \quad (1)$$

where C is the double layer capacitance (F), ϵ_r is the electrolyte dielectric constant, ϵ_0 is the dielectric constant of the vacuum, d is the charge separation distance, and A is the electrode surface area.

No redox reaction is thus involved in the charge storage mechanism in EDLCs. The active material used in EDLCs is carbon since it offers a combination of electrical conductivity, high specific surface area (SSA), and electrochemical stability over a wide range of potentials in both aqueous and nonaqueous electrolytes.³

Performance of ECs is characterized by their energy (W , joules, but usually expressed in watt hours) and power (P , watts). The energy is given by the following equation:

$$W = \frac{1}{2 \times 3600} CV^2 \quad (2)$$

where V is nominal voltage (volts). The maximum power is given by the equation

$$P = \frac{V^2}{4R} \quad (3)$$

where R is series resistance. The energy and power values are usually normalized by the weight or volume of the device or the electrode (it is very important to distinguish between those) to obtain energy and power densities.

The most important challenge ECs are facing today is to increase the device energy density to reach 10 W h/kg or more, moving them closer to batteries and cutting the cost at the same time.⁴ This can be achieved by increasing the capacitance or the cell voltage. The cell voltage (V) is mainly limited by the electrolyte stability. Increasing the energy density (eq 2) can be also achieved by increasing the capacitance, C , which is controlled by the carbon/electrolyte interface. Basically, it requires designing the carbon–electrolyte interface for optimizing the adsorption of ions from the electrolyte to maximize the charge stored per unit of weight or volume of carbon.

This Account will first summarize the current understanding of the ion adsorption on the carbon surface and the associated capacitance. Then, recent advances in designing appropriate IL mixture/carbon combinations for increasing the cell voltage will be presented, and the effect of the electrode thickness and architecture on ion transport and EC performance will be discussed. Some general considerations on comparing power and energy densities will be provided at the end to help the reader correctly interpret data and evaluate claims published in the literature.


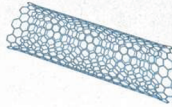
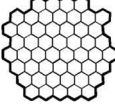
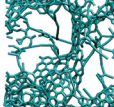
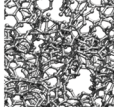

2. Carbon Materials for Supercapacitor Electrodes

Equation 1 suggests a linear capacitance increase with the area of the carbon/electrolyte interface, where the charge separation occurs. Developing high-SSA carbons is required for increasing the capacitance. Table 1 shows examples of different carbon structures that have high conductivity and high SSA and can be used in EDLCs (onion-like carbon (OLC), carbon nanotubes, graphene, activated carbons, and carbide-derived carbons).⁵

OLCs are zero-dimensional (0D) materials prepared as bulk (nonporous) nanoparticles of few nanometers diameter, usually by annealing nanodiamond powders in vacuum or argon. They offer SSA up to 500–600 m²/g fully accessible to ion adsorption and a high electrical conductivity resulting in high power^{6,7} but a limited capacitance of about 30 F/g.

Carbon nanotubes (CNTs), which are one-dimensional materials, have been extensively studied for EDLC applications within the past decade.^{3,7} Small diameter single-walled CNTs

TABLE 1. Different Carbon Structures Used in EDLCs with Onion-like Carbon (OLC), Carbon Nanotubes, Graphene, Activated Carbons, and Carbide-Derived Carbons

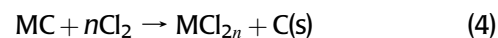
Material	Carbon onions	Carbon nanotubes	Graphene	Activated carbon	Carbide derived carbon	Templated carbon
Dimensionality	0-D	1-D	2-D	3-D	3-D	3-D
Conductivity	High	High	High	Low	Moderate	Low
Volumetric Capacitance	Low	Low	Moderate	High	High	Low
Cost	High	High	Moderate	Low	Moderate	High
Structure						

(SWCNT) with SSA up to 1000 m²/g show average capacitance values in the range of 50–70 F/g in nonaqueous electrolytes. Like OLCs, CNTs offer highly accessible outer surface area that makes them a material of choice for high power devices,^{3,7,8} despite a moderate volumetric capacitance due to low density (~0.3 g/cm³). Alternatively, CNTs can be used as substrate for preparing composite electrodes by decorating or coating the CNT surface with a thin film of redox materials.^{8–11} It is important to distinguish between SWCNT and double-walled nanotubes (DWCNT), which have a higher SSA and higher conductivity but a much higher cost compared with multiwalled nanotubes (Table 1). However, even those are usually a mix of semiconducting and metallic ones.

Graphene¹² has attracted great interest during the past 3 years for EDLC applications.⁷ As a 2D material (Table 1), graphene can potentially combine fully accessible high SSA and high conductivity. Although the theoretical SSA of a single-layer graphene can reach 2670 m²/g, one critical issue to avoid is restacking of sheets during electrode preparation. Capacitance of up to 100 F/g was reported in nonaqueous electrolytes for graphene;⁷ however, the low gravimetric density of exfoliated graphene is still an issue for designing thick electrodes to assemble large cells of hundreds of farads. Graphene can be functionalized with redox materials for enhancing energy density;^{7,13,14} however, this generally decreases the power density as well as the cyclability and narrows the operation temperature range. This is observed also for hybrid devices combining battery-like and EDLC electrodes. Capacitance of 150 F/g was reported in acetonitrile-based electrolyte with activated graphene sheets,¹⁵ which is similar to activated carbons. Such high capacitance reported for graphene electrodes is promising, and these thin-film electrodes (graphene loading from 1.5 to 2.5 mg/cm²) are of great interest for designing high power, small size devices.

Activated carbons (AC) are prepared by creating a three-dimensional porous network in the bulk of carbon materials through an activation process, which consists of a controlled oxidation of bulk carbon powders or carbonized organic precursors using various activation techniques, such as oxidation in water vapor, KOH, or CO₂. Micropores (pore size <2 nm) and mesopores (2–50 nm) created during the activation process are responsible for the high SSA, which can exceed 2000 m²/g. Low-cost activated carbons are generally obtained from the carbonization and subsequent activation of natural carbon precursors like wood, coconut shells, fruit pits, or anthracite; they are amorphous and their 3D structure contains a network of mainly sp² and some sp³ bonded atoms. The presence of oxygen, nitrogen, and other atoms in the network structure and surface termination with oxygen-containing functional groups leads to limited conductivity that requires addition of carbon black to AC electrodes. Capacitive performance of activated carbon has been greatly improved during the past years, moving from about 120 F/g in mid 2000s⁴ to more than 200 F/g in organic electrolytes.¹⁶ With a density higher than that of CNTs and graphene, about 0.5 g/cm³, activated carbon volumetric capacitance reaches 50–80 F/cm³. Due to the scalable manufacturing, reasonable cost, and high capacitance, activated carbons are widely used in commercial devices.

Carbide-Derived Carbons (CDCs) are produced by extraction of metals from carbides by a reaction like



This method allows the synthesis of micro- and mesoporous carbons with SSA of 1000–3000 m²/g with a controlled pore size, since porosity is formed by leaching out metal atoms, M, from the crystal structure of the carbide precursor. TiC-CDC with a narrow pore size distribution having a mean value that is tunable between 0.6 and 1.1 nm

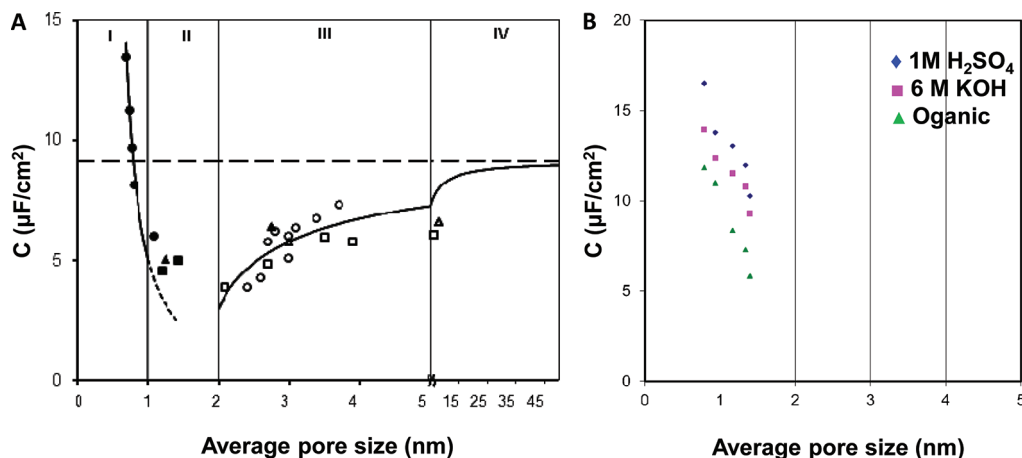


FIGURE 1. (A) Normalized capacitance vs average pore size for TiC-CDC and activated carbons tested in the same organic electrolyte.²⁶ Dots show experimental points, and the simulation of the capacitance change with pore diameter, confirming experimental results, is shown using solid lines.²⁷ (B) A similar trend was observed for activated carbons in various organic and aqueous electrolytes.²⁸

was prepared by changing the synthesis temperature.¹⁷ CDC technology allows the control of carbon growth on the atomic level, monolayer by monolayer, enabling pore size control with better than angstrom accuracy by changing process parameters, such as temperature, time, and environment.

Templated carbons are produced by the carbonization of an organic compound in nanospace of a template inorganic substance and the liberation of the resulting carbon from the template.¹⁸ The template technique allows one to prepare one-, two-, and three-dimensional carbons such as carbon nanotubes, graphene, and nanoporous carbons.¹⁸ The process allows precise control of pore size in the mesopore range and mesoporous carbons have been prepared by soft-¹⁹ and hard-template methods²⁰ using partially graphitizable carbon precursors. The soft-template method uses phenolic resin as carbon source and triblock copolymer as the template, which is a more economical, faster, and environmentally friendly route to obtain materials with large mesopores and high SSA.

Other carbons are also used in supercapacitors. Carbon nanohorns, if open to make internal cavities accessible, may show good capacitance,²¹ but this material is presently produced only in smaller quantities and mainly used for research purposes. Aerogels have a low density and their use should be limited to supporting pseudocapacitive materials, which will not be discussed in this Account.

3. Electrolytes

EC cell voltage is limited by the electrolyte decomposition at high potentials. Moving from *aqueous* to *organic* electrolytes increases the cell voltage from 0.9 to 2.5–2.7 V for EDLCs. Thus, nonaqueous electrolytes are mainly used because they

can achieve a higher cell voltage (2.7 V) than aqueous electrolytes like sulfuric acid, which are limited to about 1 V. Conventional electrolytes contain a mixture of a solvent and a salt, like tetraethylammonium tetrafluoroborate ($(C_2H_5)_4BF_4$). The use of acetonitrile (AN) as electrolyte solvent leads to highly conducting electrolytes (about 60 mS/cm at room temperature). However, the low flash point of AN ($\sim 5^\circ C$) might be an issue. Although Japan has prohibited the use of acetonitrile in supercapacitor electrolytes for safety reasons, AN-based supercapacitors are used in the rest of the world. Replacement of AN with propylene carbonate (PC) can only be achieved at the expense of the power density since the electrolyte conductivity drops by a factor of ~ 4 .

Ionic liquids (ILs), which are solvent-free electrolytes that are liquid at room temperature (organic salts), are attracting much interest because of their stability in a large voltage window, but their low conductivity at and below room temperature has been limiting their practical use to elevated temperatures.²² A careful choice of both the anion and the cation allows the design of high-voltage supercapacitors, and 3 V, 1000 F commercial devices are already available.²³ Hybrid activated carbon/conducting polymer devices also show an improved performance with cell voltages higher than 3 V.²⁴ However, ionic conductivity of these ILs at room temperature is just a few millisiemens per centimeter. Interestingly, this conductivity problem can be circumvented by selecting appropriate eutectic IL mixture–carbon combinations.²⁵

4. Capacitance versus Carbon Pore Size

Ion Desolvation in Nanopores. As mentioned above, activated carbon capacitance has doubled during the past 5 years to recently reach values as high as >200 F/g in

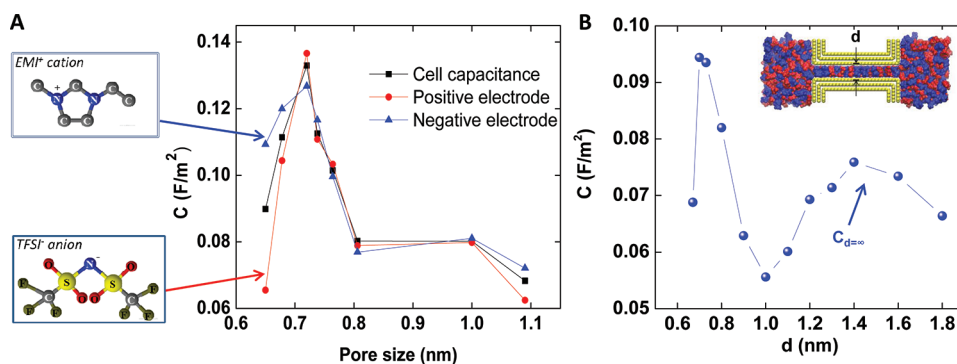


FIGURE 2. (A) Experimental normalized capacitance change vs average pore size obtained for TIC-CDC carbons in neat (EMI-TFSI) electrolyte at 60 °C and (B) calculated capacitance change vs carbon pore size from molecular dynamics (figure from ref 37).

organic electrolytes,¹⁶ and accordingly, more improvements have thus been made within the past 5 years than during the previous 20 years. One of the reasons for this substantial improvement is the appreciation of the pore size effect and observation of the ion desolvation in carbon micropores, made when studying CDC.²⁶ Figure 1a shows the specific capacitance normalized by BET SSA versus pore size of CDC and activated carbons, obtained in acetonitrile electrolyte containing 1.5 M NEt_4BF_4 salt.²⁶

Contrary to the traditional view, the normalized capacitance decreases with pore size until a critical value (~ 1 nm) is reached and then increases. Although the size of the solvated ions is larger, pores smaller than 1 nm greatly enhance the double layer charge storage. This was initially explained by the distortion of the ion solvation shell, leading to a closer approach of the ion to the carbon surface, which by eq 1 leads to improved capacitance. These results have been experimentally confirmed by many research groups^{29–32} and have drawn the interest of the modeling community who helped to understand the double layer capacitance charge in subnanometer pores (Figure 1a).^{27,33,34} Still few papers report the absence of pore size effect on capacitance,³⁵ but these claims are based on the comparison of data obtained with various carbons with broad pore size distributions and in different electrolytes. Recent modeling efforts have shown that a very precise control of the carbon pore size (like that achieved with CDCs) is needed to see the capacitance increase at small pore size.^{36–38}

Using CDC electrodes in IL electrolytes, Largeot et al.³⁹ found that the maximum capacitance was obtained when the ion size matches the carbon pore size. The “volcano” plots shown in Figure 2 rule out the way charge storage was traditionally described in EDLC materials, with ions adsorbed on both pore walls, since there is no space available for more than one ion per pore. Behind the experimental evidence of

the existence of a maximum capacitance for pore size less than the solvated ion size or for ion size close to pore size in solvent-free electrolytes, there are still numerous questions to address, like the mechanism and energetics of ion desolvation, the environment of the ions in the confined nanopores where there is not enough room to build the complete “double layer” structure, such as defined by Helmholtz. Further progress in understanding of the ion adsorption in carbon nanopores requires use of *in situ* characterization techniques and computational modeling.

***In Situ* Techniques.** Using the *in situ* electrochemical dilatometry technique, Hantel et al.⁴⁰ measured the electrode volume change during ion adsorption in CDC electrodes in nonaqueous electrolyte. Only a small expansion of less than $\sim 2\%$ was observed for the CDC with the smaller pore diameter (0.58 nm), which confirms the absence of ion intercalation (redox process) in the charge storage mechanism.

In situ study of ion adsorption in carbon pores in aqueous and organic electrolytes using the electrochemical quartz microbalance (EQCM) technique^{41,42} has shown that bulky ions like $\text{N}(\text{C}_2\text{H}_5)_4^+$ and BF_4^- solvated in propylene carbonate entered the carbon micropores without their solvation shell, but small, highly solvated Li^+ ions were losing only a part of their solvation shell to access the pores. The solvation numbers of ions confined in carbon nanopores were also estimated for a series of ions (Li^+ , K^+ , Na^+ , Cl^- , etc.) in aqueous electrolytes using EQCM, and partial desolvation was observed for ions confined in nanopores, confirming previous results in Figure 1.

Nuclear magnetic resonance (NMR) has been used to study EDLC aging⁴³ and ion adsorption in carbon nanopores in nonaqueous electrolyte.⁴⁴ Using *ex situ* solid-state NMR, Lee et al.⁴⁴ distinguished three different signals for the BF_4^- adsorption, attributed to BF_4^- adsorbed on the outer surface of the carbon, in large pores, and in small micropores, respectively. A recent communication from Deschamps et al.⁴⁵ shows

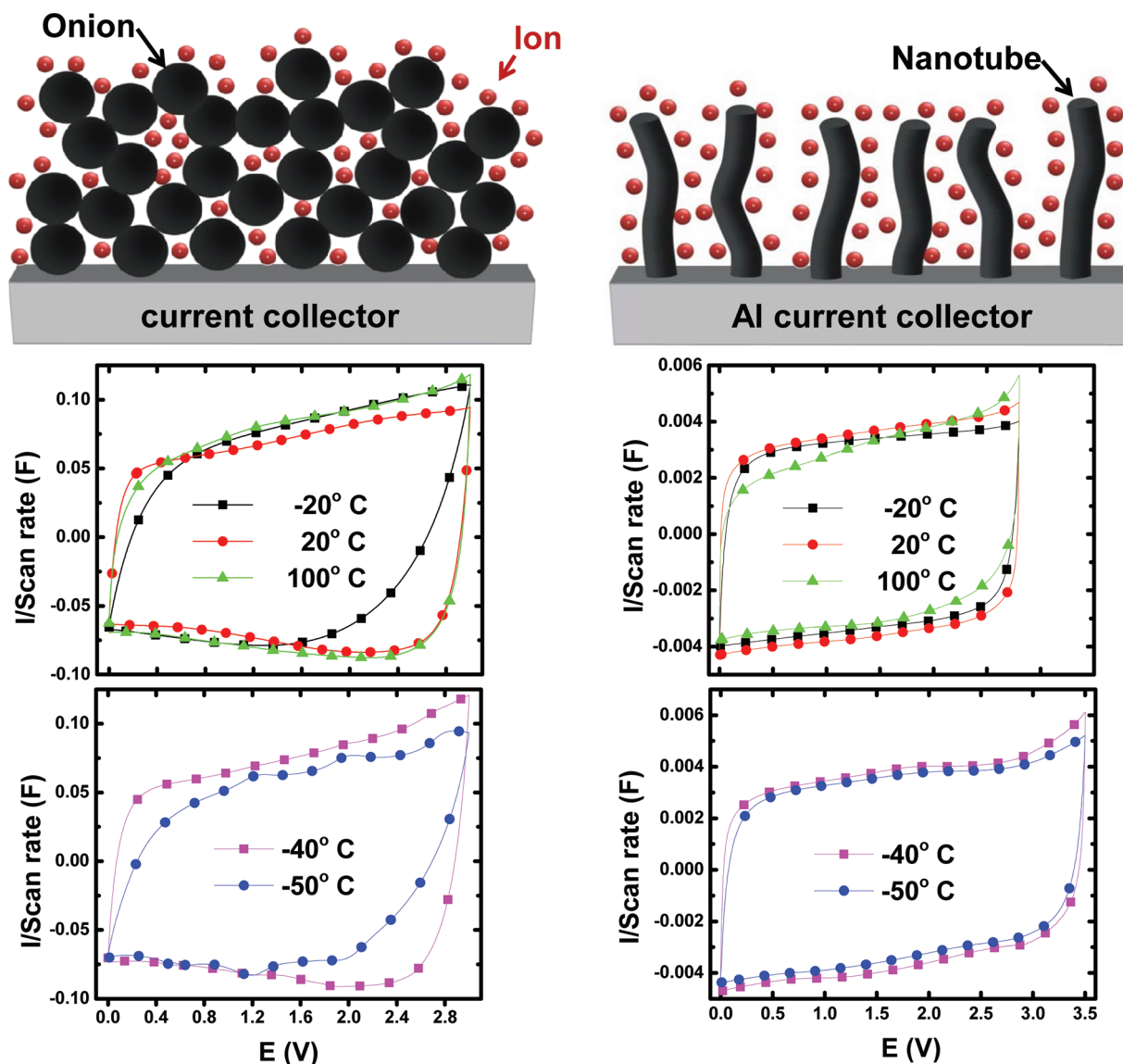


FIGURE 3. Cyclic voltammety data. (A) Schematic drawing of the OLC electrode and CVs for OLCs recorded at 100 mV/s (–20 to 100 °C) and 1 mV/s (–40 and –50 °C). (B) Schematic drawing and CVs for CNTs recorded at 100 mV/s (–20 to 100 °C) and 5 mV/s (–40 and –50 °C).

that the unevaporable fraction of solvent (acetonitrile) was roughly constant upon charging at the positive electrode while the acetonitrile was expelled from the graphene interlayer space at the negative electrode. Like recently demonstrated, *in situ* NMR measurements can help in pushing further our understanding of the ion environment inside micropores.⁴⁶

5. Modeling and Simulation

Extensive work was done to understand the electrode–electrolyte interfaces using various simulation techniques, and it is now recognized that the ions adopt a multilayered structure at the ionic liquid/graphite (planar) electrode interface.^{47,48} Such behavior is described as the “over-screening charge effect”: because of electrostatic

interactions between ions in IL, the charge carried out by the first layer of ions adsorbed at the carbon surface exceeds the one present at the carbon surface. Moving from a planar electrode surface to more complex systems, Shim et al. used a molecular dynamics approach to model ion adsorption in carbon nanotubes.⁴⁹ They confirmed that the distribution of the ions inside the pores changes with the pore size. By combining X-ray diffraction with Monte Carlo simulations in the grand canonical ensemble, Kaneko's group showed that solvent (PC) molecules were predominantly adsorbed at the carbon wall in the presence of salt, while no organization was observed in the bulk electrolyte,³⁴ thus evidencing a different environment for ions inside the carbon nanopores with ~1 nm size. From MD simulations, Feng et al.⁵⁰ found

that fully hydrated K^+ ions accumulate primarily in the central plane of slit-shaped pores for pore sizes between 1 and 1.5 nm. This phenomenon disappears when the pore width is narrower than 1 nm because of ion interactions. Kornyshev's group introduced the concept of the "superionic state".³³ Using slit-shaped pore geometry, they explained the capacitance increase in small pores with image forces in the carbon side that screen out the electrostatic interactions of ions of the same polarity inside the pore. As a result, the ion packing density, and thus the capacitance, is increased inside the pore. Using MD and DFT modeling, very recent studies^{36–38} have shown an oscillative decay of the capacitance as a function of pore size (Figure 2b), explained by the overlap of electrical double layers from the two charged carbon walls.³⁷ Figure 2b shows the calculated capacitance change versus the carbon pore size in neat ionic liquid electrolyte, obtained from MD simulation; both plots (experimental, Figure 2a, and calculated, Figure 2b) show the same capacitance increase for the pore size close to the ion size (~ 0.7 nm).

Although these studies confirmed and explained the increase of the capacitance caused by ion confinement in nanopores, these approaches failed to quantitatively predict the amplitude of this increase. The use of realistic porous carbon structures⁵¹ in the models will be required for guiding development of materials with improved capacitance.

6. Exohedral Carbon with Ionic Liquid Electrolyte for Extended Temperature Range

Recent results have shown that utilizing eutectic mixtures of IL as electrolyte in combination with a fully accessible high surface area of exohedral carbons, such as CNTs or onions, could extend the voltage window and the temperature range of operation. *N*-Methyl-*N*-propylpiperidinium bis(fluorosulfonyl)imide (PIP₁₃FSI) and *N*-butyl-*N*-methylpyrrolidinium bis(fluorosulfonyl)imide (PYR₁₄FSI) ionic liquids show melting points of 6 °C (PIP₁₃FSI) and –18 °C (PYR₁₄FSI), but the 1:1 by weight or molar ratio mixture stays liquid to –80 °C. These results demonstrate that selection of a proper combination of cations with the same anion prevents an ordered arrangement and crystallization, thereby expanding the temperature window for IL use.²⁵

Figure 3A shows the cyclic voltammograms (CV) of OLCs in the IL mixture from –50 to 100 °C.²⁵ Rectangular shape of CVs typical for a pure capacitive behavior was observed from –40 to 100 °C; which is far beyond the temperature range of conventional AN- or PC-based (–40 to +70 °C) commercial ECs.² Additionally, the cell voltage was increased to 3 V at 100 °C and 3.7 V at room temperature, which is 1 V above the cell voltage of commercial EDLCs, which means a gain of 100% in the

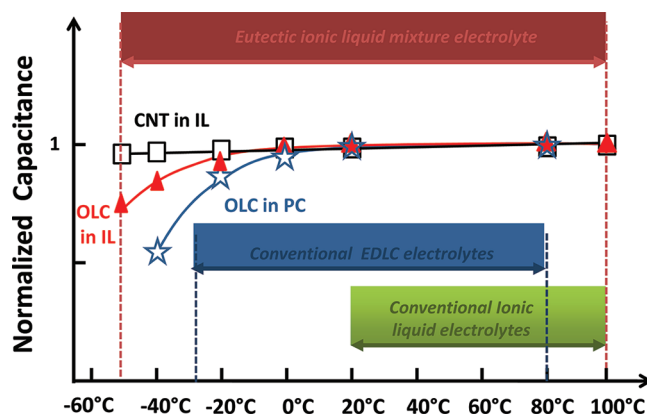


FIGURE 4. Change of capacitance versus the temperature for OLC and VA-CNT electrodes, calculated from cycling up to 2.8 V.

energy density. Using vertically aligned CNT electrodes (VA-CNTs) directly grown on an aluminum foil in the same electrolyte mixture, the low temperature of –50 °C could be reached while maintaining the capacitive behavior at 5 mV/s thanks to the large intertube distance that enhances the electrochemical accessibility of the CNT surface to the ions (Figure 3B). Figure 3C shows the change of capacitance versus the temperature for OLC and VA-CNT electrodes. As a result, the use of the (PIP₁₃FSI)_{0.5}(PYR₁₄FSI)_{0.5} mixture in conjunction with OLC and VA-CNT electrodes extends the temperature range on both the low and high temperature sides enabling EDLC applications under extreme climatic conditions (Figure 4).

7. Effect of the Electrode Thickness and Density on Performance

Typically, the performance of both batteries and supercapacitors is presented using Ragone plots (Figure 5) that show a relation between the energy density and the power density.⁵² Reporting the energy and power densities per weight of material on a Ragone plot may not give a realistic picture of the performance that the assembled device could reach since the weight of the other device components (current collectors, electrolyte, separator, and packaging) need to be taken into account (Figure 5A). This is especially true for electrodes with thickness (10 μm and less) significantly smaller than that of commercial electrodes (100–200 μm). A ten times thinner electrode will result in a 3–4 times lower energy density, but only a slightly higher power density of the device. Experimental data show that there may be an additional drop in the capacitance by a factor of 2–3 when the thickness of the nanoporous carbon electrode increases,⁵³ thus leading to an even larger drop in the energy density than shown in Figure 5A.

Since many nanomaterials have a low packing density ($<0.5 \text{ g}\cdot\text{cm}^{-3}$), all empty space in the electrode will be

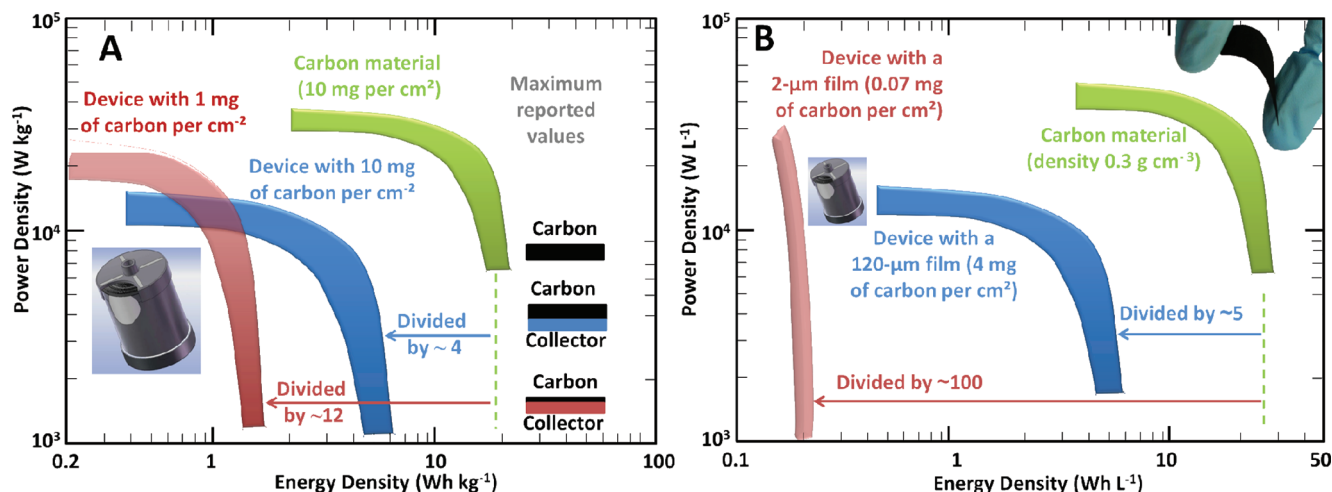


FIGURE 5. Ragone plots. Power vs energy density plots for the same electrochemical capacitors based on (A) a gravimetric (per weight) basis and (B) a volumetric basis. Calculations were performed using (A) carbon density = 0.8 g cm^{-3} , capacitance = $80\text{--}120 \text{ F g}^{-1}$, $70 \text{ }\mu\text{m}$ -thick Al current collectors, cell volume = 370 cm^3 , and cell voltage = 3 V and (B) graphene capacitance = 150 F g^{-1} (5), cell volume = 370 cm^3 , cell voltage = 3 V , and calculated cell capacitance from 75 F ($2\text{-}\mu\text{m}$ thick film) to 1700 F ($120\text{-}\mu\text{m}$ film).

flooded by electrolyte, increasing the weight without adding capacitance. Therefore, volumetric energy density (Figure 5B) is more important than the widely used gravimetric one. If we take a low-density graphene electrode (0.3 g cm^{-3}) with an extremely high gravimetric energy density of 85 W h/kg (gray area in panel A), its volumetric density will be 25.5 W h/L for the electrode and $\sim 5 \text{ W h/L}$ for the device, which is a typical value for commercial ECs with activated carbon. If a thin ($2 \text{ }\mu\text{m}$) film of the same material is used in the device, a much greater drop occurs as can be seen in Figure 5B.

The gravimetric energy density is almost irrelevant compared with areal or volumetric energy for microdevices and thin-film supercapacitors.⁵³ Therefore, microbatteries and microcapacitors should be compared with each other, not to conventional large-size devices, on Ragone plots. Ragone plots may also provide misleading information for flow and semisolid batteries,⁵⁴ where energy and power densities are decoupled. Ashby diagrams⁵⁵ may be used to show other properties such as cycle lifetime, energy efficiency, self-discharge, temperature range of operation, or cost of various EES materials and devices.

8. Summary and Outlook

Although several kinds of porous, planar, or exohedral carbons have been proposed for EDLC applications during the past decade, with graphene widely studied in the past 3 years, recent discoveries of the capacitance increase in carbon pores less than 1 nm have refocused the research efforts toward the understanding of the ion confinement in nanopores for explaining the capacitance increase when the electrolyte ion size matches the

carbon pore size. However, complete understanding of ions in confinement and at the charged interfaces is still lacking. For example, we need to improve our understanding of the effect of surface chemistry and carbon conductivity on capacitance. *In situ* experimental studies coupled with modeling/simulation will help to understand the charge storage mechanism in small pores and predict the optimized carbon structure for maximizing the capacitance increase in a given electrolyte.

The development of high-voltage electrolytes is a key objective shared with the Li battery community. Recent results have shown that a proper design of the carbon electrode structure in conjunction with an electrolyte formulation offers an opportunity for expanding the cell voltage, significantly enhancing the energy density of EDLCs and the operation temperature range of EDLCs devices.

Finally, since electrochemical capacitors are attracting more and more attention, it is our responsibility to adopt clear rules for reporting the performance of new materials for EDLCs and energy storage devices in general. Thus, special attention should be focused on the use of Ragone plots to avoid delivering a wrong message.

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BIOGRAPHICAL INFORMATION

Patrice Simon obtained his Ph.D. in 1995 in Material Science at Ecole Nationale Supérieure de Chimie de Toulouse. He joined the

CNAM in Paris in 1996 as Assistant Professor and moved to Université Paul Sabatier in 2001, where he is Professor of Material Science. He was elected as Junior Member of the Institut Universitaire de France in September 2007 and awarded the Tajima Prize by the International Society of Electrochemistry in 2009. His research is focused on the characterization of nanostructured materials for electrochemical energy storage sources, including electrochemical capacitors and Li-ion batteries.

Yury Gogotsi received his M.S. (1984) and Ph.D. (1986) degrees from Kiev Polytechnic and a D.Sc. degree from the Ukrainian Academy of Science in 1995. He holds an appointment as Distinguished University Professor and Trustee Chair of Materials Science and Engineering at Drexel University. He also serves as Director of the A.J. Drexel Nanotechnology Institute. He has coauthored two books, edited 10 books, obtained more than 30 patents, authored about 280 research papers, and received numerous international awards for his work. He currently serves as an Editor of *CARBON* (Elsevier) and is a member of the editorial board of several other journals. His research group works on nanostructured carbons and other nanomaterials.

FOOTNOTES

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The authors declare no competing financial interest.

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