

# We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

185,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index  
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?  
Contact [book.department@intechopen.com](mailto:book.department@intechopen.com)

Numbers displayed above are based on latest data collected.  
For more information visit [www.intechopen.com](http://www.intechopen.com)



---

# Classical Density Functional Theory Insights for Supercapacitors

---

Cheng Lian and Honglai Liu

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/intechopen.76339>

---

## 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 EDLs 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,  $\epsilon_0$  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,  $\mu_\alpha$  is the chemical potential of an ionic species,  $\mu_M$  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

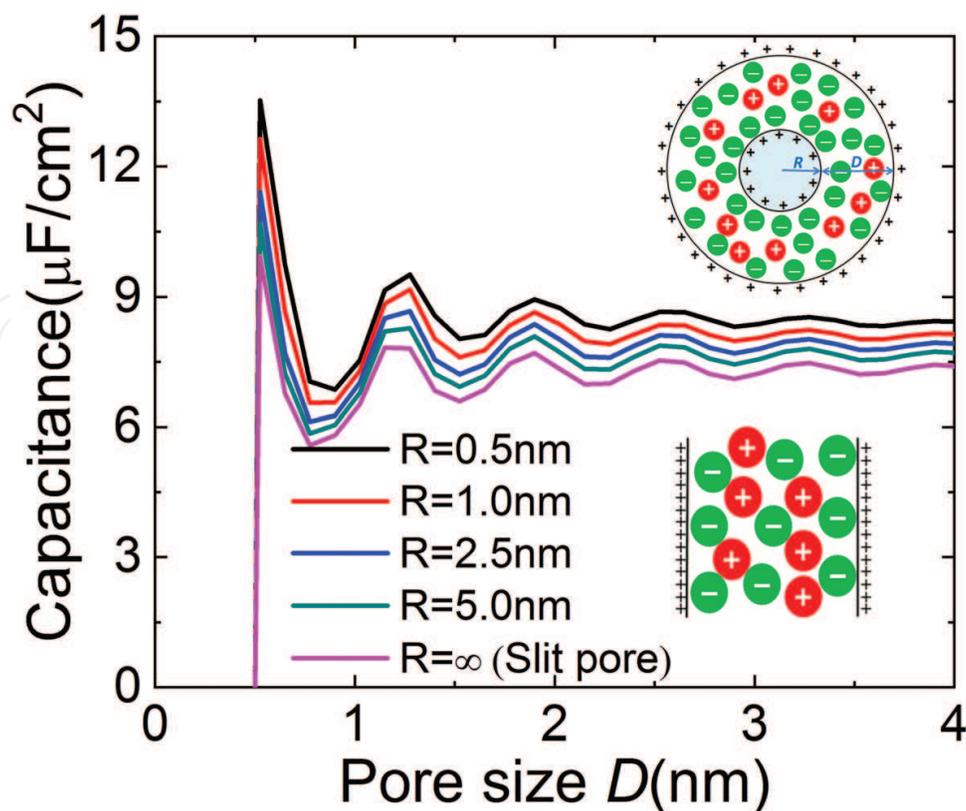
#### 3.1. Electrode geometry optimization

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.

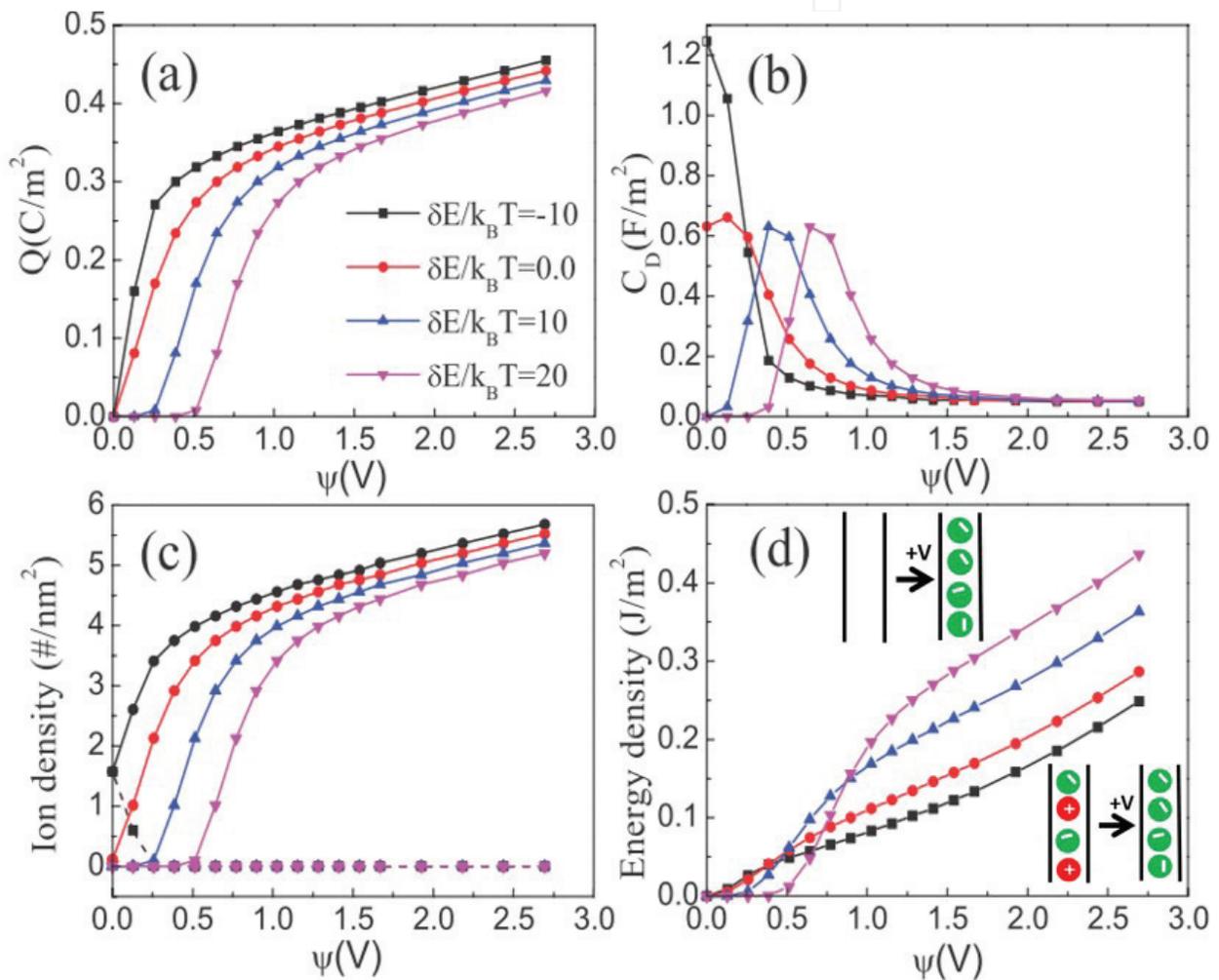
optimize EDLC performance. In particular, the spherical shell model provides a simple yet generic description of both pore size and curvature, opening up a new dimension to characterize nanoporous materials and quantify their performance for diverse applications including EDL capacitors.

### 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].  $\delta E$  stands for the resolution energy, i.e. the energy cost to transfer an ion from the bulk to the slit pore.  $\delta E$  is used as an indication of the ionophobicity of nanopores: negative  $\delta E$  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,  $\psi$ , 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,  $\delta E$ , 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  $\delta E$  means an ionophobic pore. For simplicity, we assume that  $\delta E$  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

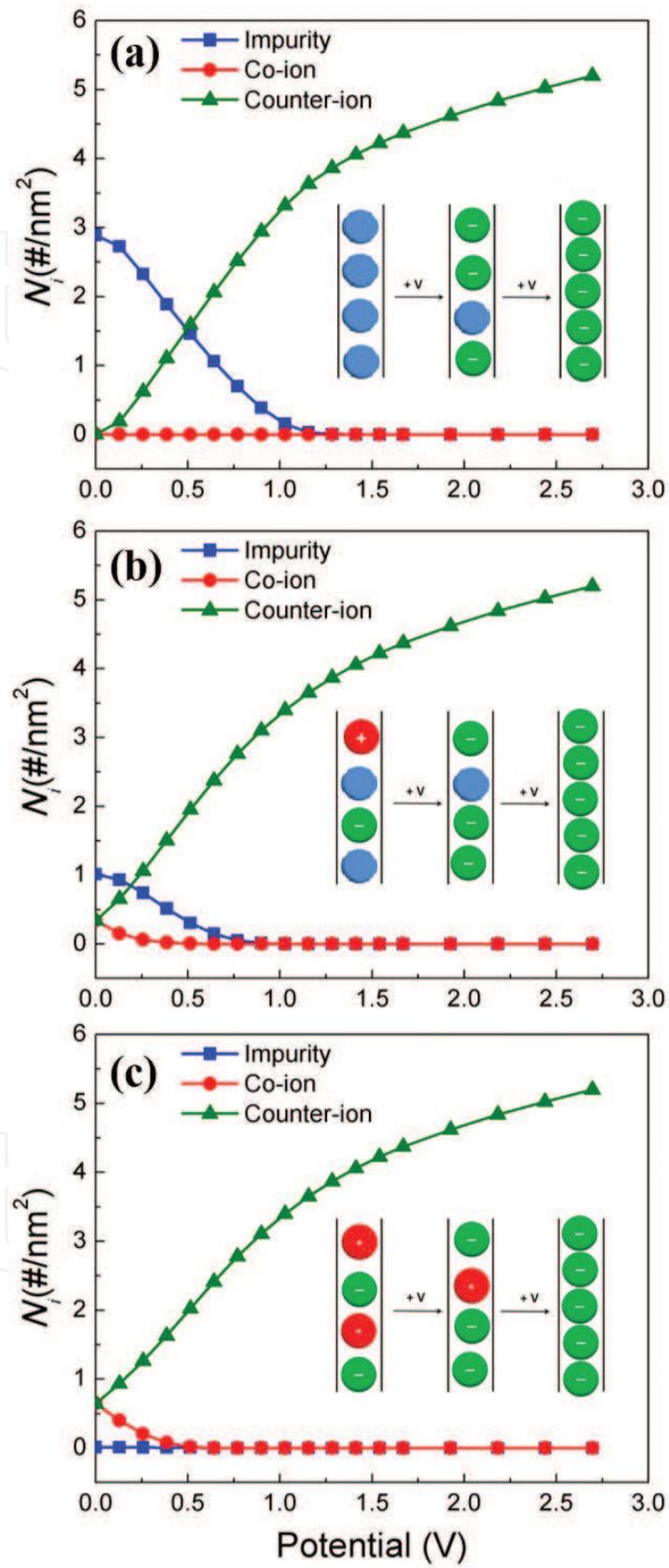
dependence on the pore size for ionic liquid and organic electrolyte EDLCs. In the previous section, we discussed the capacitance dependence on pore size for an organic electrolyte with a moderate-polarity solvent (with a dipole moment of 3.4 Debye). But how would the solvent polarity affect the pore-size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

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

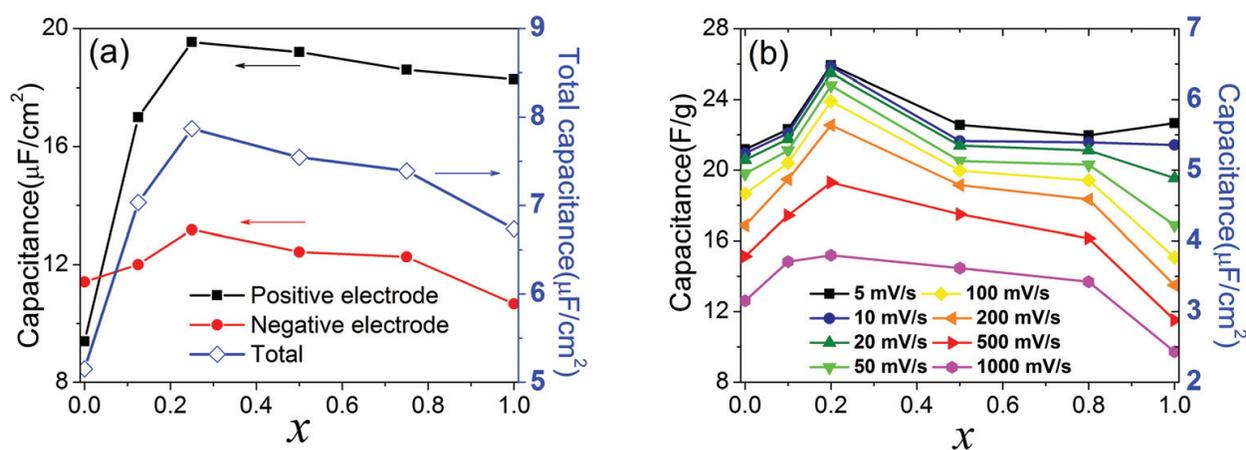


**Figure 3.** The number densities of ions and impurity molecules inside a nanopore of width  $H = 0.6$  nm with different surface adhesion energies for the impurity molecules: (a)  $\omega = -10k_B T$ ; (b)  $\omega = -5k_B T$ ; (c)  $\omega = 0.0k_B T$ .

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-BF<sub>4</sub>), 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 BF<sub>4</sub><sup>-</sup> anion relative to the TFSI<sup>-</sup> anion and the EMI<sup>+</sup> 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



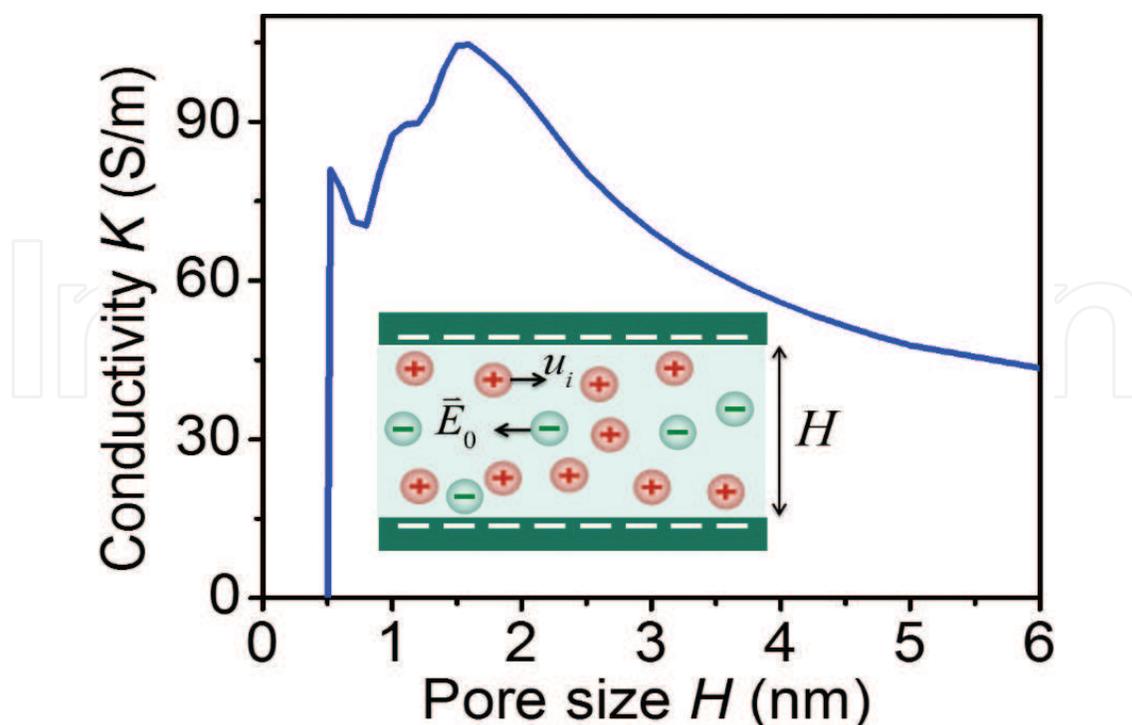
**Figure 4.** (a) Calculated integral capacitance for the positive, negative and total electrodes when the operating potential window (OPW) is fixed as 3.0 V. (b) Experimental results for a symmetric supercapacitor operating at 3.0 V. The electrode capacitance is shown as a function of the concentration 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].

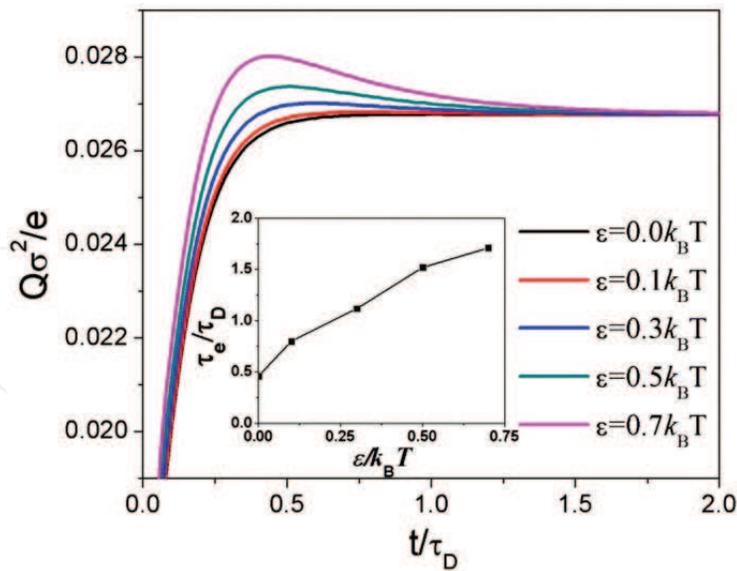
#### 4.4. Ion-ion interaction on the transport in nanopore

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  $\epsilon$ . 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.

## Acknowledgements

This research was supported by the National Natural Science Foundation of China (No. 91334203), the 111 Project of China (No. B08021) and National Postdoctoral Program for Innovative Talents (BX201700076). Cheng Lian also thanks the financial support by China Postdoctoral Science Foundation (2017 M620137) and Shanghai Sailing Program (18YF1405400). We also thank Prof. Jianzhong Wu in UC Riverside for helpful guidance and discussion.

## Conflict of interest

The authors declare no competing financial interest.

## Author details

Cheng Lian and Honglai Liu\*

\*Address all correspondence to: hlliu@ecust.edu.cn

State Key Laboratory of Chemical Engineering and School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai, China

## References

- [1] Chmiola J, Yushin G, Gogotsi Y, Portet C, Simon P, Taberna PL. Anomalous increase in carbon capacitance at pore sizes less than 1 nanometer. *Science*. 2006;**313**:1760-1763
- [2] Fedorov MV, Kornyshev AA. Ionic liquids at electrified interfaces. *Chemical Reviews*. 2014;**114**:2978-3036
- [3] Zhang LL, Zhao XS. Carbon-based materials as supercapacitor electrodes. *Chemical Society Reviews*. 2009;**38**:2520-2531
- [4] Zhai YP, Dou YQ, Zhao DY, Fulvio PF, Mayes RT, Dai S. Carbon materials for chemical capacitive energy storage. *Advanced Materials*. 2011;**23**:4828-4850
- [5] Wang DW, Li F, Liu M, Lu GQ, Cheng HM. 3D aperiodic hierarchical porous graphitic carbon material for high-rate electrochemical capacitive energy storage. *Angewandte Chemie, International Edition*. 2008;**47**:373-376
- [6] Zhu YW, Murali S, Stoller MD, Ganesh KJ, Cai WW, Ferreira PJ, Pirkle A, Wallace RM, Cychosz KA, Thommes M, Su D, Stach EA, Ruoff RS. Carbon-based supercapacitors produced by activation of graphene. *Science*. 2011;**332**:1537-1541

- [7] Chmiola J, Largeot C, Taberna PL, Simon P, Gogotsi Y. Monolithic carbide-derived carbon films for micro-supercapacitors. *Science*. 2010;**328**:480-483
- [8] Gogotsi Y, Nikitin A, Ye HH, Zhou W, Fischer JE, Yi B, Foley HC, Barsoum MW. Nanoporous carbide-derived carbon with tunable pore size. *Nature Materials*. 2003;**2**:591-594
- [9] Dash R, Chmiola J, Yushin G, Gogotsi Y, Laudisio G, Singer J, Fischer J, Kucheyev S. Titanium carbide derived nanoporous carbon for energy-related applications. *Carbon*. 2006;**44**:2489-2497
- [10] Hu S, Rajamani R, Yu X. Flexible solid-state paper based carbon nanotube supercapacitor. *Applied Physics Letters*. 2012;**100**:104103
- [11] An KH, Kim WS, Park YS, Moon JM, Bae DJ, Lim SC, Lee YS, Lee YH. Electrochemical properties of high-power supercapacitors using single-walled carbon nanotube electrodes. *Advanced Functional Materials*. 2001;**11**:387-392
- [12] Yu CJ, Masarapu C, Rong JP, Wei BQ, Jiang HQ. Stretchable supercapacitors based on buckled single-walled carbon nanotube macrofilms. *Advanced Materials*. 2009;**21**:4793-4797
- [13] Pech D, Brunet M, Durou H, Huang PH, Mochalin V, Gogotsi Y, Taberna PL, Simon P. Ultrahigh-power micrometre-sized supercapacitors based on onion-like carbon. *Nature Nanotechnology*. 2010;**5**:651-654
- [14] Portet C, Yushin G, Gogotsi Y. Electrochemical performance of carbon onions, nanodiamonds, carbon black and multiwalled nanotubes in electrical double layer capacitors. *Carbon*. 2007;**45**:2511-2518
- [15] Stoller MD, Park SJ, Zhu YW, An JH, Ruoff RS. Graphene-based ultracapacitors. *Nano Letters*. 2008;**8**:3498-3502
- [16] Liu CG, Yu ZN, Neff D, Zhamu A, Jang BZ. Graphene-based supercapacitor with an ultrahigh energy density. *Nano Letters*. 2010;**10**:4863-4868
- [17] Largeot C, Portet C, Chmiola J, Taberna PL, Gogotsi Y, Simon P. Relation between the ion size and pore size for an electric double-layer capacitor. *Journal of the American Chemical Society*. 2008;**130**:2730-2731
- [18] Chmiola J, Largeot C, Taberna PL, Simon P, Gogotsi Y. Desolvation of ions in subnanometer pores and its effect on capacitance and double-layer theory. *Angewandte Chemie, International Edition*. 2008;**47**:3392-3395
- [19] Collins PG, Bradley K, Ishigami M, Zettl A. Extreme oxygen sensitivity of electronic properties of carbon nanotubes. *Science*. 2000;**287**:1801-1804
- [20] Baughman RH, Zakhidov AA, de Heer WA. Carbon nanotubes—The route toward applications. *Science*. 2002;**297**:787-792
- [21] Gao Y, Zhou YS, Qian M, He XN, Redepenning J, Goodman P, Li HM, Jiang L, Lu YF. Chemical activation of carbon nano-onions for high-rate supercapacitor electrodes. *Carbon*. 2013;**51**:52-58

- [22] Lauw Y, Horne MD, Rodopoulos T, Webster NAS, Minofar B, Nelson A. X-ray reflectometry studies on the effect of water on the surface structure of [C4mpyr][NTf2] ionic liquid. *Physical Chemistry Chemical Physics*. 2009;**11**:11507-11514
- [23] Hayes R, Borisenko N, Corr B, Webber GB, Endres F, Atkin R. Effect of dissolved LiCl on the ionic liquid–Au(111) electrical double layer structure. *Chemical Communications*. 2012;**48**:10246-10248
- [24] Tamura K, Nishihata Y. Study on the behavior of halide ions on the Au(111) electrode surface in ionic liquids using surface X-ray scattering. *Journal of Physical Chemistry C*. 2016;**120**:15691-15697
- [25] Feng G, Huang J, Sumpter BG, Meunier V, Qiao R. Structure and dynamics of electrical double layers in organic electrolytes. *Physical Chemistry Chemical Physics*. 2010;**12**:5468-5479
- [26] Feng G, Jiang X, Qiao R, Kornyshev AA. Water in ionic liquids at electrified interfaces: The anatomy of electrosorption. *ACS Nano*. 2014;**8**:11685-11694
- [27] Porter AR, Liem SY, Popelier PLA. Room temperature ionic liquids containing low water concentrations—a molecular dynamics study. *Physical Chemistry Chemical Physics*. 2008;**10**:4240-4248
- [28] Lee AA, Kondrat S, Vella D, Goriely A. Dynamics of ion transport in ionic liquids. *Physical Review Letters*. 2015;**115**:106101
- [29] Gavish N, Yochelis A. Theory of phase separation and polarization for pure ionic liquids. *The Journal of Physical Chemistry Letters*. 2016;**7**:1121-1126
- [30] Kilic MS, Bazant MZ, Ajdari A. Steric effects in the dynamics of electrolytes at large applied voltages. I. Double-layer charging. *Physical Review E*. 2007;**75**:021502
- [31] Bazant MZ, Kilic MS, Storey BD, Ajdari A. Towards an understanding of induced-charge electrokinetics at large applied voltages in concentrated solutions. *Advances in Colloid and Interface Science*. 2009;**152**:48-88
- [32] Yochelis A. Transition from non-monotonic to monotonic electrical diffuse layers: Impact of confinement on ionic liquids. *Physical Chemistry Chemical Physics*. 2014;**16**:2836-2841
- [33] Yochelis A. Spatial structure of electrical diffuse layers in highly concentrated electrolytes: A modified Poisson–Nernst–Planck approach. *The Journal of Physical Chemistry C*. 2014;**118**:5716-5724
- [34] Jiang J, Cao D, Jiang D-e, Wu J. Kinetic charging inversion in ionic liquid electric double layers. *The Journal of Physical Chemistry Letters*. 2014;**5**:2195-2200
- [35] Qiao Y, Tu B, Lu B. Ionic size effects to molecular solvation energy and to ion current across a channel resulted from the nonuniform size-modified PNP equations. *The Journal of Chemical Physics*. 2014;**140**:174102

- [36] Lu B, Zhou Y, Holst M, McCammon J. Recent progress in numerical methods for the Poisson-Boltzmann equation in biophysical applications. *Communications in Computational Physics*. 2008;**3**:973-1009
- [37] Xu Z, Ma M, Liu P. Self-energy-modified Poisson-Nernst-Planck equations: WKB approximation and finite-difference approaches. *Physical Review E*. 2014;**90**:013307
- [38] Alijó PH, Tavares FW, Biscaia EC Jr, Secchi AR. Effects of electrostatic correlations on ion dynamics in alternating current voltages. *Electrochimica Acta*. 2015;**152**:84-92
- [39] Jiang J, Cao D, Jiang D-E, Wu J. Time-dependent density functional theory for ion diffusion in electrochemical systems. *Journal of Physics: Condensed Matter*. 2014;**26**:284102
- [40] Alijó PH, Tavares FW, Biscaia E, Secchi AR. Steric effects on ion dynamics near charged electrodes. *Fluid Phase Equilibria*. 2014;**362**:177-186
- [41] Jiang D-e, Jin Z, Wu J. Oscillation of capacitance inside nanopores. *Nano Letters*. 2011;**11**:5373-5377
- [42] Lian C, Jiang D-E, Liu H, Wu J. A generic model for electric double layers in porous electrodes. *The Journal of Physical Chemistry C*. 2016;**120**:8704-8710
- [43] Jiang D-E, Wu J. Unusual effects of solvent polarity on capacitance for organic electrolytes in a nanoporous electrode. *Nanoscale*. 2014;**6**:5545-5550
- [44] Wu J, Li Z. Density-functional theory for complex fluids. *Annual Review of Physical Chemistry*. 2007;**58**:85-112
- [45] Jiang D-E, Jin Z, Henderson D, Wu J. Solvent effect on the pore-size dependence of an organic electrolyte supercapacitor. *The Journal of Physical Chemistry Letters*. 2012;**3**:1727-1731
- [46] Wu J, Jiang T, Jiang D-E, Jin Z, Henderson D. A classical density functional theory for interfacial layering of ionic liquids. *Soft Matter*. 2011;**7**:11222-11231
- [47] Lian C, Liu K, Van Aken KL, Gogotsi Y, Wesolowski DJ, Liu HL, Jiang DE, Wu JZ. Enhancing the capacitive performance of electric double-layer capacitors with ionic liquid mixtures. *ACS Energy Letters*. 2016;**1**:21-26
- [48] Henderson D, Jiang D-E, Jin Z, Wu J. Application of density functional theory to study the double layer of an electrolyte with an explicit dimer model for the solvent. *The Journal of Physical Chemistry B*. 2012;**116**:11356-11361
- [49] Evans R. The nature of the liquid-vapour interface and other topics in the statistical mechanics of non-uniform, classical fluids. *Advances in Physics*. 1979;**28**:143-200
- [50] Robert E, Martin O, Roland R, Gerhard K. New developments in classical density functional theory. *Journal of Physics: Condensed Matter*. 2016;**28**:240401
- [51] Amin H, Le W, Walter GC. A density functional theory for colloids with two multiple bonding associating sites. *Journal of Physics: Condensed Matter*. 2016;**28**:244009

- [52] Lian C, Chen X, Zhao S, Lv W, Han X, Wang H, Liu H. Substrate effect on the phase behavior of polymer brushes with lattice density functional theory. *Macromolecular Theory and Simulations*. 2014;**23**:575-582
- [53] Jiang D-e, Wu J. Microscopic insights into the electrochemical behavior of nonaqueous electrolytes in electric double-layer capacitors. *The Journal of Physical Chemistry Letters*. 2013;**4**:1260-1267
- [54] Lian C, Liu H, Henderson D, Wu J. Can ionophobic nanopores enhance the energy storage capacity of electric-double-layer capacitors containing nonaqueous electrolytes? *Journal of Physics: Condensed Matter*. 2016;**28**:414005
- [55] Archer AJ. Dynamical density functional theory for molecular and colloidal fluids: A microscopic approach to fluid mechanics. *Journal of Chemical Physics*. 2009;**130**: Artn 014509
- [56] Zhao SL, Wu JZ. Self-consistent equations governing the dynamics of nonequilibrium colloidal systems. *Journal of Chemical Physics*. 2011;**134**: Artn 054514
- [57] Lian C, Wang L, Chen X, Han X, Zhao S, Liu H, Hu Y. Modeling swelling behavior of thermoresponsive polymer brush with lattice density functional theory. *Langmuir*. 2014;**30**:4040-4048
- [58] Stopper D, Roth R, Hansen-Goos H. Communication: Dynamical density functional theory for dense suspensions of colloidal hard spheres. *The Journal of Chemical Physics*. 2015;**143**:181105
- [59] Archer AJ. Dynamical density functional theory for molecular and colloidal fluids: A microscopic approach to fluid mechanics. *The Journal of Chemical Physics*. 2009;**130**: 014509
- [60] Marconi UMB, Melchionna S. Kinetic theory of correlated fluids: From dynamic density functional to lattice Boltzmann methods. *The Journal of Chemical Physics*. 2009;**131**: 014105
- [61] Archer AJ, Rauscher M. Dynamical density functional theory for interacting Brownian particles: Stochastic or deterministic? *Journal of Physics A: Mathematical and General*. 2004;**37**:9325
- [62] Dzubiella J, Likos CN. Mean-field dynamical density functional theory. *Journal of Physics: Condensed Matter*. 2003;**15**:L147
- [63] Merlet C, Rotenberg B, Madden PA, Taberna PL, Simon P, Gogotsi Y, Salanne M. On the molecular origin of supercapacitance in nanoporous carbon electrodes. *Nature Materials*. 2012;**11**:306-310
- [64] Palmer JC, Llobet A, Yeon SH, Fischer JE, Shi Y, Gogotsi Y, Gubbins KE. Modeling the structural evolution of carbide-derived carbons using quenched molecular dynamics. *Carbon*. 2010;**48**:1116-1123

- [65] Meunier V, Huang JS, Feng G, Qiao R, Sumpter BG. Modern theories of carbon-based electrochemical capacitors: A short review. In: Proceedings of the ASME International Mechanical Engineering Congress and Exposition 2010; Vol. 11. 2012. pp. 21-30
- [66] Huang J, Sumpter BG, Meunier V. Theoretical model for nanoporous carbon supercapacitors. *Angewandte Chemie International Edition*. 2008;**47**:520-524
- [67] Huang J, Sumpter BG, Meunier V, Yushin G, Portet C, Gogotsi Y. Curvature effects in carbon nanomaterials: Exohedral versus endohedral supercapacitors. *Journal of Materials Research*. 2010;**25**:1525-1531
- [68] Feng G, Li S, Presser V, Cummings PT. Molecular insights into carbon supercapacitors based on room-temperature ionic liquids. *The Journal of Physical Chemistry Letters*. 2013;**4**:3367-3376
- [69] Landers J, Gor GY, Neimark AV. Density functional theory methods for characterization of porous materials. *Colloids and Surfaces A—Physicochemical and Engineering Aspects*. 2013;**437**:3-32
- [70] Vatamanu J, Bedrov D. Capacitive energy storage: Current and future challenges. *The Journal of Physical Chemistry Letters*. 2015;**6**(18):3594-3609
- [71] Li S, Han KS, Feng G, Hagaman EW, Vlcek L, Cummings PT. Dynamic and structural properties of room-temperature ionic liquids near silica and carbon surfaces. *Langmuir*. 2013;**29**:9744-9749
- [72] Van Aken KL, McDonough JK, Li S, Feng G, Chathoth SM, Mamontov E, Fulvio PF, Cummings PT, Dai S, Gogotsi Y. Effect of cation on diffusion coefficient of ionic liquids at onion-like carbon electrodes. *Journal of Physics: Condensed Matter*. 2014;**26**:284104
- [73] Wang H, Pilon L. Mesoscale modeling of electric double layer capacitors with three-dimensional ordered structures. *Journal of Power Sources*. 2013;**221**:252-260
- [74] Kondrat S, Kornyshev AA. Pressing a spring: What does it take to maximize the energy storage in nanoporous supercapacitors? *Nanoscale Horizons*. 2016;**1**:45-52
- [75] Kondrat S, Kornyshev A. Charging dynamics and optimization of nanoporous supercapacitors. *The Journal of Physical Chemistry C*. 2013;**117**:12399-12406
- [76] Lee AA, Kondrat S, Kornyshev AA. Single-file charge storage in conducting nanopores. *Physical Review Letters*. 2014;**113**:048701
- [77] Kondrat S, Wu P, Qiao R, Kornyshev AA. Accelerating charging dynamics in subnanometre pores. *Nature Materials*. 2014;**13**:387-393
- [78] Cheng L, Xian K, Honglai L, Jianzhong W. On the hydrophilicity of electrodes for capacitive energy extraction. *Journal of Physics: Condensed Matter*. 2016;**28**:464008
- [79] Liu K, Lian C, Henderson D, Wu J. Impurity effects on ionic-liquid-based supercapacitors. *Molecular Physics*. 2017;**115**:454-464

- [80] Liu K, Wu J. Boosting the performance of ionic-liquid-based supercapacitors with polar additives. *The Journal of Physical Chemistry C*. 2016;**120**:24041-24047
- [81] Rochester CC, Kondrat S, Pruessner G, Kornyshev AA. Charging ultrananoporous electrodes with size-asymmetric ions assisted by apolar solvent. *Journal of Physical Chemistry C*. 2016;**120**:16042-16050
- [82] Van Aken KL, Beidaghi M, Gogotsi Y. Formulation of ionic-liquid electrolyte to expand the voltage window of supercapacitors. *Angewandte Chemie International Edition*. 2015;**54**:4806-4809
- [83] Costa R, Pereira CM, Silva AF. Structural ordering transitions in ionic liquids mixtures. *Electrochemistry Communications*. 2015;**57**:10-13
- [84] dos Santos DJ, Cordeiro MND. Effect of replacing [NTf<sub>2</sub>] by [PF<sub>6</sub>] anion on the [BMIm][NTf<sub>2</sub>] ionic liquid confined by gold. *Molecular Simulation*. 2015;**41**:455-462
- [85] Siimenson C, Siinor L, Lust K, Lust E. Electrochemical characterization of iodide ions adsorption kinetics at Bi(111) electrode from three-component ionic liquids mixtures. *ECS Electrochemistry Letters*. 2015;**4**:H62-H65
- [86] Lall-Ramnarine S, Suarez S, Zmich N, Ewko D, Ramati S, Cuffari D, Sahin M, Adam Y, Rosario E, Paterno D. Binary ionic liquid mixtures for supercapacitor applications. *ECS Transactions*. 2014;**64**:57-69
- [87] Kondrat S, Oshanin G, Kornyshev AA. Charging dynamics of supercapacitors with narrow cylindrical nanopores. *Nanotechnology*. 2014;**25**:315401
- [88] Péan C, Merlet C, Rotenberg B, Madden PA, Taberna P-L, Daffos B, Salanne M, Simon P. On the dynamics of charging in nanoporous carbon-based supercapacitors. *ACS Nano*. 2014;**8**:1576-1583
- [89] Pean C, Rotenberg B, Simon P, Salanne M. Understanding the different (dis)charging steps of supercapacitors: Influence of potential and solvation. *Electrochimica Acta*. 2016;**206**:504-512
- [90] He Y, Huang J, Sumpter BG, Kornyshev AA, Qiao R. Dynamic charge storage in ionic liquids-filled nanopores: Insight from a computational cyclic voltammetry study. *The Journal of Physical Chemistry Letters*. 2015;**6**:22-30
- [91] Lian C, Gallegos A, Liu H, Wu J. Non-scaling behavior of electroosmotic flow in voltage-gated nanopores. *Physical Chemistry Chemical Physics*. 2017;**19**:450-457
- [92] Lian C, Zhao S, Liu H, Wu J. Time-dependent density functional theory for the charging kinetics of electric double layer containing room-temperature ionic liquids. *The Journal of Chemical Physics*. 2016;**145**:204707