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Efficient storage mechanisms for building better supercapacitors

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and P. Simon^{2,4,6*}

Supercapacitors are electrochemical energy storage devices that operate on the simple mechanism of adsorption of ions from an electrolyte on a high-surface-area electrode. Over the past decade, the performance of supercapacitors has greatly improved, as electrode materials have been tuned at the nanoscale and electrolytes have gained an active role, enabling more efficient storage mechanisms. In porous carbon materials with subnanometre pores, the desolvation of the ions leads to surprisingly high capacitances. Oxide materials store charge by surface redox reactions, leading to the pseudocapacitive effect. Understanding the physical mechanisms underlying charge storage in these materials is important for further development of supercapacitors. Here we review recent progress, from both *in situ* experiments and advanced simulation techniques, in understanding the charge storage mechanism in carbon- and oxide-based supercapacitors. We also discuss the challenges that still need to be addressed for building better supercapacitors.

The urgent need for efficient energy storage devices has resulted in a widespread and concerted research effort into electrochemical capacitors, also called supercapacitors, in the past ten years. These devices consist of two high-conductivity electrodes separated by an electrolyte containing mobile ionic species. As in conventional capacitors, charge is stored at the surface of the electrodes through an excess of electrons on one side of the device and electron holes on the other side, on application of a voltage between the electrodes¹. Unlike conventional capacitors, however, the charge on the electrodes is then balanced by the adsorption of cations and anions, respectively, at their surface. The excellent performance of supercapacitors is due to the highly reversible ion adsorption mechanism. In contrast to batteries, charging is not limited by diffusion of ions in the bulk of the electrodes, and hence higher power densities can be achieved. Supercapacitors can therefore complement and sometimes even replace batteries when high power delivery or uptake is needed².

Two distinct families of supercapacitors can be considered. The principal one, electrochemical double-layer capacitors (EDLCs), uses porous carbon electrodes with high accessible surface area. This acts as an 'electric sponge', which adsorbs the ions from the electrolytes on charging and releases them at discharge. After years of incremental developments, the discovery of a different charging mechanism in nanoporous carbons (with pore size smaller than 1 nm) has spurred further research into EDLCs³. As a consequence, recent work has not only been directed towards new materials and architectures, but is also aimed at understanding the physical mechanisms underlying the charge storage in such materials. The development of *in situ* experiments, in particular spectroscopy and diffraction, as well as advanced simulation techniques for the realistic description of complex interfacial

processes, has radically modified our understanding of nanoporous carbon-based supercapacitors.

The second family of supercapacitors, known as pseudocapacitors, is based on redox reactions that occur largely (but not exclusively) on oxide-based material surfaces⁴. Fundamental studies on pseudocapacitors remain scarce, because of the difficulty of characterizing the oxide surfaces and determining the details of the charge transfer mechanism. But the recent development of nanostructured oxides and of hybrid carbon/oxide electrodes is progressively changing the way we think about pseudocapacitive charge storage.

Despite the recent progress in both the performance and fundamental understanding of the mechanisms involved in supercapacitors, this body of work has not been placed in the broader context of capacitive storage. Existing reviews in the literature either focus on the properties of the materials⁵⁻⁷ or on the electrolytes^{8,9}. Here we review both chemical and physical aspects of the capacitive storage mechanism in carbon- and oxide-based supercapacitors. We discuss the latest advances, which have implications not only for supercapacitors but also for other applications in which voltage-driven ion adsorption in nanoporous structures plays a key role.

Electrochemical double-layer capacitors

Charge storage in supercapacitor electrodes makes use of the electrostatic attraction between the ions of an electrolyte and the charges present at the electrode surface, which allows the formation of oppositely charged layers at the electrolyte/electrode interface. Supercapacitors use mainly porous carbon as electrode materials, thus benefiting from the high surface area available for ion adsorption. The charge separation occurring upon polarization at the electrode/electrolyte interface can be described in a crude approach

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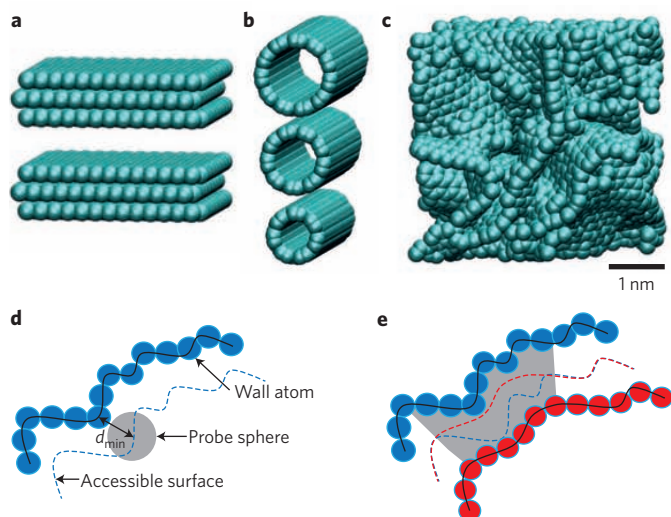


Figure 1 | Examples of nanoporous carbon structures. **a-c**, Although ordered structures such as slit pores (**a**) and nanotubes (**b**) exist, most supercapacitors use disordered nanoporous carbons (**c**). The definition of the accessible surface depends on the choice of the probe and on the nature of the porosity. **d,e**, In mesopores, the whole surface is accessible (**d**), whereas in micropores (**e**) some regions of the pores are inaccessible to probe molecules or ions. In **e**, blue and red spheres represent wall atoms at opposite sides of a micropore, and the blue and red dashed lines represent the closest surfaces to these that are accessible by the probe sphere. Where the dashed lines cross, the pore wall is inaccessible, as indicated by the grey-shaded area in **e**.

using the double-layer capacitance model proposed by Helmholtz in 1853 (ref. 10):

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

where ϵ_r is the electrolyte relative permittivity, ϵ_0 is the vacuum permittivity, d is the effective thickness of the double layer (charge separation distance) and A is the electrode surface area. Note, however, that all these quantities (except for ϵ_0) are ill-defined for the interfaces at play in the present case of highly disordered materials.

Until 2005, it was believed that the best strategy for increasing capacitance consisted in maximizing the electrochemical double-layer charging. The challenge at that time was therefore to develop new mesoporous carbons with the highest specific surface area. Then, following original work from the group of Aurbach^{11,12}, the discovery of a different, more efficient storage mechanism in nanopores (pore size less than 1 nm: that is to say, less than the size of solvated ions)³ led to a change of view: not only the surface area but also the pore size and the carbon nanostructure drive the electrochemical performance. The community thus had to reconsider the way that charge is stored at the carbon/electrolyte interface in ultra-small pores. Since then, much effort has been directed towards the basic understanding of charge storage mechanisms at the nano- and subnanoscales, considering both sides of the interface: the carbon structure and the electrolyte organization, including the (de)solvation of ions and their interactions under extreme confinement.

In this section, we show how the development and the use of new techniques, both theoretical and experimental, have been at the origin of major advances in carbon-based supercapacitors. First, more realistic structural models for porous carbon structures have been developed by coupling modelling and characterization techniques such as small-angle X-ray scattering (SAXS) or neutron scattering (SANS), which greatly improve our understanding of their electrochemical behaviour. In addition, the combination of advanced

electrochemical techniques such as electrochemical quartz crystal microbalance (EQCM), spectroscopies such as nuclear magnetic resonance (NMR) or infrared, and characterization techniques (SAXS), together with modelling, have led to the elucidation of electrolyte organization in carbon nanopores at null potential and under polarization, as well as the charge storage mechanism and the ion dynamics in the pores. These points are detailed below.

Structural models for nanoporous carbons. Nanoporous carbons generally consist of defective nanoscale graphitic units, with pores ranging from micropores (pore size <2 nm) to mesopores (from 2 to 50 nm). Unlike slit pores or nanotubes (Fig. 1a,b), they do not display any three-dimensional (3D) long-range ordering (Fig. 1c). Because the electrochemical performance of carbons is driven by the porous carbon/electrolyte interface, accurate and reliable characterizations of the porous network are needed for designing better supercapacitors. Specific surface area and pore size distributions of porous material are generally obtained from gas adsorption techniques, using theoretical models. But such methods suffer from several limitations when applied to microporous carbons.

Choosing an appropriate molecular probe is essential, as pores inaccessible to gas molecules may be accessible to ions from the electrolyte, depending on thermodynamic conditions (Fig. 1d,e). This is specifically true when N_2 adsorption at 77 K is used to measure the carbon specific surface area. The quadrupole moment of the N_2 molecule limits the access of the gas to small micropores, and reduced flexibility of the porous carbon network structures at low temperatures does not necessarily reflect the ambient temperature properties. As a result, N_2 sorption does not give accurate porosity values for ultramicropores (<0.7 nm). Without a quadrupole moment and with a smaller diameter (0.335 nm compared with 0.363 nm), Ar atoms can access small micropores more easily than N_2 . Combined with a higher experimental measurement temperature and a simpler theoretical analysis, this makes Ar adsorption at 87 K more suited than N_2 for the characterization of microporous carbons¹³. A complementary approach involves using the adsorption of supercritical gas or subcritical fluids (CO_2) at ambient temperature, which improves the adsorption kinetics.

The choice of the probe and of the experimental conditions is only part of the challenge, as the microscopic features must then be extracted from the experimental isotherm by means of an appropriate model. The Brunauer–Emmett–Teller (BET) analysis¹⁴ is not recommended for microporous carbons, as recently confirmed by the International Union of Pure and Applied Chemistry¹⁵, as it overestimates the surface of large micropores (>0.7 nm) by 10 to 40%, owing to enhanced bilayer gas adsorption on carbon pore walls. In addition, the BET surface area of ultramicropores (<0.7 nm) is underestimated owing to incomplete monolayer formation. Reliable porosity values for larger micropores (>0.7 nm) can be experimentally obtained by the subtracting pore effect method (SPE) using a high-resolution α_s -plot, at low relative pressure (from $P/P_0 = 10^{-6}$)^{16,17}. Moving from measurements of surface area to measurements of pore size distribution, quenched solid density functional theory analysis can provide reasonable structural information from high-resolution adsorption isotherms¹⁸.

All of this illustrates the difficulty of measuring the surface area of nanoporous carbons. Furthermore, the very concept of ‘surface’ by itself could be questionable, as it depends on the approach (that is, the probe) used to measure it¹⁹. Therefore, methods based on molecular probes should be complemented by alternative direct characterization techniques such as SAXS and NMR spectroscopy, which can assess the whole pores of nanoporous carbons that are accessible to the electrolyte ions, and thus are directly relevant to the electrochemical measurement. Despite such limitations, it remains reasonable to discuss the dependence of the capacitance per unit surface area on pore size based on Ar adsorption data, to provide a

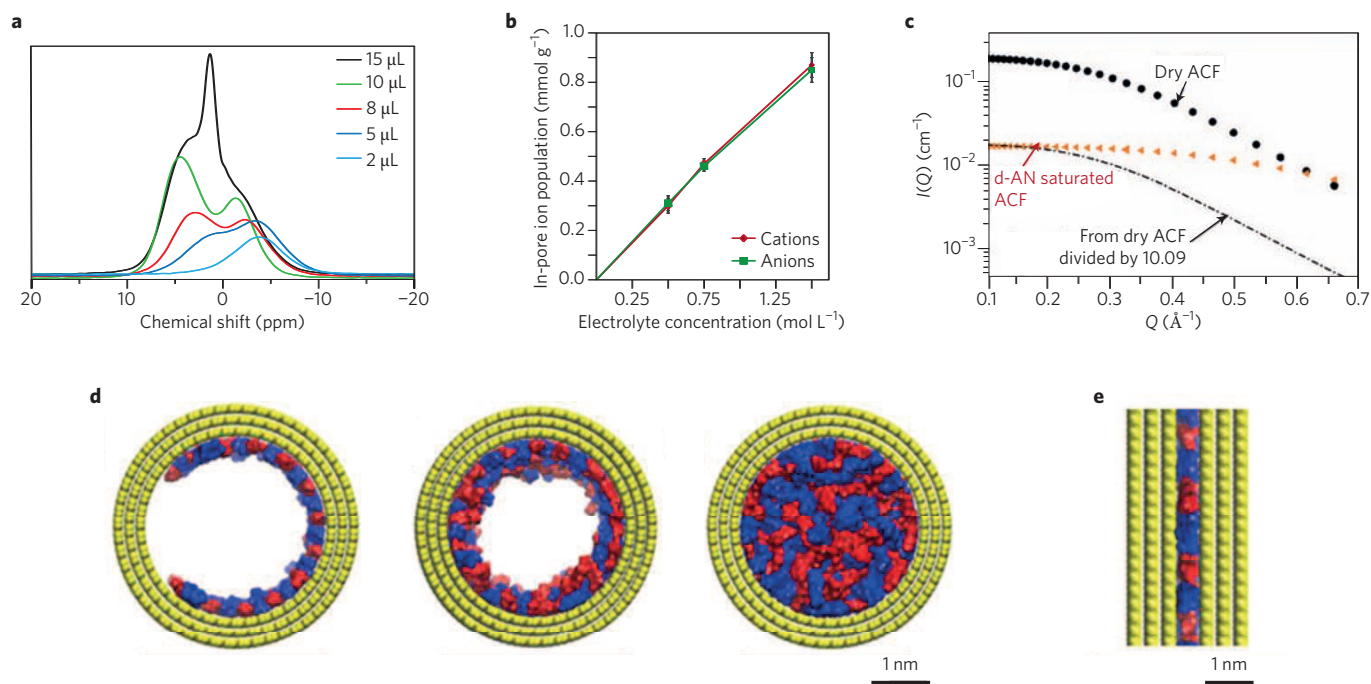


Figure 2 | Characterization of pore wetting at null potential. **a**, NMR spectra with different electrolyte loadings inside nanoporous carbon. ppm, parts per million. **b**, Number of ions adsorbed inside the pores with respect to the electrolyte concentration. **c**, Neutron scattering experiments on dry or electrolyte-saturated activated carbon electrodes. Q , scattering vector; I , intensity; ACF, activated carbon fabric; AN, acetonitrile. **d,e**, Adsorption of ionic liquids inside a mesopore and a micropore from molecular dynamics simulations (yellow, pore wall atoms; red, cations; blue, anions). Figure reproduced from: **a**, ref. 25, American Chemical Society; **b**, ref. 26, NPG; **c**, ref. 27, American Chemical Society; **d,e**, ref. 28, American Chemical Society.

method for comparison between samples and preparation method. Nevertheless, gravimetric capacitance (farad per gram of carbon) or volumetric capacitance (farad per volume of electrode) is preferred, as these are based on experimental, measured values, free from any theoretical model or structural considerations.

Revealing the ‘real’ structure of nanoporous carbons is much more complex, because it is not currently possible to resolve such structures by resorting only to experimental approaches. To that end, combinations of experimental and modelling techniques have been proposed. One may, for example, use synchrotron X-ray diffraction and SAXS experiments to obtain short- and long-range structural information on the porous carbon network. But scattering techniques usually give access to 1D structural information, and the corresponding data must be transformed into 3D structures by the use of hybrid reverse Monte Carlo simulation^{20,21}. Combinations of NMR, pair distribution function analysis of X-ray data, and Raman spectroscopy with lattice simulations have recently been used to evaluate the size of the graphene domains in the porous carbons²². Alternatively, quenched molecular dynamics has been used successfully to describe the structure of nanoporous carbons without resorting to experimental structural data^{23,24}.

We finally note that most studies so far have focused on the structure of the nanoporous carbon only, whereas the ability to predict the key features of the structure needed to optimize the charge storage also requires a deeper understanding of the structures and dynamics of the confined electrolyte.

Wetting of the pores at null potential. Until recently, the charging of supercapacitors was assumed to arise from a simple mechanism of the applied potential driving the ions into the porous carbon network. The first *in situ* NMR studies have shown that this is not the case: even at low electrolyte loadings, NMR signals are observed that are shifted towards lower frequencies, as shown in Fig. 2a (refs 25–29), owing to the aromatic ring-current effects of graphitic domains and magnetic susceptibility of the carbon. The results

indicate that ions (along with the solvent) are adsorbed within the pores. The starting situation at 0 V is therefore better characterized by the interpenetration of the two heterogeneous structures — the solid carbon material and the electrolyte. Molecular dynamics simulations further confirmed this picture, showing that an ionic liquid in contact with a nanoporous carbon electrode spontaneously fills the highly confined nanopores, even without any applied field^{30–32}.

NMR spectroscopy is quantitative and thus provides the concentrations of ions adsorbed inside the electrode. The latter follow a linear trend with respect to their counterparts inside the bulk electrolyte²⁶ (Fig. 2b), thereby confirming the affinity of the ions for the carbon. As the ions diffuse between pores during the signal acquisition, however, they experience various environments, resulting in relatively broad NMR spectra³³. It is therefore not straightforward to determine the population of the various adsorption sites (for example mesopores versus micropores) using this technique. Another approach is SANS or X-rays. In an empty porous carbon, the signal at small wave vectors originates from the contrast between the carbon atoms and the pore voids. For example, nanopores with a characteristic length scale d of 1–2 nm display a signature around $2\pi/d \approx 3–6 \text{ nm}^{-1}$. When the pores are filled with the electrolyte, this contrast vanishes and the signal decreases. An example of the application of *in situ* SANS to a typical activated carbon, either empty or loaded with an organic electrolyte, is shown in Fig. 2c (ref. 27). The decrease in the scattering intensity depends on the wave vector, revealing an incomplete wetting of the smallest pores.

In contrast, Bañuelos *et al.* combined SANS and molecular dynamics simulations to investigate the adsorption of a room-temperature ionic liquid (RTIL) inside a hierarchical porous carbon at various loadings²⁸ and concluded that the RTIL covers the pore surfaces uniformly, rather than leaving some pore surfaces unsaturated. Their pictures of the wetting of mesopores and micropores are shown in Fig. 2d and e, respectively. Different results were observed in the case of aqueous electrolytes³⁴, suggesting that the surface chemistry of the carbon and the nature of the electrolyte strongly

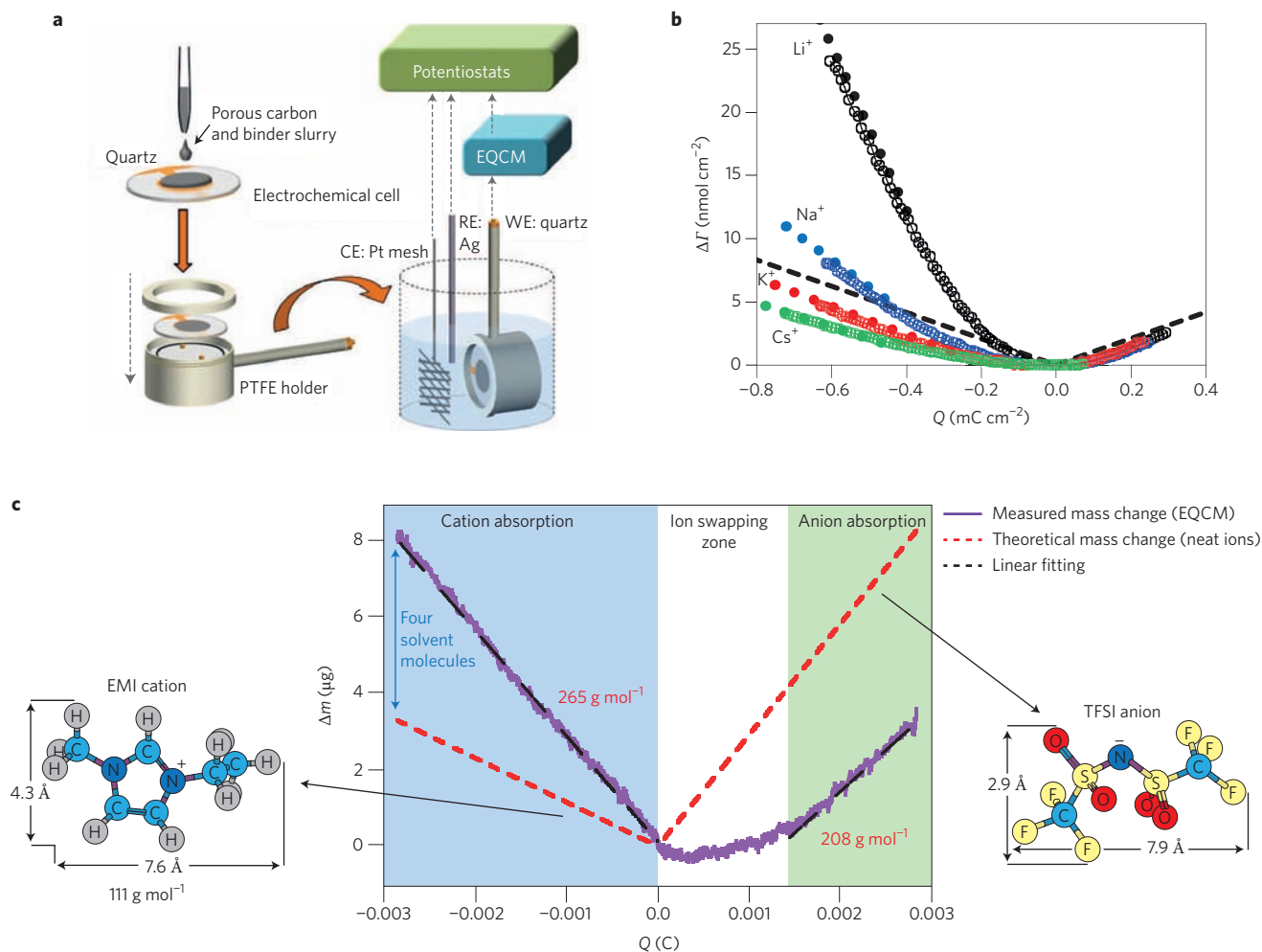


Figure 3 | Desolvation of the ions in electrified nanopores. **a**, EQCM set-up. RE, reference electrode; CE, counter electrode; WE, working electrode. **b**, Variation of the adsorption of ions with respect to the accumulated charge per unit area in aqueous electrolytes with various alkali cations. Dashed lines represent the theoretical mass change (Faraday's law for neat ions). **c**, Variation of the mass with respect to the accumulated charge in an organic electrolyte. EMI, 1-ethyl-3-methylimidazolium; TFSI, bis(trifluoromethylsulfonyl)imide anion. Figure reproduced from: **b**, ref. 39, American Chemical Society; **c**, ref. 43, American Chemical Society.

affect the wetting properties. Recently, Kondrat and Kornyshev have proposed to use 'ionophobic' pores for designing a new generation of supercapacitors³⁵. Their idea, which remains to be realized experimentally, is built on the fact that such pores would be filled for high voltage only; this could potentially result in larger energy densities and rapid rates of charge and discharge.

Desolvation in nanopores. The discovery that ions could access carbon pores smaller than their solvated ion size has revitalized research into ion confinement in carbon nanopores. From electrochemical measurements, it was proposed that ions lose a part of their solvation shell to access these small nanopores (<1 nm). In addition, the capacitance was strongly enhanced when the carbon pore size was in the same range as the ion size^{3,36-38}. Although such observations were made using carbon with tailored pore sizes, the use of conventional electrochemical techniques failed to give quantitative information on the extent of desolvation. The development of *in situ* techniques such as EQCM has led to important advances in addressing this issue. Figure 3a shows a schematic of an EQCM set-up; the change of the quartz resonance frequency reflects the change of weight of the active material during the polarization.

The use of EQCM to study ion adsorption in porous carbons was pioneered by Levi and Aurbach³⁹⁻⁴¹. Figure 3b shows typical

changes of ion population as a function of the charge accumulated in a porous carbon electrode during polarization in aqueous electrolyte with varying alkali cations³⁹. In this example, from the associated mass change and comparison with the theoretical mass change expected for the adsorption of bare ions from Faraday's law, it was shown that the adsorbed Li⁺, Na⁺, K⁺ and Cs⁺ ions are tightly attached to 2.0, 0.8, 0.1 and 0.0 water molecules on average. The confinement of the ions is therefore accompanied by a substantial decrease in their solvation number (number of solvent molecules around the ion), thus confirming previous results⁴².

EQCM was also used in organic electrolytes in combination with carbons of 1-nm average pore diameter⁴³. A solvation number between three and four could be calculated for 1-ethyl-3-methylimidazolium cations confined in the 1-nm pores, much smaller than the eight molecules for cations in the bulk electrolyte. The joint use of NMR spectroscopy and EQCM allowed the effects from the cations and anions to be separated and the cation solvation number to be determined²⁶. These results clearly indicate that the partial desolvation of the ions occurs when accessing small pores. The decrease in the ion solvation number could also be quantified directly in molecular dynamics simulations³¹. Importantly, these studies point out a difference in the energy storage mechanism depending on the electrode polarity, as described below in more detail.

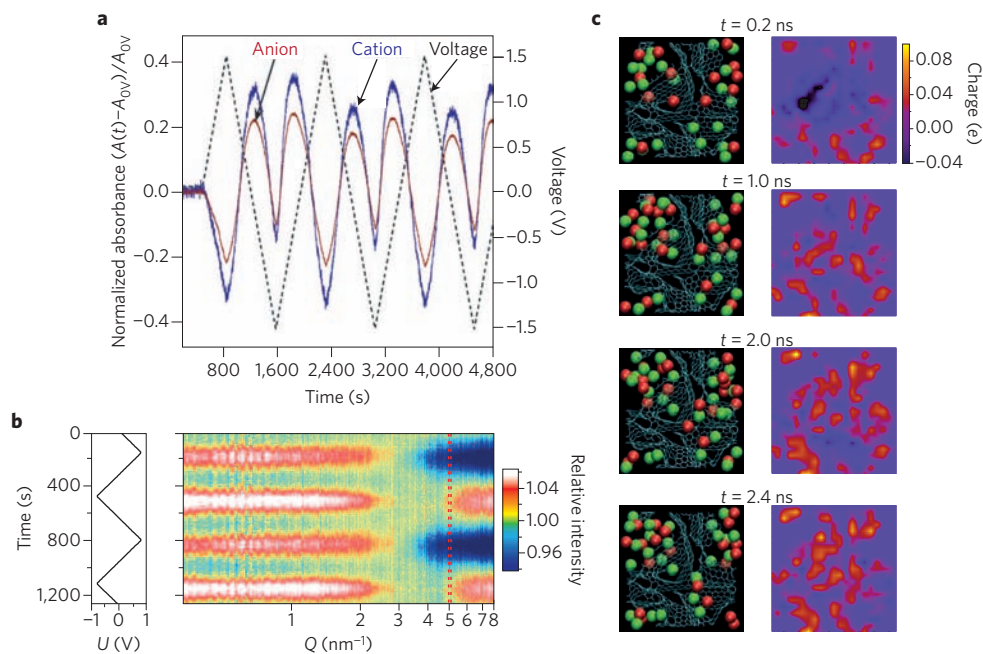


Figure 4 | Characterization of the charging dynamics of supercapacitors. **a**, Temporal variation of the normalized infrared absorbance for various charge–discharge cycles (ionic liquid electrolyte). **b**, Temporal variation of the SAXS intensity (right panel) for various charge–discharge cycles (aqueous CsCl electrolyte). Q , scattering vector. The evolution of the applied potential U with time is shown in the left panel. **c**, Time evolution of the local charge on the carbon atoms on charging in a molecular dynamics simulation (turquoise sticks, C–C bonds; red spheres, cations; green spheres, anions). Figure reproduced from: **a**, ref. 60, American Chemical Society; **b**, ref. 61, RSC; **c**, ref. 65, American Chemical Society.

Charge storage mechanism. Although the basic principle underlying charge storage in EDLCs, namely the adsorption of ions at the surface of the electrode, is well established, the corresponding microscopic mechanisms have remained elusive until recently. The Gouy–Chapman–Stern theory, which has been the cornerstone of theoretical electrochemistry for over a century, predicts that near an extended surface, the electrode charge is balanced by the polarization of the electrolyte. The decay of the ionic charge distribution and of the electrostatic potential occurs over the ‘Debye length’, typically in the 1–10 nm range, which depends on the electrolyte concentration and solvent permittivity. But this picture is of limited help in understanding the interfacial structure and thermodynamics in the case of supercapacitors, owing to the strong ionic correlations at high electrolyte concentration or in pure ionic liquids⁴⁴ and to the marked effects of confinement^{30–32,45}. The behaviour of such electrolytes near metallic walls, noticed as early as 1952⁴⁶, has called for a paradigm change^{44,47}, and recent advances in simulation techniques⁴⁸ have shown that it is also important to consider the electrolyte structure at the electrode surface^{49,50}. Recent claims based on surface force apparatus experiments have also revived the debate on the differences between electrochemical interfaces involving pure ionic liquids and those of solvent-based electrolytes^{51–54}.

In the case of planar graphitic electrodes, the Gouy–Chapman–Stern theory predicts an increase in the capacitance with the applied potential. This theory does not, however, capture two important features, namely the ionic correlations and the finite surface area accessible to the ions. This explains why it fails at reproducing, even qualitatively, experimental results in highly concentrated electrolytes⁴⁷. Mean-field theories accounting for these effects and molecular simulations^{44,55} show that the differential capacitances may display various shapes (the ‘camel’ or ‘bell’ shapes) depending on the nature of the electrolyte. But these capacitance values remain too small to be exploited efficiently in supercapacitor devices.

An important consideration for extreme confinement, when pore sizes are comparable to the diameter of the ions, is that the electronic charge inside the electrode is compensated by an imbalance in the

number of co- and counter-ions inside the pores. In such a ‘super-ionic state’, the local breakdown of electro-neutrality in the interstitial fluid is compensated by the creation of a corresponding charge on the metallic surface that efficiently screens the interactions between like-charged ions^{56,57}. Several processes may lead to the overall excess of counter-ions inside an electrode: adsorption of counter-ions, swapping of co-ions for counter-ions, or desorption of co-ions⁵⁸. For a given combination of electrodes and electrolyte (nature of the ions, presence and choice of a solvent), one or several of these mechanisms are observed as a function of voltage. NMR, molecular dynamics, infrared spectroscopy, SAXS and EQCM suggest that ion swapping is the most common process at low voltage, but for large ion sizes and/or at high voltage, adsorption of the sole counter-ions is also observed, as illustrated in Fig. 3c. Desorption of co-ions seems to be less frequent. Recent *in situ* NMR measurements on a solvent-based electrolyte have shown that the charge storage mechanism can differ depending on the electrode polarization; ion swapping was observed for positive polarization, whereas counter-ion adsorption dominated for negative polarization. This suggests that multiple factors may influence how excess ionic charge is achieved, including relative sizes and mobilities of co/counter-ions, kinetic phenomena and ion rearrangement over multiple cycles. Coupling NMR with EQCM also showed that both counter-ion adsorption and ion swapping are accompanied by the entrance or departure of solvent molecules²⁶. In pure ionic liquids, molecular simulations suggest that the exchange occurs almost without changing the volume occupied by the liquid inside the electrode³⁰, but this conclusion should be strengthened by considering further combinations of cations and anions, and requires experimental confirmation.

The fundamental understanding of the microscopic charging mechanisms achieved in the past five years provides a strong basis for the design of better supercapacitors, by suggesting new strategies for the optimization of charge storage through appropriate combinations of electrode structures, ions and solvent. The widespread use of experimental and simulation tools developed to establish these mechanisms will be the key to the success of this endeavour.

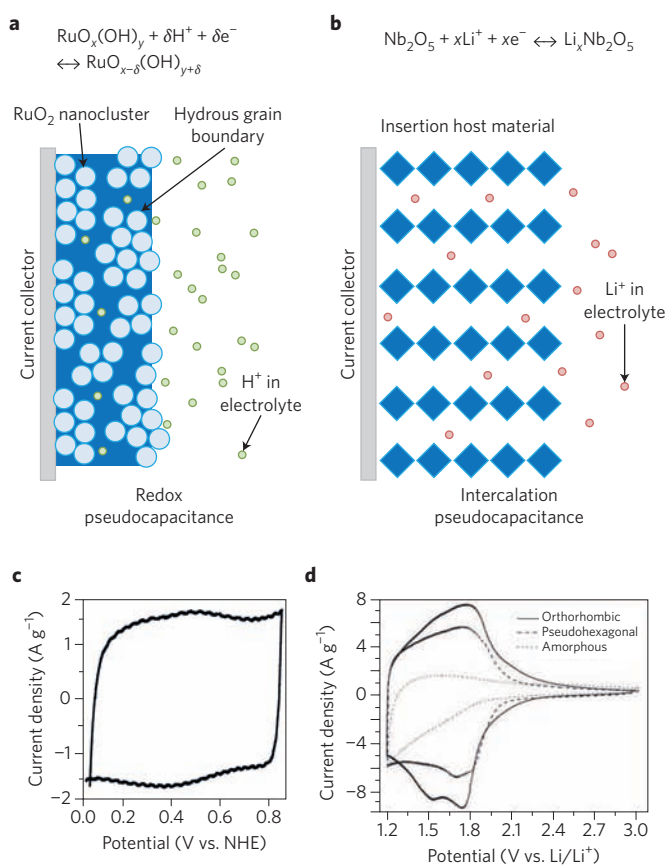


Figure 5 | Different types of pseudocapacitive behaviour.

a, Redox pseudocapacitance in RuO_2 occurs in the near-surface region. **b**, Intercalation pseudocapacitance in Nb_2O_5 (T-phase) is a bulk effect from Li^+ insertion. **c**, Cyclic voltammetry experiments show the RuO_2 to have the traditional capacitor 'box'. **d**, Cyclic voltammetry experiments show that the orthorhombic Nb_2O_5 (T-phase) exhibits redox peaks with little voltage offset. Figure reproduced from: **a, b**, ref. 66, RSC; **c**, ref. 69, American Chemical Society; **d**, ref. 67, Wiley.

Dynamics of charging and discharging. The key feature of supercapacitors, for example with respect to batteries, is their very high power density: they are able to charge or discharge within a few seconds. The increase in capacitance should therefore not be achieved at the price of a decrease in power. Conventional theories predict that liquids suffer from noticeable slowdown of their dynamics when they are strongly confined, disqualifying in principle the use of microporous carbons for supercapacitors. Fortunately, such effects have not been observed in experiments performed on carbide-derived carbons (CDCs), for which a maximal characteristic discharge time of 20 seconds was obtained for the smallest average pore size³. This trend is further confirmed by electrochemical impedance spectroscopy. This technique offers the possibility of measuring in-pore resistivities in the low-frequency region. These resistivities are usually of the order of 50 to 200 ohm cm for electrolytes made of organic ions dissolved in acetonitrile at room temperature — only slightly higher than for the same liquids under bulk conditions⁵⁹.

The fast charging of supercapacitors impedes the application of the usual *in situ* techniques to monitor their dynamical behaviour. In many cases, the time needed to record a spectrum or a diffractogram is longer than their charging time. However, techniques such as infrared spectroscopy or SAXS have been used to study charge/discharge cycles of supercapacitors at a low scan rate of 5 mV s^{-1} . Figure 4a and b shows the relative evolution of the signal with time and potential, in two different experiments. In one case, a supercapacitor made of

1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquid and a CDC electrode is studied by infrared spectroscopy⁶⁰. In the second case, the adsorption of an aqueous CsCl electrolyte inside a microporous activated carbon is studied by SAXS⁶¹. In both cases, the response of the liquid closely follows the applied potential, with a lag of only a few seconds. These observations are consistent with a timescale of seconds for charging microporous supercapacitors. NMR and magnetic resonance imaging (MRI) studies have highlighted the role of the cell design in the timescale of ionic response during charging. Using a non-optimal 'shifted' cell design to allow electrodes to be studied independently, *in situ* NMR experiments revealed a lag between the applied potential and charge build up on the electrode even at a low scan rate, which is due to ohmic drop²⁵. This issue was subsequently addressed through the use of MRI which allows spatial resolution of the two electrodes in a conventional cell design⁶².

The microscopic origin of the observed fast charging has been studied using molecular simulations. In particular, molecular dynamics provides the trajectories of the molecules and is perfectly suited for extracting transport properties such as diffusion coefficients. Recent work has shown that the diffusion coefficients of the ions are generally one to two orders of magnitude smaller in the electrodes than in the bulk liquid^{59,63}, but strong variations are observed with the filling of the electrode in the case of ionic liquids^{63,64}. Indeed, Kondrat *et al.* have shown that in slit pores, the ions can even diffuse faster than in the bulk at intermediate voltages⁶³. In CDCs, this effect is not observed but the good connectivity between the pores was shown to be an important characteristic, allowing the larger pores to play the role of electrolyte reservoirs as shown in Fig. 4c (ref. 65). Injecting molecular dynamics results into an equivalent circuit model then leads to estimated charging times of 1 to 10 s for CDC electrodes⁶⁵, further demonstrating the good predictive power of these simulations.

Oxide-based supercapacitors

In the 1970s, Conway and others recognized that certain materials undergo redox reactions at or near their surface and yet their electrochemical properties are similar to those of supercapacitors, which store energy at the electrical double layer formed at the electrode/electrolyte interface¹. These pseudocapacitive materials lead to much higher levels of charge storage than EDLCs, owing to the redox reactions⁴. For this reason, over the past several years there has been growing interest in pseudocapacitors because of the prospect of achieving the high energy density of traditional battery electrode materials combined with the long cycle life and power density of EDLCs⁶⁶.

The mechanism of pseudocapacitance. The most widely investigated pseudocapacitors are RuO_2 and MnO_2 . As the field has developed, certain metrics have emerged that provide a more rigorous identification of pseudocapacitance. In particular, materials exhibiting high energy density at high discharge/charge rates display electrochemical signatures that are representative of pseudocapacitive behaviour. An especially good model system in which to characterize pseudocapacitance is Nb_2O_5 , as 70% of its theoretical capacity for lithium can be stored in only 1 minute (125 mAh g^{-1} for 1-minute discharge)⁶⁷. Moreover, charge storage by means of redox reactions takes place in the bulk of the material and not only at the surface as is commonly thought⁶⁸. The charge storage mechanism involved here, intercalation pseudocapacitance, is not controlled by semi-infinite diffusion and instead exhibits the fast kinetic response observed in double-layer capacitors (leading to high power) despite the fact that charge storage arises from redox reactions. A comparison between intercalation pseudocapacitance and the redox pseudocapacitance⁶⁹ that characterizes RuO_2 is shown in Fig. 5. Some of the key electrochemical responses associated with pseudocapacitance include: (i) a linear dependence of the potential on the state of charge; (ii) a charge-storage capacity mostly independent of rate; and (iii) redox

peaks with small voltage offsets⁷⁰. Materials that do not show such features should not be considered pseudocapacitive. The recent paper by Brousse *et al.* points out the limitations in describing materials such as Ni(OH)₂ or cobalt oxides as being pseudocapacitive⁷¹.

Pseudo-intercalation reactions. Another important consideration for pseudocapacitive materials is that the structure does not undergo a phase transformation on intercalation. In this regard, when MoO₂ is prepared as a nanoscale material, its characteristic monoclinic-to-orthorhombic phase transition, which occurs on lithiation, is suppressed and the material shows the pseudocapacitive responses mentioned above. The gravimetric capacity for nanoscale MoO₂ for 2-minute discharge rate is nearly 200 mAh g⁻¹, far exceeding the energy density of any other material at this rate⁷². Additional studies show that pseudocapacitive behaviour is preserved even in 40- μ m-thick Nb₂O₅ films. Such films have been incorporated in a hybrid cell comprising a Nb₂O₅ negative electrode and activated carbon as the positive electrode⁶⁸. Although this device showed very good performance, it was limited by the energy density of the carbon electrode, which stores energy by means of the electrical double layer.

One of the more popular approaches to developing pseudo-capacitor materials involves the synthesis of nanoscale materials⁷³. Growing evidence indicates that electrochemical characteristics tend to become more capacitor-like when the crystallite is smaller than 20 nm. For example, the potential dependence on state of charge (see (i) above) can become linear owing to a larger number of surface sites for charge storage or the suppression of a phase transition. Kinetics are also influenced by the small crystallite size, as the decrease in diffusion distance leads to higher power density. In addition, the use of sweep voltammetry to separate diffusion-controlled kinetics from capacitive processes shows nanoscale materials to be more capacitor-like⁶⁶. Thus far, the charge storage mechanisms for only a few 2D materials prepared in the form of nanosheets have been characterized. In the case of TiO₂, a surface-controlled response reported for this material is expected, as nearly the entire surface of the sample is exposed to electrolyte⁷⁴.

To account for the role of nanostructuring, Simon, Dunn and colleagues recently proposed that pseudocapacitance can be intrinsic or extrinsic to a material⁶⁸. An intrinsic pseudocapacitor shows the various electrochemical signatures of double-layer capacitors regardless of particle size or shape: MnO₂ is a good example of intrinsic behaviour^{71,75,76}, although the structural behaviour and charge storage of the material changes from one allotrope to another⁷⁷, as shown by *in situ* synchrotron X-ray diffraction analyses⁷⁸. In contrast, the extrinsic term applies to materials that show pseudocapacitor characteristics only as nanoparticles. With these materials, the diffusion distance is less than $(Dt)^{1/2}$, where D is the diffusion coefficient and t the time. These materials do not show pseudocapacitive behaviour in the bulk state. The extent to which nanostructuring produces pseudocapacitance is likely to cover a wide range of transition metal oxides, sulfides and nitrides, and is currently an active area of research. As shown with MoO₂, the extrinsic pseudocapacitor approach provides the exciting opportunity of creating materials that possess both the high energy density of battery materials and the high power density of capacitors.

Hybrid supercapacitors

The desire to increase the energy density of EDLCs coupled with the growing interest in pseudocapacitor materials has led to the design of composite hybrid materials^{79,80}. The development of these fast charge/discharge materials is providing the basis for creating the next generation of hybrid supercapacitors.

The most advanced hybrid supercapacitors are based on the use of high-rate Li₄Ti₅O₁₂ (LTO), another lithium-ion insertion material. This material retains a lithium capacity in excess of 120 mAh g⁻¹ at a charge/discharge rate of 30C (full discharge in 2 min). Moreover,

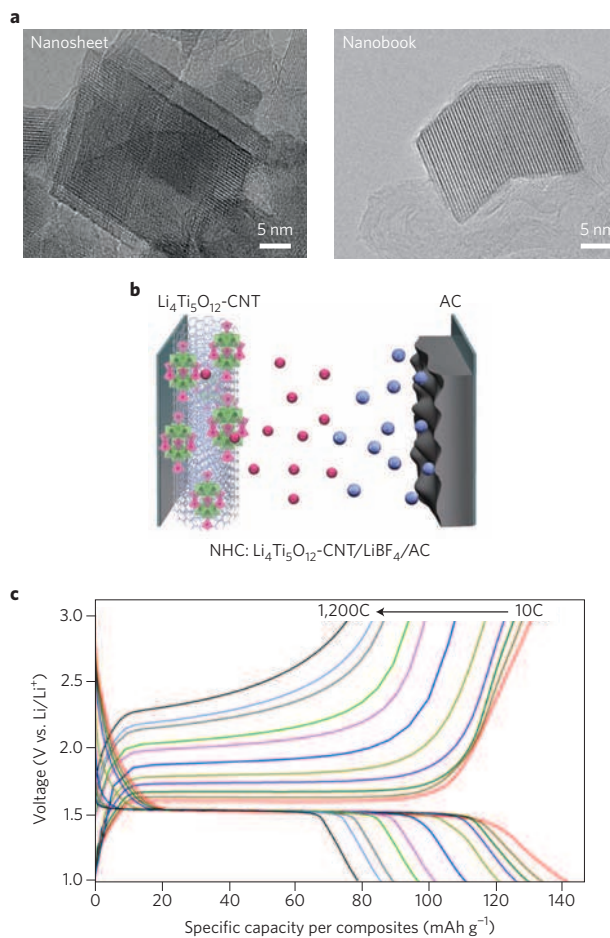


Figure 6 | Nano-hybrid supercapacitor set-up and characterization.

a, High-resolution transmission electron microscope images of nanocrystalline Li₄Ti₅O₁₂ prepared as 'nanosheets' and/or 'nanobooks' that are fabricated in composites with CNTs using ultracentrifugation (~75,000g). **b**, Nano-hybrid capacitor (NHC) using an activated carbon (AC) and dimension-controlled Li₄Ti₅O₁₂ nanocrystals composited with single-walled CNTs. **c**, Discharge curves at various C-rates (from 10 to 1,200) after charging at a fixed rate of 10C. Figure reproduced from: **a,c**, ref. 85, American Chemical Society; **b**, ref. 84, RSC.

in contrast to MnO₂ and RuO₂ which operate in aqueous electrolytes within a limited potential window (about 1 V), LTO functions in high-voltage non-aqueous electrolytes. LTO cannot be defined as a pseudo-capacitive material, as it shows a voltage plateau and undergoes a phase change during lithiation. Because it exhibits zero strain and supports rapid Li⁺ ion transport during the (de)intercalation reaction, however, LTO is suitable for use in high-rate electrodes in hybrid supercapacitors, devices that combine a faradaic battery electrode with a capacitive electrode. The first generation of commercial hybrid supercapacitors, called the Li-ion capacitor, was based on combining a negative graphite electrode of a Li-ion battery with a capacitive porous-carbon positive electrode⁸¹. The use of ultrafast Li-ion intercalation materials such as LTO could greatly increase the power capability of such devices, while preserving high energy density⁸².

In recent work, ultracentrifugation synthesis has been explored to further extend the performance of high-rate and pseudocapacitive materials such as RuO₂ (ref. 83). The ultracentrifugation process enables the preparation of nano-sized, dimension-controlled (1D to 2D) materials, directly bound on high-surface-area carbons such as carbon nanotubes (CNT) or disordered porous carbons⁸⁴. Dimension-controlled 2D-LTO is shown in Fig. 6a. High-resolution

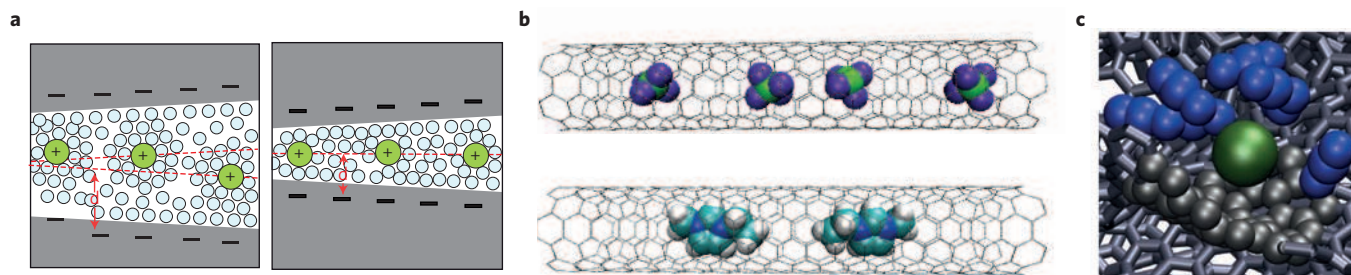


Figure 7 | Evolution of the picture of the electrode/electrolyte interface in the past decade. **a**, Ions (green spheres) surrounded by solvent molecules (blue spheres) residing in pores with size between 1 and 2 nm (left), and less than 1 nm (right), as pictured in 2006. **b**, Adsorption of BF_4^- anions (top) and 1-ethyl-3-methylimidazolium cations (bottom) inside carbon nanotubes that are positively or negatively charged, as seen in 2010 (green, B; violet, F; turquoise, C; blue, N; white, H; black sticks, C-C bonds of the nanotubes). **c**, Adsorption of partially desolvated PF_6^- ion in a disordered nanoporous carbon, as simulated in 2013 (green, PF_6^- ; blue, acetonitrile molecules; black, C atoms in contact with the anion; black sticks, C-C bonds of the electrode). Figure reproduced from: **a**, ref. 3, AAAS; **b**, ref. 32, American Chemical Society; **c**, ref. 31, NPG.

transmission electron microscopy images clearly demonstrate that 2D-LTO nanosheets nucleate from the CNT surface and are firmly attached to it. Fast Fourier transform analysis revealed the d -spacing of lattice fringes as 4.81 Å, corresponding to the (111) plane of the 3D spinel structure⁸⁵. The surrounding interstitial carbon influences the growth direction, shape and size of the 2D-LTO crystals. One fascinating nanoscale morphology is that which occurs from two interconnected LTO nanosheets (a ‘nanobook’; Fig. 6a). These dimension-controlled LTO show ultrafast charge/discharge behaviour when operated in excess of 300C (full discharge in 12 s) and as high as 1,200C (full discharge in 3 s), as shown in Fig. 6c.

Energy storage devices based on hybrid supercapacitors are being commercialized, and this underscores the importance of these new materials. A three- to fivefold increase in energy density compared with conventional carbon-based EDLCs has been achieved by combining a negative electrode made of ultracentrifugation-prepared LTO nanosheets with a porous-carbon positive electrode. Although the stability of the nanostructured electrode/electrolyte interfaces is still an important issue to be solved, this technology has the potential to become an alternative to EDLCs⁸⁴.

Outlook

Supercapacitor electrodes, which used to be a black box, can now be probed at the molecular scale using a variety of experimental and simulation techniques. Our view on the structure of the interface has profoundly changed in the past ten years, as summarized in Fig. 7. The discovery of a new storage mechanism inside nanoporous carbons has enabled large improvements in the energy density of commercial EDLC devices, which now reach specific energies beyond 6–7 Wh kg^{-1} . These devices are now used in power electronics, in cars (stop/start systems), and in public transport systems such as trams and buses. The next challenge will be to push this limit further (>10 Wh kg^{-1}), thus establishing supercapacitors as ideal candidates in other key applications.

If we consider only porous carbon-based supercapacitors, the possibilities are virtually infinite. On the electrode side of the interface, it is possible to tune the carbon porosity, composition (by activation or using dopants) and microstructure⁸⁶. The impact of carbon doping remains to be understood. For example, including nitrogen in the structure enhances the performance thanks to an additional faradaic contribution, so far limited to aqueous electrolytes⁸⁷. On the electrolyte side, numerous cations, anions and solvent molecules can be used. The development of high-throughput techniques, such as the ones already applied to battery materials and electrolytes⁸⁸, will be a big step forward in that direction⁸⁹. But there is still a need for systematically defining the good descriptors that can be extracted from simulations in order to select a few promising systems among thousands of candidates. Clearly such descriptors can only be designed

from the knowledge gained from the combination of all the information extracted from the combination of all the information extracted from *in situ* experiments and understanding at the molecular level. Once the relationships among the carbon morphology, the pore size distribution, the size of the ions and the capacitance of the systems are established, the key for enhanced energy densities will depend on surface functionalization⁹⁰ and on improvement of the operating potential by formulating better electrolytes^{91,92}.

The potential for improvement is even larger for oxide-based pseudocapacitors. Although recent studies have shed some light on the main features of the various mechanisms involved (for example simple surface redox reactions versus pseudo-intercalation), their molecular aspects remain mostly unknown. There is, therefore, an explicit need to adapt the *in situ* experiments and simulations that have been successfully applied to carbon-based supercapacitors for oxide materials. But there are challenges due to the difficulty in obtaining well-defined interfaces both structurally and chemically. Certain oxide supercapacitors operate in aqueous solvents for which acid/base effects must be taken into account, whereas other oxide systems involve the development of nanostructured, nanocrystalline metal oxide particles operating in non-aqueous electrolyte. Two-dimensional materials such as MoS_2 and the compounds known as MXenes have recently been tested for supercapacitor applications^{93,94}. Here also, pseudocapacitive effects are at play, but it is likely that the microscopic mechanisms derived for oxide materials will not be relevant for these materials. The use of *in situ* characterization techniques^{95,96} will be a decisive step towards improving the energy density of these materials.

Fundamental understanding of ion adsorption and charge storage in supercapacitors is essential for applications and technologies. In the area of energy storage, adsorption processes in porous carbons are of central importance for several technologies. One noteworthy example is redox flow batteries⁹⁷, both aqueous and non-aqueous, which are rapidly progressing towards commercialization because of both centralized and distributed systems that store energy from renewable sources. Biofuel cells, both enzymatic and microbial, represent a well-established sustainable technology in which adsorption processes on porous carbon electrodes are critical for achieving the redox processes involved in energy conversion⁹⁸. Other emerging energy technologies include flow capacitors⁹⁹ and ‘blue energy’. The latter is based on extracting the energy associated with the mixing of fresh river and salty seawater¹⁰⁰ or on osmotic power harvesting under salinity gradients¹⁰¹. In addition, applications of ion adsorption in carbon-based systems extend beyond energy storage to areas such as biosensors¹⁰² as well as gas-phase sensors for detection of toxic gases¹⁰³, while the use of carbon electrodes for desalination represents an increasingly attractive technology for drought-stricken areas. As these examples show, the experimental and theoretical tools developed and the knowledge gained for supercapacitors provide the basis for the development of a wide range of current and future technologies.

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Competing interests

The authors declare no competing financial interests.