Ions in Subnanometer Pores

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Desolvation of Ions in Subnanometer Pores and Its Effect on Capacitance and Double-Layer Theory**

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The study of charged solid–liquid interfaces, manifested as "double layers", represents a problem of both practical and scientific importance. Double layers are present in all electrolyte solutions and have been traditionally studied using planar noble-metal electrodes and mercury drops.[1] However, in the ionic channels in cells[2] or the small-diameter pores of electrochemical double-layer capacitors (EDLCs),[3] ions are in a very confined situation, which is different from that of a planar solid/electrolyte interface. By using nanoporous carbon with pores smaller than the size of an ion and a single associated solvent molecule, we show that the implicit assumption that double layers are governed only by ion/electrode charge separation may be short-sighted. Other factors may play a more dominant role than previously thought, for example, increasing the confinement of the ions leads to an increase in the capacitance. Including the effect of partially desolvating ions in the current double-layer theory could lead to a better understanding of the behavior of ions in confined environments.

Carbon is conductive, nearly ideally polarizable, and has pore sizes that can vary from smaller than the ionic size of electrolyte ions to many times larger than these ions.[4] The utility of using porous carbon species for studying double-layer charging was realized when using them as the active material in electrochemical capacitors, because the formation of a double-layer within their pores is assumed.[5] In EDLCs—also called supercapacitors or ultracapacitors because of the high specific charge they can store—symmetric positive and negative electrodes made from high-surface-area carbon ($>1000\ m^2\,g^{-1}$) are immersed in an electrolyte solution, with the entire construct housed in a hermetic can. The fundamental processes occurring at the electrodes are very different from those taking place in batteries. While batteries store the electrical energy in chemical bonds, EDLCs store it directly in the double layer. Attention directed towards EDLCs has greatly lagged behind that given to other power sources, such as batteries and fuel cells,[6] possibly due to the poor fundamental understanding of the electrode processes.

Helmholtz noted the adsorption of oppositely charged ions from solution on an electrode surface with an excess or deficiency of charge,[7] thus coining the term "double layer". It was later postulated that because of thermal fluctuations, a gradient of ionic-charge density may exist adjacent to the oppositely charged electrode and that the ion excess decays to the bulk concentration away from the electrode.[8] This "diffuse layer" and the Helmholtz layer constitute the double layer. These phenomenological models assume that only the forces between the electrode and the ions dictate charge storage whereas the solvent merely acts as a continuum that can be represented by a macroscopic dielectric permittivity. More advanced models have been proposed which highlight the possibility that the solvent may be inadequately described by a constant dielectric permittivity. Instead, these models note that the permittivity should decrease in close vicinity of the electrode as a result of the decreasing ability of the solvent to screen charge.[9] However, individual solvent-molecule and ion contributions have not been widely addressed.

It was shown by using various experimental techniques that ions carry with them a dynamic sheath of specifically adsorbed solvent molecules.[10] Contemporary thinking holds that because of the magnitude of the solvation energy,[11] ions must enter the narrow pores of double-layer capacitor carbons with the solvent shells intact.[12] This assumption led to numerous efforts directed towards the development of mesoporous carbons (with an average pore size of >2 nm)[13] containing pores able to accommodate a full double layer, which consists of a layer of solvated ions (which is about 1.5-nm thick) and a diffuse layer (that can be several nanometers thick depending on the electrolyte concentration).[4] However, recent studies show an increase of the capacitance in small pores, which seems to contradict the generally accepted double-layer theory.[14]

Various porous-carbon samples obtained from the same precursor (with all the pores being smaller than the size of the solvation shell) were used as active materials in double-layer capacitors to probe the belief that ions remain solvated during charging and test the hypothesis that increasing the confinement of the ions by decreasing the pore size points to a different charge-storage mechanism.

Porous carbon with tailored porosity was synthesized from TiC by using the procedure reported previously.[15] The porosity was characterized by means of argon sorption at 77 K (see Figure 1 a,b and the Supporting Information). Electrochemical testing was carried out on large electrodes

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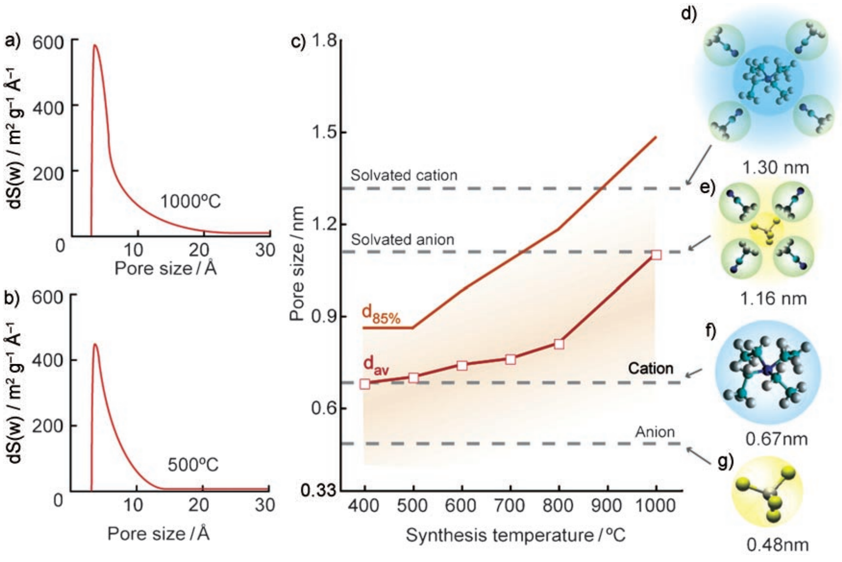

Figure 1. Pore-size evolution and comparison with the sizes of the electrolyte ions. Pore-size distributions calculated assuming slit-shaped pores for TiC-CDC synthesized at a) 1000 and b) 500 °C (fitted DFT distribution curves). A plot of the average pore size, d_{av}, versus the synthesis temperature (c) shows the pore-size increase from the size of the unsolvated cation (about 0.67 nm) to about 1.0 nm. The schematic representations of the d) solvated $(CH_3CH_2)_4N^+$ cation, e) solvated BF_4^- anion, f) bare cation, and g) bare anion show their sizes, as calculated in reference [17], in relation to the average pore sizes shown in (c). In general, the pore-size distribution shifts to larger pore sizes with increasing synthesis temperature, but the majority of pores are still smaller than the size of the solvated ions. Also, at all synthesis temperatures, at least 85 % of the pores, $d_{85\%}$, are smaller than the size of the ion with a sheath of solvent molecules coordinated around it. The smallest pore size resolvable using this technique is 0.33 nm.

(area: 4 cm^2)[16] to eliminate edge effects. The experiments were performed using high-purity electrolytes in a three-electrode configuration amenable to studying the processes at both the positive and negative electrodes. The electrolyte was 1.5 M tetraethylammonium tetrafluoroborate (TEA-TFB) in acetonitrile—an electrolyte that is commonly used in EDLCs because of its high conductivity and the relatively small ion size, which gives a large capacitance. From the pore-size distributions for the titanium-carbide–derived carbon (TiC-CDC), it is apparent that all samples have pores smaller than the solvated ions (see Figure 1), which will not allow ions to enter completely solvated.

The cyclic voltammograms obtained between 0 and 2.3 V, thereby monitoring the current response at each electrode for samples synthesized at 500 (Figure 2a) and 800 °C (Figure 2b), are representative of all the samples studied. These voltammograms show no electron-transfer processes occurring on either electrode within the studied potential range. Such processes would appear as peaks at the corresponding potentials, thus indicating redox reactions. Also, the different potential range traduced for the positive and negative electrodes at different synthesis temperatures indicates a different behavior as the pore size is changed.

From Figure 3 it is apparent that the double-layer capacitances caused by the anion (C_-) and cation (C_+) at the positive and negative electrodes, respectively, have different behaviors with regards to the pore size. The anion/positive electrode has a relatively constant double-layer capacitance at pore sizes between 0.8 and 1.1 nm. At average pore sizes below 0.8 nm, there is a sharp increase in the double-layer capacitance. For the cation/negative electrode, there is a slight increase in the capacitance upon decreasing the pore size from 1.1 to 0.75 nm, but at pore sizes below this value, the capacitance decreases slightly, which may be attributed to the presence of pore bottlenecks smaller than the ion or to an insufficient electrical conductivity of the CDC produced at 400 °C.[14] The maximum in capacitance for each ion/electrode system is shifted to smaller pores for the smaller ion (anion). A similar dependence was observed for the capacitance normalized by the area. It should also be noted that the sharp increase in capacitance for the anion/positive electrode system is far more profound than that of the cation/negative electrode one. If we used the ammonium salt $(CH_3)_4NBF_4$ instead (where the anion and cation have roughly the same size), the capacitance would be expected to be similar at both electrodes.

This increase in capacitance cannot come for purely electrostatic reasons. Most of the pores considered herein are equal to (or smaller than) a single ion with a single associated solvent molecule (Figure 4), and decreasing the pore size decreases the volume available for double-layer accumulation. Therefore, the ions must be at least partially stripped of solvent molecules to occupy the carbon pores in this study. Also, the results point to a charge-storage mechanism whereby the partial removal of this solvation shell

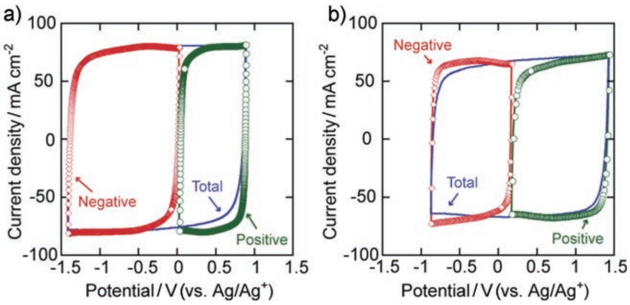

Figure 2. Cyclic voltammograms (CVs) taken at a scan rate of 20 mV s^{-1} on samples synthesized at a) 500 and b) 800 °C. The plot of total current density versus potential represents the response of both the positive and negative electrodes as the potential is scanned. The positive- and negative-electrode responses are separated from one another by using a third silver quasi-reference electrode placed between the electrodes. As the current in the cell is limited by the lower-capacitance electrode, the different sizes of the voltage windows in a CV plot are indicative of different capacitance values at the positive and negative electrodes. This is most clearly reflected in the TiC-CDC sample synthesized at 500 °C.

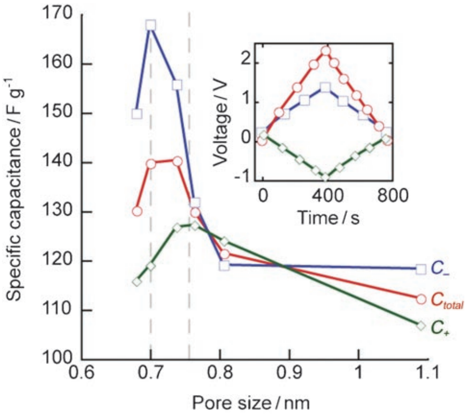

Figure 3. Dependence of the capacitance on the pore size. The specific capacitances calculated from a constant current discharge (inset, colors as for main plot) for the anion/positive electrode (C_-) and cation/negative electrode (C_+) systems show similar behaviors until a critical pore size of about 0.8 nm is reached. At pore sizes below this value, the anion/positive electrode and cation/negative electrode capacitances diverge.

and the increased confinement of the ions leads to an increased double-layer capacitance.

Unfortunately, theoretical work is still not mature enough to be able to explain this anomalous capacitance increase found in carbons with extremely small pores. Following the work of de Levie,[18] electrochemical capacitors have largely been modeled either by using mechanistic models derived from fitting the experimental data to electrical transmission line models[19,20] or by making modifications to the original models[21] proposed by Helmholtz,[7] Grahame,[22] Stern,[8] and others.[9] Recent modeling work[23] and experiments[17] suggest that the structure of water and the solvation of ions are different in nanopores than in bulk; for instance, Tanimura et al.[24] showed by means of molecular dynamics simulations that alkaline cations are stripped of their hydration shells and passed into the interior of a carbon nanotube at a charge density below 3 μF cm^{-2} (at 1 V), which is a quantity that is easily accessible experimentally. This result is not surprising considering that desolvation of ions by voltage-gated ion channels happens readily[2] at much lower potentials. The flux of ions across these channels can be as high as 10^7 s^{-1}, which shows not only that this process happens, but also that it happens extremely quickly. The most recent study[25] attempted to provide an explanation of the capacitance increase in small pores observed by our group.[16]

Although more work is needed to completely understand this phenomenon, the anomalous capacitance increase found in moving to carbon materials with pores of atomic dimensions may result from multiple possible scenarios. The energy involved in desolvating the ions upon charging and resolvating them upon discharging could operate in the form of a reversible energy-storage mechanism; for example, if we calculate the energy stored on each electrode of the TiC-CDC sample prepared at 800 °C, we arrive at a value of about 150 kJ mol^{-1}, which is very close to the solvation energy of $(CH_3CH_2)_4NBF_4$ in acetonitrile.[26] A lower capacitance of the cation, relative to that of the anion, may be attributed to its larger size per unit charge, which leads to a smaller solvation energy. The ethyl arms of the TEA cation may also "hide" acetonitrile molecules, thus hindering the full removal of the solvation shell. If the actual charge-storage mechanism is related to the energy of desolvation, the larger solvation energy of the anion would lead to its higher measured capacitance. This rationale also explains why the capacitance of aqueous solutions is, in general, higher than that of aprotic solutions. Solvation energies for the same ion in water are generally twice as high as those in an aprotic solvent. Similarly, the capacitance generally doubles in moving from organic to aqueous electrolytes.[27] This process can be compared to Li$^+$ insertion into graphite in Li-ion batteries,[28] with complete removal of the solvation shell and a change in the oxidation state. In the case of the supercapacitors tested herein, we anticipate a partial desolvation and the presence of both ions and solvent molecules in the pores, with no charge transfer as evidenced in Figure 2.

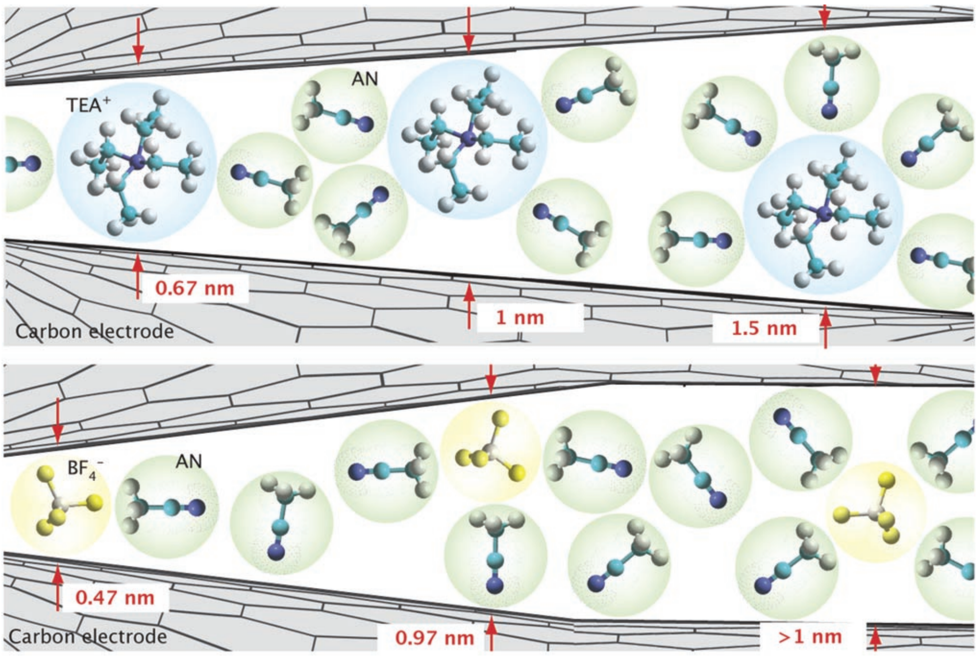

Figure 4. Geometric confinement of ions in extremely small pores. Both anions and cations enter the pores with no solvent-molecule screening charge at pore sizes below 1.5 and 1 nm, respectively. Therefore, it can be asserted that in all our experiments, the ions enter the pores either bare or with partial solvent shells (TEA$^+$ = tetraethylammonium, AN = acetonitrile).

Decreasing the pore size may allow a larger number of ions to be accommodated inside the same volume of carbon. Also, the closer proximity of both pore walls to the ions—and no possibility for the solvent molecules to screen charge—could lead to an excess charge density on the electrode side. The conductance properties of carbon have led some researchers to assume a space-charge capacitance on the electrode side of the double layer,[29,30] but this theory does not apply in the present study because of the lack of graphitic structure.

To measure the capacitance in the series of carbon materials studied herein (with pores smaller than the size of the solvated ion), there must be at least a partial removal of the solvent shell. The results show that a decrease in the pore size causes an increase in the number of solvent molecules removed, along with a similar increase in the capacitance. This result points to a mechanism in which removing the solvent shell leads to some form of charge/energy storage. Recasting the theory of double layers in electrochemistry to take into account solvation effects could lead to a better understanding of charge storage in electrochemical capacitors and ion transport in biological systems—and may even open up new opportunities in areas such as water desalination.

Experimental Section

Supercapacitor cells (4 cm^2) were assembled in a glove box under argon atmosphere (with O_2 and H_2O contents below 1 ppm). The electrode films were composed of CDC (95 wt%) and poly(tetrafluoroethylene) (PTFE, 5 wt%). The weight density of active material was kept constant at 15 mg cm^{-2}, thus leading to a thickness that varied between 250 and 270 μm, depending on the type of TiC-CDC. The active material was laminated onto a treated aluminum current collector. PTFE plates and stainless steel clamps were used to maintain the stack under pressure (0.5 MPa). A porous polymeric separator (composed of two 25-μm-thick PTFE layers) was inserted between the two electrodes. A silver wire (2 mm) placed between the electrodes acted as quasi-reference electrode. We assumed that the concentration of silver ions at the silver electrode did not change during cycling, and therefore, that its potential remained constant. The cell was then immersed into an electrolyte, which consisted of tetraethylammonium tetrafluoroborate (1.5 M) in acetonitrile, and put into an airtight box. The electrolyte salt (35309 from Acros Organics, CAS 429-42-5) was dried under vacuum for at least 24 h at 80 °C. Extra dry acetonitrile (32681 from Acros Organics, CAS 75-05-8) was used as purchased. All tests were done at room temperature in excess of electrolyte.

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