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Classical Density Functional Theory Insights for Supercapacitors

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Abstract

The most urgent issue for supercapacitor is to improve their energy density so that they can better compete with batteries. To design materials and interfaces for supercapacitor with higher energy density requires a deeper understanding of the factors and contributions affecting the total capacitance. In our recent works, the classical density functional theory (CDFT) was developed and applied to study the electrode/electrolyte interface behaviors, to understand capacitive energy storage. For porous electrode materials, we studied the pore size effect, curvature effect, and the surface modification of porous materials on the capacitance. Through CDFT, we have found that the curvature effects on convex and concave EDLs are drastically different and that materials with extensive convex surfaces will lead to maximized capacitance; CDFT also predicts oscillatory variation of capacitance with pore size, but the oscillatory behavior is magnified as the curvature increases; an increase in the ionophobicity of the nanopores leads to a higher capacity for energy storage, and a pore-like impurity can enter the pore, makes the pore ionophobic and storage more energy. We also find the mixture effect, which makes more counterions pack on and more co-ions leave from the electrode surface, leads to an increase of the counterion density within the EDL and thus a larger capacitance.

Keywords: supercapacitors, classical density functional theory, porous electrode, ionic liquid, electrical double layer

1. Introduction

Capacitive energy storage is the key component for sustainable energy systems, e.g. by storing the renewable but intermittent energy and making it accessible upon demand. The most commonly used energy storage devices are batteries and supercapacitors. A battery stores

energy by electrochemical reactions, while a supercapacitor stores energy through physico-chemical adsorption, including formation of electric double layer and surface redox reactions. A battery has high energy density but low power density, while a supercapacitor boasts of high power density due to the fast surface physical and chemical processes. There are two types of supercapacitors: electric double-layer capacitors (EDLC) store electrical energy through formation of electric double layer at electrode/electrolyte interface, while pseudocapacitors store electrical energy by reversible redox reaction (including ion intercalation). Supercapacitors are becoming increasingly important for electrical energy storage due to their advantages on rapid charge/discharge rate, a virtually unlimited life, a wider range of working temperature, a very high efficiency, etc. However, the main drawback, a low energy density, has been limiting supercapacitors in the applications requiring many rapid charge/discharge cycles for short-term power needs. It is the most urgent issue to improve the energy density of supercapacitors [1]. The EDLC performance is strongly correlated with electrosorption of ionic species at the inner surfaces of microporous electrode [2].

To design new materials and interfaces for EDLC with higher energy density, one requires a deeper understanding of the factors and contributions affecting the total capacitance of an EDLC. The most widely used electrode material for EDLC is porous carbon. Many types of carbon-based materials have been used for EDLC [3, 4], such as activated graphene oxide [5], activated carbon [6], carbide-derived carbon [7–9], carbon nanotube [10–12], onion-like carbon [13, 14] and graphene [15, 16]. The gravimetric capacitance of those carbon materials is quite sensitive to their structure, especially the porosity and specific surface area. The pore size can greatly affect the ion partitioning and packing inside the pore, which causes a large change on the capacitance. The relationship between the pore size and the capacitance of ionic liquids has been investigated by Simon and Gogotsi [1, 17, 18]. This important work reveals a clear physical insight into the pore size-dependent capacitance and suggests that the capacitance maximum can be achieved by optimally matching the pore size and ion size. Carbon nanotube has been reported as a novel EDLC electrode material [19, 20]. The reported capacitance of single-wall carbon nanotube is 180 F/g in aqueous electrolyte [11]. The onion-like carbon was also reported as a promising EDLC electrode and exhibit very large power density at discharging rate of up to 200 V/s [13, 21]. Moreover, graphene-based material also has been developed to be attractive EDLC material and its unique electronic structure could have large influence on the charge capacitive behavior [6, 15]. The pseudocapacitors and EDLC show distinctly different electrochemical behavior in cyclic voltammetry. Pseudocapacitance may contribute more capacitance than double-layer capacitance for the same surface area.

In general, the electrode-electrolyte interface is the most key issue of supercapacitors, fundamental understanding on this should be crucial. Experimental tools such as Atomic Force Microscopy (AFM) and X-ray reflectometry were applied to study the structural properties of EDLCs at the electrode surface [22–24]. However, it's difficult for experimental method to directly detect the nanoscale electrode-electrolyte interface. Computational methods, such as molecular dynamics (MD) simulations, were also used to investigate the distribution of ions near electrified interfaces [25–27]. Analytical methods [28–37] are computationally more efficient than MD simulations thereby suitable for a systematic investigation of the key parameters for relatively large systems. CDFT can be used to account for the ionic steric effects and electrostatic

correlations neglected in the Poisson-Nernst-Planck (PNP) or Poisson-Boltzmann (PB) equations, a conventional microscopic theory for EDLs. The non-mean-field effects are significant for room-temperature ionic liquids (RTILs) due to strong electrostatic interactions and high ion densities [38–40].

In this work, we discuss the impurity effect on the charging and capacitive behaviors based on the CDFT. CDFT had been successfully used in studying the EDL structure and the capacitance of ionic liquids and organic electrolytes systems [41–44]. It has been shown that the CDFT predictions are able to capture the essential results from earlier experimental and simulation studies and provides microscopic insights into the electrochemical behavior of ionic liquids as the working electrolytes for supercapacitors [45–47].

This paper is structured as follows. First, we describe our coarse-grained models of RTILs and porous materials and provide a brief introduction to the classical DFT method. Next, we discuss the pore structure of electrode and the electrolyte effect on the EDL structure and the capacitive performance of EDLCs. Finally, we summarize the main results and possible future work.

2. Classical density functional theory

We use a non-primitive model to represent the ionic species, impurities, and solvent molecules in the electrolyte solution [48]. The model system consists of charged hard spheres for ionic species and a hard-sphere dimer for solvent molecules. The pair potential between two arbitrary spheres/segments in the system, i and j , is given by

$$u_{ij}(r) = \begin{cases} \infty, & r < \frac{\sigma_i + \sigma_j}{2} \\ \frac{Z_i Z_j e^2}{4\pi\epsilon_0 \epsilon r}, & r \geq \frac{\sigma_i + \sigma_j}{2} \end{cases} \quad (1)$$

where r is the center-to-center distance, e is the elementary charge, ϵ_0 is the permittivity of free space, $\epsilon = 1$ is the local dielectric constant for the vacuum.

CDFT [44, 49–52] was used to obtain the EDL structure and capacitance for the carbon materials in contact with the electrolyte solution. The details of the CDFT calculations have been published before [42, 45, 47, 48, 53, 54]. Briefly, we obtained the surface charge densities at various electrical potentials. Given the number densities of ions and solvent molecules in the bulk and the system temperature, the pore size, the pore geometry, and the surface electrical potential, we solve for the density profiles of cations, anions and impurities, as well as the solvent segments inside the pore by minimization of the grand potential.

$$\begin{aligned} \beta\Omega[\rho_M(\mathbf{R}), \{\rho_a(\mathbf{r})\}] = & \beta F[\rho_M(\mathbf{R}), \{\rho_a(\mathbf{r})\}] + \int [\beta\Psi_M(\mathbf{R}) - \beta\mu_M] \rho_M(\mathbf{R}) d\mathbf{R} \\ & + \sum_a \int [\beta\Psi_a(\mathbf{r}) - \beta\mu_a] \rho_a(\mathbf{r}) d\mathbf{r} \end{aligned} \quad (2)$$

where $\beta^{-1} = k_B T$, $R \equiv (\mathbf{r}_{\delta+}, \mathbf{r}_{\delta-})$ represents two coordinates specifying the positions of two segments in each solvent molecule, μ_α is the chemical potential of an ionic species, μ_M is the chemical potential of the solvent, $\Psi_a(\mathbf{r})$ stands for the external potential for ions, $\Psi_M(\mathbf{R})$ is the summation of the external potential for a solvent molecule, i.e. $\Psi_M(\mathbf{R}) = \sum_{i=\delta+, \delta-} \varphi_i(\mathbf{r}_i)$, and F is the total intrinsic Helmholtz energy. The number densities of the positive and negative segments of the solvent are calculated from

$$\rho_{\delta+}(\mathbf{r}_{\delta+}) = \int d\mathbf{R} \delta(\mathbf{r} - \mathbf{r}_{\delta+}) \rho_M(\mathbf{R}) \quad (3)$$

$$\rho_{\delta-}(\mathbf{r}_{\delta-}) = \int d\mathbf{R} \delta(\mathbf{r} - \mathbf{r}_{\delta-}) \rho_M(\mathbf{R}) \quad (4)$$

The intrinsic Helmholtz energy F includes an ideal-gas contribution and an excess contribution due to intermolecular interactions F^{ex} .

$$\beta F = \int [\ln \rho_M(\mathbf{R}) - 1] \rho_M(\mathbf{R}) d\mathbf{R} + \beta \int V_b(\mathbf{R}) \rho_M(\mathbf{R}) d\mathbf{R} + \sum_a \int [\ln \rho_a(\mathbf{r}) - 1] \rho_a(\mathbf{r}) d\mathbf{r} + \beta F^{ex} \quad (5)$$

Where V_b stands for the bonding potential of the solvent molecule. The detailed expression for each contribution and the numerical details can be retrieved from Ref. [45, 48]. In evaluation of the Coulomb energy, we calculate the mean electrostatic potential (MEP) from the density distributions of the ions by using the Poisson equation

$$\nabla^2 \psi(\mathbf{r}) = -\frac{4\pi e}{\epsilon} \rho_c(\mathbf{r}) \quad (6)$$

Eq. (9) can be integrated with the boundary conditions that defined by the operation potential. The surface charge density Q is obtained from the condition of overall charge neutrality. The differential capacitance C_d of the EDLs could be calculated by a derivative of the surface charge density Q with respect to the surface potential.

Time-dependent density functional theory (TDDFT) is an extension of the CDFT to describe dynamic or time-dependent processes based on the assumption of local thermodynamic equilibrium [54–62]. For ion diffusion in an electrolyte solution near electrodes, TDDFT asserts that the time evolution for the local density profiles of ionic species, $\rho_i(\mathbf{r}, t)$, follows the generalized diffusion equation

$$\frac{\partial \rho_i(\mathbf{r}, t)}{\partial t} = \nabla \cdot \{ D_i \rho_i(\mathbf{r}, t) \nabla [\beta \mu_i(\mathbf{r}, t) + \beta V_i(\mathbf{r})] \} \quad (7)$$

Where D_i stands for the self-diffusivity of ion i , $\beta = 1/(k_B T)$, k_B is the Boltzmann constant, T stands for the absolute temperature, $\mu_i(\mathbf{r}, t)$ is the local chemical potential and could be obtained by a derivative of the intrinsic Helmholtz energy F with respect to the density, and $V_i(\mathbf{r})$ denotes the external potential arising from the electrodes. With TDDFT, we could capture the ion dynamics inside the nanopores.

3. Electrode effect on the capacitive performance

3.1. Electrode geometry optimization

Whereas practical porous electrodes involve micropores with complicated morphology and pore size distributions [63, 64], theoretical modeling of EDLCs is mostly based on simplistic models to represent the pore geometry and the electrolyte-electrode interactions [65]. Specifically, three types of electrode structures are commonly used in theoretical investigations [66–68]: (i) planar surfaces (e.g., a flat surface or slit pores); (ii) cylindrical pores with their concave inner surfaces or cylindrical particles with their convex outer surfaces (e.g., carbon nanotubes); and (iii) spherical surfaces (e.g., onion-like carbons). The slit and cylindrical pore models are conventionally used for porous materials characterization [69]. Despite the fact that a great variety of porous carbons have been utilized in EDLCs, the effects of the pore size and geometry on the EDL structure remain poorly understood [70]. At the heart of the issue is the question: What is the microscopic structure of porous electrodes and how does the capacitance of EDLCs depend on the electrode pore geometry and electrolyte composition? Recent simulations and experiments indicate that both the pore size and geometry play an important role in determining the capacitance of EDLCs [25, 68, 71–73]. An important question is whether this behavior is generally valid, given the slit-pore model or solid particles used in theoretical calculations and the diversity of pore structure for realistic carbon electrodes. Specially, how does the pore structure and curvature affect the capacitance dependence on the pore size? To address these questions, we propose in this work a generic model to represent both pore size and curvature of carbon electrodes using the CDFT. CDFT is an ideal computational tool for examining the pore size and geometry effects, as it is computationally efficient and applicable over a wide range of pore sizes ranging from that below the ionic dimensionality to mesoscopic scales.

Figure 1 shows the integral capacitance as a function of pore width D at different inner core radii. In all cases, the surface electrical potential is fixed at $\psi_0 = 1.5$ V. As observed in an previous work for an ionic liquid in slit pores [41], the EDL capacitance exhibits the oscillatory dependence on the pore size. The distance between neighboring peaks (or valleys) is approximately equal twice the ion diameter. The oscillatory variation of the integral capacitance is closely affiliated with the layering structures of ion distributions inside the nanopores. The layer-by-layer distributions of cations and anions are evident near the charged surfaces [41].

As inner radius R decreases, the capacitance increases significantly. This is also expected from the increased EDL capacitance at both the inner and outer surfaces. The oscillatory dependence of the capacitance on the pore size is consistent with those corresponding to individual EDLs. Our results show that the EDLs have a smaller influence on the overall ion distributions inside the pore as the pore size falls, leading to a diminishing difference in average counterion and coion densities. On the other hand, a smaller inner core radius results in more counterions in the pore thus a larger capacitance.

This work illustrates the curvature and pore size effect of realistic porous electrodes and suggests the significant role of convex surfaces for the synthesis of new porous electrodes to

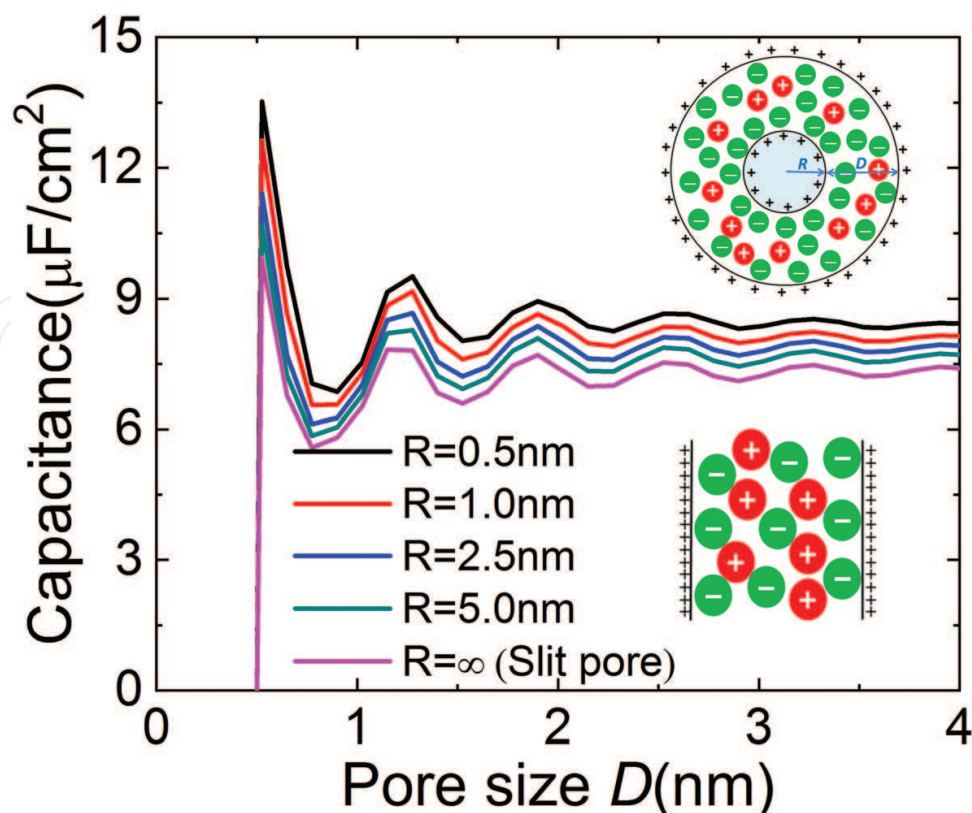


Figure 1. The overall integral capacitance versus the pore size for spherical shells of different inner radii. Reproduced from Ref. [41] with permission. Copyright 2016 American Chemical Society.

optimize EDLC performance. In particular, the spherical shell model provides a simple yet generic description of both pore size and curvature, opening up a new dimension to characterize nanoporous materials and quantify their performance for diverse applications including EDL capacitors.

3.2. Electrode surface modification

Energy storage via electrosorption depends not only on the electrical potential and the geometric compatibilities of the electrode pores and ionic species but also on specific interactions between mobile ions and the surface properties of electrode materials. While existing theoretical reports are mostly devoted to analyzing electrostatic interactions and confinement effects, relatively little is known on how specific ion-surface associations may influence the EDLC performance. Very recently, Kondrat and Kornyshev found that the capacitive performance is sensitive to the ion affinity with nanopores: their theoretical results show electrodes with ionophobic nanopores may have slightly lower, the same, or even higher energy storage capacity than the ionophilic ones, all depending on the electrode voltage [74–76]. The capacitance voltage curve is shifted to substantially higher voltages as the pore ionophobicity increases. Within an ionophobic pore, the stored energy could be higher than for ionophilic

pores when the electrodes are operated at sufficiently high voltages [74]. It has also been shown that the charging kinetics of an empty ionophobic nanopore is much faster than that of an ionophilic nanopore at similar conditions [75, 77]. Experimentally, the ionophobicity may be controlled by modifying the surface properties of nanoporous materials or by introducing special functional groups to the ionic species.

We discussed the effects of non-electrostatic ion-surface interactions based on the classical density functional theory (CDFT) [54, 78]. δE stands for the resolution energy, i.e. the energy cost to transfer an ion from the bulk to the slit pore. δE is used as an indication of the ionophobicity of nanopores: negative δE promotes adsorption of ions within the pore (viz., an

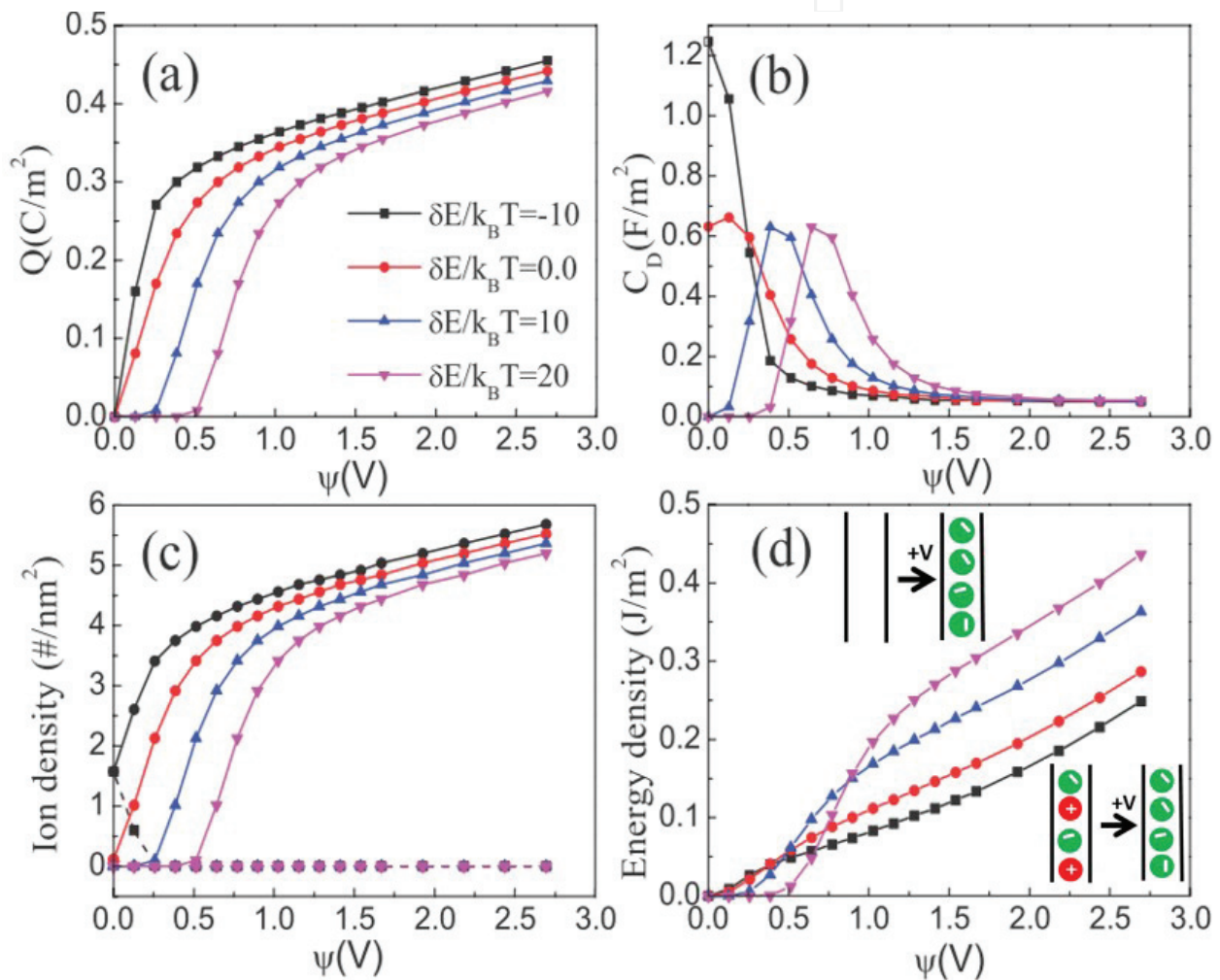


Figure 2. Theoretical predictions for the surface charge density (a), the differential capacitance (b), the average cation and anion densities inside the nanopore (c), and the energy stored per surface area (d) for an EDLC containing an organic electrolyte. Because of the system symmetry, the results are the same if the surface potential, ψ , is extended to the negative values. Here the concentration of the organic electrolyte is fixed at 1.0 M, the pore size is $D = 0.6$ nm. The ionophobicity of the nanopores is reflected in the ion resolution energy, δE , which represents the ion transfer energy from the bulk reservoir into the nanopore. In (c), the solid lines are average densities inside the pore for the counterions, and the dashed lines are for the coions. Because of their small values, the curves for the average coion densities collapse into the same zero line. Reproduced from Ref. [54] with permission. Copyright 2016 IOP Publishing.

ionophobic pore), while a positive δE means an ionophobic pore. For simplicity, we assume that δE is independent of the ion valence, the pore size, and the surface electrical potential.

In an ionophobic pore with a large ion resolution energy, both counterions and coions are nearly excluded from the nanopore at low surface electrical potential. In this case, counterions are inserted into the empty pore only when the electrical potential is sufficiently large to overcome the surface repulsion. The differential capacitance increases with the surface potential until it reaches a maximum. A further increase of the surface electrical potential leads to saturation of counter ions inside the pore and thus a decline of the capacitance. In both ionophobic cases shown in **Figure 2(b)**, the capacitance versus potential curve has a two-hump camel shape, and the capacitance value at the minimum is close to zero, in stark contrast to the maximum for an ionophilic pore. **Figure 2(b)** indicates that the peak capacitance shifts to a higher potential as the ionophobicity increases. In other words, we may find a bell shape to the two-hump camel shape transition in the capacitance-electrical potential curves by changing the surface ionophobicity. **Figure 2(d)** shows that, at low electrical potential, the energy density ($E(\psi) = \int_0^\psi C_D(x)x dx$) for an ionophilic pore is higher than that of an ionophobic pore, while the trend is opposite at high potentials. Because the peak of the camel shape differential capacitance shifts to higher potential, a more ionophobic pore offers higher storage energy. On the other hand, increasing ionophobicity prohibits counter ions from entering the pore, thus reduces the energy density at low potential. From the discussions above, we find that an ionophobic nanopore prevents counterion insertion and shifts the saturation point to a higher voltage. The energy stored in the EDLC can be promoted by the ionophobicity only when the electrode voltage is larger than a critical value [54].

4. Electrolyte effect on the capacitive performance

4.1. Solvent effect

Commercial EDLC devices mainly use the organic electrolyte in which a salt such as tetraethylammonium tetrafluoroborate is dissolved in an organic solvent such as acetonitrile (ACN) or propylene carbonate. It is very intriguing to unravel the role of the solvent during EDL charging inside small pores. By introducing a molecular dipole into our electrolyte, CDFT also allows us to examine the capacitance of an organic EDLC for different pore sizes and solvent polarity.

Our previous work illustrates the dependence of the capacitance on the pore size for the electrolyte/electrode models [45, 53]. For an ionic liquid EDLC, the capacitance oscillates with the pore size with a dampened magnitude around an average value of about $7.5 \mu\text{F}/\text{cm}^2$. The maximum capacitance occurs when the pore size is about the same as the ion diameter, which coincides with the anomalous increase of capacitance observed by Largeot et al. [17] Whereas a similar peak appears for the organic electrolyte, there is no significant oscillation as the pore size increases, and the capacitance at the first peak is less dramatic in comparison with the asymptotic value. The theoretical results thus offer a reconciliatory picture of the capacitance

dependence on the pore size for ionic liquid and organic electrolyte EDLCs. In the previous section, we discussed the capacitance dependence on pore size for an organic electrolyte with a moderate-polarity solvent (with a dipole moment of 3.4 Debye). But how would the solvent polarity affect the pore-size dependence of capacitance in a wide range of organic electrolyte EDLCs?

Our CDFT calculations provide valuable insights into the effects of the dipole moment of the solvent in an organic electrolyte [43]. We found an optimal dipole moment that yields a maximum in the large-pore capacitance. These theoretical results further illustrate the rich behavior of the organic electrolytes inside porous electrodes. Moreover, it provides new considerations that can be taken into account when designing new experiments to select organic electrolytes for EDLCs.

4.2. Impurity or additive

RTIL has been used as electrolytes widely to increase the capacitive performance of electrochemical capacitors [82]. However, there are always some small amounts of impurity (e.g., water, alkali salts, and organic solvents) in RTIL, which may affect the electrochemical behavior of electrochemical devices. To understand the impurity effect, the RTIL with different impurities in the porous carbon electrodes is studied via CDFT. With a different type of binding energy with the surface or ionic species, the impurity shows a different influence on the EDL microstructures and contributes differently to the integral capacitance. It is noted that the impurity can be considered as either a contaminant or an additive to the ionic liquid, all depending on the interaction between the impurity and the electrode or ions [79, 80]. Meanwhile, the capacitance strongly oscillates with the variation of the pore size similar to that for the pure ionic liquid electrolyte. With strong binding of impurity to the ionic species, the RTIL/impurity mixture may lead to an enhanced capacitance oscillation. In certain pores, a significant increase in the capacitance can be obtained. The theoretical results provide insights for further investigation of supercapacitors aiming at rational design of porous electrode materials and charge carriers.

We also demonstrate that, under conditions favoring impurity accumulation in the nanopores of the electrode, impurity can change the EDL charging mechanism even at low bulk densities, shown in **Figure 3**. As the adhesion energy of impurity molecules with the electrode surface increases, the capacitance-potential curves can change from the bell shape to the two-hump camel shape, with the peak shifting toward a higher charging potential. Qualitatively the impurity effect on the charging behavior is similar to the solvent effect as studied by Rochester and coworkers [81]. Whereas the amount of impurity and solvent in the bulk is considerably different, the concentration effect can be compensated by the change in the transfer energy to yield a same charging behavior. As an ionophobic pore could be beneficiary for improving charge storage and charging dynamics, introduction of impurity molecules inside the pore makes it essentially more ionophobic thus enhances the energy storage. Our theoretical results suggest that special attention should be given to the nature of impurity and operation voltages when the surface properties nanoporous electrodes are modified to enhance the performance of EDLCs. It is worth noting that association between ions and impurity molecules, which

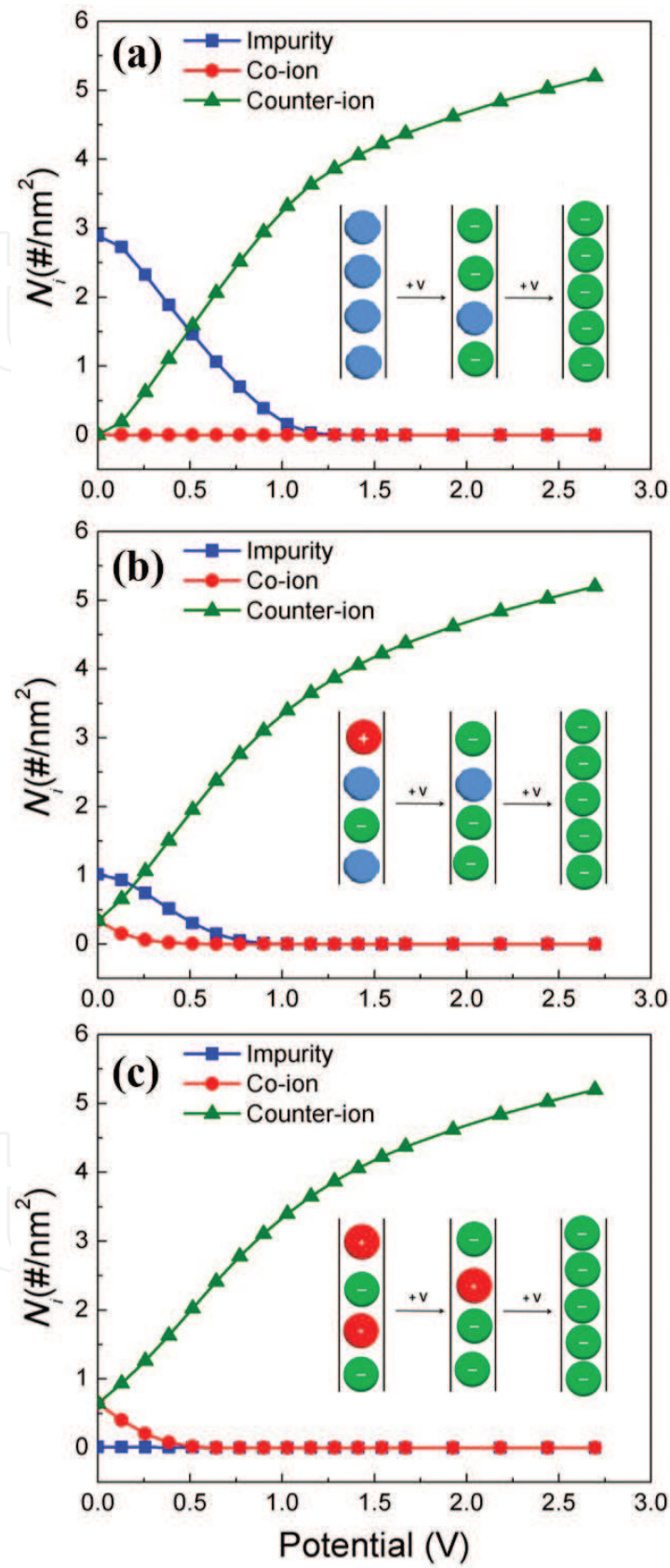


Figure 3. The number densities of ions and impurity molecules inside a nanopore of width $H = 0.6$ nm with different surface adhesion energies for the impurity molecules: (a) $\omega = -10k_B T$; (b) $\omega = -5k_B T$; (c) $\omega = 0.0k_B T$.

might happen for impurity molecules with large polarity, may give rise to different pictures of the charging behavior. For impurity molecules without affinity to ionic species, their accumulation inside the pore will increase the charge storage and capacitance, regardless of the polarity. The effects of ion binding with impurity molecules on the charging mechanism and energy density will be investigated in the future work. From a practical prospective, the impurity can be considered as either a contaminant (undesirable) or an additive (desirable) to room-temperature ionic liquids. Based on this study and our previous work [80], we suggest new experimental strategies to introduce additives into ionic liquids with specific surface binding affinity to the porous electrodes (e.g., by surface modifications). While significant efforts have been devoted to formulation of ionic liquid mixtures and selection of solvents [47], much less is known on how supercapacitor performance may be influenced by potent additives at a low concentration.

4.3. Ionic liquid mixture

Formulating RTIL mixed electrolytes was recently proposed as an effective and convenient strategy to increase the capacitive performance of electrochemical capacitors [82]. However, little is known about how the properties of EDLCs containing RTIL mixtures would be affected by the electrolyte composition [83–86]. Here, we investigate the EDL structure and the capacitance of two RTILs, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMI-TFSI) and 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF₄), and their mixtures with onion-like carbon electrodes using experiment and the CDFT. The principal difference between these ionic liquids is the smaller diameter of the BF₄[−] anion relative to the TFSI[−] anion and the EMI⁺ cation in **Figure 4**. We find that the capacitance versus the composition of the RTIL mixture exhibits a volcano-shaped trend; in other words, there exists a composition of the ionic mixture that yields a maximal integral capacitance [47]. The mixture effect, which makes more counterions pack on and more co-ions leave from the electrode surface, leads to an

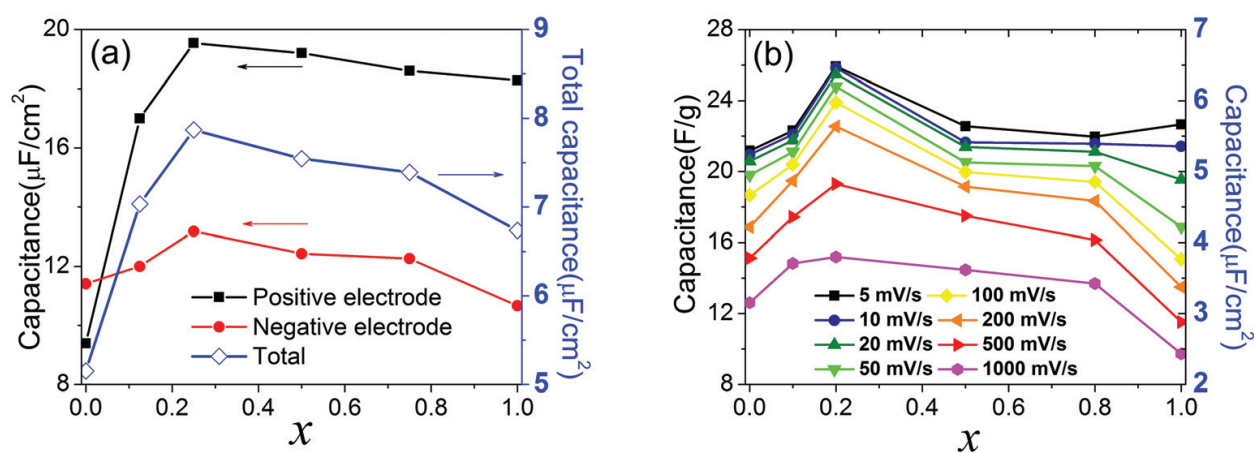


Figure 4. (a) Calculated integral capacitance for the positive, negative and total electrodes when the operating potential window (OPW) is fixed as 3.0 V. (b) Experimental results for a symmetric supercapacitor operating at 3.0 V. The electrode capacitance is shown as a function of the concentration of the RTIL mixture for different scan rates. Reproduced from Ref. [82] with permission. Copyright 2016 American Chemical Society.

increase of the counterion density within the EDL and thus a larger capacitance. These theoretical predictions are in good agreement with our experimental observations and offer guidance for designing RTIL mixtures for EDL supercapacitors with optimal performance [47].

4.4. Ion-ion interaction on the transport in nanopore

The charging kinetics of EDLs has a pivotal role in the performance of a wide variety of nanostructured devices. Despite the prevalent use of ionic liquids as the electrolyte, relatively little is known on the charging behavior from a microscopic perspective [33, 75, 77, 87–90]. Here, we study the charging kinetics of ionic liquid EDLs using the TDDFT that captures the molecular excluded volume effects and electrostatic correlations [39]. We found that the thermodynamic non-ideality plays a pivotal role in electrodiffusion and such effect cannot be captured by the lattice-gas model for the excluded volume effects. In particular, TDDFT predicts “wave-like” variation of the ionic density profiles that has not been identified in previous investigations [34]. This unusual charging behavior can be explained in terms of the oscillatory structure of ionic liquids near the electrodes. For ion transport in narrow pores with a high gating voltage, in **Figure 5**, the conductivity shows an oscillatory dependence on the pore size owing to the strong overlap of electric double layers [91].

Besides, our new TDDFT is able to account for the molecular excluded volume effects, electrostatic correlations, and the dispersion interactions. Our results show that the dispersion interaction between ions makes the surface charge be a non-monotonic function of time shown in **Figure 6**. However, the dispersion interaction between the electrode and ionic-liquid does not

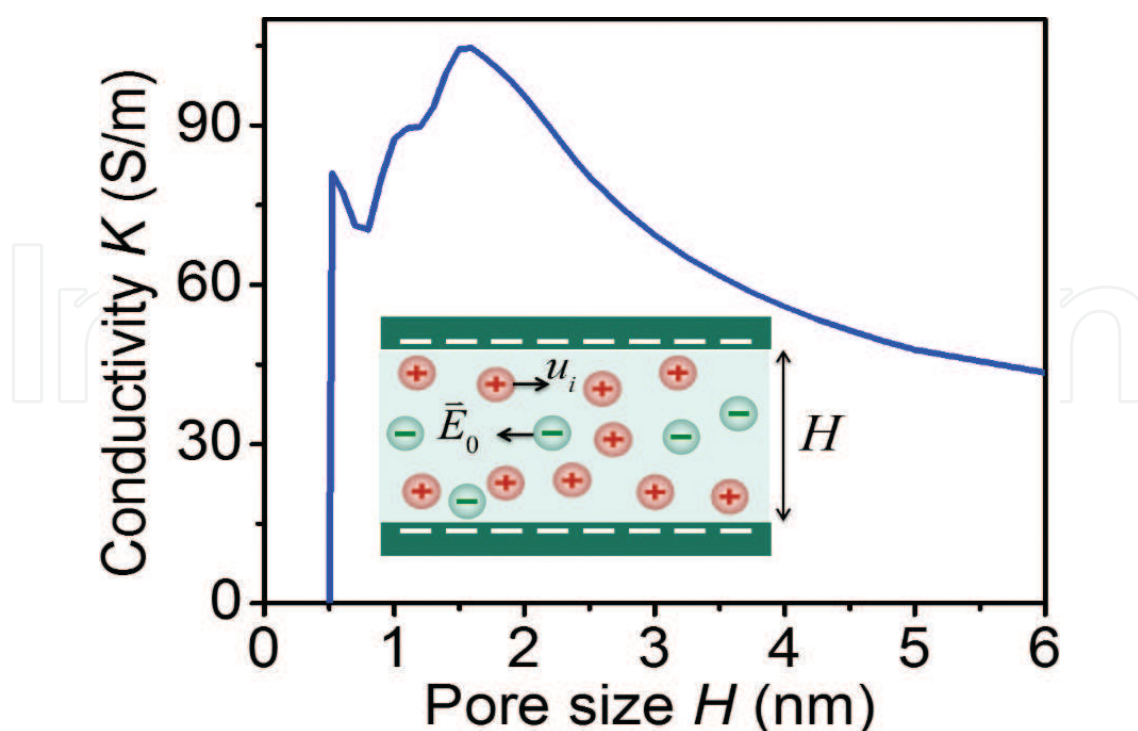


Figure 5. The conductivity shows an oscillatory dependence on the pore size [91]. Copyright 2017 Royal Society of Chemistry.

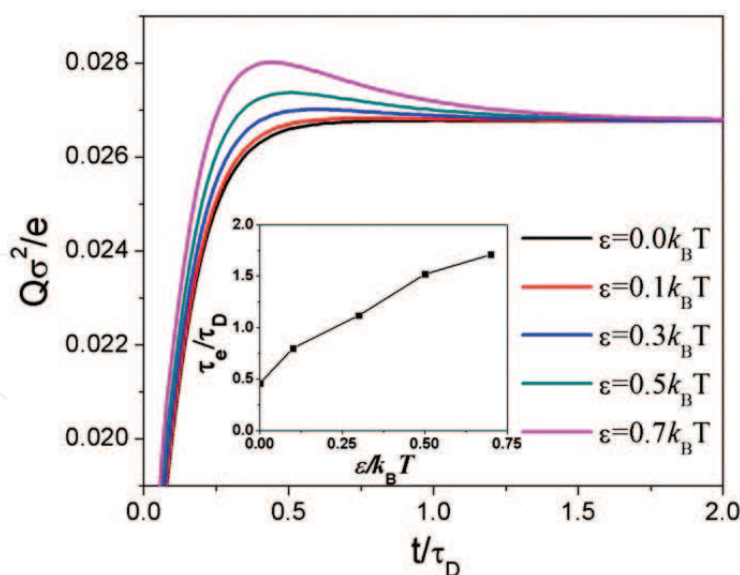


Figure 6. Evolution of surface charge density for different strengths of dispersion forces. (Inset) The time toward equilibrium as a function of the dispersion energy parameter ϵ . Reproduced from Ref. [92] with permission. Copyright 2016 American Physical Society.

change the monotonic evolution of surface charge density [92]. Both the ion-ion and the electrode-ion dispersion interactions increase the duration of the EDL charging process [92]. We also identified significant influence of the gating potential on the scaling behavior of the conductance with changes of pore size and the salt concentration. For ion transport in narrow pores with a high gating voltage, the conductivity shows an oscillatory dependence on the pore size owing to the strong overlap of electric double layers [91]. We hope these theoretical work enables a way to tune the charging behavior of electric double layer capacitors (EDLCs) by an appropriate choice of electrodes and ionic liquids.

5. Conclusion and perspective

In our recent works, the CDFT was developed and applied by us to study the electrode/electrolyte interface behaviors, to understand capacitive energy storage. As a statistical mechanical tool and an alternative to molecular dynamics or Monte Carlo simulation methods, CDFT offers a powerful and efficient mathematical framework to describe the equilibrium and dynamic properties of many-body systems in terms of the one-body density profiles. It allows one to precisely tune the parameters such as ion diameter, solvent dipole, and pore size over a large range and to focus on the most important physical problems to be addressed, using a computationally efficient coarse-grained approach to model real fluids. Through CDFT, we have found novel behaviors of electrolytes inside nanopores, such as capacitance oscillation, optimal dipole moment, and wave-like charging. Further development of CDFT for complex pore structures and charging kinetics would allow us to directly predict power density and energy density for supercapacitors.

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Conflict of interest

The authors declare no competing financial interest.

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