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Electric double layer capacitance for ionic liquids in nanoporous electrodes: Effects of pore size and ion composition

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ABSTRACT

The energy density of an electric double layer (EDL) capacitor, a type of supercapacitor, depends on the ion distribution within the micropores of electrodes that are typically made of amorphous carbon. By using coarse-grained models and the classical density functional theory, we investigate the distributions of ionic species among different idealized nanopores in contact with an asymmetric ionic liquid mixture and the effects of the bulk electrolyte composition on capacitive energy storage. We find that a charged pore is always small-ion selective, provided all ions have the same valence and similar non-electrostatic interactions. While small ions enhance both the EDL capacitance and the accessibility of micropores, an ionic mixture containing ions of different sizes may yield a capacitance higher than those corresponding to pure ionic liquids. The increased capacitance may be attributed to more efficient ion packing near the charged surface. At certain conditions, the improvement is on a par with the anomalous capacitance rise for pure ionic liquids in electrodes with ultranarrow pores.

1. Introduction

This volume commemorates the life of Lesser Blum, who completed his work among us in April 2016. The sadness we feel is for the loss of such a great mind, a pioneer in molecular theories of ionic systems, and a genuine friend. Through us, his work and intellectual life will continue. Lesser is survived by his signature contributions to analytical solutions of the Ornstein-Zernike equation via the mean spherical approximation (MSA) [1–4], which provide a systematic improvement of the Debye-Hückel theory for aqueous electrolyte solutions. In recent years, correlation functions derived from the very same method were broadly used within the framework of classical density functional theory (DFT).

Recent years have witnessed tremendous advances in the synthesis of novel electrode materials [5–7]. These materials typically contain micropores of different sizes with large specific surface areas, promising broad applications to the next generation of electrochemical devices with much enhanced energy and power densities. When they are in contact with an organic electrolyte or a room temperature ionic liquid (RTIL), commonly used for supercapacitors, the micropores have enormous effects on the ionic composition under confinement and, subsequently, the electric double layer (EDL) structure [8]. The ionic systems in the micropores may have properties drastically different from those corresponding to the bulk electrolyte. For example, a confined organic electrolyte can effectively reduce its dielectric constant by as much as 90% of the bulk value due to the change in the local ion composition [9]. While extensive work has been devoted to studying ion selectivity by nanopores in various aqueous systems [10,11], a complete understanding is yet to be established on how ions from a non-aqueous ionic mixture are distributed in the micropores of electrodes and how the bulk electrolyte composition affects the performance of various electrochemical devices.

In comparison to alternative electrochemical methods for energy storage, EDL capacitors have unique advantages in terms of the power density and the cycling life. The capability of an EDL capacitor for energy storage is largely determined by its energy density, which is closely related to the distribution of ionic species within different micropores. While tuning the composition of a bulk electrolyte is relatively straightforward, device optimization requires a good understanding of ion partitioning between micropores and its connection with the overall EDL capacitance. Experimental measurement of the density profiles of an ionic liquid inside the micropores of an

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electrode have been proved difficult due to confinement effects. As a result, most experimental work thus far has been focused on either single electrode surfaces or in bulk ionic liquids. Conventional methods such as *in situ* atomic force microscopy [12] are not a viable option due to the nature of the electrochemical devices and charged species in the system. For example, use of a charged tip would alter the structure of the electric double layer. Some more useful techniques are X-ray and neutron scattering. However, even in these cases, the diversity of pore sizes in a given electrode material will render pore specific information thus of limited utility. Therefore, modeling methods are valuable to provide even a qualitative understanding of the distribution of ionic species within charged pores.

Room-temperature ionic-liquid (RTIL) mixtures have superior operating potential windows and the ability to charge-discharge over long periods of time without losing performance [13]. However, there are many possible ionic liquid mixtures; each composition has the possibility to produce enhanced electrochemical properties for applications to energy storage. Besides, the RTIL properties are quite different from those for a dilute solution of electrolyte in an aqueous medium. The difference is manifested not only in terms of the dielectric constant, ion size and shape, but also in the ion concentration, conductivity, and more importantly, in issues arising from the decomposition of water within a charged pore [14]. As a result, the ion distribution in conventional EDL is fundamentally different from that in an ionic liquid. As shown in previous experimental and theoretical studies [15–17], an ionic liquid EDL exhibits a lamellar structure [6], formed by layers of alternating cations and anions near the electrode surface. While the previous studies are mostly focused on ion distributions near a planar surface, the question of how asymmetric ionic liquids form layered structures within charged pores remains unanswered.

Previously, we have studied the partitioning, selectivity, and ionic distributions of asymmetric ionic liquid species within nanoporous electrodes [8]. In that study, we found that ion selectivity by the micropores of an electrode in contact with a room-temperature ionic liquid is fundamentally different from that of ion channels or nanopores in aqueous systems. The effects of ion size and valence on selective adsorption of ionic species by a slit pore were examined in details with Monte Carlo simulations [18]. A charged pore in contact with an ionic mixture attracts smaller ions of the same valence not only when the surface bears the opposite charge or stronger attraction but also when it has the same charge exerting a stronger electrostatic repulsion. It follows naturally from this, that we should address the impact of the ion selectivity and the ionic distributions within the pore, on the capacitance for ionic liquid mixtures. We also hope to give insight into how asymmetric ionic liquid mixtures affect electrochemical stability seen in experiments [13].

2. Methods

We use a coarse-grained model to capture the primary features of ionic-liquid mixtures. Cations and anions are represented as charged hard spheres as in the primitive model of electrolyte solutions. A microporous electrode is modeled as slit pores with an applied surface potential range of ±1.5 V. The slit pore model is commonly used in experimental characterization of porous materials by gas adsorption to determine pore-size distribution [19]. Ion confinement between two parallel walls has been one of the most popular models for studying confined electrolyte due to its simplicity [20]. As in a conventional model of electric double layer, we do not take into account electrostatic screening due to electrons at the electrode surface or any material specific effects.

The coarse-grained model accounts for electrostatic correlations and excluded volume effects not included in the conventional theories of EDL, mostly based on various modifications of the Poisson-Boltzmann equation. Because of its simplicity, we can easily tune the wall potential, the pore width, and the mixture composition of the bulk electrolyte [21]. Although the coarse-grained model lacks specific chemical detail, we have demonstrated previously that it is able to capture the transition from the "bell" shape to the "camel" shape in the dependence of the differential capacitance on the surface potential [22], describe layer-by-layer distributions of cations and anions near a charged surface [17], and predict the anomalous increase of capacitance for ionic liquids in ultra-narrow pores [23].

The electrolyte used in this model mimics an asymmetric ionic liquid mixture containing tetrafluoroborate (BF_4^-), bis(trifluoromethylsulfonyl)imide ($TFSI^-$), and 1-ethyl-3-methylimidazolium ($EMIm^+$). The diameter of cations ($EMIm^+$) was chosen to be $\sigma_+ = 0.5$ nm, and those for anions (BF_4^- and $TFSI^-$) were 0.30 nm and 0.50 nm, respectively. These values of ion diameters are close to those of the actual ions, and were selected to approximately account for excluded volume effects. Similar methods have been successfully used in our previous studies of RTIL in porous electrode materials [21–23].

The pair potential (u_{ij}) between charged species includes a hard-sphere part to represent excluded volume effects and the Coulombic part for electrostatic interactions:

$$u_{ij}(r) = \begin{cases} \infty & r < \frac{\sigma_i+\sigma_j}{2} \\ \frac{Z_iZ_je^2}{4\pi\varepsilon_0 r} & r \geq \frac{\sigma_i+\sigma_j}{2} \end{cases} \tag{1}$$

where r represents the center-to-center distance, e is the unit charge, ε_0 is the permittivity of the free space, σ_i and Z_i are the diameter and valence of ionic species i, respectively. The primitive model is valid only when the van der Waals forces and polarizability play a minor role in inter-ionic interactions. The unity dielectric constant is used in Eq. (1) because all components are considered explicitly in our model. It should be noted that the dielectric constant might be slightly larger than unity due to ion polarizability ignored in our model. However, we expect that such effects will not change the qualitative behavior of our theoretical results.

Each ion species within the pore is subject to an external potential due to the confinement and the surface charge:

$$\beta V_i(z) = \begin{cases} -2\pi l_B Z_i HQ/e, & \frac{\sigma_i}{2} \leq z \leq H - \frac{\sigma_i}{2} \\ \infty, & \text{otherwise} \end{cases} \tag{2}$$

where z is the perpendicular distance from a surface of the slit pore, $\beta = 1/(k_BT)$, k_B is the Boltzmann constant, T is temperature, $l_B = \beta e^2/(4\pi\epsilon_0)$ denotes the Bjerrum length, Q represents the surface charge density, and H is the surface-to-surface separation (*viz.*, the width of the pore). The Bjerrum length is taken as 55.69 nm, corresponding to electrostatic interactions in a vacuum at room temperature. As the dielectric constant of amorphous carbons is not much different from that of an ionic liquid, the polarizability of the electrode has but a small effect on the distribution of ions within the pore.

To study the effect of ion composition, the total number density of the bulk ionic liquid was fixed at 4.64 nm^{-3}, or 3.84 M. The value is typical for common ionic liquids. Three ionic systems were considered in this work: neat (symmetric) ionic liquid ($x = 0.0$), symmetric and asymmetric ionic liquids of equal composition ($x = 0.5$), and a neat asymmetric ionic liquid ($x = 1.0$), where x stands for the molar fraction of BF_4^- in the anion mixture. The three ionic liquids have the same concentration of cations.

Using the coarse-grained model for ionic liquids in slit pores, we calculate the density distributions of all ionic species from the classical density functional theory (cDFT) [17]. At a given

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temperature (T) and bulk density (ρ_i^0) for each species (i), the ionic density profile is

$$\rho_i(z) = \rho_i^0 \exp\left[-\beta V_i(z) - \beta Z_i e\Phi(z) - \beta\Delta\mu_i^{ex}(z)\right] \tag{3}$$

where $\Delta\mu_i^{ex}(z)$ is the local excess chemical potential. Different from the PB equation, cDFT accounts for the thermodynamic non-ideality due to electrostatic correlations and the excluded volume effects. The local electrical potential, $\Phi(z)$, is related to the local charge density by the Poisson equation

$$\frac{\partial^2\Phi(z)}{\partial z^2} = -\frac{e}{\varepsilon_0}\sum_i Z_i\rho_i(z) \tag{4}$$

The density profile and the Poisson equation can be solved self-consistently given a surface potential and appropriate boundary conditions. The numerical details for cDFT calculations as well as the analytical expression for the excess chemical potential have been reported in our previous publications [17].

From the ionic density profiles, we can calculate the surface charge density,

$$Q = -\frac{1}{2}\sum_i Z_i e\int_0^H \rho_i(z)dz \tag{5}$$

where a factor of 1/2 accounts for two surfaces of a slit pore. The surface charge is given as the negative value of the total charge of all ions within the pore divided between the two pore walls. The condition of overall electroneutrality for the entire slit pore follows Gauss' Law. As indicated above, our cDFT calculations neglect the specific properties of electrode materials such as surface structure and defects. Given an electrical potential at the surface, the surface charge is determined exclusively by the ionic distributions.

Also from the density profiles of ionic species inside the pore, we can obtain the excess absorption of ions:

$$\Gamma_i = \frac{1}{H}\int_0^H \left[\rho_i^{pore}(z) - \rho_i^{bulk}\right]dz \tag{6}$$

The excess ion absorption as defined above is equivalent to the difference between the average density of a species (i) within the pore and that of the same species in the bulk.

3. Results and discussion

The main purpose of this work is to offer insight into important parameters determining the electric double layer (EDL) capacitance given by ionic liquids confined within nanopores. As one might expect, the distribution of ion species within the pore is dependent on the pore width, the surface electrical potential, as well as the ionic composition in the bulk. = The knowledge can be useful for a judicious selection of porous electrodes and electrolytes and for understanding their compatibility to optimize the performance of EDL capacitors.

First we analyze the capacitance versus the pore width for the three ionic liquids mentioned above (Fig. 1). For the symmetric neat ionic liquid, $EMIm - TFSI (x = 0)$, the capacitance is strongly dependent on the pore size. As reported in our early work [23], the oscillation of capacitance with respect to the pore size can be attributed to the overlap of EDLs. Upon introducing a smaller counterion, BF_4^-, at equal mole fraction ($x = 0.5$), we observe not only that it makes small pores more accessible but that it also leads to a significant increase of the capacitance except for a very narrow range of pores with the pore size comparable to the diameter of $TFSI^-$ (viz., 0.5nm $< H <$ 0.6nm). The slight decrease of (or little change in) the capacitance in this pore regime is due to their equal accessibility to the narrow pore. Because BF_4^- and $TFSI^-$ ions have the same one-body electrostatic energy due to the surface charge and because formation of multilayers of ions is prohibited in the narrow pore, the presence of BF_4^- allows for accommodation of slightly more coions, $EMIm^+$, explaining the minor reduction of the capacitance. For large pores ($H >$ 1.0nm), the influence of the pore size on the capacitance is much reduced in comparison to that for the symmetric system. The capacitance is largest when the pore size is the same as the BF_4 diameter because, in this case, the coions are totally excluded. When the pore size increases from $H =$ 0.3 nm to 1.0 nm, the capacitance oscillates due to the strong layering of cations and anions inside the micropore pore.

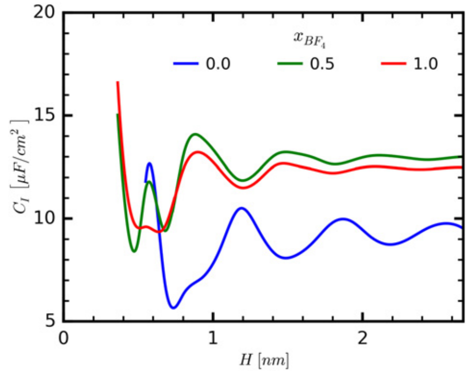

Fig. 1. Integral capacitance versus the pore size for a neat symmetric ($x = 0.0$) and a neat asymmetric ($x = 1.0$) ionic liquid and for their equal molar mixture ($x = 0.5$). In all cases, the surface potential is fixed at 1 V.

Also shown in Fig. 1 is the variation of capacitance with respect to the pore width for the asymmetric neat ionic liquid, $EMIm\text{-}BF_4$ ($x = 1$). For most cases, the capacitance is larger than that for the symmetric ionic liquid because it contains counterions of smaller size. For the reasons discussed above, the symmetric ionic liquid has a higher capacitance in a narrow range of the pore size because of equal accessibility of both counterions. Except in the range of very small pores ($H <$ 0.5 nm), the mixed ionic liquid has a capacitance higher than that of either symmetric or asymmetric neat ionic liquid, suggesting that the EDL capacitance can be optimized by tuning the electrolyte composition. Although $TFSI^-$ is inaccessible to an extremely narrow pore ($H <$ 0.5 nm), its presence in the bulk effectively reduces the BF_4^- concentration thus a (slightly) smaller capacitance.

Fig. 2 shows the ionic density profiles inside a large slit pore ($H =$ 2.55 nm). In all cases, the layer-by-layer distributions of ionic species are evident and have been discussed in our earlier work [17]. The layering of ionic species near a charged surface is also in good agreement with X-ray refectory measurements [24]. Different from conventional models of EDL, we see strong oscillation of the local ion densities regardless of the size symmetry of cations and anions. At the same surface potential (here 1 V), the contact density of BF_4^- is larger than that of $TFSI^-$ because the smaller the counterion, the closer it is distributed near the charged surface. When the charged pore is in contact with an equal molar mixture of BF_4^- and $TFSI^-$, it exhibits a strong selection of the small counterions. While the adsorption of the large counterions ($TFSI^-$) is significantly reduced, its density profile remains oscillatory inside the pore due to strong electrostatic interactions and correlation effects.

From Fig. 3 we observe a strong adsorption of small counterions (BF_4^-) into the pore even at very low concentrations. As shown in Fig. 2 for ionic distributions, the absorption of small counterions is primarily due to their accumulation in the Stern layer. The surface excess shows a maximum $x = 0.2$, arising from more efficient

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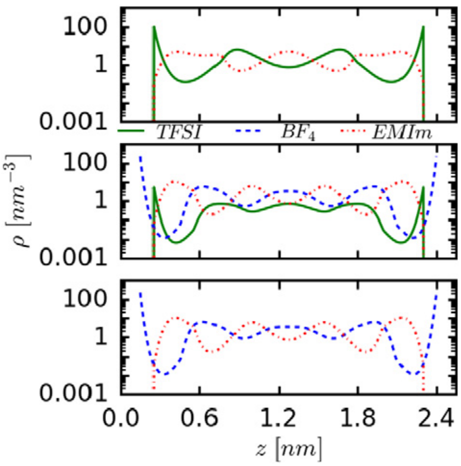

Fig. 2. The ionic density profiles inside a slit pore ($H = 2.55$ nm). The top panel is for the symmetric neat ionic liquid ($x = 0.0$), the bottom panel is for the asymmetric ($x = 1.0$) neat ionic liquid, and the bottom panel is for their equal molar mixture ($x = 0.5$). In all cases, the surface potential is fixed at 1 V.

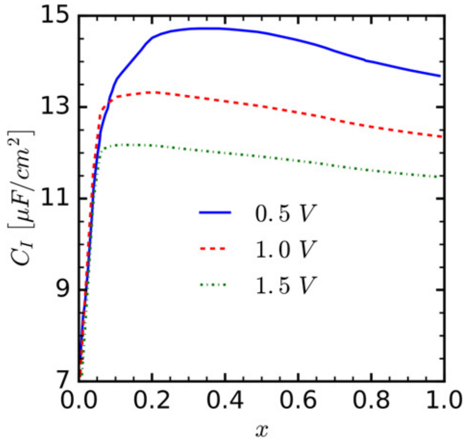

Fig. 4. Capacitance versus the mole fraction of the small ions (BF_4^-) in different mixed ionic liquids. Here the pore width is $H = 0.8$ nm.

packing as the small anions intercalate into the layer-by-layer structure formed between the larger cations and anions. This mixed packing of small and large counterions allows the cations to locate closer with anions, increasing their overall ion concentration inside the pore. With still increasing *x*, we see more adsorption of the larger counterions in the pore, as shown in the surface excess for $TFSI^-$. The surface excess for cations first rises with the BF_4^- concentration due to stronger ion pairing and slightly falls as the surface excess for $TFSI^-$ increases.

As discussed above, we expect that the EDL capacitance can be optimized by tuning the ionic composition. To illustrate the composition effect, we present in Fig. 4 the dependence of the capacitance on the mole fraction of BF_4^- in a narrow slit pore, $H = 0.8$ nm, at three representative surface potentials, 0.5 V, 1.0 V, 1.5 V. At low concentrations of BF_4^- ($x < 0.05$), the EDL structure is dominated by one type of counterions ($TFSI^-$). In this case, the capacitance is relatively insensitive to the surface potential because the EDL structure becomes saturated at a low voltage ($<$ 0.5 V) [22]. The voltage effect becomes more significant at high BF_4^- concentrations when the EDL structure is determined by close packing of two counterions with significant difference in size. The integral capacitance rises rapidly in the presence of small counterions. Similar to the surface excess discussed above, the capacitance reaches a maximum at an intermediate concentration and falls slightly as the concentration is further increased. When the surface potential is fixed, the overall charge neutrality of the slit pore explains the coincidence of the surface excess and the integral capacitance. The electrolyte composition corresponding to the maximum capacitance varies with the surface potential because of the competing effects of the surface charge and ion pairing inside the pore. Relative to that of a symmetric neat ionic liquid, the composition effect is most significant at low surface potential, which may be affiliated with the decline of capacitance at high voltage.

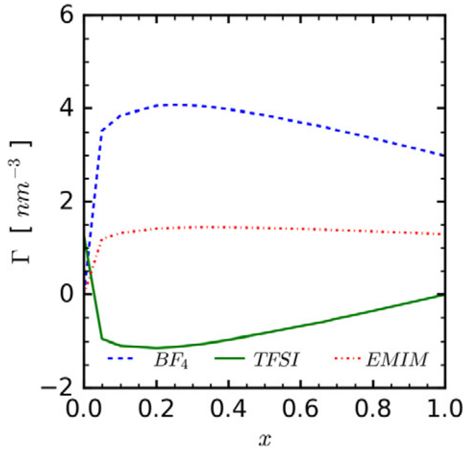

Fig. 3. Surface excess (Γ) for different ionic species versus the mole fraction of the small ions (BF_4^-). Here the pore width is $H = 1.18$ nm and the surface potential is 1 V.

A charged surface in contact with a room temperature ionic liquid results in an EDL structure that is distinctively different from that described in conventional electrokinetic models. As shown in Fig. 5, the local mean electrical potential (MEP) inside a slit pore exhibits a sinusoidal shape, corroborating the layer-by-layer ion distributions discussed above. Each layer signifies a complete charge inversion, indicating that EDL charging is not simply a surface phenomena but accompanied by a disorder-order transition from ions in a near random state to a lamellar phase. Clearly, the periodicity of the ordered structure is closely correlated with the diameters of both cations and anions, and the propagation of the local electrostatic potential is significantly dampened when the cations and anions are different in size. Because a charge pore is strongly small ion selective, the local electrical potential for the asymmetric neat ionic liquid is not much different from that for the equal molar mixtures of BF_4^- and $TFSI^-$ in the bulk.

4. Conclusions

Using a charged hard-sphere model for room temperature ionic liquids (RTIL) complemented with a slit-pore model for porous electrodes, we have studied the electric double layer (EDL) capacitance of symmetric and asymmetric neat ionic liquids and their mixtures and inspected how electrical charge is stored within the micropores of carbon electrodes. We found that the EDL capacitance is closely correlated with ionic distributions, in particular with the surface excess of counterions. The EDL capacitance can be maximized by tuning the composition of the ionic mixture in the bulk. In general, adoption of small counterions will increase the EDL capacitance due to the formation of a thinner layer of counterions in direct contact with the surface. Nevertheless, a mixed ionic liquid provides efficient packing of ionic species near the charged surface by intercalating thus a higher capacitance than that of neat ionic liquids.

The EDL structure affects the capacitance from two sources. First, the contact layer of counterions near the charged electrode, which

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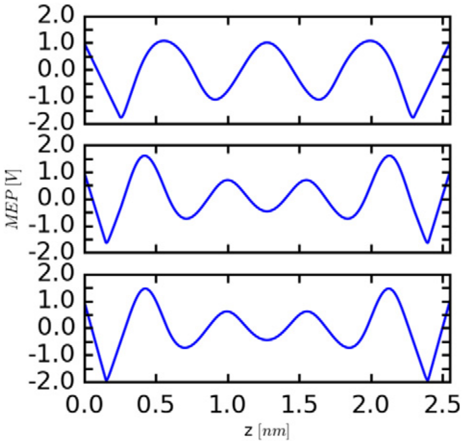

Fig. 5. The local mean electrical potential (MEP) inside a slit pore. Here the pore width is $H = 2.55$ nm, and the surface potential is 1 V. As in Fig. 2, the results correspond to three ionic liquids (from top to bottom $x = 0, 0.5, 1$).

is often called the Stern layer in the continuum model, is reduced in width, thus increasing the capacitance. The second contribution is from the increased layer-by-layer ordering induced by small counterions. Better ordering means better, more optimized, packing of charge carriers and therefore a stronger, more stable capacitance in variation with respect to the pore width. As the pore width increases, the ordering of ion distribution inside the pore remains relatively unchanged. This was observed in Fig. 1, where, as we introduce the mixture of small and large anions, the oscillation of capacitance with respect to the pore size is muted by pore width equal to 1.4 nm compared with the symmetric ionic liquid which being more coarse has capacitance oscillations for pore width past 2.5 nm.

Furthermore, it was observed, that for mixtures near the limit of large pore size, the capacitance is comparable to what is seen for ultra-narrow pores with a symmetric ionic liquid. This increased ordering of the ionic liquid structure implies amorphous carbon electrodes can still yield high capacitance with the right mixture of ionic liquid without the need for expensive, or exclusive, designer electrodes with engineered pore size distributions. It has also been shown in experiment, that these ionic liquid mixtures have better cycling performance: longer lifetime with very little degradation of performance [13]. As it is shown, the general structure of the ionic liquid mixture does not vary wildly as the potential is increased. The compact, ordered, layering of cations and anions delivers stability to the device while charging and discharging.

From our previous work [8] at zero applied electrode potential, as well as work currently under review for non-zero potentials, we found that an increase of the small ion concentration in the mixture enhances small ion selectivity. From this, it was gathered a pore exposed to the bulk would only increase in concentration of the small counterions, thus increasing capacitance with the pore width. Under an applied potential, the selectivity is much more acute. This concept has been shown experimentally by Dyatkin et.al. [25] who found, for a single material, capacitance increased with the grain size of the electrode.

Classical density functional theory (DFT) will no doubt be a useful tool in design and optimization of the next generation of EDL capacitors containing room temperature ionic liquids. In our DFT calculations, the electrical potential at the carbon surface is fixed such that the ionic distribution is uncorrelated with the electronic structure of the carbon atoms. Besides, we assume that the electrical conductivity is the same as that of an ideal metal. The polarization effect is significant only when ionic distributions are considered at conditions of a constant surface charge density. From a practical perspective, of prime interest to the field of energy storage is the ability to obtain enhanced capacitance for microporous electrodes with a simple ionic liquid mixture which would otherwise be obtained using designer electrodes if a neat ionic liquid is used. Future theoretical and experimental investigations of the EDL capacitors to enhance the performance of EDL for capacitive energy storage should be focused on expanding the operating potential window of ionic liquids as well as the pore size distribution of electrode materials. Subsequent work with this system, currently in progress, uses this model to accurately predict capacitance of real carbon electrodes (e.g., carbide derived carbons) using experimental data for pore size distributions. This can be done by assuming, to a first approximation, that each pore is independent and that a material is simply a linear combination of these pores as given by weights of probability from the pore size distribution. The coarse-grained model offers great insight into how capacitance is determined from ionic distributions within the electric double layer of confined pores. It is generally applicable to ionic systems in porous materials, including other ionic-liquid mixtures, current or those yet to be discovered.

Atomistic molecular dynamics (MD) simulations have been broadly employed to investigate the capacitance of EDLCs. In comparison with the simple model used in this work, one key advantage of MD simulation is richer representation of molecule configurations and captures the chemical details of the electrode/electrolyte interface. However, MD simulation is not necessarily more quantitative in describing physiochemical properties of ionic liquids than the classical DFT calculations based on the primitive model. For example, non-polarizable force fields typically overestimate ion-ion interactions, resulting in smaller diffusion coefficients and higher viscosities compared with experimental results. By incorporating the fundamental measure theory (FMT) and the mean-spherical approximation (MSA), classical DFT provides a systematic way to improve the conventional theory of EDL and enables semi-quantitative description of electrostatic phenomena over a broad range of the pore size, from that comparable to the ionic size to macroscopic scales. Existing publications of classical DFT to EDLCs are mostly limited to the primitive model that describes each ionic species as a charged sphere. Because the simple model is by no mean accurate by an atomistic perspective, further development is needed to extend the classical DFT calculations using atomistic models. The atomistic details are important for understanding surface reactions and for establishing concrete connection between the molecular models and chemical species.

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