Increasing Energy Storage in Electrochemical Capacitors with Ionic Liquid Electrolytes and Nanostructured Carbon Electrodes

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Supporting Information

ABSTRACT: The potential pathways to increase the energy storage in electric double-layer (EDL) supercapacitors using room-temperature ionic liquid electrolytes and carbon-based nanostructured electrodes are explored by molecular dynamics simulations. A systematic comparison of capacitances obtained on nanoparticles of various shape and dimensions showed that when the electrode curvature and the length scale of the surface roughness are comparable to ion dimensions, a noticeable improvement in the capacitive storage is observed. The nanoconfinement of the electrolyte in conductive electrode pores further enhances the capacitance due to mismatch in ion-electrode surface interactions and strong electrostatic screening. We show that nanoporous structures made of arrays of conductive carbon chains represent a synergy of all three favorable factors (that is, high curvature, atomic scale roughness, and nanoconfinement) and can generate non-Faradic capacitance ranging from 260 to 350 F/g, which significantly exceeds the performance of the current generation of nanostructured electrodes.

SECTION: Energy Conversion and Storage; Energy and Charge Transport

Electric double-layer capacitors (EDLCs or supercapacitors) have been extensively explored as promising energy storage devices in which the charge/energy is stored through ion rearrangement in the interfacial layer between the electrode and electrolyte. Substantial efforts have been dedicated to improve the energy density of EDLCs through design of nanostructured electrodes with a high specific surface area and understanding the interplay between various phenomena defining the performance of these devices. Several experimental, theoretical, and simulation studies conducted on this topic over the past few years clearly demonstrated the complexity of physical phenomena and correlations governing the EDL capacitance. For example, it was shown that the capacitance could be strongly influenced by thermodynamic conditions,1 electrolyte chemical structure,2-4 and nanoconfinement,5,6 as well as by the electrode surface roughness/nanostructure5,8 and conductivity. While our detailed understanding of these complex systems is still in its infancy, there is sufficient evidence that envisioned breakthroughs for supercapacitors must come from the optimal design of nanostructured electrode/electrolyte combinations.

Utilization of nanostructured electrodes provides several beneficial factors; (i) it can significantly increase the surface area exposed to the electrolyte and hence available for EDL formation, (ii) when the nanoscale structural features on the electrode surface, for example, surface curvature or atomic scale roughness, are comparable to the size of ions comprising the EDL, additional geometric factors can facilitate the ion separation in the EDL and lead to a capacitance enhancement, and finally, (iii) as has been demonstrated in several experiments2-5 and simulations9-12 as well as explained by theoretical models,13-15 the confinement of the electrolyte in charged nanoporous electrodes can be accompanied by qualitatively different physical behavior, for example, strong (exponential-like) screening of electrostatic interactions between ions due to electronic polarization of the electrode can lead to super ionic states of densely packed ions of the same charge14 which can also result in the enhancement of capacitive storage.6,10 However, the plethora of possible nanostructured electrode architectures as well as the complicated interplay between electrode/electrolyte structural characteristics and the capacitor performance makes the
rational design of novel supercapacitors a daunting task. The most frequently utilized electrodes, such as activated or carbide-derived carbon (CDC), are structurally heterogeneous amorphous materials consisting of a variety of nanostructural elements, including flat graphene sheets, 1D and 2D curved surfaces, and even carbon single chains.\(^{16}\)

Moreover, the content of these structural elements as well as their characteristic shape and size distributions can depend on (and hence can be controlled by) electrode preparation conditions (e.g., high- or low-temperature synthesis of CDC). In this Letter, we attempt to provide guidance to the process of designing optimal nanostructured electrodes by systematically analyzing several correlations between EDL capacitance and nanostructural features of electrodes. Specifically, we focus on two important questions: Which nanostructured elements are most beneficial to manipulate with in order to increase the energy storage in EDLC? What are the theoretically possible limits of the energy storage in EDLCs that can be achieved using nanostructured electrodes and room-temperature ionic liquids (RTILs)\(^{2}\)? Addressing these questions provides guidance toward designing the next generation of nanostructured electrodes for high-energy-density supercapacitors.

For EDLCs, RTILs are widely considered the electrolyte of the future. RTILs are solventless electrolytes with many properties that make them attractive for electrochemical energy storage: high chemical and thermal stability, negligible vapor pressure, a broad electrochemical stability potential window, and an immense parameter space in terms of ion selection and resulting properties. While there are a number of studies of the EDL in RTIL electrolytes on flat surface electrodes, studies of complex electrode geometries, such as those of exohedral carbon nanomaterials, are rare in the literature and so far focused on organic electrolytes.\(^{17}\)

For the purpose of this work, we divided the nanostructured electrodes in two categories, open-structure (or exohedral) and nanofluidic confinement electrodes. In our definition, the open-structure electrodes are those where the electrode nanostructural features are sufficiently separated from each other by an electrolyte such that there is no electrolyte nanofluidic confinement. In other words, the pore size or the separation between nanoscale features (e.g., nanotubes or fullerenes) is significantly larger than the dimensions of electrolyte molecules (i.e., RTIL ions), and hence, the EDLs formed on such electrode surfaces are in contact with the bulk electrolyte. This definition would include flat surfaces as well as porous systems with wide pores, for example, for a typical RTIL electrolyte, this would correspond to pores wider than 40 Å, which is about five times larger than the size of individual ions and about twice the width of highly structured EDLs near flat surfaces in typical RTILs. The kinetic limitations in EDLCs currently observed\(^{16,19}\) for RTIL electrolytes (charging rate and temperature of operation) are addressed by the use of these exohedral materials, and therefore, this type of electrode has received significant attention. In contrast, electrodes with relatively narrow pores or with arrangement of nanoscale features (e.g., nanotube bundles) where the separation between those structural features is comparable to a single ion in size will be categorized here as nanofluidic confinement electrodes. In such electrodes, the electrolyte experiences confinement between the electrode surfaces, and therefore, the formed EDL is not in direct contact with the bulk electrolyte. As we will show below, the physical phenomena and behavior of the electrolyte in such confined environments can be significantly different than that on open-structure electrodes.

The simulation setup consisted of two electrodes and a RTIL electrolyte being placed between the electrodes. The simulations for open-structure electrodes such as fullerenes, nanotubes, and single carbon chains were performed using the constant electrode charge methodology described in ref 30, while simulations for flat and nanoscale surfaces as well as for electrodes with nanofluidic confinement (slit nanopores and single-chain arrays) were conducted using a constant applied potential approach, as described in ref 20. In the former approach, the partial atomic charges for surface atoms were predefined and homogeneously distributed. In the latter approach, electrodes were modeled as conductors with charges determined using self-consistent iterations for electrostatic energy minimization with respect to electrode charges.\(^{21,22}\) Positions of electrode atoms were fixed in all simulations. For description of the RTIL electrolyte, a combined explicit atom/charged atom force field that has been developed and validated previously\(^{20,23,24}\) was utilized. The equations of motion were integrated using the RESP algorithm\(^{25}\) as described in ref 26. The temperature was maintained at 393 K using Nosé–Hoover thermostat chains.\(^{27}\) More detailed descriptions of the systems setup and simulation methodologies and protocols are given in the Supporting Information. For each system, production runs over 10 ns were conducted for each value of the potential difference investigated. The collected statistics on electrode charges and ion densities were subsequently used to derive electrode potentials and capacitances. The potentials of zero charge (PZCs) were computed from the simulations with uncharged electrodes. The electrode potential was defined as the difference between the Poisson potential on the electrode surface and in bulk electrolyte minus the PZC. The differential capacitance (DC) was computed as the numerical derivative of the electrode charge versus electrode potential as described in ref 28. The integral capacitance (IC) was computed as the electrode charge at a given potential divided by the electrode potential.

Open Structures. While the role of electrolyte chemistry on the formation of the EDL and the capacitance was investigated both by experiments and simulations, understanding of the influence of the electrode surface geometry on the EDL capacitance is still rather poor. We begin our discussion by analyzing the capacitance generated on electrodes with several common surface geometries such as atomically flat, rough, and curved. Figure 1 compares the ICs at 4 V potential difference between electrodes for the following electrode geometries: (i) flat surfaces consisting of graphene layers; (ii) atomically rough or nanopatterned surfaces, (iii) cylindrical electrodes consisting of (3,3), (5,5), and (7,7) metallically conducting single-walled carbon nanotubes (SWCNTs) with corresponding nanotube radii of 1.9, 3.4, and 6.1 Å, respectively; (iv) spherical particle electrodes with radii of 1.9, 3.45, and 6.4 Å represented here by C\(_{20}\), C\(_{60}\), and C\(_{180}\) fullerenes, respectively; and (v) carbynes, single carbon chains. The latter represent an ideal case of a single-chain conductor. While the stability and conductive properties of isolated C\(_{20}\) and (3,3) SWCNTs are not practical, these structural elements can be embedded into other structures and also represent a limiting case of highly curved surfaces in porous carbons such as CDC or activated carbon. Similarly, the electrochemical stability and feasibility of manufacturing electrodes comprised of linear carbon chains is yet to be proven, but from a fundamental understanding point
of view, this system represents the limiting case where the thickness (diameter) of the electrode nanostructure becomes comparable to single-atom dimensions. To facilitate the comparison of capacitances obtained on electrodes with different geometries, we have normalized them per unit mass of electrode atoms that are in direct contact with the electrolyte. Where it was possible to define a surface area, we also report the capacitance per unit of specific surface area.

For an atomically flat graphite electrode, the IC of the RTILs ranges between 4.5 and 5.3 μF/cm² or 55 and 70 F/g, depending on the electrolyte chemical structure. For example, the average IC shown in Figure 1 for a basal plane (flat) graphite electrode is 65 F/g (4.93 μF/cm²) for [C₅min][TFSI], 61.6 F/g (4.67 μF/cm²) for [pyr₁₃][FSI], and 56.6 F/g (4.3 μF/cm²) for [C₅min][TFSI]. In our normalization of capacitance, we assume that the surface graphene layer is exposed to electrolyte with both sides at surface. Decreasing further the radius of the curvature is small. This allows us to conclude that the curvature effects can only contribute a modest extent to the capacitance enhancement observed experimentally on, for example, onion-like carbon electrodes where the outer layer radius of the onion typically is much larger than 6 Å. A significant (i.e., more than doubling) increase in capacitances for spherical electrodes (compared to those for flat surfaces) would require a curvature radius as small as 1.9 Å, as in the C₂₀ fullerene.

Next, we analyze the capacitance near atomically corrugated nanopatterned surfaces. The rough edges of the nanopatterned surfaces are expected to generate large local electrostatic fields, promoting the ion segregation near the electrode surface at low electrode potentials and therefore generating a larger capacitance than on atomically flat surface electrodes. Atomically rough surfaces can be populated with random structural features using chemical etching or other surface modifications. For the particular case illustrated here, the atomically rough surfaces were generated from graphite ABAB stacking in such a way that small surface grooves 7.1 Å deep and 35 Å wide were exposed to the electrolyte (see Figure 1). These surfaces with groove widths comparable to the ion sizes have modified the EDL structure and accumulation rates (versus electrode potential) of the electrolyte near the surface, generating surprisingly large capacitance per specific surface.

Figure 1. The capacitance as a function of electrode surface curvature radius and geometry for various open structure electrode geometries as obtained from MD simulations at the 4 V potential difference between electrodes. For majority of the open structures (i.e., flat surfaces as well as well-separated nanotubes, spherical particles, and carbon chains), the DC is almost independent of the potential in the potential window between 0 and 4 V, and hence, the ICs on individual electrodes are very similar. However, for atomically corrugated nanopatterned surfaces, the charge accumulation/separation is asymmetric with electrode polarity, and therefore, an average value for positive and negative electrodes is shown. The ICs obtained for rod-like carbon chains immersed in [EMIM][TFSI] (green ▲), [pyr₁₃][FSI] (turquoise ◆), [BMIM][PF₆] (blue ▼), and an all-trans carbon chain in the [pyr₁₃]/[TFSI] (pink △) are shown.
area. For example, the average (over two electrodes) IC of the electrode with a corrugated surface shown in Figure 1 is 157 F/g (or 7.5 μF/cm²), which is factor of 2−3 higher than those obtained on atomically flat basal plane graphite. Note that in the case of a nanopatterned surface, we observed a noticeable asymmetry in the capacitance as a function of electrode polarity, with the negative electrode generating up to 20% larger IC than the positive one. More detailed discussion of correlations between the capacitance and EDL structure on atomically corrugated surfaces can be found in refs 7 and 8. Finally, our simulations reveal that the largest enhancement of the capacitance is obtained for electrodes made of conductive carbon chains (carbynes). Linear chains of carbon were observed experimentally in TiC−CDC and B₄C−CDC. We modeled carbynes both as a 1D sequence of carbon atoms (i.e., rod-like −C≡C≡C− or −C≡C≡C≡C−) as well as sequences of atoms arranged in a zigzag shape (all-trans) conformation. Both geometries have produced similar capacitances of around 240−250 F/g. This enhancement was obtained for several different electrolytes (i.e., [pyr][FSI], [EMIM][TFSI], [BMIM][PF₆]), therefore indicating that the chemical structure of the electrolyte does not play an important role and the observed increased values of the capacitance is primarily correlated with the electrode geometry/curvature. Due to extreme curvature effects and atomic-scale corrugation, electrodes comprised of single carbon chains immersed in RTILs can generate a capacitance that is up to a factor of 4 larger than the capacitances on flat surfaces with one side exposed toward the electrolyte, or almost double the IC of a single graphene layer immersed in electrolyte with both sides exposed to the electrolyte. Taking into account the relatively weak dependence of the capacitance on the chemical structure of the electrolyte, we believe that the capacitances shown in Figure 1 for the linear chains are close to a theoretical limit that can be expected for open structures.

**Electrodes with a Nanoconfined Electrolyte.** Recent experiments have indicated that when the electrolyte is confined into pores with at least one dimension comparable to ion sizes, then a twofold capacitance enhancement can be observed. Theoretical models and molecular simulations showed that for slit-like nanopores, the primary mechanism for the observed capacitance enhancement is an abrupt separation of ions inside of the nanopores due to expulsion of co-ions when the electrode potential reaches a certain threshold. The complete ion separation is facilitated by strong screening of electrostatic interactions between ions confined in nanopores with polarized conductive walls, which leads to an effective short-range ion−ion electrostatic interaction, as illustrated in Figure 2a for two positive ions inside of negatively charged slit-pores as a function of ion separation and pore width.

**Figure 2.** (a) The total electrostatic energy between two ions inserted into a porous electrode consisting of an array of carbon chains and a slit geometry pore as a function of the distance between the ions and the separation between the chains/walls. For comparison, the unscreened electrostatic energy is also shown as a black line. Also shown are the 5kT energy level and the corresponding separations for each curve. (b) The separations between two ions at which the electrostatic repulsion is reduced below 5kT plotted as a function of the pore width.
between ions promotes dense packing of the counterions inside of nanopores upon complete ion separation and, hence, maintains the high capacitance.

Taking into account the intrinsically high capacitance observed for carbon single chains in open structures, it is reasonable to assume that combining the high atomic roughness and the curvature of linear carbon chains with a nanoconfinement effect can lead to a further capacitance enhancement. To test this hypothesis, we have conducted simulations of RTILs in contact with model electrodes comprised of an array of single chains, as illustrated in Figure 3. First, we confirmed that the relatively low volumetric density of conductive atoms in this nanoporous electrode structure still provides sufficient screening of electrostatic interactions between intercalated ions. Figure 2a clearly shows a fast (exponential) decrease of the repulsion energy between inserted ions both for the slit and for carbon chain array geometries. Comparing the separation between ions at which the electrostatic repulsion energy is comparable to thermal fluctuations (below $kT$), it is clear that only 10–20% higher ion separations are required to reach this energy level for the linear chain confinement compared to the slit-pores. Figure 2b shows that the scaling of these separations as a function of nanoconfinement dimensions (width in the slit-pore or separation between single chains) is very similar. Therefore, in single-chain conductive arrays, one can expect sufficient screening of electrostatic interactions between inserted ions needed to retain a relatively high density of the counterions inside of the nanopores even when all co-ions are expelled.

Next we investigate the non-Faradic capacitance enhancement that can be obtained in such nanoporous electrode structures. The IC obtained from simulations of an [EMIM]-[TFSI] RTIL electrolyte on carbon chain arrays with spacing ranging between 6.6 and 8.0 Å is shown in Figure 4 as a function of chain separation and is compared to the corresponding values obtained for electrodes with slit-pore geometries. Examination of Figure 4 reveals the following major trends/observations:

(i) The IC values ranging between 240 and 347 F/g obtained for carbon chain arrays are almost a factor of 6 larger than the average IC on a flat surface, clearly indicating a remarkable capacitance enhancement. For comparison, experimental CDC systems generated capacitances of 140–160 F/g in subnanometer pores, while previous simulations of slit-like nanopores reported a 133 F/g maximum in the IC. For our best geometry, the IC per unit mass of electrode in the chain array is about 40% larger than that of an isolated single chain (open structure).

(ii) The IC is asymmetric with respect to the electrode polarity. Specifically, the positive electrode generates systematically lower capacitances than the negative electrode. Similar asymmetry in capacitance enhancement was previously observed for this RTIL electrolyte in slit-like nanopores. This asymmetry is a consequence of details of the chemical structure and the distribution of partial atomic charges in electrolyte ions that, in turn, leads to different interactions between ions and the electrode surface.

(iii) The variation of the IC as a function of the distance between chains is rather broad; however, high values of the capacitance are observed over a broad range (a couple of Å) of chain separations. On the negative electrode, a maximum capacitance of 340–350 F/g is reached between 6.8 and 7.2 Å of chain separation. The relatively broad maxima in the IC indicate a potential flexibility in the design and fabrication of these nanoporous structures with optimal energy storage. In contrast, for slit nanopores, both simulations and experiments showed that only a very narrow range of pore widths (~0.5 Å) generates the capacitance enhancement.

Examination of the ion density inside of electrodes showed that at 0 V for chain arrays with separations > 7.6 Å, the RTIL had no problem wetting the electrodes. However, for arrays with chain separations < 7.5 Å, the ions did not wet the electrode, that is, they did not intercalate inside of the electrode at atmospheric pressure. We observed a similar effect for slit-like nanopores for slit widths < 7.0 Å, and Merlet et al. observed this near-PZC in their simulations of nanoporous CDC electrodes. In these systems, the steric repulsion of ions due to nanoconfinement is larger than attractive dispersion interactions between RTILs and electrode atoms therefore creating “ionophobic” conditions at 0 V. Overcoming this steric repulsion requires either an external pressure or electrostatic potential to be applied on the electrodes. For the latter, Figure 5 shows the density of ions inside of electrodes as a function of chain separation in the electrode at a 3 V potential difference. For electrodes with ionophobic conditions (<7.5 Å), we can see that when the potential is applied, only counterions intercalate inside of the electrode, therefore leading to an almost complete separation of ions. For a wider spacing of chains, more ions intercalate into the electrode, but the electrolyte is no longer completely separated (we see some fraction of co-ion intercalation). Note that the charge built on the electrode is primarily defined by the difference of counterions and co-ions intercalated. From Figure 5, we can see that while the overall number of EMIM and TFSI ions increases with increasing spacing between the chains, the difference between these two (and hence the total charge) stays almost constant. This is consistent with the observed relatively broad and flat peaks in the IC as a function of chain separation discussed in Figure 4.

The mechanisms of charge accumulation (and the capacitance enhancement) on electrodes and the asymmetry of capacitance as a function of electrode polarity can be further studied by examining the DC and ion densities as a function of the electrode potential, as shown in Figure 6 for the system with a 7.2 Å spacing between electrode chains. For the investigated combination of an electrolyte and array of chains, the DC versus electrode potential shows a minimum at low

![Figure 4](image-url)

**Figure 4.** The IC as a function of distance between carbon chains or the width of the slit nanopore for the positive and negative electrodes. The dashed line corresponds to 66 F/g, which is the typical range of ICs on a flat surface.
voltages due to low wettability of the pores by the electrolyte. A maximum at +2 V of 420 F/g and two maxima on the negative electrode at −0.8 (of 375 F/g) and −1.5 V (of 420 F/g) can be clearly identified in Figure 6a. Interestingly, the DC remains surprisingly high (300−350 F/g) even at potentials larger than ±2 V and remains above 250 F/g for an electrode potential in the range of ±4 V. The latter is quite impressive compared to flat electrodes or nanopores with slit-pore geometries where the DC drops quickly as the electrode potential magnitude increases above 2−2.5 V.

Shown in Figure 6b are the densities of inserted ions as a function of the electrode potential. Near PZC, densities of both ions are almost zero, consistent with relatively poor wettability of pores with this separation and with the observed minimum in DC (near PZC) shown in Figure 6a. For this type (i.e., ionophobic) of electrodes, simulations using the primitive model by Kiyohara et al.36,37 predicted that intercalation of the electrolyte into pores is accompanied by a first-order phase transition at a certain value of the electrode potential, which would compensate for the steric repulsion between the electrolyte and the nanopore. As we can see from Figure 6b in our chemically realistic system for the selected separation of chains, the behavior on positive and negative electrodes is different. On the negative electrode, we observe an almost linear increase of the counterion (EMIM cation) and the total ion densities as the magnitude of the electrode potential increases. There are no sharp jumps in the ion density that can be associated with the phase transition observed by Kiyohara et al. The depletion of the co-ion (TFSI anion) from the negative electrode occurs at a relatively low voltage, that is, the TFSI is essentially completely removed at about −1.8 V. At potentials below −1.8 V, the dominant mechanism for the charge accumulation on the negative electrode is the counterion densification inside of nanopores. However, the changes in the composition/density versus potential on the positive electrode are strikingly different from the negative electrode. As the electrode potential changes sign from negative to positive, a sharp increase of the TFSI density is observed near PZC. Surprisingly, concomitant with the increase of TFSI, the density of EMIM also increases due to strong bonding to TFSI and the inability of the positive electrode to expel the EMIM co-ion. The overall density of ions increases sharply, which is consistent with the first-order phase transition observed by Kiyohara et al. in their simulations using the primitive model. In the potential range between +0.3V and +4.0V the EMIM co-ion density decreases. Interestingly, in this potential range, the total ion density stays almost constant, consistent with the ion swapping mechanism.

Analysis of the total ion density/composition inside of the electrodes shows that the mechanism of charge accumulation can strongly depend on the electrode polarity as well as geometric dimensions of nanopores and the specific interaction between electrolyte ions and the electrode. For the RTIL/ single-chain array systems investigated in this work, we observed various mechanisms of ion intercalation/exchange inside of the nanoporous electrodes. These mechanisms included (a) a continuous ion swapping inside of the nanopore...
with increasing electrode potential (the dominant mechanism for wider nanoparticles that correspond to ionophilic conditions at PZC, i.e., chain separations > 7.5 Å), (b) a continuous increase of the ion density toward superionic states (e.g., as was shown in Figure 6b for the negative ionophobic electrode with a 7.2 Å chain spacing as well as observed by Kondrat et al. in their coarse-grained simulations for slit nanopores), and (c) a change in the electrolyte composition accompanied by clear sharp jumps (phase transitions) in one or both ion densities (this mechanism has been observed in both ionophobic and ionophilic chain array electrodes as well as in our previous studies of slit nanopores). However, despite the variety and specificity of the observed mechanisms for each system, Figure 4 shows that enhanced values of capacitance are obtained for electrodes with ionophobic as well as ionophilic conditions, indicating that the capacitance is primarily sensitive to the extent of ion separation with an applied potential independent of what mechanisms are responsible for this process.

Finally, we would like to point out that the synthesis and stability of linear carbon chains (carbynes) is quite a controversial issue, and fabrication of their arrays is not realistic at the moment. Short (∼10 atoms long) chains have been observed in interstellar space, and longer chains were reported in confinement inside of nanotubes; however, the presence of linear carbon was observed in highly disordered CDC. Moreover, conductivity measurements on those CDC materials have shown 1D hopping for electrical conductance mechanisms, confirming the presence of linear carbon chains in those amorphous materials. The presence of 1D chain elements might explain why low-temperature CDC with a small average pore size and fairly low conductivity shows higher capacitance values compared to materials with 2 orders of magnitude higher conductivity produced or annealed at higher temperatures and containing 2D carbon sheets. Simulations presented here clearly showed that single-chain structural elements can generate several times higher capacitance (per mass) compared to that of a flat graphene surface. Hence, we speculate that despite having overall lower conductivity, the low-temperature CDC might have enough single-chain structural elements that would lead to increased capacitance compared to high-temperature CDC, which is overall more conductive but has “flatter” surface (i.e., lower capacitance) structural elements.

In conclusion, our systematic analysis of correlations between the nanoscale structure of carbon-based electrodes and capacitive energy storage of the EDLC with RTIL electrolytes showed that atomic-scale roughness and curvature of electrode surfaces as well as nanoconfinement of electrolytes can provide noticeable enhancement of the capacitance when the dimensions of these nanostructural characteristics are comparable to electrolyte ion sizes.

Increasing the curvature of the electrode results in an effectively larger volume of the interfacial layer, which allows more counterions per surface area (compared to a flat surface) to compensate for the electrode surface charge, therefore leading to increased capacitance. Open-structure electrodes comprised of single nanotubes or spherical fullerenes showed increasing capacitance with increasing nanoparticle curvature. However, the effect becomes significant only at large curvatures. For example, while a maximum capacitance increase of ∼50% compared to a flat basal plane graphene surface was observed for the smallest radius nanotube (R = 1.9 Å), for more realistic nanotubes (R = 3.4 and 6.4 Å), a capacitance increase of only 15–20% was obtained. For spherical particles, the capacitance increase was more pronounced (e.g., for C60 fullerenes, R = 3.45 Å, an 80% capacitance increase compared to the flat electrode was observed). However, from practical points of view, increasing the curvature in two dimensions and preserving the conductive properties of electrode nanoparticles might be challenging.

The atomic-scale roughness of the electrode surface can also increase the capacitance. The large local electrostatic fields generated at the atomically rough surface edges facilitate the ion segregation near the surface at lower voltages (less than 2 V), allowing therefore higher capacitance. Just roughening of the flat surface can increase the capacitance by a factor of 2.5 compared to the flat surface if the dimensions of surface roughening patterns are comparable to the electrolyte ions’ dimensions.

The nanoconfinement of RTIL electrolytes inside of conductive electrode nanopores leads to significant screening of electrostatic interactions between ions, which can facilitate the separation of co-ions and counterions as well as allow denser packing of counterions inside of nanopores (i.e., super ionic states). As has been shown experimentally and in simulation/theoretical studies, the nanoconfinement can lead to a factor of 2 increase in the capacitance.

In attempt to explore the maximum possible capacitive non-Faradic energy storage, we have investigated the synergistic effect of all three beneficial characteristics by studying the electrodes comprised of conductive single-chain arrays that combine the nanoconfinement effect with maximized atomic roughness and the curvature possessed by a single-chain conductor. The capacitances on the order of 340–350 F/g obtained for the arrays of linear carbon chains are close to a theoretical limit of non-Faradic capacitance that can be achieved using RTIL electrolytes. So far, experimentally, this magnitude of capacitance was only observed when Faradic redox processes were involved, that is, in pseudocapacitors. For example, electrodes comprised of doped polymer chains with single-chain electronic conductivity as large as 80 kS/cm showed similarly large capacitances. However, the charge storage in these electrodes involves fast redox reactions between the electrolyte and polymer chains, which leads to chemical degradation of the electrode after a few thousands cycles. Nanostructured electrode/electrolyte combinations with non-Faradic charge storage, that in principle can have an infinite lifespan due to the absence of chemical reactions, typically report capacitances below 200 F/g. However, very little effort to maximize the interplay of all beneficial nanostructural characteristics discussed above has been made so far. Our simulations clearly demonstrate that significantly higher energy storage is possible for the non-Faradic capacitors if the fabrication and preparation of nanoporous carbon electrodes can be directed to maximize the content of atomically rough and highly curved surfaces. The ideal structural element that contains both of these properties is a carbon single chain. Therefore, optimizing processing conditions to allow the maximum content of carbon single-chain segments, like those believed to be present in low-temperature CDC electrodes, is a promising direction for designing a new generation of nanostructured electrodes.
A detailed description of the simulation setup and protocols. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

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