EQUILIBRIUM AND DYNAMIC CHARGE STORAGE IN NANOPORES WITH ROOM TEMPERATURE IONIC LIQUIDS

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Abstract

Electrochemical capacitors store electrical energy physically in the electrical double layers at the electrode/electrolyte interfaces. In spite of their high power density and extraordinary cyclability, the widespread deployment of electrochemical capacitors is limited by their moderate energy density. The current surge in interest in electrochemical capacitors is driven by recent breakthroughs in developing novel electrode and electrolyte materials. In particular, electrodes featuring sub-nanometer pores and room-temperature ionic liquids are promising materials for next-generation electrochemical capacitors. To realize the full potential of these materials, a basic understanding of the charge storage mechanisms in them is essential. In this dissertation, using atomistic simulations, we investigated the charge storage in sub-nanometer pores using room-temperature ionic liquids as electrolytes.

These simulations of the equilibrium charge storage in slit-shaped nanopores in contact with room-temperature ionic liquids showed that the capacitance of the nanopores exhibits a U-shaped scaling behavior in pores with width from 0.75 to 1.26 nm. The left branch of the capacitance scaling curve directly corresponds to the anomalous capacitance increase and thus confirms prior experimental observations. The right branch of the curve indirectly agrees with experimental findings that so far have received little attention. We also found that the charge storage in sub-nanometer pores follows a distinct voltage dependent behavior. At low voltages, charge storage is achieved by swapping co-ions in the pore with counter-ions in the bulk electrolytes. As voltage increases, further charge
storage is due mainly to the removal of co-ions from the pore, leading to a capacitance increase. The capacitance eventually reaches a maximum when all co-ions are expelled from the pore. At even higher electrode voltages, additional charge storage is realized by counter-ion insertion into the pore, accompanied by a reduction of capacitance. The molecular origins of these phenomena were elucidated by a new theoretical framework we developed specifically for the charge storage in nanopores using solvent-free electrolytes.

These simulations of the charging dynamics of sub-nanometer pores in contact with room-temperature ionic liquids showed that the charging of ionophilic pores, of width comparable to the size of ion, is a diffusive process. Such a process is often accompanied by overfilling and followed by de-filling. In sharp contrast to conventional expectations, charging is fast because ion diffusion during charging can be an order of magnitude faster than in the bulk, and charging itself is accelerated by the onset of collective modes. Further acceleration can be achieved using ionophobic pores by eliminating overfilling/de-filling and thus leading to charging behavior qualitatively different from that in conventional, ionophilic pores.

Overall, our studies indicated that electrodes with sub-nanometer pores and room-temperature ionic liquids can potentially enable the development of electrochemical capacitors with concurrently high power and energy densities. The fundamental insights gained in our studies help guide the rational design and optimization of these materials to realize their full potentials.
Dedication

For my wife, Mrs. Yujie Zhang, our first coming baby, my mother, Mrs. Sulan Li and father, Mr. Zhanyun Wu.
Acknowledgments

I would like to express my deep gratitude to my committee for their continued support and encouragement: Dr. Rui Qiao, my committee chair; Dr. John R. Saylor; Dr. Steve J. Stuart and Dr. Xiangchun Xuan. I offer my sincere appreciation on the learning opportunities provided by the committee. I would like to offer special thanks to my advisor, Dr. Rui Qiao for his countless encouragement. His words: “The purpose of living is not to cover the shortages but to explore the talents” has become my motivation to overcome the difficulties I met in work and life.

The completion of this works cannot be accomplished without the contribution from others collaborators, Dr. Bobby G. Sumpter and Dr. Jinsong Huang at Oak Ridge National Lab; Professor Alexei Kornyshev and Dr. Svyatoslav Kondrat at Imperial College in London. The theory of charging dynamics part of this work was first put forward by Dr. Svyatoslav Kondrat and Professor Alexei Kornyshev and we took the chance to learn the essence of the theory from them during a workshop at London and found similar observations on our simulations.

My grateful thanks are also extended to my labmates, Dr. Guang Feng, Dr. Ping He, Mr. Ying Liu, Mr. Xikai Jiang, Mr. Yadong He and Mr. Fengchang Yang. Dr. Guang Feng and Dr. Ping He constantly encourage me when I was in trouble at beginning of the study and life in U.S. Mr. Ying Liu helped me finish the implementation of green function solver and Mr. Xikai Jiang took part of my work on verifying the effect of diffusion coefficient variation.
I would also like to extend my thanks to staff at Mechanical Engineering department, Ms. Garrett Teri, Ms. Boyce Tameka, Ms. Dockins Gwen, Ms. Poole Kathryn for their honest work. The same thanks is given to the technicians at Mechanical Engineering department, Mr. Cole Jamie, Mr. Justice Michael, and Mr. Bass Stephen for their helps.

Finally, I would thank my wife, Mrs. Yujie Zhang and my parents, Mrs. Sulan Li and Mr. Zhanyun Wu for their love and supports throughout my study.
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CHAPTER 1

Introduction

1.1. Background

The quality of living in modern society is highly affected by the ready availability of cheap energy. The main sectors of energy consumption include transportation and electric power, as shown in Figure 1.[1] A large fraction of the total energy consumption is fulfilled by the combustion of fossil fuels, which creates significant CO$_2$ emission and thus contribute to global warming.[2] One possible way to reduce the global warming is to combine electricity generation from renewable energy sources with little or even zero CO$_2$ emission (e.g., wind, solar, tidal energy) and low-emission transportation technologies (e.g., plug-in hybrid electric vehicles and all electric vehicles. [3]

Utilizing renewable electricity in daily operations and powering electric vehicles require economical and reliable electrical energy storage (EES) technologies. For example, electricity generated from renewable energy sources is often intermittent e.g., no electricity is generated from solar sources in night time and electricity generated from wind farms is often subject to large hour-to-hour variation.[4] To address this issue, electricity generated during a particular period of time can be stored in EES and delivered later. In addition, EES allows off-grid usage of the electricity for driving electric vehicles and this helps
reduce or eliminate the distributed CO$_2$ emission from combustion of gasoline, another key source of CO$_2$ emission. Lastly, EES is useful for shaving the demand peak and storing the unused electricity. For example, with EES, electricity generated during low-demand time can be stored and delivered during peak hours. Thus the on-peak power supply can be met without building more or large thermal plants.

Among the many available EES technologies, batteries and electrochemical capacitors have been identified by the Department of Energy (DOE)[3] as two of the most important EES systems due to their potential application in high-profile applications such as electric vehicles and grid-scale energy storage. In this dissertation, we focus on electrochemical capacitors (ECs). The key characteristics of ECs include their high power density, excellent reliability, extraordinarily long service time, and capability to operate in
very wide temperature range.[5] Because of these characteristics, they are ideally suited for retrieving energy from repetitive and fast processes that are currently being wasted, e.g., they can be used for harvesting energy during braking of vehicles or large machines.[6,7] In addition, thanks to their excellent reliability, ECs are excellent candidates to provide burst energy to adjust the wind turbine blades in changing wind directions.[8] Finally, with a very short charge/discharge time (typically on the order of several seconds), large-scale ECs are also useful for the power regulation in electricity grid to fulfill the peak demand and avoid costly shut downs. [9-11]

1.2. Concept of Electrochemical Capacitors

Electrochemical capacitors (ECs), is also known as supercapacitors or electrical double layer capacitors (EDLCs). Similar to conventional dielectric capacitors, ECs store charge physically.[5,12] Charges are physically brought to the electrode surface and form charge separation to store energy(so called electrical double layers will be discussed later). However, ECs are distinctly different from conventional electrostatic and electrolytic capacitors in that they store much more energy. For instance, the capacitance of a typical capacitor is a few hundreds of μFs, while a handheld EC can reach capacitance as high as 5000 F.[13] Furthermore, the components of ECs are different from those of the conventional capacitors. Conventional capacitors are composed of parallel conducting plates and the dielectric materials sandwiched between them, while typical ECs are composed of porous electrodes and electrolytes.[5]
To understand the charge storage mechanism of ECs and why the energy stored in ECs is much larger than conventional capacitors, we can examine the basic setup of an EC. A simple EC can be set up by inserting two conductors (electrodes) into a beaker containing an electrolyte, for example, two carbon rods in salt water, and connecting them to a power source (see Figure 2). Driven by an external power source, positive/negative electrode carries positive/negative charge and ions in the electrolytes are attracted to the electrodes surface carrying opposite charges. Together with the electrical charge on the electrode surface, the ions adsorbed onto and adjacent to the electrode surface form an electric double layer (EDL, see Figure 2). After the external power source is removed, the net charge on the electrode remains, thus the EDL remains in place, storing energy.

The charge storage ability of an EDL is characterized by the capacitance. If we adopt the simplest model for EDL, i.e. the Helmholtz model, the capacitance of an EDL near a planar surface is given by

$$C = \frac{\epsilon_0 \epsilon_r}{d} A$$  \hspace{1cm} (1.1)

where $\epsilon_0$ is the dielectric constant of vacuum, $\epsilon_r$ is the dielectric constant of the electrolyte, $d$ is the thickness of EDL (typically the size of an ion), and $A$ is the surface area of the electrode. The thickness of the EDL is on the order of the ions’ diameter (typically less than 1 nm), which is orders of magnitude smaller than the thickness of the dielectric medium found in typical dielectric capacitors. The surface area of porous electrodes is
usually very large. For example, the surface area of carbide-derived carbon, one type of nanoporous material that has received significant attention in the recent years, can reach 3000 m$^2$/g.[14] Thus, it is evident from Equation 1.1 that with large surface area of electrode, $A$, and atomic scale EDL thickness, $d$, a very large amount of charge can be stored in ECs. For example, carbide-derived carbon shows specific capacitance up to 130 $F/g$,[14] while the specific capacitance for a typical conventional dielectric capacitors is about a few hundreds of $\mu F/g$. Because of this, ECs are often called supercapacitors and can be good candidates for many EES applications.

![Figure 2. A simple EC set up. A simple EC can be set up by immersing a pair of electrode in electrolytes (e.g., salt water). Inset is a zoomed-in view of the EDL.](image)

From the basic mechanism of charge storage in ECs discussed above, we can infer the key characteristics of ECs. In the absence of chemical reactions, the storage and release of charge in ECs are driven mostly by electrostatic interactions. As such, the deterioration
of performance due to chemical reaction, an important limitation of batteries, is eliminated. Consequently, ECs have excellent cyclability and, an EC can go through millions of full charge/discharge cycles (a typical battery can only go through several hundreds to a few thousands of cycles before failing).[15] In addition, since charging/discharging is not limited by slow kinetics of chemical reactions, charge storage/release occurs on order of seconds in typical ECs.[5] Therefore ECs can deliver hundreds to thousands of times the power of a similar-sized battery. However, a major drawback of ECs is that the amount of charge stored physically in them is much less than that chemically stored in batteries. Thanks to aggressive research investments, this issue is being addressed and some recent ECs have shown significantly improved energy density that is already comparable to that of traditional lead-acid batteries.[3]

A quantitative way of comparing the performance of various EES devices is the Ragone plot (see Figure 3). We observe that the performance of current-generation ECs is intermediate between conventional capacitors and batteries, which can be perceived as a weakness of the ECs, e.g., they can neither compete with batteries on energy density nor compete with conventional capacitor on power density. Therefore, at present, ECs are mostly used in applications demanding high power density but requiring only moderate energy densities. Indeed, batteries in hybrid-bus are being replaced by ECs to capture the energy generated during many stops of a bus, and then release the power to help the bus get started from dead stop.[16] However, for ECs to break into mainstream markets so many of their unique advantages such as excellent cyclability can be harnessed, it is
imperative to improve their energy density while not sacrificing their excellent power density.

**Figure 3.** Ragone plot of various energy storage devices. Power density and energy density of capacitors, ECs, batteries and fuel cells are compared in the plot. Source: U.S. Department of Energy, basic research needs for electrical energy storage, 2007 [3]

To improve the performance of ECs, a more detailed understanding of the design and operation of ECs is necessary. However, as shown in Figure 4, a practical EC does not differ fundamentally from the simplistic EC illustrated in Figure 2. A practical EC is made of four main components: electrodes (cathode, anode), electrolytes, separators and current collector. As mentioned earlier, the surface area of the porous electrode must be large to ensure high capacitance and thus high energy density. Prior researches [20,21] have shown that the energy density and power density of an EC are given by

\[ E = c \times \frac{V^2}{2} \times SSA \]  
\[ P = \frac{V^2}{4R_s} \]
where $c$ is capacitance, $V$ is the operation voltage, SSA is the specific surface area of the electrode and $R_s$ is effective internal resistance of the EC. Prior researches[3,20-23] have established that $c$, $V$, SSA and $R_s$ are mostly affected by the selection of electrode and electrolyte materials. It is thus clear that the energy and power densities of an EC are controlled primarily by its electrode and electrolyte materials. Below we summarize the available electrode and electrolyte materials for ECs.

**Figure 4.** A sketch of a practical EC. A practical EC is made of porous electrodes, electrolytes, separator, and current collectors. During charging, counter-ions enter and co-ions leave nanopores to store charge. During discharging, counter-ions leave and co-ions enter nanopores to release energy.

1.3. **Materials for Electrochemical Capacitors**

1.3.1. Electrode Materials

Electrodes are used to provide the surface area (and to a less extent, the volume) for forming EDLs and for passing electric current. The most important properties of porous electrode materials in ECs are their specific surface area (surface area per weight or volume)
and their pore size. According to IUPAC[17], the pore in the materials can be divided in several groups in term of the pore size: micropores (< 2 nm), mesopores (2 nm - 50 nm) and macropores (> 50 nm). Because few practical electrode material feature only pore with a uniform size, the nanopores in electrode materials are usually characterized by their pore distribution.

Carbon based porous materials are popular electrode candidates due to their high electric conductivity, chemical stability and low cost.[18-21] Carbon porous materials can have rather different forms depending on different the source materials, forming conditions, and chemical/physical processing.

Popular carbon materials used in ECs include: activated carbons, templated carbons, carbide-derived carbons, carbon nanotubes and graphenes.[21] The properties and characteristic of these materials are summarized in Table 1.

Table 1. A comparison of various carbon electrode materials for electrochemical capacitors

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<tr>
<th>Carbon</th>
<th>Typical Pore Size (nm)</th>
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<th>Energy Density (Wh/kg)</th>
<th>Power Density (kW/kg)</th>
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<td>1000-3500[22]</td>
<td>3-5[22]</td>
<td>7-10[22]</td>
</tr>
<tr>
<td>Carbon nanotube</td>
<td>0.5-6[25]</td>
<td>120-500[28]</td>
<td>7[26]</td>
<td>20[26]</td>
</tr>
<tr>
<td>Graphene</td>
<td>0.6-5[27]</td>
<td>2630[29]</td>
<td>70[27]</td>
<td>250[27]</td>
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Below we give a brief description of these carbon materials. Activated carbons (ACs) are the most widely used for ECs due to their large surface area and moderate cost. ACs are generally produced from physical (thermal) and/or chemical activation of various types of carbonaceous materials (e.g., coconut shells).[28,29] A porous network in the bulk of the carbon particles is produced after activation. Nanopores inside ACs usually have a relatively broad size distribution.[29,30] Longer activation time or higher temperature leads to large mean pore size.[30] Surface areas of ACs is ~ 1000 m²/g.[28] Specific capacitance of ACs can reach 100-120 F/g in organic electrolyte.[21]

Templated carbons (TCs) are nanostructured carbons produced by the templating method[20] and they have been used in some ECs. TCs have rather controllable pore size and pore types. In general, the preparation procedure of templated carbons begins with the infiltration of a carbon precursor (e.g., carbon diamonds, carbon fibers, carbon powders) into a template structure (e.g., silica MCM48, MCM41, and SBA-15), followed by carbonization treatment and finally finished with the removal of the template.[31-33] A schematic representation in Figure 5 shows the general concept of the templating technique and various porous carbons obtained from different templates.[20] The pores of TCs can be controlled to obtain different types pores, micropore (<1-2nm), mesopore (5-50nm) and macropore (60-100nm). Another example of a highly ordered TC obtained from SBA-15 silica and pitch is shown in Figure 9(c).[41]
Figure 5. Schematics of templating technique. (a) Macroscopic representation showing the general concept of the templating technique; (b) microscopic synthesis of macroporous carbons using silica spheres as template, (c) mesoporous carbons using SBA-15 as template and (d) microporous carbons using Zeolite Y as template. Reproduced with permission from ref. [20] © 2009 Royal Society of Chemistry.

Carbide-derived carbons (CDCs) are gaining interest recently because the pore size in them can be generated with sub-nanometer resolution and the sub-nanometer pores in them can store large amount of charge compared to their counterparts.[34] Atomic level control of pore size can be achieved because the rigid metal carbide lattice is used as a template and metal is extracted layer by layer.[35] Take Ti$_2$SiC$_2$ for instance, Ti and Si are extracted to form carbon structure by the reaction:[35-37]
$Ti_3SiC_2 + 8Cl_2(g) = SiCl_4(g) + 3TiCl_4(g) + 2C$

Figure 6 illustrates how carbon structure is formed by the above reaction. The pore size distribution can be fine-tuned by controlling the chlorination temperature and the choice of starting carbide.[35] The produced CDC exhibits a specific surface area up to 2430 m$^2$/g and a specific capacitance up to 170 F/g.[36] The microstructure of a CDC obtained from $Ti_3SiC_2$ at 1200 °C is shown in Figure 9(b). The manufacture of CDCs is less complicated and adaptable to industrial size processes [36] because of the easy removal of gases.

![Figure 6](image_url)

**Figure 6.** A schematic of the lattice structure change of $Ti_3SiC_2$. The lattice structure of $Ti_3SiC_2$ with and without Ti and Si atoms shown in figure left and right, respectively. Reproduced with permission from ref. [37] © 2006, Elsevier.

Carbon nanotubes (CNTs) have unique advantages for being electrode materials, such as extraordinary electronic conductivity, superior mechanical properties, and excellent thermal conductivity.[26,38-40] Two types of CNTs are typically used: single wall nanotubes (SWNTs) consisting of a single graphite sheet wrapped into a cylindrical tube (see Figure 7(A-D))[26]; multi-wall nanotubes (MWNTs) comprised of a concentrically array of SWNT (see Figure 7(E)). CNT are usually synthesized by carbon-
arc discharge, laser ablation of carbon, catalytic decomposition of hydrocarbons and electrolysis.[41] The diameter of nanotubes can range from a few angstroms to tens of nanometers.[38] Good capacitance (180 and 102 F/g for SWNT and MWNT electrodes, respectively) and power density (20 kW/kg at an energy density of 7 Wh/kg for SWNT electrodes) have been reported.[26] Highly ordered CNTs on SiC are also shown in Figure 9(d).

Figure 7. Atomistic structure of SWNTs. (A-C) The side view and top view of the nanotubes are presented (D) Tunneling electron microscopic view of a SWNT. (E) Transmission electron microscope (TEM) image of a MWNT containing a concentric array of SWNTs. Reproduced with permission from ref. [26] © 2002, American Association for the Advancement of Science.

Graphene is another outstanding candidate for electrode material, having similar advantages with CNTs but with larger theoretical specific surface area.[44-46] Most significantly, the quantum capacitance of graphene was recently found to be
Figure 8. An illustration of the chemical route to synthesize chemically derived graphene. Reproduced with permission from ref. [48] © 2010, Royal Society of Chemistry.

Figure 9. Carbon structure used as electrodes materials for ECs. (a) Transmission electronic microscopy (TEM) image of a disordered microporous carbon. Reproduced with permission from ref. [21] © 2008, Rights Managed by Nature Publishing Group. (b) TEM image of CDC produced at 1200 °C from Ti$_3$SiC$_2$. Ordered graphite pattern (graphite ribbons) can be found in CDC. Reproduced with permission from ref. [36] © 2006, Elsevier. (c) TEM image of a template carbon prepared using SBA-15 silica as template and pitch as carbon source. Reproduced with permission from ref. [49] © 2001, Elsevier. (d) SEM image of an array of carbon nanotubes (labelled CNT) supported on a SiC substrate. Reproduced with permission from ref. [21] © 2008, Rights Managed by Nature Publishing Group.
21 \mu F/cm^2,[45] which sets the upper limit of EDL capacitance for all carbon-based materials. Graphene can be made via many physical and chemical preparation. Chemical approaches, which produce chemically derived graphene, are popular. As illustrated in Figure 8, graphite is first oxidized to graphene oxide (GO) and this is followed by GO reduction to obtain chemically derived graphene.[47] The pore size in graphene, however, is quite difficult to fine-tune and has been found to distribute over a rather wide range of 0.6-5nm in a recent study.[25] Using electrodes made of chemically derived graphene, specific capacitance of 135 F/g and 95 F/g with aqueous electrolyte and organic electrolytes, respectively has been demonstrated recently.[48]

1.3.2. Electrolyte Materials

The performance of ECs is not only determined by electrode materials but also strongly affected by electrolyte materials. Importantly, the operation voltage and internal resistance of ECs are mainly constrained by the properties of the electrolytes. It is evident from Equation 1.2 and Equation 1.3 that high operation voltage and low internal resistance are preferred properties for electrolytes, because energy and power density are both proportional to the square of operating voltage and power density is inversely proportional to the internal resistance.

The electrolytes used in ECs can be classified into three categories: aqueous electrolyte, organic electrolyte, and room temperature ionic liquids (RTILs). Aqueous electrolyte has high ion concentration and low internal resistance. However, the operation voltage of aqueous electrolyte is limited to ~1V due to the decomposition of water at
voltage large than 1V.[20] Compared to aqueous electrolyte, organic electrolyte (e.g., TEA·BF₆ dissolved in ACN) has higher operation voltage 3-3.5V, but application of organic electrolytes is limited by factors such as high cost, low conductivity, flammability toxicity and low dielectric constant which results in a small capacitance.[18] RTILs are an emerging class of electrolyte for ECs. RTILs are solvent-free electrolytes, but unlike molten salt such as NaCl, they remain in liquid state at room temperature. In some sense, RTILs are similar to organic electrolytes that RTILs can be converted to organic electrolytes by adding organic solvents.[50] Several properties make RTILs promising candidate electrolytes for ECs, e.g., wide operation voltage windows (up to 6 V)[51], low vapor pressure, and high thermal and chemical stability. The latter are important consideration for safe operations. A comparison of various electrolytes is shown in Table 2.

Table 2. A comparison of various electrolytes for electrochemical capacitors

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Operation Voltage</th>
<th>Conductivity</th>
<th>Safety</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous electrolytes</td>
<td>Low (~1V)[20]</td>
<td>High</td>
<td>Safe</td>
</tr>
<tr>
<td>Organic electrolytes</td>
<td>Medium (~3V)[18]</td>
<td>Low</td>
<td>Non-safe</td>
</tr>
<tr>
<td>RTILs</td>
<td>High (up to 6V)[51]</td>
<td>Often low</td>
<td>Safe</td>
</tr>
</tbody>
</table>

1.4. Recent Experimental Progresses

In the previous sections, we identified the principal advantages and limitations of (ECs) and established that improving the performance of ECs hinges on developing better
electrode and electrolyte materials. While the development of ECs has been rather incremental from the time it was first invented till the early 2000s, there has been several recent experimental breakthroughs that greatly improved the performance of ECs and significantly challenged the prevailing view of charge storage mechanisms in ECs. In this section, we review some of the more important developments of ECs on the experimental front. The experimental development of ECs has several active fronts, and each has led to impressive improvement of EC performance.

The first front focuses on increasing the specific area of the electrode materials. In this regard, Zhu et al. [25] proposed an industrial scalable method to synthesize porous carbon with surface area up to 3100 m$^2$/g. This carbon has a continuous three-dimensional network of highly curved, atom-thick wall that form primarily 0.6 to 5 nm width pores. ECs made of this carbon yield high capacitance and energy density with organic and ionic liquid electrolytes.

The second front focuses on improving the specific capacitance of the electrode. Conventionally, the ECs communities believed that nanopores with diameters smaller than the diameter of solvated ions do not contribute to charge storage (i.e., the specific capacitance of such pores is effectively zero). This traditional view implies that the energy density of ECs cannot be improved by increasing the specific surface area of an electrode, which is best achieved by introducing very narrow (e.g., sub-nanometer) pores into the electrode may not be effective at all. This view has been challenged by the experimental work done by the Gogotsi group at Drexel University. Specifically, Chmiola et al. [34] shows that the specific capacitance of ECs increases as pore size decreases below 1 nm.
This discovery challenged the conventional presumption that pores smaller than solvated electrolyte ions do not contribute to energy storage.[28,52] As shown in Figure 10, the specific EDL capacitance varied with pore size from 0.6 to 2.25 nm. In region I of Figure 10, the pore width is substantially larger than twice the size of solvated ion and capacitance does not decrease too much. In region II of Figure 10, pore width decreased to less than twice the solvated ion size, accompanying with capacitance decrease. In even smaller pores (region III in Figure 10), which are narrower than the size of solvated ions, however, the capacitance increases as the pore size reduces. Chmiola and colleagues attributed such an anomalous enhancement of the specific capacitance to the distortion of ions’ solvation shell, which allows a closer approach of the ion center to the electrode surface. While such simplistic interpretation is subject to debate, their experiments nevertheless challenged the long-held presumption that pores smaller than solvated

![Figure 10](image.png)

**Figure 10.** Plot of specific capacitance of the carbons filled by organic electrolyte. Insets are the sketch of organic electrolyte molecular used in experiment. Reproduced with permission from ref. [34] © 2006, American Association for the Advancement of Science.
electrolyte ions do not contribute to energy storage. Such a discovery triggered a great wave of fundamental and applied research on charge storage using ECs.

Later, Largeot et al. [53] further investigated the relationship between ion size of electrolyte and double layer capacitance using RTILs, EMI-TFSI, to find out the optimal pore size to achieve highest capacitance. Capacitance is observed to increase as pore size decreases and reach the maximum around the size of ion (≈0.7 nm) (see Figure 11). Similar EDL capacitance enhancement trend is also observed in aqueous electrolyte although the magnitude is moderate.[17]

![Figure 11](image1.png)

**Figure 11.** Plot of specific capacitance of DCD carbon filled by ionic liquids electrolyte. The sketches of electrolyte ion with the size of ion are shown besides. Reproduced with permission from ref. [53] © 2008, American Chemical Society.

The third front in experiment studies of ECs focuses on developing electrode-materials with different structures to help maintain ECs’ high power density. Generally, it is expected that adapting narrow pores will slow down the transport of ions during charging and discharging. Korenblit et al. [24] developed templated CDC with hierarchical
structures to overcome the impedance to the ion transport and power performance from narrow micropores. Here, mesoporous channels are templated into CDC to serve as ion-highways that allow for fast ionic transport into the bulk of the CDC particles. The templated CDC exhibits a specific surface area up to 2430 m$^2$/g and a specific capacitance up to 170 F/g [39]. Yoo et al. [54] reported an “in-plane” fabrication approach for ultrathin ECs based on electrodes comprised of pristine graphene and multilayer reduced graphene oxide. The 2D in-plane design took advantage of the atomic thickness and flat morphology of graphene. By using layer by layer assembly of graphene oxide, the design help ions to access all graphene layers without having to travel meandering paths.[54] Finally, by growing graphenes directly on metal substrates, Miller et al. [55] fabricated ECs in which the access of ions to electrode surface is facile. While the resulting ECs have lower energy density, the power density is very impressive. In fact, the fabricated ECs can be used as 120Hz filter. The time constant of the graphene ECs is 200 microseconds, much smaller than that of typical resistor-capacitor (RC) ECs (~1s). The very fast response of these ECs allow them compete with aluminum electrolyte capacitors for usage in electronic circuits, e.g., in portable electronics where the size of the device is an important design consideration.

1.5. Recent Progresses in Theoretical and Simulations

Triggered by the recent breakthroughs in experimental studies of ECs (perhaps most importantly by the results shown in Figures 10 and 11), there have been significant interest from theoretical communities to understand the charge storage in ECs. Given that
there are many choices for electrolyte and electrode materials and how they may be paired, gaining fundamental insights on the charge storage in nanopores is not only interesting from a scientific perspective but also useful for practical development of ECs as they can guide the rational design and selection of electrode and electrolyte materials to help optimize ECs’ performance.

The charge storage in narrow pores filled with novel electrolytes such as RTILs, however, cannot be understood using the classical EDL theories and ion transport theories. Specially, the classical Gouy-Chapman-Stern theory was developed for dilute electrolytes and is rigorous only in the limit of infinite dilution and low electrode voltages. The RTILs, however, are solvent free electrolytes. Likewise, the Poisson-Nernst-Planck model, which has been used to predict charging dynamics in nanopores, is rigorous only in the limit of negligible ion-ion correlations, which is again opposite to the strong ion-ion correlations found in RTILs. While these issues pose challenges for understanding the charge storage in nanopores, they also create new opportunities for fundamental research to advance basic understanding of EDLs in novel materials. Below we summarize the recent advances in theoretical and simulation studies of the charge storage in ECs. We will first focus on charge storage in terms of the thermodynamics limit (i.e., equilibrium charge storage). We will then present studies of charge storage under dynamics conditions.

1.5.1. Thermodynamics of Charge Storage in Nanopores

Huang et al. [17,56] published the first works on the mechanisms of anomalous enhancement of capacitance in nanopores. The authors proposed two heuristic theoretical models for the EDL in such nanopores. The essential idea is that the classic Helmholtz
model for EDLs (see Equation 1.1) does not take into account the curvature of the nanopores, which can be large in micropores and mesopores. For mesopores, the authors assumed that pores are cylindrical, solvated counter-ions enter mesopores and approach the pore wall to form an electric-double-cylinder capacitor (EDCC) (see Figure 12(a)). The capacitance of such a capacitor is given by

\[
\frac{C}{A} = \frac{\varepsilon_r \varepsilon_0}{b \ln(b/(b - d))}
\]  

(1.4)

where \( b \) is the radii of the outer cylinders and \( d \) is the separation distance between inner and outer cylinders. In the limit of wide nanopores, the EDCC model is reduced to classical Helmholtz model. For micropores, the geometrical confinement prevents the formation of double cylinders as in mesopores. Therefore, the authors assumed that solvated (or desolvated) counter-ions line up along the pore axis to form an electric wire in cylinder capacitor (EWCCs) as shown in Figure 12(b). In some way, EWCCs can also be viewed

\[\text{Figure 12. Schematic diagrams of the EDLs in nanopores. a) A negatively charged mesopore with solvated cations forming an electric double-cylinder capacitor (EDCC). The radius of the inner and outer cylinders are } b \text{ and } a \text{ respectively. b) A negatively charged micropore of radius } b \text{ with cations of radius } a_0 \text{ lining up to form an electric wire-in-cylinder capacitor (EWCC). Reproduced with permission from ref. [17] © 2008, WILEY.}\]
Figure 13. Fitting of experiment data on capacitance of CDC micropores using the EDCC model. (a) In CDC micropores filled with organic electrolyte (1.5M TEABF$_4$ in CH$_3$CN). The three panels show the capacitance of the negative and the positive nanopores (left and central panels) and the total capacitance (right panel) of the two pores arranged in serial. (b) In CDC micropores filled with RTILs (EMI-TFSI). (c) In activated carbon electrode filled with aqueous KOH electrolyte. Reproduced with permission from ref. [17] © 2008, WILEY.
as EDCCs, but the key quantity for EWCCs is no longer $d$, but rather the radius of the inner cylinder $a_0$, which is the effective size of ions. The authors showed that the EDCC/EWCC model can fit the experimental data on capacitance in nanopores quite well for diverse electrode and electrolyte materials (e.g., organic electrolytes, ionic liquids, and aqueous electrolyte, see Figure 13). Importantly, the EWCC model can explain the anomalous enhancement of capacitance in sub-nanometer pores.

While the EDCC/EWCC models offer useful insights on role of pore curvature on capacitance and help rationalize some experimental observations, these models are based on simplistic assumptions as described above. Importantly, they do not take into account any molecular details of the electrolyte ion except ion size. Some of the underlying assumptions, while seemingly justified *posteriori* based on the good fitting of the experimental data by the models, are not fully corroborated from first principle. Detailed analysis at molecular level can help resolve these limitations. Indeed, several molecular dynamics (MD) simulations have been performed to study the EDL at nanoconfinement. For example, Yang *et al.* [57] simulated the EDL capacitors in CNT forests in organic electrolytes. (see Figure 14 for their MD model) They observed a very moderate capacitance enhancement as the effective pore size decreases below 1 nm.
**Figure 14.** Illustration of the filled nanotube forest treated by MD simulation. (Left) The nanotube model. (Right) Cross-section perpendicular to the nanotubes. Reproduced with permission from ref. [57] © 2009, American Chemical Society.

In another MD study, Shim and colleagues [58] explored the EDLs capacitance of CNT filled with RTILs (EMI'BF₄⁻) as a function of CNT diameter \( d_0 \) (0.7 < \( d_0 < 2 \) nm). A snapshot of their MD system is shown in Figure 15. The specific capacitance \( \bar{c} \) is found to increase as \( d_0 \) decreases from 2.02 nm to 0.94 nm. One of the main factors responsible for this behavior is the growing difference of internal solvation via counter-ions and via co-ions, which leads to a progressively more important role for the internal counterions when the pore size decreases. As \( d \) further decreases, however, \( \bar{c}_T \) starts to decrease. This is attributed to a rapid transition from strong internal exclusion to the complete lack of internal solvation for very small CNTs. The reported trend for the variation of specific capacitance with \( d_0 \) is in good agreement with available experiment data, although the capacitance obtained from MD simulation is ten times smaller than what was observed experimentally. The authors’ analysis shows that the charge contributed by the counter ions is not monotonically distributed, rather the charge form multilayers with alternating signs. This interesting behavior, which was also observed in wide nanopores, was attributed to the orientational alignment of bulky ions inside the pores. Based on these MD observations,
an electric multi-charge layer capacitance (EMLC) model, which assumed $n$ concentric layers of charge distributed inside CNT was proposed to explain the capacitance behavior of CNT nanopores. Figure 16 shows that the capacitance of nanopore computed from MD simulation can be fitted to the predictions of the EMLC model reasonably well.

![Figure 15](image1.png)

**Figure 15.** Electrochemical capacitor modeled by Shim and Kim. The system consists of a CNT (diameter 2.02 nm) as micropore and EMIBF$_4$ as an electrolyte. Reproduced with permission from ref. [58] © 2010, American Chemical Society.

![Figure 16](image2.png)

**Figure 16.** Capacitance computed from MD results fitted by EMLC model. (a) A schematic of the EMLC model; (b) MD results and experiment results of $\bar{c}_t$ (unit: $\mu F/cm^2$) and their fits via the EMLC model. The fit is shown as dotted lines. Reproduced with permission from ref. [58] © 2010, American Chemical Society.
The above molecular simulations shed light on the unique features of EDLs nanoconfinement, e.g., the multilayer charge distribution and the orientational ordering of bulky ions inside nanopores. While these simulations manage to reproduce some aspects of the experiment observations well, they do not provide systematic theories for the charge storage in nanopores and offer limited guidance for practical development of ECs.

Skinner et al. [59] explored the upper limit of the capacitance of the EDL formed at the metal/RTIL interfaces. They first worked on the EDLs near open planar electrodes in contact with RTIL reservoirs to explain the large capacitance of EDLs not predicted by the classical mean-field theories. Their essential idea is to consider the image charge effects of the ions near the electrode surfaces. By taking into account the image charge effect, they demonstrated the EDL capacitance can be significantly larger than that predicted by the Helmholtz model since repulsion of bound ions on electrodes is very weak. At low voltage or small ion density, the capacitance is inversely proportional to the repulsion of bound ions according to Equation 1.5.

\[
C(0) \cong \frac{4}{15\alpha} \left(\frac{4\pi}{Na^3}\right) eS = \frac{4}{15\alpha} \left(\frac{4\pi}{Na^3}\right) C_H
\]  

where \(\alpha\) is a factor depending on the structure of dipole position, \(a\) is the size of ions, \(N\) is bulk density of ions, and \(C_H\) is the Helmholtz capacitance. The variations of capacitance and the density of bound ions as a function of the electrode voltage are shown in Figure 17.
Following the above work, Skinner et al. [60] extended their model from open planar electrode to narrow pores to elucidate the high volumetric capacitance of $\sim 100$ F/cm$^3$ observed in experiments. They show that charges confined within narrow pores create an infinite series of image charges in two electrode walls (see Figure 18(a)). This leads to an electrostatic interaction $U$ between ions which decays exponentially as a function of their lateral distance. By neglecting entropic effects, they derived an analytical expression for the differential capacitance $C$ at small electrode voltages $(V - V_t)$:

$$C \cong 32\pi^3 \left( \frac{e}{4\pi \varepsilon_0 \varepsilon d} \right) \ln^{-3} \left[ 8\pi^2 \left( \frac{e}{4\pi \varepsilon_0 \varepsilon d} \right)^2 \frac{a}{d} C_H \right] \left( \frac{V - V_t}{V} \right)$$

(1.6)

where $d$ is pore size, $a$ is ion size, and $V - V_t$ is the voltage that drive ions into the pores. Equation 1.6 suggested that at low ion density, capacitance increased as voltage and pore size decreased. These results can be understood physically by noting that as pore size decreases, the exponential screening among ions increases, resulting in decreasing energy...

\[\text{Figure 17. The area densities of bound ions and the capacitance as a function of the applied voltage.} \]  
The area density of bound ions is shown as dashed lines, measured by left vertical axis and the capacitance is shown as solid line, measured by right vertical axis. Reproduced with permission from ref. [59] © 2010 The American Physical Society.
and therefore enhanced capacitance. Similarly, as voltage decreases, less ions will be inside the slit nanopore, resulting in decreasing ion-ion interaction, thus high capacitance. Figure 19 shows the capacitance as a function of the voltage, plotted for different pore widths, d = a, 1.5a, 2a.

![Figure 18](image_url)

**Figure 18.** A schematic depicting anions neutralizing a positively charged nanopore. (a) When pore width is wide enough to form independent EDLs, each anion has one image charge. (b) When pore width can accommodate only single layer of ion, each anion has an infinite series of image charges. Reproduced with permission from ref. [60] © 2011 The American Physical Society.

![Figure 19](image_url)

**Figure 19.** The capacitance of a 2D metal pore, as a function of the electrode voltage. The width of the pore is d. The top x-axis shows ion density for the case with d/a = 1. Reproduced with permission from ref. [60] © 2011 The American Physical Society.
The research above highlighted a unique phenomenon for ions confined in narrow pores, i.e. the predominance of image charge effect in regulating the interactions between ions. Specifically, the image charge effect reduces the repulsion of bound ions near electrodes, and this is the root of capacitance enhancement in subnanometer pores. Such an idea has been independently pursued by the Kornyshev group at Imperial College. Specifically, Kondrat et al. [61] derived a simple phenomenological model to understand the charge storage mechanism in nanopores. The model takes into account the exponential screening of ion-ion interactions in nanopores. Specially, their model takes into account the exponential screening of ion-ion interactions by the metallic pore walls, and they concluded that the screened electrostatic interactions between ions lead to a “superionic” state, which in turn causes capacitance enhancement as pore width decreases. The total free energy of an ionic liquid confined inside a nanopore, \( F \) is given by

\[
F = U + E_s + \sum_{\alpha=\pm} \mu_{\alpha} \rho_{\alpha} - TS
\]  

(1.7)

where \( U \) is the internal energy due to ion-ion electrostatic interaction, \( E_s \) is the free energy for transferring an ion from the bulk into the pore, \( \mu_{\pm} \) is the chemical potential of the cation/anion and \( S \) is the entropy. The free energy can be minimized numerically with respect to the ion density \( \rho_{\pm} \), and the differential capacitance can be found by numerically differentiating the net ionic charge inside the pore with respect to the electrode voltage. The prediction of the differential capacitance of pores with different pore widths is shown in Figure 20 as a function of voltage \( V \). At zero voltage the capacitance increases with decreasing pore width, in agreement with the experimental observations.
Figure 20. Differential capacitance of nanopores as a function of pore width and applied voltage. (a) Differential capacitance of nanopores as a function of the pore width (L is the pore width; d is the ion diameter). The capacitance increases with decreasing pore width at zero voltage (solid line, in accordance with experiment observations). (b) Variation of the nanopore capacitance as a function of the electrode voltage in two different pores. Reproduced with permission from ref. [61] © 2011 IOP Publishing Limited.

Following the above work, Kondrat et al. [62] performed Monte Carlo (MC) simulations of a restricted primitive model of ionic liquid in slit-like metallic nanopores to study the charge storage in nanopores using RTILs. The MC simulations confirmed several essential predictions of their phenomenological model. For example, the anomalous enhancement of nanopore capacitance in narrow pores was recovered in the MC
simulations (see Figure 21(b)). For narrow pores, the capacitance-voltage curve exhibits a peak before dropping down to zero at higher voltages (see Figure 21(a)). This peak results from the saturation of the total ion density in a pore, which occurs before the pore was filled solely with counter-ions.

Figure 21. Anomalous capacitance behavior inside narrow metallic nanopores. (a) Variation of the differential capacitance as a function of voltage for a few pore widths. (b) Variation of the differential capacitance at zero potential as a function of pore width. Experiment data and mean field results are shown in (b). Reproduced with permission from ref. [62] © 2011, Royal Society of Chemistry.
1.5.2. Charging Dynamics of Nanopore

In the preceding section, we summarized the theoretical and simulation studies of the charge storage inside nanopores under equilibrium conditions (i.e., at infinitely slow charging rates). Practical ECs, however, mostly operate under fast charging/discharging conditions. Therefore, understanding the charge storage and release under dynamic conditions is very important. Below we summarize the current understanding of the charging dynamics in ECs.

1.5.2.1. Theories for the Charging of EDLs

The de facto theory for understanding the charging of nanopores in ECs is the equivalent circuit model. In this model, an EC is modeled using an “equivalent circuit”, which consists of “capacitors” (due to the double layers forming at the electrode surfaces), and “resistors”. (which account for the resistance posed by the electrolyte for charge transport during charging/discharging)[63] A schematic sketch of a circuit model is shown in Figure 22. The model parameters, e.g., the double layer capacitance $C_D$ and bulk resistance $R_b$, can be fit from experimental data or estimated for certain systems, e.g., flat surfaces. For charging dynamics of dilute electrolyte in parallel-plate electrodes, the relaxation time of EDL is given by $\tau_c = R_b C_D = \frac{\lambda_D L}{D}$, where $\lambda_D$ is Debye length of the double layer, $L$ is distance ions traveled and $D$ is the ions diffusion coefficient. Although the model provides some insights on the factors governing charging dynamics, the applicability of the model remains questionable and using it to fit experimental data often incurs difficulties and ambiguities.
Figure 22. An equivalent RC circuit model for a parallel-plates EC.

An alternative theoretical approach for understanding the charging dynamics of a nanopore is to solve the time-dependent Poisson-Nernst-Planck (PNP) equations within the entire EC (i.e., without distinguishing the EDLs and bulk electrolytes \textit{a priori}) Biesheuvel \textit{et al.} [64] analyzed the response of a model microelectrochemical system to a time-dependent applied voltage by solving the PNP model. The model shown in Figure 23 consists of a symmetric binary electrolyte between parallel-plate blocking electrodes. Specifically, a porous electrode of thickness $L_e$ is separated from bulk electrolyte by a stagnant diffusion layer of thickness $L_{sd}$. The characteristic pore $h_p$ is defined as the ratio of the pore volume to the pore area, and is much larger than the Debye screening length, $\lambda_D$. Hence, the pore space is mostly filled with quasi-neutral electrolytes and it exchanges ions with a charged thin double-layer “skin” on the electrode surface. The volume-averaged potential $\phi(x, t)$ and salt concentration $c(x, t)$ in the pore space vary as counter-ions enter (coions leave), the thin double layers, thus changing the mean surface charge density $q(x, t)$ and total excess salt density $w(x, t)$. Based on the matched asymptotic analysis for thin double layers, the authors showed that the electric-circuit shown in Figure 22 is a zero-
order, linear approximation of the PNP model. The linearized problem for low voltages or early times, can be interpreted by a classical RC circuit model. The porous electrode can be modeled as a “transmission line” (nanopores) in series with “resistor,” (the SDL) as shown in Figure 24.

Figure 23. A model electrochemical cell considered by Biesheuvel et al. Reproduced with permission from ref. [64] © 2010, The American Physical Society.

Figure 24. Equivalent-circuit interpretation of the charging of a porous electrode. Linearized charging dynamics of a porous electrode can be interpreted as equivalent-circuit model. The quasi neutral solution in the pore acts as a serial of resistors coupled with the EDL capacitors, which is named as transmission line model. Reproduced with permission from ref. [64] © 2010, The American Physical Society.

Following the above work, Biesheuvel et al. [65] proposed a porous-electrode theory that can include the EDL model to describe the dynamics of charging and salt
storage in porous electrodes. In the description of EDLs, they considered two limits: the classical Gouy-Chapman-Stern (GCS) model for thin DLs compared to the macroscopic pore dimensions (valid for macro pores) and a modified Donan model for strongly overlapping EDLs (valid for micropores). For both EDL models, the porous electrode theory can be reduced to two coupled nonlinear PDEs for the salt concentration and EDL charge density within the porous electrode. Analytical and numerical results for salt concentration, potential, and surface charge density were present for the steady state for the transient development toward the steady state. Typical numerical simulation results are presented in Figure 25, where a negative charged EDL turns positive after applying the voltage. These results showed that very rich behavior can emerge during ion transport and ion absorption in porous electrodes.

The theories presented above are expected to be valid for electrolytes in which ion-ion correlations are weak. As such, they cannot be used to understand the charging of nanopores using RTILs. Recently, Kondrat et al. extended their earlier work on thermodynamics of charge storage in nanopores,[61,62] and developed a new phenomenological model to predict the charging of single nanopores by RTILs. [66] The starting point of their theory is by the formulation of the free energy of a nanopore + RTIL system as
Figure 25. Numerical results for charging of porous electrode. The profiles of salt concentration $c$, pore potential $\phi$, diffuse layer charge density $q$, and salt adsorption $w$ in the electrode as a function of time are shown. The evolution of the profile goes as direction of arrow, starting from solid then dashed, and finally solid. Filled circles denote the initial condition, and open triangles denote the steady state. The EDLs are initially negatively charged. Then voltage is applied and the EDL eventually become positively charged. This sign reversal, coupled with the nonlinear dynamics of ion transport, leads to the complicated behavior seen in the Figure. Reproduced with permission from ref. [65] © 2011, American Physical Society.
\[ F[\rho_{\pm}] = \frac{1}{2} \sum_{\alpha,\beta} \int dR_1 \int dR_2 \rho_\alpha(R_1)U_{\alpha\beta}(R_1, R_2) \rho_\beta(R_2) + \sum_\alpha h_\alpha \int dR \rho_\alpha(R) + F_0[\rho_{\pm}] \]  

where \( R = (x,y) \) are lateral coordinates, \( \rho_\alpha = \pm (R) \) are the two-dimensional ion densities, \( U_{\alpha\beta} \) is the electrostatic interaction, \( h_\alpha \) is ion self-energy and \( F_0 \) is the “reference” free energy in the local density approximation. The evolution of ion density follows the mass conservation law

\[ \frac{\partial \rho_{\pm}}{\partial t} = -\nabla J_{\pm} \]  

where \( J = -D \rho_{\pm} \nabla (\beta \frac{\partial F}{\partial \rho_{\pm}}) \) is the ionic flux, \( D \) is the diffusion coefficient and \( F \) is the total free energy of the system. Equations 1.8 and 1.9 together form a closed model for charging of nanopores using RTILs. By solving the closed model, the evolution of ion and charge density inside the pore can be obtained.

Using the above model, Kondrat \textit{et al.} studied the charging dynamics inside two types of nanopores, i.e., ionophilic pores that are pre-wetted by RTILs and ionophobic pores that are empty at potential of zero charge (PZC) state. Their analysis showed that charging of initially empty (i.e. ionophobic) pores proceeds in a front-like manner (see Figure 26), while the charging of initially filled (i.e. ionophilic) pores is diffusive (see Figure 27); in both cases, the accumulated charge inside a nanopore grows as the square root of time. In addition, their analysis showed that the finalization of the charging process seems to be faster for empty pores (see Figure 28).
**Figure 26.** Front-like propagation of counter ions into a initially empty nanopore after a voltage jump is applied on the pore walls. Reproduced with permission from ref. [66] © 2013, American Chemical Society.

**Figure 27.** A representative example of the diffusive charging of initially filled pores. The inset shows that there is a small "congestion" zone close to the pore entrance that moves along the pore and relaxes in the end of the charging process. Reproduced with permission from ref. [66] © 2013, American Chemical Society.
Figure 28. Charging of pores predicted by the model developed by Kondrat et al. Panel (a) is for ionophilic pores an panel (b) is for ionophobic pores. The thin vertical lines indicate the time when the "fronts" from two ends meet each other, which was identified as a beginning of the final charging stage (stage III). Stage III appears to be faster in ionophobic pores. Reproduced with permission from ref. [66] © 2013, American Chemical Society.

1.5.2.2. Dynamics of RTILs in Nanoconfinement

All of the existing theoretical models require the diffusion coefficient of ions as an input parameter. At present, there is no first principle theory for ion diffusion in novel electrolytes such as RTILs. Usually, the diffusion coefficient of ions inside nanopores is inferred from the dynamics of ions in the bulk. This assumption may be reasonable for large pores, but become increasingly problematic where the pore size reduces. Below we summarize the works on the dynamics of ions confined inside nanopores.
Li et al. [67] reported the influence of silica and carbon solid walls on the structure and dynamic properties of confined RTIL ([C₄mim][Tf₂N]) by MD simulation and nuclear magnetic resonance (NMR) experiments. (see Figure 29) They found that the temperature-dependent diffusion coefficients of [C₄mim][Tf₂N] confined in silica or carbon mesopores exhibit divergent behavior. The loading fraction (f = 1.0, 0.5, and 0.25) has a large effect on the diffusion coefficient in the silica pore. The ion diffusion coefficient displays weaker temperature dependence as the loading fraction decreases. (see Figure 30(a)) The diffusion coefficients of mesoporous carbon-confined [C₄mim][Tf₂N] are relatively insensitive to the loading fraction and exhibit a temperature dependence that is similar to that found in bulk RTILs at all loading levels. (see Figure 30(b)) These phenomena were attributed to the unique surface heterogeneity, dissimilar interfacial microstructures, and interaction potential profile of RTILs near silica and carbon walls.

**Figure 29.** Cross-sectional views of the silica and carbon mesopores filled with a RTIL. [C₄mim][Tf₂N] is the RTIL used. Reproduced with permission from ref. [67] © 2013, American Chemical Society.
Figure 30. Diffusion coefficients of C₄mim+ confined in (a) silica and (b) carbon mesopores as a function of temperature at different loading fractions (f). Reproduced with permission from ref. [67] © 2013, American Chemical Society.

Hung et al. [68] studied the structure and dynamics of RTILs [EMIM+][NTf₂⁻] confined inside a slit graphitic nanopore at different surface charge density (see Figure 31). The results shown in Figure 32 indicate that in general, the diffusion of ions inside pores is slower than that in the bulk. However, the diffusion of ions inside charged nanopores can also be comparable or even larger than the diffusion of bulk ions. This implies that the slow diffusion of ions in bulk does not mean slow ion diffusion in charged nanopores. This is an important observation and it points to the need for research on ion diffusion under conditions relevant to the charging of nanopores.
Figure 31. MD system modeled by Hung et al. to study dynamics of RTILs. (a) Schematic representation of the ions [EMIM+]\([\text{NTf}_2^-]\). (b) A snapshot of [EMIM+]\([\text{NTf}_2^-]\) confined inside a slit graphitic nanopore. The top and bottom walls of the pore are positive and negatively charged, respectively. Reproduced with permission from ref. [68] © 2011, American Chemical Society.

Figure 32. Log-log plot of the MSD of ions confined inside a slit graphitic nanopore. Surface charge densities on its two walls is \(\sigma = \pm 16.0 \ \mu\text{C/cm}^2\). The first ionic layer is close to the negatively charged pore wall, whereas the third layer of ions is near the positively charge pore wall. The dashed and solid lines denote the MSD of ions in the parallel direction and in the z-direction, respectively. Reproduced with permission from ref. [68] © 2011, American Chemical Society.

1.6. Research Objectives

ECs were first invented in 1950s but they have gained significant attention only recently because their performance, in particular energy density, cannot meet the need of mainstream applications. The current surge in interest in ECs and the impressive improvement of their performance are driven largely by recent breakthroughs in
development of novel materials for ECs such as ultra-porous nanopores featuring well-aligned micropores and RTILs capable of working at large (>3V) voltages. To greatly accelerate the development of ECs, a trail-and-error approach is both ineffective and cost-prohibitive given the vast varieties of possible materials that can be engineered and tested. Instead, research that allows the device level performance of ECs to be predicted based on the choice of electrode and electrolyte materials is needed.

Predicting the performance of ECs at device level must be built upon effective models for the charge storage at the single-nanopore level. The charge storage mechanisms in single nanopores are understood reasonably well in conventional EC materials where the classical EDL theories are valid. The charge storage mechanisms in many emerging materials, in which the classical EDL theories are expected to fail, however, are only beginning to be understood. The limited understanding of the charge storage in these materials is the weakest link in the current fundamental and applied researches on ECs.

In this dissertation, we focus on the charge storage mechanisms in novel EC materials at the single-nanopore level. In particular, we seek to address the following pressing issues at the frontier of EC materials development:

- **How does the capacitance of nanopores filled with RTILs vary with pore size?**

Recent experiments have shown that the capacitance of subnanometer pores filled with ionic liquids or organic electrolytes increases anomalously as the pore size decreases, thereby opening a new avenue for developing ECs with high energy density. However, this observation has been challenged by recent experimental studies, in which the capacitances
were found to be nearly pore-width independent for pores from 0.7 to 15 nm. The sharp contrast in the observed capacitance scaling was ascribed to the discrepancy in the specific surface area (used for determining the specific capacitance) probed by different methods. The debate about anomalous capacitance is in part fueled by the absence of a complete theoretical description of all the intricate processes taking place at the nanoscale. While several theoretical and heuristic models have been proposed to explain the anomalous enhancement of capacitance in sub-nanometer pores, many issues remain open. First, the polarizability of pore walls, which has been suggested to play an essential role in charge storage in nanopores, is usually neglected in atomistic simulations. Second, existing theoretical models are mostly based on extremely simplistic models for RTILs, and it is not immediately clear whether important physics are missed because of such simplifications. Finally, many subtle but important differences exist between experimental observations and theoretical predictions despite some agreements between them. For example, while the anomalous enhancement of capacitance reported in experiments are for integral capacitance, similar findings from theoretical studies and prior MC simulations are actually for differential capacitance measure at zero potential.[62] In fact, using the data presented in the prior MC simulations, one can show that, for an applied voltage of $\phi_w = 1.5$ V (which can be justified, assuming a symmetric capacitor, for an experimental potential drop of 3 V between the two electrodes), $C_{\text{int}}$ increases as the pore width decreases from 1.2 to 1.0 nm but decreases as the pore width further decreases, which disagrees with the experimental trend. The experimental trend of $C_{\text{int}}$ is recovered if $\phi_w < 1.0$ V. In this work, we will use MD simulations to understand the variation of EDL capacitance in
subnanometer pores with different pore sizes. We will use coarse-grained, but nevertheless more realistic RTIL models in these simulations. We will also build an analytical model for quantitatively relating the structure of EDLs in nanopores to their capacitance.

- **How does the capacitance of a nanopore filled with RTILs depend on operation voltages?** There is only limited theoretical works on how operating condition such as electrode voltage, which is a critical design parameter for ECs, affects charge storage in sub-nanometer pores. So far, only the variation of differential capacitance, $C_{\text{diff}}$, of a pore filled with ionic liquid has been examined. On the basis of MC simulations, Kondrat et al.[62] showed that $C_{\text{diff}}$ is constant at low voltage and reaches a maximum at certain voltage. At slightly higher voltages, $C_{\text{diff}}$ drops rapidly to zero. They “speculate that the peak in the capacitance vs. voltage curve is related to the ‘complete filling’ of the pore above a certain voltage”[62] but no further mechanistic explanation of this behavior was given. Similar behavior has also been observed by Skinner et al.,[60] although $C_{\text{diff}}$ did not drop to zero rapidly at larger voltages. Likewise, they did not provide a mechanistic explanation for the scenario that the pore is filled with RTILs at zero electrode voltage. Hence, the mechanisms of these observations remain elusive. Understanding these observations is helpful to set foundation to optimize operation condition for specified electrolyte. Here, we seek to clarify the relation among applied potential, EDL structure change and capacitance of EDLs by integrating molecular modeling with the analytical model which connects EDL structure and capacitance.

- **How do sub-nanometer pores connected with RTIL reservoirs charge?** Much of recent works on ECs resort to RTILs and ultra-nanoporous electrodes to reach high
energy density. However, an emerging issue in these developments is that the power density of ECs is often compromised [69] because ion transport in RTILs is slow in bulk and can be even slower in nanoconfinement, leading to sluggish charging dynamics and thus low power density. [67, 68, 70, 71] Given that an essential advantage of ECs compared to other energy storage devices is their high power density, this issue must be resolved. Fundamental research on charging of ECs is necessary to resolve this issue. While a few theoretical models have been proposed to delineate the charging of sub-nanometer pores using RTILs, some of the underlying assumptions of these models (e.g., constant ion diffusion coefficient through charging) are problematic and these models have yet to be validated through experiments (which is extremely difficult) or simulations. In this work, we simulate the charging of a single nanopore using RTILs under the action of an impulsively applied voltage. We seek to address the following issues. First, are there ‘universal features’ in the charging of such pores? Second, does the slow ion transport in bulk RTILs necessarily imply slow ion transport during charging? Finally, is it feasible to accelerate charging by tailoring the size, geometry, and the surface properties of nanopores? Resolving these issues can shape and guide the development of novel materials for ECs.

The rest of this dissertation is organized as follows. Chapter 2 describes the methodology and model used in this dissertation. Chapter 3 and 4 examine the thermodynamics of charge storage in nanopores, e.g., how the specific capacitance of EDLs in nanopores varies with the pore width and operation voltage under equilibrium conditions. Chapter 5 presents the study on the charging dynamics of nanopores when RTILs are used as electrolytes. Finally, conclusions are presented in Chapter 6.
Chapter 2

Methodology

In this dissertation, MD simulations are used to study the equilibrium and dynamic charge storage in sub-nanometer pores. The nanometer length scale of the electrode pore and ions can be directly resolved in such simulations. While such simulations are computationally intensive, they involve relatively few assumptions (especially when compared to analytical theories) and thus can provide a more accurate description of the physical phenomena we intend to study. In this Chapter, the MD methods are described, with a focus on how the polarizability of electrode walls, which has been suggested to play an essential role in charge storage in nanopores but is not included in conventional MD simulations, is modeled.

2.1. Molecular Dynamics Method

MD is a powerful method that allows one to understand the macroscopic properties of materials or transport processes to be understood using the molecular structure of materials and operating conditions as inputs.[72] In essence, an MD simulation starts by prescribing the initial coordinates (sometimes also velocities) of all the molecules inside the system. Next, the interactions between all molecules inside the system are computed using the atom configurations and force fields describing the interactions between atoms as input. The computed forces are then used to update the velocity and coordinates of the
atoms by following Newton’s law. The latter two steps are repeated until enough statistics are obtained.

Because all molecules are explicitly simulated, MD simulations are suitable for studying problems that span limited length and time scales (e.g., a few to ten nanometers in space and a few to tens of nanoseconds in time). Numerous textbooks and research papers have been published on the MD methods, and thus we will not elaborate on the basics of the MD methods here.

The application of MD methods to the simulation of charge storage in nanopores, however, has its own challenge. Specifically, in most classical MD simulations, the polarizability of surface is neglected and the charge on the surface is specified before the simulation and never updated. The nanopores in ECs, however, have strong metallic nature and, as a first approximation, can be taken as ideally polarizable objects. In general, the distribution of surface charge of a polarizable electrode is non-uniform because a charge near a conductor induces counter-charges on the conductor’s surface, which distribute in such a way that potential of the conductor remains uniform (shown in Figure 33(b)). These induced charges act to attract the original charge towards the conductor. The induction of charge on the conductor surface and the ensuing attraction on the original charge are historically termed the “image charge effects”. This is because, for a charge outside the conductor, the attraction it experiences due to the image charge effects is equal to the attraction by a counter-charge located at the mirror image position of the original charge. Image charge effects also affect the apparent interactions between charges, e.g., the
electrostatic interaction energy between two ions located at 0.4 nm above a planar conductor with a separation of 0.5 nm is halved due to the image charge effects.

Generally, there are two approaches to model polarizable electrodes (or equivalently, to account for the image charge effects). One way is to manipulate the charge distribution on the electrode and the other way is to keep constant potential on the electrode. These methods are mathematically equivalent to each other. Imposing charge on the electrode surface can be easily implemented with native MD technology. The difficulty is to impose correct surface charge distribution dynamically as the charge distribution changes with the change of position of ion nearby. Because of this difficulty, the polarizable nature of electrode surface is entirely neglected and uniform charge distribution is imposed on nanopores [57,58]. In our work, we implemented the method developed by Raghunathan et al. [73] to directly enforce constant electrical potential on the walls of the

![Diagram](image_url)

**Figure 33.** Concept of image charge effects. When a charge (shown as an anion here) is located near a polarizable electrode, a non-uniform surface charge is induced on the electrode surface so that the electrode potential on the electrode surface remains uniform. The electrostatic interaction between the original charge and the induced charges is equivalent to the interaction between the original charge and a fictitious image charge (shown as cation here).
electrode pores. The implementation of this method will be discussed in details in the following section. Our implementation here follows a similar route as taken by Clint earlier[74,75] but several improvements were made.

2.2. Method for Modeling of Polarizable Electrodes

The essence of the image charge effect is encapsulated in the Poisson equation:

\[ \nabla^2 \phi = -\rho_e/\varepsilon \]  

(2.1)

with the boundary conditions

\[ \phi|_{\text{conductor surface}} = \phi_w \]  

(2.2)

where \( \phi \) is the electrical potential, \( \rho_e \) is the charge density due to atomic charges inside the domain, \( \varepsilon \) is the permittivity of the medium (for explicit-solvent simulations, \( \varepsilon \) is typically taken as the vacuum permittivity \( \varepsilon_0 \)), and \( \phi_w \) is the prescribed electrical potential on the conductor surface. Note that:

1. The body of the conductor does not explicitly appear in these equations – only the surface of the conductor is necessary in defining the problem.

2. The image charge effects, i.e., induction of charges on the conductor surface by charges in the system, are not explicitly presented in these equations. Rather, such effects are implicitly embedded in the equipotential boundary condition (Equation. 2.2). The induced charge density on conductor surface is computed by \( \sigma_w = -\partial\phi/\partial n \), where \( n \) is the surface normal direction.

To model the image charge effects, i.e., solving Equation 2.1 and Equation 2.2 we enforce the equipotential condition on the conductor surface as given by Equation 2.2.
Without losing generality, we consider the system shown in Figure 34. To solve the potential inside the system (shaded region in Figure 34), we perform the decomposition:

$$\phi = \phi_{inf} + \phi_c$$  \hspace{1cm} (2.3)

where $\phi_{inf}$ is the electrical potential in the original system and its periodic images. It is governed by:

$$\nabla^2 \phi_{inf} = -\rho_e / \varepsilon$$  \hspace{1cm} (2.4)

here $\rho_e$ is the charge density in the original system. Since the solution domain of Equation 2.4 is infinite, no explicit boundary condition for $\phi_{inf}$ is needed. $\phi_c$ is a correction potential inside the original system (shaded region in Figure 34). It is governed by a Laplace equation:

$$\nabla^2 \phi_c = 0$$  \hspace{1cm} (2.5)

with the boundary condition:

$$\phi_c |_{conductor surface} = \phi_w - \phi_{inf} |_{conductor surface}$$  \hspace{1cm} (2.6)

where $\phi_{inf} |_{conductor surface}$ is the solution of $\phi_{inf}$ on the conductor surface. It is easy to prove that the superposition of $\phi_{inf}$ and $\phi_c$ satisfies Equation 2.1-2.2. Since Equation 2.4 is a Poisson problem in periodic domain, it will be solved by using the Particle Mesh Ewald (PME) method, i.e., $\phi_{inf} = \phi_{real} + \phi_{rec}$, where $\phi_{real}$ and $\phi_{rec}$ are the real space and reciprocal space potential in PME. With this choice, Equation 2.3 and 2.6 can be re-written as triplet decomposition:

$$\phi = \phi_{real} + \phi_{rec} + \phi_c$$  \hspace{1cm} (2.7)

$$\phi_c |_{conductor surface} = \phi_w - (\phi_{real} + \phi_{rec}) |_{conductor surface}$$  \hspace{1cm} (2.8)

The equipotential condition on conductor is rigorously satisfied by the triplet decomposition, and the electrostatic force acting on a charge $i$ due to the image charge
effects is given by $F_{i}^{img} = -q_i \nabla \phi_c$. The algorithm for computing electrostatic forces in a system that features image charge effects is summarized in Algorithm 1.

**Algorithm 1.** Computing electrostatic force in presence of image charge effects

1. Compute $\phi_{real}$, $\phi_{rec}$ and the electrostatic force acting on any charge $i F_i^{PME} = -q_i \nabla (\phi_{real} + \phi_{rec})$ by using the PME algorithm. Note that $\phi_{rec}$ is computed on a 3D FFT grid in the PME algorithm.
2. Compute $\phi_{rec}$ on conductor surfaces by interpolation of $\phi_{rec}$ available at the FFT grid, and compute analytically $\phi_{real}$ at any point $r_j$ on conductor surfaces by
   
   $$\phi_{real}|_{r_j} = \frac{1}{4 \pi \varepsilon_0} \sum_{i=1}^{N} q_i \text{erfc}(\beta r_{ij})/r_{ij}$$

   where $N$ is the number of charges in the system, $r_{ij}$ is the distance between charge $i$ and point $j$ on the conductor and $\beta$ is the parameter determining the relative weight of real space and reciprocal sum of the potential in PME.
3. Solve Equation 2.5 with boundary condition given by Equation 2.8. Details of this will be discussed next.
4. Compute the force acting on any charge $i$ due to the image charge effects by $F_i^{img} = -q_i \nabla \phi_c$
5. The total electrostatic force acting on charge $i$ is $F_i^{total} = F_i^{PME} + F_i^{img}$
Figure 34. Decomposition of potential $\phi$ into a potential $\phi_\infty$ and a correction potential $\phi_c$. Dash line denotes the simulation box, and the shaded region denotes the original system. Only two periodic images are shown here for clarity. $\phi_\infty$ can be solved by standard electrostatics algorithms (such as particle mesh Ewald) in molecular dynamics. The boundary condition for $\phi_c$ is obtained by using Equation 2.8 after $\phi_\infty$ is solved.

2.3. Implementation Details

The choice of grid spacing and discretization scheme used in solving $\phi_c$ govern the accuracy and the efficiency of the algorithm described in Section 2.2. For this boundary value problem, the accuracy of the solution is also strongly affected by the smoothness of boundary value. From Equation 2.8 and the fact that $\phi_{rec}$ is smooth, we conclude that the smoothness of $\phi_c$ on the conductor surfaces is dictated by the variation of $\phi_{real}$ on the conductor surface as computed by Equation 2.9. In typical molecular simulations, the closest approach between charges is $\sim 0.1$ nm, and the term $\text{erfc}(\beta r_{ij})$ in Equation 2.9 varies significantly over several angstroms. Therefore, the grid spacing on the conductor surface should be $\sim 0.1$ nm. In practice, the grid spacing is taken as the same as the FFT grid spacing in PME solver. Finally, Equation 2.5 is discretized on a three-dimensional compact stencil consisting of twenty seven points, which is a 4th order accuracy.
2.3.1. Method for Solving Discretized Laplace Equation

Many fundamental studies of interfacial phenomena deal with simple geometries, in which translational/rotational/mirrored symmetries of the surfaces exist. Here we exploit the symmetries of simple geometries to implement the algorithm described in previous sections by Green’s function method. In addition, the implementation of the Green’s function method is accelerated using Fast Fourier Transform (FFT).

2.3.2. Assemble $\phi_c$ using Green’s function method

We propose to solve Equation 2.5 (i.e. step 3 of Algorithm 1) using the Green’s function method when only simple conductor geometries are involved. Due to the linear nature of Equation 2.5, the solution of Equation 2.5 with the whole boundary is a summation of the solution with every boundary point. Assuming that there are M points on the conductor surface, the solution of linear Equation 2.5 can be written:

$$\phi_c = \sum_{i=1}^{M} \phi_{c,i} G(i)$$  \hspace{1cm} (2.10)

where $\phi_{c,i}$ is the boundary value of $\phi_c$ at point $i$ on the conductor surface (computed by Equation 2.8) and $G(i)$ is the Green function for point $i$. $G(i)$ is the solution of Equation 2.5 under condition that the boundary value of point $i$ taken as 1 and the boundary values of all other points on the conductor surface taken as 0. If we compute $G(i)$ before each simulation and store it in the computer memory, then the solution only needs to be assembled to provide the $\phi_c$ at each time step of the simulation.

A limitation of the above approach is that if $G(i)$ must be stored for each boundary point $i$, the memory cost becomes expensive (for typical system, the size of one Green’s
function is about 2 Mb. Actually, there is unnecessary to store Green’s function for each boundary point. For simple conductor surface geometries, \( G(i) \) for one point on the surface can be obtained easily by translating/rotating/mirroring the Green’s function at another point on the surface. For example, in the parallel electrode system shown in Figure 34, one need only to store the Green’s function for one arbitrary point \( i \) on the lower electrode. The Green’s function for other points on the lower electrode can then be obtained by shifting the Green’s function for point \( i \) in the horizontal plane. The Green’s function for points on the upper electrode can be obtained by rotation of the Green’s function corresponding to point \( i \) on the lower electrode. More details about shifting, rotation and mirroring Green’s function can be obtained from ref.[74].

2.3.3. Assemble \( \phi_c \) by Circular Convolution

The most expensive part of our algorithm for solving the correction potential \( \phi_c \) is assembling \( \phi_c \) from Green’s functions. Here, we propose to assemble \( \phi_c \) by circular convolution to reduce the computation cost. Because the computational domain for \( \phi_c \) is rectangular cuboid (see Figure 35), each Green’s function \( G_i \) is stored in the form of a three-dimensional (3D) matrix termed \( GM \). Likewise, because the surface of the electrodes considered in this work have rectangular shape, the boundary value of \( \phi_c \) on each grid point \( i \), \( \phi_{c,i} \) is stored in a two-dimensional (2D) matrix termed \( VE \).

The essential idea of the assembling \( \phi_c \) through circular convolution can be illustrated using a one dimensional (1D) example. For a line discretized into three points, the Green’s function of the first point, \( G(1) \) is \([1 2 1]\). Due to periodic boundary condition,
$G(2)$ is $[1 \ 1 \ 2]$ and $G(3)$ is $[2 \ 1 \ 1]$. The boundary values of the three points $\phi_{c,i}$ are $[1 \ 2 \ 3]$. $\phi_c$ can be assembled using Equation 2.10

$$\phi_c = \sum G_i \times \phi_{c,i} = [1 \ 2 \ 1] \cdot 1 + [1 \ 1 \ 2] \cdot 2 + [2 \ 1 \ 1] \cdot 3 = [9 \ 7 \ 8]$$

while $\phi_c$ can be further converted into circular convolution and computed using FFT:

$$= F([1 \ 2 \ 1]) \cdot F([1 \ 2 \ 3]) \text{ Fourier Inverse Transfer} \rightarrow [9 \ 7 \ 8]$$

By converting the direct assembly of $\phi_c$ into circular convolutions, the computation complexity is reduced from 2D $3 \times 3$ operation into 1D $3 \times 1$ operation. In general, for a vector with size $n$, the computation complexity of direct assembly is $\sim o(n \times n)$. The method above, by leveraging the efficiency of FFT in computing convolutions, has a computational complexity of $\sim o(n \log(n)).$[76]

The extension of the above method to situations in which the $GM$ is a 3D matrix straightforward since assembling. $\phi_c$ in 3D space, can be decomposed into assembling 1D $\phi_c$ vectors (shown in Figure 35). Since the above method is based on the method of circular convolution, it requires that the matrix $GM$ for a point $i$ on the electrode surface can be obtained by circular shifting of the matrix $GM$ for another point $j$ on the electrode surface in a certain dimension (e.g., the y-dimension in Figure 35(b)). In our MD simulations, we considered only two types of geometries, i.e., parallel plates (Figure 35(a)) and slit-shaped nanopores connected with reservoirs (Figure 35(b)). In the first type of system, circular
convolution can be performed in both $x$- and $y$- directions. In the second type of system, circular convolution can be performed only in the $y$-direction.

**Figure 35.** Assembly of $\phi_c$ vector-by-vector in 3D space. For clarity, different layers (three layers are shown here) are marked with different colors and only their boundaries are delineated using solid lines. The solid lines also denote the individual vectors from which the $\phi_c$ in the entire domain is assembled. The dashed lines are guides for eyes. (a) System with two parallel plates as electrodes. Here circular convolutions is possible in box $x$- and $y$-direction. (b) System with slit-shaped pore as electrode. Here circular convolution is possible only in the $y$-dimension.
CHAPTER 3

Equilibrium Charge Storage in Nanopores-Effects of Pore Size

In this Chapter we use molecular simulations to investigate EDLs in slit-shaped nanopores with polarizable walls in equilibrium with RTILs. We will focus on how the capacitance of the nanopore varies as a function of the nanopore size, which is one of the most important design parameters of electrode materials. Much of the work described in this chapter has been previously published in ref. [88]. As summarized in Chapter 1, there are outstanding controversies on whether the anomalous enhancement of capacitance observed in recent experiments does exist. In addition, prior simulations and theoretical studies, which providing useful insights, cannot fully clarify the charge storage in such nanopores. Our simulations reproduced the anomalous capacitance enhancement when the pore width reduces below a critical value, but also revealed that capacitance increases as the pore width increases beyond another critical value. We provide mechanistic insights into these scaling behaviors by delineating the relation between the structure and the capacitance of the EDLs in these pores. We show that the EDLs inside sub-nanometer pores filled with RTILs represent a new capacitor regime in which the ubiquitously used transmission-line model for ECs fails qualitatively.
3.1. MD System and Methods

3.1.1. MD System

Figure 36(a) shows a schematic of the MD system that consists of a slit-shaped pore in contact with a reservoir of RTILs. The entire electrode surface (the horizontal pore walls and the vertical walls blocking the RTIL reservoir) is modeled as an equipotential surface with a net charge. The magnitude of surface charge and electrical potential of the pore walls was not directly controlled, but determined from the ion distribution obtained in the MD simulations using Faraday cage effect (discuss in details later). Ions were modeled using semi-coarse grained models that 1) resolve their geometrical anisotropy and van der Waals interactions, which are important in determining EDL capacitance,[50] and 2) assign the

![Figure 36. Schematics of the simulation system and ions. (a) A schematic of the simulation system featuring a slit-shaped nanopore in equilibrium with a RTIL reservoir. The electrode features an equipotential surface that carries a net charge that is balanced by ions inside the simulation box (denoted by the red dashed line). (b) Schematics of the semi-coarse grained model for the cation and the anion. The red sphere in the cation and the green sphere in the anion denote the atoms which carry charges of $+e$ and $-e$, respectively.](image)

60
charge of each ion to one of its atoms (Figure 36(b)). These models were adopted in spirit of the hard sphere model[61] which has been shown to capture key features of EDLs in nanopores. Simulations in which the charge of each ion was distributed on its multiple atoms yielded qualitatively similar results, in agreement with our prior finding that charge delocalization plays a relatively unimportant role in determining the thermodynamic properties of EDLs.[50] We note that, however, charge de-localization plays a key role in determining dynamics of RTILs. Hence caution must be used if the present RTIL model is to be used to study EDL dynamics.

3.1.2. Simulation Method

Simulations were performed using a customized MD package Gromacs.[77] The methods for enforcing electrical potential on an electrode surface and for computing electrostatic interactions are the same as that used in ref.[78]. Using the Faraday cage effect, the total charge on the electrode surface was controlled by fixing corresponding amount of charges inside the electrode (denoted by the shaded regions in Figure 36(a) and by adjusting the number of ions inside the system to balance these charges. The length of the pores was $\geq 6.0$ nm but varied slightly for different pores. The RTIL layers adjacent to each vertical plate are thicker than 3 nm so that bulk-like RTILs are found at positions away from the plate. The electrode was cut from a cubic lattice (lattice constant: 0.17 nm) and its atoms were frozen. A united atom coarse grain model for the cation consisted of a 7-atom ion featuring a ring with the geometry of the native imidazolium. The anion was modeled as a 5-atom ion with the geometry of $\text{BF}_4^-$. The charge of each ion was located on one of its atoms as shown in Figure 36(b). A background dielectric constant of 2.0 was
used to account for the electronic polarization of the ions. The Lennard-Jones parameters for all atoms were the same as those of carbon.[78]

3.1.3. Evaluation of Integral Capacitance

To compute the integral capacitance, two systems were simulated for each pore width: in a quasi-potential of zero charge (qPZC) system, the net charge of the entire electrode was zero; in a charged (CHG) system, the net charge of the entire electrode was positive, and the anion sketched in Figure 36(b) serves as the counter-ion. The potential of the pore wall with respect to the RTIL reservoir in these two systems was determined to be $\phi_{qPZC}$ and $\phi_{CHG}$, respectively. The surface charge densities of the pore wall were determined as $\sigma_{qPZC}$ and $\sigma_{CHG}$ by averaging the net charge over the whole electrode surface.\(^1\) $\phi_{qPZC}$, $\phi_{CHG}$, $\sigma_{qPZC}$, and $\sigma_{CHG}$ for the various pores studied are summarized in

Table 3. In the qPZC systems, $\sigma_{qPZC}$ deviates slightly from zero due to the different affinity of ions to the horizontal pore wall and the open vertical walls. The integral capacitance of each pore was computed using $C_{int}=\Delta\sigma/\Delta\phi$, where $\Delta\sigma = \sigma_{CHG} - \sigma_{qPZC}$ is the increase of pore surface charge density as the pore is electrified by $\Delta\phi = \phi_{CHG} - \phi_{qPZC}$ volts. $\Delta\phi$ of all pores studied is within 0.1 V from the target value of 1.68 V (cf.

\(^1\) For equilibrium study, averaging the charge density over the entire electrode surface is acceptable, although there is some error for the charge density near the pore mouth, so called “mouth effects”. In dynamic study, however, the region near pore mouth become important and the surface charge density is averaged based on the region 0.5 - 1 nm away from the pore mouth.
Table 3), which is similar to the experimental potential.[53] Since $\sigma_{\text{CHG}} >> \sigma_{\text{qPZC}}$ and $\sigma_{\text{qPZC}} \approx 0$ in all pores, the computed capacitance approximates well the integral capacitance defined by $C_{\text{int}} = \sigma_{\text{CHG}} / (\phi_{\text{CHG}} - \phi_{\text{PZC}}),[79]$ where $\phi_{\text{PZC}}$ is the surface potential of a neutral pore.

Table 3. Surface charge density ($\sigma$) and electrical potential ($\phi$) in the qPZC and CHG systems for various nanopores. The electrical potential in bulk RTILs is taken as zero.

<table>
<thead>
<tr>
<th>pore width W (nm)</th>
<th>qPZC system</th>
<th>CHG system</th>
<th>$\Delta \phi$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\sigma_{\text{qPZC}}$ (C/m$^2$)</td>
<td>$\phi_{\text{qPZC}}$ (V)</td>
<td>$\sigma_{\text{CHG}}$ (C/m$^2$)</td>
</tr>
<tr>
<td>0.75</td>
<td>-0.007</td>
<td>0.117</td>
<td>0.172</td>
</tr>
<tr>
<td>0.78</td>
<td>-0.005</td>
<td>0.0104</td>
<td>0.150</td>
</tr>
<tr>
<td>0.84</td>
<td>-0.003</td>
<td>-0.035</td>
<td>0.118</td>
</tr>
<tr>
<td>0.91</td>
<td>-0.001</td>
<td>-0.138</td>
<td>0.108</td>
</tr>
<tr>
<td>1.04</td>
<td>0.006</td>
<td>-0.266</td>
<td>0.115</td>
</tr>
<tr>
<td>1.12</td>
<td>0.007</td>
<td>-0.283</td>
<td>0.121</td>
</tr>
<tr>
<td>1.17</td>
<td>-0.002</td>
<td>-0.084</td>
<td>0.148</td>
</tr>
<tr>
<td>1.26</td>
<td>-0.005</td>
<td>-0.028</td>
<td>0.157</td>
</tr>
</tbody>
</table>

3.2. Capacitance Variation in Slit Nanopores

3.2.1. MD Predictions

Figure 37(a) shows the variation of capacitance ($C_{\text{int}}$) with the center-to-center width ($W$) of the pores, where a U-shaped $C_{\text{int}}$-$W$ curve is observed. The trend revealed by the left branch of the $C_{\text{int}}$-$W$ curve agrees with that reported experimentally (see Figure 37(b)): it simultaneously captures the sharp increase of $C_{\text{int}}$ as $W$ decreases from
0.91 to 0.75 nm and its slight change as $W$ decreases from 1.12 to 0.91 nm, the latter was not found by prior analytical model.[17] We note that the pore width reported in ref. [53] is most likely the “accessible width”, which is about one van der Waals diameter (~0.3 nm) smaller than the “center-to-center width” used in Figure 37(a). If $C_{\text{int}}$ in Figure 37(a) is plotted against the “accessible width”, it would shift toward smaller pore width by ~0.3 nm, suggesting that the capacitance enhancement would appear in a narrower pore width range (0.45 to 0.61 nm) than experiments (0.7 to 0.8 nm).[53] Such a difference can be attributed to the fact that the counter-ion in our simulation (~0.52 nm in diameter) is smaller than that used in the experiments (the largest dimension of both anions and cations is ~0.8 nm).[53] Nevertheless, the trend of the capacitance scaling, the focus of the present study, bears a close resemblance to the experimental one.

The sharp increase of $C_{\text{int}}$ with $W$ ranging from 1.12 to 1.26 nm has not been directly reported experimentally but is indirectly supported by measurements. Figure 37(b) shows that the experimental capacitance of a 1.1 nm pore is ~7 $\mu$F/cm$^2$, [53] whereas the experimental capacitance of planar electrodes made of glassy carbon in the same electrolyte is ~12 $\mu$F/cm$^2$.[24,80] This difference implies that the capacitance of pores larger than 1.1 nm should increase toward the planar surface value with increasing $W$. Figure 37(a) does show that the capacitance increases with increasing pore width but it does not approach $C_{\infty}$ in an asymptotic way since the capacitance in a 1.26 nm pore is higher than $C_{\infty}$. This suggests that as the pore width further increases, capacitance will decrease again and eventually reaches $C_{\infty}$. How $C_{\infty}$ is reached as $W$ increases, e.g., by a damped oscillation or by a smooth decay, is an interesting question, and may be pursued in future
studies. However, we expect the capacitance will not vary significantly in wider pores based on the insights obtained from the analysis below. Specifically, as will be shown later, the pore capacitance is controlled primarily by the change of ion solvation in pores as the pore becomes electrified. When pore width $W$ increases, the solvation experienced by ions in different pore becomes increasingly similar. Hence the change of their solvation upon pore electrification will not differ significantly as $W$ increases, which subsequently resulting a weaker dependence of capacitance on $W$. The capacitance scaling trend shown in Figure 37 was also observed in simulations in which the charge of cation and anion was distributed among all their atoms, although the capacitance increases less sharply (~20% less sharper compared to the data herein) as pore size varies from 0.91 to 0.75 nm.

Figure 37. EDL capacitance computed from MD simulations. (a) Variation of EDL capacitance from MD simulations in pores with center-to-center width from $W = 0.75$ to 1.26 nm. $C_\infty$ denotes the capacitance of an open planar electrode. (b) Variation of EDL capacitance in pores filled with EMI-TFSI electrolyte reported in ref. [81]. The experimental capacitance, $C_{\infty,\text{exp}}$, was measured on planar glassy carbon electrodes in the same electrolyte.[80] The statistical error for the 1.17 nm
pore is relatively large because ion diffusion in this pore is very slow (due to the nearly crystal-like packing inside the neutral pore), which renders simulation difficult.

The above results suggest that the dependence of the nanopore capacitance on the pore width is more complex than previously expected in experimental and theoretical studies. In view of the ongoing debate on the anomalous capacitance enhancement in sub-nanometer pores, our results strongly support the existence of the anomalous capacitance enhancement. Additionally, the sharp increase of capacitance over very narrow pore widths (0.75 - 0.91 nm and 1.12 - 1.26 nm) and the U-shaped $C_{\text{int}}-W$ curve for $W < 1.26$ nm (and the possibly oscillatory $C_{\text{int}}-W$ curve for $W > 1.26$ nm) indicates that, for the pore-width dependent capacitance to be observed experimentally, it is essential that the electrode materials used in experimental characterization feature unimodal and narrow pore-width distribution. When electrodes with multimodal and/or wide pore-width distribution are used, the capacitance variation in different pores can be averaged out. In this regard, we note that most of the electrodes used in ref. [81], where the capacitance was found to be nearly pore-width independent, are based on activated carbons. Since such electrodes are prone to a relatively wide pore-width distribution, it is possible that the independence of capacitance on pore width observed in those experiments is caused by the averaging effect.

### 3.2.2. EDL Structure inside Nanopores

The capacitance scaling shown in Figure 37(a) is ultimately controlled by the different EDL structures in various pores. Figure 39 shows the cation and anion density profiles across pores with $W = 0.75, 0.78, 0.84, 0.91, 1.04, 1.12, 1.17$ and $1.26$ nm in the qPZC system and in the CHG system. We observe that, when the pore is neutral or nearly
neutral, a large amount of ions accumulate inside the pore. In pores with $W = 0.75$ and 0.78 nm, cations and anions form a monolayer in the pore center, due to the wall confinement. In wider pores, anions always form one layer near each wall, which is an expected behavior for molecules confined in pores wider than twice their diameter. The cation distribution, however, shows more complex behavior: in pores with $W = 0.84$ and 0.91 nm, they reside rather uniformly across the accessible width of the pore; in pores with $W = 1.12$ nm, they accumulate in a narrow band near the pore central plane; in pores with $W = 1.17$ and 1.26 nm, they form a distinct layer near each pore wall. The different cation distributions in these pores are mainly driven by the tendency of cations to maximize their “solvation” by anions.\(^2\) We computed the solvation number of cations across these pores (i.e., the number of anions within $r_1$ from a cation, where $r_1$ is the first local minimum of the cation-anion radial distribution function) and found that its distribution profile resembles the cation density profile. The ion distribution profiles in electrified pores are simpler. In pores with $W = 0.75$ and 0.78 nm, limited amount of cations (co-ions) and mostly anions (counter-ions) form a monolayer in the pore center. In wider pores, counter-ions form two distinct layers, while co-ions accumulate mainly in the pore center.

The observed ion distributions are closely related to the geometry of the ions used here. For example, in neutral pores with $W = 1.17$ and 1.26 nm, contact pairs of cations

\(^2\) The “solvation” in RTILs refers to the electrostatic and van der Waals interactions between a cation and its surrounding anions (and vice versa). This is qualitatively similar to organic electrolytes consisting of ions solvated by solvent molecules. The quotation marks are removed for later usage of solvation in for simplicity.
and anions are positioned side-by-side across the pore. Such crystal-like packing of cations and anions results in strong solvation of these ions, which in turn leads to a distinct layer of cation/anion near each pore wall and significantly slowed ion diffusion inside the pores (the diffusion coefficients of both ions are less than 1/10 of their bulk value). In neutral pores with \( W = 1.12 \text{ nm} \), however, the pores are too narrow to accommodate a contact pair of cation and anion positioned across the pore, and cations must reside in the pore center to maximize their solvation. Since ions used in this study are representative of RTILs in which the cation shape is strongly anisotropic and the anion is quasi-spherical, the results obtained here are relevant to this broad class of RTILs.

3.2.3. Physical Origins of Capacitance Variation

To gain mechanistic insights into the capacitance scaling behavior shown in Figure 37(a) and its relation with the EDL structure shown in Figure 39, we derive a model for the EDL capacitance. Consider a pore in equilibrium with an RTIL reservoir. Under an electrifying potential \( \phi \), the pore surfaces acquire a charge density of \( \sigma \) (throughout this work, the electrical potential in reservoir is taken as zero). The electrochemical potential of an ion \( i \) inside the pore, \( \mu_{i,\text{pore}(\phi,\sigma)} \), is the free energy cost for inserting the ion into the pore, which is equal to its electrochemical potential in the reservoir (\( \mu_{i,\infty} \)):

\[ \text{------------------------} \]

\( ^3 \) This can be deduced from the ion distribution profile shown in Figure 3. Specifically, the separation between the cation density peak near one pore wall and the anion density peak near the opposite wall is 0.32 nm, which is nearly the closest approach (~0.3 nm) between the charged atoms in the anion and in the cation.
\[
\mu_{i, \text{pore}(\phi, \sigma)} = E_{i \rightarrow \text{all}}(\sigma) + \Delta E_{\text{all others}}(\sigma) - T \Delta S(\sigma) = \mu_{i, \infty} \tag{3.1}
\]

where the first term on the right-hand side is the interaction energy between the inserted ion and all species in the pore including the walls, and \((\sigma)\) is used to emphasize that the configuration of all species (including ion \(i\)) used to determine \(E_{i \rightarrow \text{all}}\) corresponds to the state at which the pore has a surface charge density of \(\sigma\); the second term is the change of interaction energy between all other species as the ion is inserted into the pore, and it includes the cavitation energy cost when the ions around the inserted ion are separated from each other to generate a cavity to accommodate the inserted ion; the third term stands for entropic effects. Splitting the energy between ion \(i\) and all species into an electrostatic part \(E_{i \rightarrow \text{all}}^{\text{elec}}(\sigma)\) and a non-electrostatic part \(E_{i \rightarrow \text{all}}^{\text{non-elec}}(\sigma)\), we have

\[
E_{i \rightarrow \text{all}}^{\text{elec}}(\sigma) + E_{i \rightarrow \text{all}}^{\text{non-elec}}(\sigma) + \Delta E_{\text{all others}}(\sigma) - T \Delta S(\sigma) = \mu_{i, \infty} \tag{3.2}
\]

Using the superposition principle in electrostatics, the energy of an ion \(i\) due to its electrostatic interactions with all species inside a polarizable slit-shaped pore with a surface potential of \(\phi\) is

\[
E_{i \rightarrow \text{all}}^{\text{elec}}(\sigma) = q_i \phi + \sum_{j \neq i} E_{i \rightarrow j}^{\text{elec}}(\sigma) + E_{i, \text{self}}(\sigma) \tag{3.3}
\]

where \(q_i\) is the charge of ion \(i\), \(j\) is the index of all ions, \(E_{i \rightarrow j}^{\text{elec}}(\sigma)\) is the electrostatic interaction energy between ions \(i\) and \(j\) given by[82]

\[
E_{i \rightarrow j}^{\text{elec}}(\sigma) = \frac{q_i q_j}{\varepsilon \varepsilon_0 W} \sum_{n=1}^{\infty} \sin\left(\frac{n \pi z_i}{W}\right) \sin\left(\frac{n \pi z_j}{W}\right) K_0\left(\frac{n \pi R_{ij}}{W}\right) \tag{3.4}
\]
where $\varepsilon_0$ and $\varepsilon_r$ are the vacuum permittivity and background dielectric constant, respectively; $z_i$ and $z_j$ are the distance of ion $i$ and $j$ from the lower pore wall, respectively; $K_0$ is the zeroth order modified Bessel function of the second kind, which decreases sharply as its argument increases; $R_{ij}$ is the lateral ion-ion separation, i.e., separation between ions $i$ and $j$ in direction parallel to the pore wall; $E_{i,\text{self}}$ is the self-energy of ion $i$, which depends on the pore width $W$ and ion’s position inside the pore.[82,83] Using Equation (3.2) and (3.3), we obtain

$$\phi = \left[ \mu_{i,n} - \sum_{j \neq i} E_{i \rightarrow j}^{\text{elec}}(\sigma) - E_{i,\text{self}}^{\text{elec}}(\sigma) - E_{i \rightarrow all}^{\text{non-elec}}(\sigma) - \text{ETS}(\sigma) \right] / q_i \quad (3.5)$$

where $\text{ETS}(\sigma) = \Delta E_{\text{all-others}}(\sigma) - T\Delta S(\sigma)$. Applying Equation (3.5) to an electrified pore (surface potential: $\phi$; surface charge density: $\sigma$) and a neutral pore (surface potential: $\phi_{\text{PZC}}$) with the same width, and using $C_{\text{int}} = \sigma / (\phi - \phi_{\text{PZC}})$, we obtain

$$C_{\text{int}} = \frac{q_i \sigma}{\Delta E_{i \rightarrow all}^{\text{elec}}(0 \rightarrow \sigma) + \Delta E_{i \rightarrow all}^{\text{non-elec}}(0 \rightarrow \sigma) + \Delta E_{i,\text{self}}^{\text{elec}}(0 \rightarrow \sigma) + (\text{ETS}(\sigma) - \text{ETS}(0))} \quad (3.6)$$

where $\Delta E_{i \rightarrow all}^{\text{elec}}(0 \rightarrow \sigma) = \sum_{j \neq i} E_{i \rightarrow j}^{\text{elec}}(\sigma) - \sum_{j \neq i} E_{i \rightarrow j}^{\text{elec}}(0)$ is the change in electrostatic interaction energy of an ion $i$ with other ions as the pore surfaces acquire a charge density $\sigma$ (note that the number of counter/co-ions and their positions inside the pore change accordingly during this process). $\Delta E_{i \rightarrow all}^{\text{non-elec}}(0 \rightarrow \sigma) = E_{i \rightarrow all}^{\text{non-elec}}(\sigma) - E_{i \rightarrow all}^{\text{non-elec}}(0)$ and $\Delta E_{i,\text{self}}(0 \rightarrow \sigma) = E_{i,\text{self}}(\sigma) - E_{i,\text{self}}(0)$ are the changes in non-electrostatic energy and in self-energy of an ion $i$ as the pore surfaces acquire a charge density $\sigma$, respectively. The first three terms in the denominator of Equation (3.6) are expected to dominate over the remaining terms that represent higher order interactions and entropic effects.
$\Delta E_{i,\text{self}}(0 \rightarrow \sigma)$ is small and can be neglected. Consequently, for scaling of capacitance, we have

$$C_{\text{int}} \approx q_i / \left[ -\Delta E_{\text{ions}}^{\text{elec}}(0 \rightarrow \sigma)/\sigma - \Delta E_{i \rightarrow \text{wall}}^{\text{non-elec}}(0 \rightarrow \sigma)/\sigma \right] \approx q_i / \left[ -\Delta E_{i \rightarrow \text{wall}}^{\text{tot}}(0 \rightarrow \sigma)/\sigma \right]$$  (3.7)

where $\Delta E_{i \rightarrow \text{wall}}^{\text{tot}} = \Delta E_{i \rightarrow \text{ions}}^{\text{elec}} + \Delta E_{i \rightarrow \text{wall}}^{\text{non-elec}}$. Equation 3.7 correlates the capacitance of EDLs in a pore with the variation of ion energy (and ultimately the variation of EDL structure) as the pore is electrified.

To understand the physical meaning of Equation 3.7, we consider a pore electrified by a positive potential $\phi$. Here, each cation inside the pore is affected by two factors when the pore becomes electrified: 1) its energy due to the interaction with the pore walls increases by $q_i \phi$, and 2) its energy due to the interaction with others species becomes more negative (and stabilized) when the pore acquires net negative space charge, i.e., $\Delta E_{i \rightarrow \text{wall}}^{\text{tot}} < 0$.

While the first factor tends to drive the cations out of the pore, the second factor tends to hold them inside. Consequently, for each unit negative space charge the pore gains (or, for each unit positive surface charge the pore walls gain), if the energy gain of cations due to their interactions with other species inside the pore is significant, i.e., $-\Delta E_{i \rightarrow \text{wall}}^{\text{tot}} / \sigma$ is large, it will be difficult to remove them from the pore. This tends to lead to a small net negative space charge in the pore and accordingly to a small capacitance, as predicted by Equation 3.7. Below we delineate the physical origins of the capacitance scaling shown in Figure 37(a) by analyzing the energy change of cations inside each pore as it becomes positively electrified. A similar analysis has also been performed for anions but is not shown for brevity.
Figure 38 shows the variation of $\Delta E_{i\rightarrow \text{ions}}^{\text{tot}}(0 \rightarrow \sigma)/\sigma$ and its two components for cations. We observe that 1) the scaling of capacitance in these pores can be explained by the scaling of $\Delta E_{i\rightarrow \text{all}}^{\text{tot}}(0 \rightarrow \sigma)/\sigma$ using Equation 3.7, and 2) $\Delta E_{i\rightarrow \text{all}}^{\text{tot}}(0 \rightarrow \sigma)/\sigma$ is dominated by $\Delta E_{i\rightarrow \text{ions}}^{\text{elec}}(0 \rightarrow \sigma)$. The latter observation indicates that, as a pore is electrified, the change of a cation’s energy due to the change in its electrostatic interactions with other ions, $\Delta E_{i\rightarrow \text{ions}}^{\text{elec}}(0 \rightarrow \sigma)$, is more important than the change in its non-electrostatic interactions with other species. These observations indicate that $\Delta E_{i\rightarrow \text{ions}}^{\text{elec}}(0 \rightarrow \sigma) + \Delta E_{i\rightarrow \text{all}}^{\text{non-elec}}(0 \rightarrow \sigma)$ in Equation (3.6) indeed dominates over the term $ETS(\sigma)-ETS(0)$, and Equation 3.7 is justified. They also indicate that we can understand the capacitance scaling in Figure 37(a) by elucidating the physical origins of the scaling of $\Delta E_{i\rightarrow \text{ions}}^{\text{elec}}(0 \rightarrow \sigma)/\sigma$ shown in Figure 38.

![Figure 38](image_url)

**Figure 38.** Variation of $\Delta E_{i\rightarrow \text{all}}^{\text{tot}}(0 \rightarrow \sigma)/\sigma$ and its two components in the pores studied. The ion energy in the qPZC system is used to approximate the ion energy in neutral pore.
In pores within $0.75 \leq W \leq 0.91$ nm, $\Delta E_{i\rightarrow ions}^{elec}(0 \rightarrow \sigma)/\sigma$ becomes less negative as $W$ decreases, and this is caused by two factors. Firstly, the screening of electrostatic interactions increases as $W$ decreases. As first pointed out in ref. [62] and shown in Equation (3.4), the electrostatic interaction between two ions confined in a polarizable pore decreases sharply as $R_{ij}/W$ increases. Consequently, as the same amount of net negative space charge is introduced into a pore by adding anions or removing cations, the energy gain of a cation inside a narrower pore tends to be smaller. Secondly, the degree of a two-dimensional nature of ion solvation increases as $W$ decreases. As $W$ decreases from 0.91 to 0.75 nm, cations/anions inside the pores are increasingly solvated by their counterparts located near their equator (the line connecting the north and south poles of an ion is assumed to be normal to the pore walls) because of wall confinement. As such, anions introduced into (and the cations removed from) narrower pores during pore electrification tend to have a larger lateral distance $R_{ij}$ from the cations remaining inside the pores, which leads to a less negative $\Delta E_{i\rightarrow ions}^{elec}(0 \rightarrow \sigma)/\sigma$ in narrower pores according to Equation (3.4).

In pores within $0.91 < W \leq 1.12$ nm, $\Delta E_{i\rightarrow ions}^{elec}(0 \rightarrow \sigma)/\sigma$ changes slightly as $W$ changes, and this can be understood as follows. As $W$ decreases from 1.12 to 0.91 nm, the increased screening of electrostatic interactions tends to make $\Delta E_{i\rightarrow ions}^{elec}(0 \rightarrow \sigma)/\sigma$ less negative. However, as these pores become positively electrified, the newly added anions can distribute near the north/south pole of the remaining cations in the pore due to two effects: 1) the pores are wide enough to allow three-dimensional solvation of ions, and 2) during pore electrification, cations originally located near neutral walls (interfacial cations) are removed and leave more space for the anions to be added into the pore. Of these effects,
the second one is more important in the 0.91 nm pore as there are more interfacial cations in the neutral 0.91 nm pores (see Figure 39). Since a displacement of interfacial cations would decrease the lateral anion-cation distance \( R_{ij} \), the second effect tends to make \( \Delta E_{\text{elec}}^{i-\text{ions}}(0 \rightarrow \sigma)/\sigma \) more negative as \( W \) decreases from 1.12 to 0.91 nm. This effect counteracts the increased screening of electrostatic interactions in narrower pores and the result is that \( \Delta E_{\text{elec}}^{i-\text{ions}}(0 \rightarrow \sigma)/\sigma \) changes slightly as \( W \) decreases from 1.12 to 0.91 nm.

In pores within \( 1.12 < W \leq 1.26 \) nm, \( \Delta E_{\text{elec}}^{i-\text{ions}}(0 \rightarrow \sigma)/\sigma \) becomes less negative as \( W \) increases, and this trend is mainly caused by the qualitative change of ion solvation structure as \( W \) changes. As shown in Figure 39, in a neutral 1.12 nm pore, cations are located mostly in the center of the pore to maximize their solvation by anions located near the two walls. As the pore walls become positively electrified, the number of anions solvating each cation increases but the solvation structure of these cations remains largely unchanged because they are still located at the pore center. In comparison, the 1.26 nm pore follows a qualitatively different scenario. As shown in Figure 39 and described earlier, when these pores are neutral, cations and anions form contact pairs and are positioned side by side across the pore. Such a solvation structure leads to small lateral separation \( R_{ij} \) between a cation and its solvation anions, which in turn leads to strong electrostatic interactions according to Equation (3.4). As the pore walls become electrified, the solvation structure of cation changes drastically: cations are displaced into pore center and can no longer be positioned side-by-side with anions across the pore. Such a change in cation solvation structure increases the lateral separation \( R_{ij} \) between a cation and some of its solvation anions, and thus weakens their electrostatic interactions. Consequently, as the pore walls of a 1.26 nm
Figure 39. The upper panels of each figure show the ion density in the qPZC systems, and the lower panels show the ion density in the CHG systems of each slit studied. The pore wall surface charge density and surface potential for each system are shown in Table 2. The position of ions is based on the location of their charged atoms.
pore become electrified, the energy gain of each cation due to its electrostatic interaction with anions, is reduced by the above weakening mechanism. Since this weakening mechanism exists in the 1.26 nm pore but not in the 1.12 nm pore, \( \Delta E_{\text{lec}}^{i\rightarrow \text{ions}}(0 \rightarrow \sigma)/\sigma \) tends to be less negative in the 1.26 nm pore.

The above discussions demonstrate that the scaling of EDL capacitance in pores is controlled by the screening of electrostatic interactions in different nanopores, and, more importantly, by the ion solvation structure inside nanopores and how it changes as nanopores are electrified. In particular, large capacitance can be expected if the ion solvation is weak (as in the 0.75 nm pore) or if the electrification of a pore disrupts the strong ion solvation structure inside it (as in the 1.26 nm pore). These insights have rich ramifications in the design of electrode materials and electrolytes for optimizing the capacitance of ECs. Specifically, they suggest that one can optimize the capacitance of a nanopore through the manipulation of ion solvation inside the pore by tailoring the size, shape, and other chemical details of ion pairs for the nanopore. Such an approach goes beyond the state-of-the-art practice in which the capacitance of a nanopore is optimized by matching the size of the counter-ion with the nanopore width[53] and provides richer opportunities for enhancing the capacitance of ECs by enabling one to exploit the vast chemical diversity of RTILs.[84]

3.3. A New Capacitor Regime

To understand the collective behavior of EDLs in ECs (e.g., their charging kinetics), each pore in ECs is often represented by an equivalent circuit with capacitors connected in
parallel and with resistors in serial.[63] Such a transmission line model has been extensively used in ECs research, and it implicitly requires that, at equilibrium, the potential drop between the pore wall and the bulk electrolyte occurs *entirely* inside each pore, *i.e.*, the potential drop between the pore center and the bulk electrolyte is zero. However, this assumption is not valid from our simulation.

Figure 40 shows the distribution of electrical potential across the half-width of several pores studied in this work. The total potential drop from each pore surface to the bulk RTIL is shown in Table 3. We observe that the potential at the pore center generally deviates strongly from zero: the electrical potential at the pore center increases from -1.10 to 0.44 V as the pore width varies from 0.75 to 1.26 nm while the total potential drop from the electrode surface to the bulk RTIL is close to 1.68 V in all pores. The deviation of electrical potential at the pore center from its value in the bulk electrolyte can be understood qualitatively as follows. The electrochemical potential of an ion *i* in RTILs, $\mu_i$, depends both on the average electrical potential at its position (cf. the second term in Equation (3.3) and its interactions with surrounding ions (cf. the third term in Equation (3.3)). Since the interactions of an ion located at the pore center with its surrounding ions differ significantly from that of the same ion located in the bulk RTILs (due to the different ion solvation structure at these positions), and $\mu_i$ of an ion at the pore center is equal to that in the bulk RTILs, the electrical potential at the pore center should deviate from that in the bulk.
The non-validity of the potential assumption suggests that the transmission line model breaks down in pores studied here, and a capacitor regime qualitatively different from that in wide pores emerges. Specifically, although the charges on the pore wall are balanced by ions enclosed between the pore wall and the pore central plane, there exists a significant potential drop between the pore center and the bulk electrolyte, which has no analogy in classical capacitors. Consequently, although the pore walls and the EDLs together can still be viewed as capacitors, they can no longer be described by the transmission line model. The transmission line model will be accurate when pore width becomes large enough so that the EDLs near opposing pore walls no longer interact with each other. Since the thickness of EDL in RTILs is usually 1-3 nm, we expect that the transmission line model will be accurate in pores wider than 2-6 nm.

![Figure 40. Distribution of electrical potential normalized across half-width of the pores. The inset shows a schematic of the transmission line model widely used to model EDLs in ECs.](image)

### 3.4. Conclusion
In summary, we studied the EDLs in nanopores filled with RTILs using MD simulations that account for the geometrical anisotropy of ions and the polarizability of pore walls. The results show that the scaling of pore capacitance exhibits a more complex behavior than previously reported, and the possible oscillating capacitance as a function of pore width scaling behavior revealed helps settle the debate on the validity of anomalous capacitance enhancement in sub-nanometer pores and points to opportunities for new experimental studies.

Furthermore, using a newly developed mechanistic model for nanopore capacitance, we rationalized the observed scaling behaviors and showed that ion solvation structure in nanopores and its response to pore electrification play a critical role in controlling the capacitance. This insight lays the theoretical basis for optimizing pore capacitance through the manipulation of ion solvation inside nanopores by tailoring the chemical details of ion pairs for a given pore, e.g., pore size.

Finally, we showed that the assumption of potential drop inside EDLs in nanopores filled with RTILs is not valid. The invalidity of a fundamental assumption of the transmission line model suggests that this model breaks down qualitatively thus a new capacitor regime emerges. The results suggest that the predictions of the transmission line model, which is used ubiquitously in ECs research, must be carefully reassessed in the future.
CHAPTER 4

Equilibrium Charge Storage in Nanopores—Effects of Electrode Voltage

In Chapter 3, we analyzed the physics origin of the capacitance scaling of nanopore filled by RTILs. The capacitance of different nanopores were studied under similar operation condition e.g., electrode voltage difference is within 5% for all simulations. In practice, how operating conditions affect the charge storage in nanopore is not well understood. In this Chapter, we aim to elucidate the impact of operating conditions such as electrode voltage on the capacitance of nanopore. Much of the work described in this chapter has been previously published in ref. [94].

4.1. Method and simulation system

The MD simulations were performed using a customized version of the package Gromacs.[85] The same MD system with Chapter 3 is used here, which consists of an electrode featuring a slit pore and a RTIL reservoir in direct contact with the electrode (see Figure 36). The dimensions of the slit pore and RTIL reservoir were chosen so that the effects associated with the slit pore entrance do not affect the ion density profile in the pore interior. The electrical polarizability of the electrode and the pore surfaces is modeled self-consistently within the framework of classical electrostatic theories using the method developed in ref.[73]. The force fields for cation (a 7-atom ion featuring a ring with the geometry of the native imidazolium) and anion (a 5-atom ion with the geometry of BF₄⁻)
ion) were the same with the force fields of ions in Chapter 3. The geometry of ions is shown
Figure 36. The net charge of each ion is localized on one of its atoms (see Figure 36). These
force fields have been found to predict properties of EDLs well compared to fully detailed
force fields.[86] We also confirmed that distributing the net charge of each ion evenly on
its constituent atoms does not change the trends reported here. Simulations were performed
in the NVT ensemble (T = 400 K). Temperature is controlled by Nose-Hoover thermostat.
Each system was simulated three times using different initial configurations and each
simulation consisted of an equilibrium run of 20 ns and a production run of 20 ns.

4.2. Results and Discussion

To quantify the charging of the pore as a function of the electrode voltage $\phi$, we
first examine the occupancy of ions inside pore by introducing an area-based number
density $\rho_s$. Specifically, taking advantage of the fact that ions form a single layer inside the
pore, we define $\rho_{s,+} = \int_0^W \rho_{s,+}(z)dz$, where $\rho_{s,+}(z)$ is the number density of cation across the
pore and $W$ is the pore width. $\rho_{s,-}$ is similarly defined. Essentially, $\rho_s$ represents the number
of ions enclosed between the two parallel pore walls per unit area. Figure 41(a) shows the
variation of $\rho_s$ for cations and anions as the electrode voltage increases. Using the data in
Figure 41(a), the pore wall surface charge densities $\sigma$, $C_{\text{int}}$, and $C_{\text{diff}}$ were computed and
shown in Figure 41(b) and Figure 41(c). These results indicate that the charge storage
inside the pore examined here exhibits the following characteristics: 1) for $\phi < 1$ V, charge
storage is mainly achieved by swapping cations inside the pore with anions in the bulk
electrolyte (hereafter referred to as ion-swapping), and both $C_{\text{diff}}$ and $C_{\text{int}}$ depend only
weakly on the electrode voltage; 2) as electrode voltages increase further, additional charge storage inside pore is achieved mainly by the removal of cations from the pore and both $C_{\text{int}}$ and $C_{\text{diff}}$ increases. Both $C_{\text{int}}$ and $C_{\text{diff}}$ reach their maximum at ca. 1.7-2 V, close to the point at which cations are completely removed from the pore; and 3) as the electrode voltage increases even further, more anions enter the pore and capacitance decreases. At $\phi \approx 2.89$ V, the steric limit of anion packing is not yet reached and $C_{\text{diff}}$ is nonzero.

Some of the above observations are similar to those revealed in prior studies. For example, the overall trend of $C_{\text{diff}}$ in Figure 41(c), in particular, the existence of a potential $\phi_m$ at which $C_{\text{diff}}$ is maximized, is similar to those reported earlier by Skinner et al. and Kondrat et al.[60,62] and closely resembles the trend reported in experimental characterization of capacitance of microporous electrodes featuring primarily 0.94 nm-wide pores in contact with 1-propyl-2,3-(IM$_{311}$-TFSI) RTIL.[87] However, our results present key differences from prior theoretical works. For example, Figure 41(c) shows that, similar to that observed experimentally in ref. [87] and theoretically in ref. [60], $C_{\text{diff}}$ decreases moderately as voltages increases from $\phi_m$ to $\sim 1.5 \phi_m$ as compared to the rapid decay of $C_{\text{diff}}$ toward zero reported in ref. [62]. In addition, in this work, as $\phi$ increases toward $\phi_m$, $C_{\text{diff}}$ increases rapidly and the charge storage in the potential window 1 V < $\phi$ < 1.7 V is achieved mainly by the removal of co-ions from the pore with few counter-ions inserted. As $\phi$ increases beyond $\phi_m$, further charge storage is achieved by insertion of counter-ions into the pore. These observations contrast sharply with those reported in ref.[62], in which charge storage at $\phi < \phi_m$ is governed by ion-swapping and extra counter-
ion insertion, and charge storage at $\phi > \phi_m$ is entirely determined by ion-swapping. These differences highlight the rich behavior of charge storage in sub-nanometer pores.

Figure 41. (a) Variation of the area-based number density, $\rho_s$, of cations and anions (see text for definition) as a function of the electrode voltage $\phi$. (b) Surface charge density, $\sigma$, of the slit pore walls as a function of the electrode voltage. The solid curve is a cubic spline interpolation of the MD data. (c) Variation of the integral and differential capacitance of the pore as a function of
The three state points 0, 1, and 2 discussed in the text have electrode voltages of \( \phi = \text{PZC} \), 1.07 and 1.97 V, respectively.

The analysis on mechanisms underlying the variation of modes of charge storage with electrode voltage focuses on \( C_{\text{int}} \) instead of \( C_{\text{diff}} \) since \( C_{\text{int}} \) is the most important observable of ECs. Also we note that both \( C_{\text{int}} \) and \( C_{\text{diff}} \) show similar dependence on the electrode voltage in the system (cf. Figure 41(c)). To understand the evolving mode of charge storage inside the pore as a function of electrode voltage, consider a positively polarized electrode pore. As the voltage of the electrode increases by \( \Delta \phi \), the pore wall surface charge density increases by \( \Delta \sigma \) and the net charge inside the pore changes by \( -\Delta \sigma \), which can be achieved in three possible modes: insertion of anions into the pore without removal of cations from the pore (\textit{i.e.}, pure anion insertion), removal of the cation from the pore without insertion of anion into the pore (\textit{i.e.}, pure cation removal), and insertion of anions into the pore accompanied by removal of the same amount of cations from the pore (\textit{i.e.}, ion swapping). Charge storage will proceed by one or several of these modes so that the system’s free energy is minimized. We note two key features of the ion-ion interactions inside the system of Figure 41: 1) since all ions are distributed within a monolayer inside the pore, insertion or removal of ions strongly affect the separation between ions (especially for ions with the same charge) already inside the pore, and 2) ion-ion interactions are screened by polarizable pore walls and this decreases (increases) exponentially as the ion-ion separation in the plane parallel to pore walls increases (decreases). To examine the energetics of ion-ion interactions inside a pore as it becomes charged, note that the insertion of anions into the pore tends to increase the system’s energy.
by reducing the anion-anion separations inside the pore (thus enhancing their repulsion), but this is partially offset by the increased cation-anion attraction. Removal of cations from the pore tends to increase the system’s energy by reducing anion-cation attractions, but this is offset by a reduction of cation-cation repulsions and anion-anion repulsions (anion-anion separation increases as the removal of cations leaves space for anions).

At low electrode voltage ($\phi < 1.0$ V), the number of anions and cations inside the pore does not differ significantly. As the electrode voltage increases by $\Delta\phi$, the change of the system’s energy after inserting an anion into the pore is similar to that after removing a cation from the pore. Therefore, the system does not exhibit notable preference between anion insertion and cation removal. As such, charge storage is realized by simultaneous insertion of anions and removal of cations, i.e., ion swapping. Since each removed cation leaves more space than that occupied by each inserted anion, a small amount of net anion insertion is also observed in Figure 41(a). As the electrode voltage increases to higher values ($1.0$ V $< \phi < 1.97$ V), the pore is filled with more anions than cations (e.g., the ratio of $\rho_-$/$\rho_+$ is 2.82 at $\phi = 1.50$V). In such a situation, inserting anions will reduce anion-anion separation and sharply increase anion-anion repulsion (recall ion-ion interactions increases exponentially as their separation decreases). Meanwhile, the enhancement of cation-anion attraction is moderate as cations inside the pore is already surrounded by many anions, and the newly inserted anions are located at position away from the cation and contribute little to cation-anion attraction. On the other hand, removing bulky cations form inside the pore leaves larger spaces for the anions inside the pore and greatly reduces their repulsion, even though the cation-anion attraction is also reduced. Since the overall energetics of the
system at large voltage is dominated by anion-anion repulsions, removing cations is more favorable than inserting anions. As a result, the additional charge storage inside the pore is achieved predominantly by cation removal when the electrode voltage increases. Such a trend is particularly clear at high electrode voltages (e.g., \( \phi > 1.5 \) V), where additional charge storage as the electrode voltage increases is nearly exclusively achieved by cation removal. As electrode voltage increases beyond \( \phi \approx 1.97 \) V, all cations are removed from the pore and additional charge storage is achieved by anion insertion. Clearly, the mode of charging at moderate electrode voltages revealed here, i.e., the predominance of cation removal as voltage increases from 1 to 2 V, is related to the asymmetry of cation and anion sizes. Since the sizes of cations and anions in ref. [62] are exactly the same, the different modes of charging found in this work and in ref. [62] are likely caused by the different ions studied.

To understand the variations of \( C_{\text{int}} \) as a function of the electrode voltage \( \phi \), we use a model we developed in a previous work. As shown in ref. [88], by neglecting the cavity energy and entropic effects, the scale of \( C_{\text{int}} \) of a nanopore follows

\[
C_{\text{int}} \sim \frac{e}{-\Delta E^{\text{elec}}_{i-\text{ions}}(0 \rightarrow \sigma)/z_i\sigma}
\]

(4.1)

where \( z_i \) is ion \( i \)'s valence, and \( \Delta E^{\text{elec}}_{i-\text{ions}}(0 \rightarrow \sigma) = E^{\text{elec}}_{i-\text{ions}}(\sigma) - E^{\text{elec}}_{i-\text{ions}}(0) \) is the change of ion \( i \)'s energy due to its electrostatic interactions with ions inside a pore as the surface charge density of the pore increases from 0 to \( \sigma \) under the action of an electrical potential. Equation 4.1 is applicable to both cation and anion. Essentially, Equation 4.1 correlates the capacitance of a pore with the variation of electrostatic ion energy as the pore becomes
electrified. To understand Equation 4.1, consider a neutral pore. As the electrical potential on the pore wall increases from zero to \( \phi \), removal of a cation \( i \) from the pore is affected by 1) the increase in electrode potential, which tends to drive cation \( i \) out of the pore, 2) the decrease in net ionic charge inside pore, which creates an increased attraction (hereafter referred to as ionic attraction) to cation \( i \) and hinders its removal. Consequently, for each unit positive charge the pore wall gains (or, each unit negative ionic charge the pore gains), if the attraction rendered by ions inside the pore to cations increases weakly (i.e., \(-\Delta E_{+\rightarrow \text{ions}}^{\text{elec}}(0 \rightarrow \sigma)/\sigma \) is small), it will be easy to remove a large amount of cations from the pore at a given \( \phi \), which tends to lead to large \( C_{\text{int}} \). Similar interpretation applies to anions.

Equation 4.1 can be used to understand the variations of \( C_{\text{int}} \) for \( \phi < 1.97 \) V. We can apply this equation to the cations since cation removal plays a key role for the charge storage inside the pore with a wall potential of \( \phi < 1.97 \) V. Figure 42 shows the variation of \(-\Delta E_{+\rightarrow \text{ions}}^{\text{elec}}(0 \rightarrow \sigma)/\sigma \) for \( \phi < 1.97 \) V. We observe that, as \( \phi \) increases from 0.5 to 1.97 V, \(-\Delta E_{+\rightarrow \text{ions}}^{\text{elec}}(0 \rightarrow \sigma)/\sigma \) decreases by 27%. According to Equation 4.1, \( C_{\text{int}} \) should increase by \( \sim 36\% \) in this potential window, as compared to the 50% increase observed in Figure 41(c). The good agreement confirms that, for \( \phi < 1.97 \) V, the larger \( C_{\text{int}} \) at higher \( \phi \) is mainly caused by the smaller \(-\Delta E_{+\rightarrow \text{ions}}^{\text{elec}}(0 \rightarrow \sigma)/\sigma \) at higher \( \phi \). This behavior can be understood by examining the ionic charge distribution near cations at different \( \phi \). To illustrate this, we show in the following why \(-\Delta E_{+\rightarrow \text{ions}}^{\text{elec}}(0 \rightarrow \sigma)/\sigma \) at \( \phi = 1.97 \) V is smaller than that at \( \phi = 1.07 \) V. Let's first define three state points 0, 1, and 2 (cf. Figure 41(b)) corresponding to slit pores held at \( \phi = \text{PZC}, 1.07 \) and 1.97 V. We next note that
−ΔE_{+⇒ions}(0 → \sigma_2)/\sigma_2 < −ΔE_{+⇒ions}(0 → \sigma_1)/\sigma_1 is mathematically equivalent to
−ΔE_{+⇒ions}(\sigma_1 → \sigma_2)/(\sigma_2 − \sigma_1) < −ΔE_{+⇒ions}(0 → \sigma_1)/\sigma_1 where \sigma_1 and \sigma_2 correspond to \phi_1 = 1.07 \text{ V} and \phi_2 = 1.97 \text{ V}. The latter is the net result of two factors: 1) the different modes of charge storage in potential window \phi < 1.07 \text{ V} and 1.07 \text{ V} < \phi < 1.97 \text{ V} and 2) the rapid decay of the ion-ion interactions inside the present pore as their separation increases.

Figure 42. Variation of −ΔE_{+⇒ions}(0 \rightarrow \sigma)/\sigma as a function of the electrode potential.

To quantify the ionic charges near each cation inside the pore, we define an ionic charge distribution function \( g_e(r) \) in spirit of a radial distribution function: \( g_e(r) = (\rho_{s,+}(r) - \rho_{s,-}(r))e \), where \( \rho_{s,+}(r) \) and \( \rho_{s,-}(r) \) are the average local area-based number density of cation and anions at distance \( r \) from each cation inside the pore and \( e \) is the unit charge. The change of the ionic charge distribution function of cations inside the pore \( \Delta g_e(r) \) as the electrode voltage varies is shown in Figure 43(a) and (b). Figure 43(a) shows that, as \( \phi \) increases from 0 to 1.07 \text{ V}, the increased “effective” negative ionic charge near each cation
inside the pore is mainly due to the insertion of anions at a distance of 0.5-0.65 nm from it and the removal of cations at a distance of 0.6-0.8 nm from it. Specifically, as $\phi$ increases from PZC to 1.07 V, anions (cations) enter (leave) the pore. During this process, the energy of a cation inside the pore becomes more negative because it is “effectively” surrounded by a larger number of negative charges, which originates either from packing of more anions or removal of cations near the cation. As $\phi$ increases from 1.07 to 1.97 V, few anions enter the pore, but many cations leave the pore. During this process, the energy of each cation that remained inside the pore also becomes more negative because it is surrounded by more negative ionic charges. However, these negative ionic charges originate mostly from the removal of cations near the remained cations. Since the separation of cations inside the pore is large at 1.07 V, cations are removed at distances far from where the cations remained in the pore. Indeed, Figure 43(b) shows that, as $\phi$ increases from 1.07 to 1.97 V, the increased “negative” ionic charges near each cation inside the pore is mostly due to the removal of cations from a distance 0.7 to 1.2 nm from it. Hence, per each unit surface charge density the pore wall gains, although the increase of the negative ionic charge near the cations remained inside the pore is the same for the two potential windows these effective negative ionic charges are distributed closer to the cation in the first potential window. Since the interactions between these effective charges and the cations that remained inside the pore decays rapidly as their separation increases, it follows that $-\Delta E_+^{elec}_{\rightarrow ions}(\sigma_1 \rightarrow \sigma_2)/(\sigma_2 - \sigma_1)$ is smaller than $-\Delta E_+^{elec}_{\rightarrow ions}(0 \rightarrow \sigma_1)/\sigma_1$, and $C_{\text{int}}$ at 1.97 V is larger than that at 1.07 V.
Figure 43. The ionic charge distribution function of the cation changes as a function of voltage. Ionic charge distribution function of the cations changed as the electrode voltage on the pore wall increases from ~0 V to 1.07 V (panel a) and from 1.07 V to 1.73 V (panel b). Contributions to $\Delta g_e(r)$ by the addition of anions to the vicinity of cation and by the removal of cations from the vicinity of cations are also shown. To facilitate the comparison of $\Delta g_e(r)$ in these two cases, $\Delta g_e(r)$ is scaled by change of the pore wall surface charge density $\Delta \sigma$ in each potential window.

However, Equation 4.1 cannot easily account for the decrease of $C_{\text{int}}$ as $\phi$ increases beyond 1.97 V. Specifically, since anion insertion dominates the increased charge storage as $\phi$ increases beyond 1.97 V, we computed the variation of $-\Delta E_{\text{elec ions}} (0 \rightarrow \sigma) / \sigma$ for $1.97 \text{ V} \leq \phi \leq 2.98 \text{ V}$ and found that it remains essentially constant. Thus, Equation 4.1 predicts $C_{\text{int}}$ to be a constant in this potential window, while Figure 41(c) indicates that $C_{\text{int}}$ decreases as $\phi$ increases. The decrease of $C_{\text{int}}$ for this potential window is likely caused by entropic effects that are neglected in Equation 4.1. For $\phi > 1.97 \text{ V}$, the area-based number density of ions inside the pore increases as $\phi$ increases (cf. Figure 41(a)), which tends to
reduce the entropy per unit area. Such an effect becomes more and more important as $\phi$ increases and tends to hinder the insertion of additional anions into the pore, thereby reducing $C_{int}$.

4.3. Conclusion

In summary, we utilized MD simulations to determine how charge storage inside a sub-nanometer pore in equilibrium with an RTIL reservoir depends on the electrode voltage. We showed that, at low voltages, charge storage of the pore is achieved by swapping co-ions in the pore with counter-ions in the RTIL reservoir. As voltage increases, additional charge storage is due mainly to the removal of co-ions from the pore and capacitance increases. This change of charge storage mode is caused by the asymmetry in size of the counter-ions and co-ions and by the fact that, at high potential, the counter-ion/counter-ion repulsion dominates the system’s energy. It follows that the removal of co-ions is more effective in reducing this energy than the insertion of counter-ions.

The capacitance increases because, at higher potential, the stabilization of co-ions inside the pore by the ionic charges inside the pore per unit surface charge on the pore wall becomes weaker, which is in turn caused by the short-ranged nature of the electrostatic interactions in sub-nanometer pores. At even higher electrode voltage, additional charge storage is realized by counter-ion insertion into the pore and the capacitance reduces due to entropic effects. These results illustrate that the charge storage in sub-nanometer pores exhibits rich behaviors as the voltage changes. The various trends depend on the specific nature of RTILs (e.g., cation/anion size asymmetry) and the generic features of sub-
nanometer pores (e.g., short-ranged electrostatic interactions). Clearly, harnessing this behavior could be useful for improving the performance of ECs.
CHAPTER 5

Charging Dynamics of Nanopore

In the previous chapters, we focused on the thermodynamics of charge storage in nanopores, i.e., how much charge can be stored inside the nanopores under equilibrium conditions (or at infinitely slow charging rates). Those studies help understand the maximal energy density of ECs. Since ECs must work under fast/discharging conditions in practice, it is essential to understand the charging dynamics of nanopores. In this Chapter, we focus on the charging dynamics of sub-nanometer pores connected to RTIL reservoirs. Much of the work described in this chapter has been previously published in ref. [89].

5.1. Methods

We investigate the charging of a pair of slit nanopores in two metallic electrodes, which mimics the nanopores in graphene-based nanoporous electrodes. The MD system consists of a pair of identical slit pores and two reservoirs separating the pores. The access width of pores was 0.53 nm and 0.66 nm, the pore length is 12.09 nm, and periodic boundary conditions were applied in all directions. Figure 44 shows a schematic of the side view of the simulation system. In the simulations, the negative electrode pore is grounded and the electrical potential difference between the walls of the two nanopores is enforced using the method described in Chapter 2. Figure 45 shows a few snapshots of the MD system illustrating the charging of the nanopores.
Figure 44. A schematic of the MD system for studying charging dynamics in nanopores. The blue lines denote the simulation box. The red lines denote the image planes of the electrode pore walls. For the system featuring 0.53 nm wide nanopores, the dimension of the simulation box in the $x$, $y$ and $z$ directions are 46.02, 3.12, and 3.77 nm, respectively. For the system featuring 0.66 nm wide nanopores, the dimension of the simulation box in the $x$, $y$ and $z$-directions are 46.02, 3.12, and 3.90 nm, respectively.

Figure 45. Charging of narrow electrode pores with RTILs. (a) Side-view snapshot of one half of the MD system featuring an electrode pore (width: 0.53 nm) and part of the RTIL reservoirs connected to it. (b-d) Top-view snapshots of the ionic structure inside the negative electrode pore when a voltage of 3V is imposed impulsively between the positive and the negative electrode pores. The blue and orange spheres represent cations and anions, respectively. Wall atoms are not shown for clarity. A 3 ns movie of charging process is provided in ref. [89].

Three types of nanopore are modeled: ionophobic, ionophilic pores with smooth walls, ionophobic pores with walls featuring surface defects. A pore is ionophilic if it is
pre-wetted by ions at the potential of zero charge (PZC) otherwise, it is considered ionophobic. The is tuned by varying the Lennard-Jones interaction parameters between the ions and pore walls (see below). To model ionophobic pores with surface defects, twelve groups of surface defects are grafted on the walls of 0.53 nm wide pore. As shown in Figure 46, each group of the surface defects consists of three wall atoms protruding from the geometrical plane of the pore wall to the central plane of the pore. Because the pore width is only 0.53 nm, these surface defects effectively block the pore exit locally.

**Figure 46.** Snapshots of the ionophobic pore with local defects (panel a: side view; panel b: top view). The two pores in the system have the same surface defects and only the negatively charged pore is shown here. Atoms in grey (available in color copies) denote the wall atoms on defect-free portion of the wall and atoms in pink denote the surface defects.

In each of the MD systems, there are 6048 atoms on the electrode surface. The number of ions inside the entire system was tuned so that, at PZC, the ion density in the RTIL reservoirs matched that of a bulk system at 400 K and 1 atm within 1% (such an elevated temperature was chosen to ensure that the model RTIL remains in the liquid phase). There are 1180 and 1200 pairs of ions in the system featuring 0.53 nm and 0.66 nm wide ionophilic nanopores, respectively. There are 1024 pairs of ions in the system
featuring 0.53 nm wide ionophobic nanopores. There are 1180 pairs of ions in the system featuring 0.53 nm ionophilic nanopores with surface defects.

**Force fields.** Cations have the same geometry as the BF$_4^-$ ion, which has a rather spherical shape. Its constituent atoms were modeled as LJ particles and a unit charge was assigned to its central atom. The anion is identical to the cation except that its central atom is negatively charged. To account for the electronic polarizability of RTILs, a background dielectric constant of 2.5 was used during the calculation of the electrostatic interactions.

The LJ potential describing the non-electrostatic interactions between atoms is given by $\phi_{LJ}(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$. The LJ parameters of all atoms in the MD system are the same, i.e., $\sigma = 0.336$ nm and $\epsilon = 0.36$ kJ/mol. Using such parameters, the two ionophilic nanopores are both wetted by RTILs at PZC. To produce an ionophobic nanopore, the LJ parameters for the non-electrostatic interactions between pore wall atoms and atoms of cations/anions were taken as $\sigma = 0.336$ nm and $\epsilon = 0.12$ kJ/mol. The LJ parameters for the non-electrostatic interactions between ions were not changed.

With the above RTIL models, the self-diffusion coefficient of ions in bulk RTILs at 400 K and 1 atm was found to be $D_+ = D_- = 2.32 \times 10^{-9}$ m$^2$/s, which is about 1-2 order of magnitude larger than that of typical RTILs at similar conditions.[86] Such a high diffusion coefficient is useful in the present study because simulating large MD systems featuring polarizable electrodes is computationally demanding and the fast diffusion of ions allows the entire process of charging a nanopore to be simulated using currently available computational resources. As shown in Section Chapter 1, the essential features
of ion diffusion revealed using these simple ion models are also observed in simulations using more sophisticated RTIL models.

**Simulation procedure.** MD simulations were performed using a customized Gromacs code.[85] Pore walls were maintained as equi-potential surfaces with their image planes coinciding with the geometric plane of wall atoms. In the method [64] we used, the electronic polarizability of pore walls is taken into account on the continuum electrostatics level. This method is in good agreement[60,90] with other models of polarizable electrodes[50,91].

In MD simulations, a time step of 3 fs was used, and a Nose-Hoover thermostat with the time constant 10 ps was used to control the temperature of RTILs. The non-electrostatic interactions were computed with a cutoff length of 1.5 nm and the neighbor list was updated every step. To take into account the electronic polarizability of pore walls, the electrostatic interactions were computed using the PME method and by solving an auxiliary Laplace equation. In the PME part, we used a real space cutoff of 1.5 nm, and the FFT grid spacing of 0.13 nm. The auxiliary Laplace equation was discretized using the compact fourth-order stencil on the same grid as the FFT grid and solved during each simulation step. Because of the significant computational cost in computing electrostatic interactions, each of the charging cases required about twenty one days of simulation time.

The system was first equilibrated for 2 ns at PZC at 400 K. After the system reached the equilibrium, a voltage difference of 3V was impulsively imposed between the negative and positive electrodes, and the system was evolved in the NVT ensemble for 6 ns. Each charging case was repeated 50 (5) times for ionophilic (ionophobic) pores, with
independent initial configurations, to obtain reliable statistics. To compute the equilibrium charge at a given applied voltage, a separate system with 50% shorter pores were setup and run for 20 ns. We determined the integral capacitance of the ionophilic pores at 3 V to be 12.6 and 8.1 μF/cm² for the 0.53 and 0.66 nm wide pores, respectively; this is comparable to the experimental values [92,93]. The corresponding capacitance of the 0.53 nm-wide ionophobic pore is 11.4 μF/cm².

**Joule effect.** It is known that the temperature of an ionic liquid inside nanopores tends to rise above the thermostat temperature during charging (see, e.g., ref. [94]), due to the so-called ‘Joule effect’. Indeed, in the simulations the RTIL temperature inside the 0.66 nm-wide pore rises from 400 K to a maximum of 422 K after 250 ps, but returns to 400 K by t ≈ 550 ps, and remains close to 400 K thereafter. To assess how this ‘over-heating’ affects charging, we performed extra simulations in which RTILs' temperature inside the pore is controlled by a canonical velocity rescaling method [95]. With overheating eliminated by this method, we verified that the extracted diffusion coefficients agree within the statistical error with those obtained by the ‘conventional’ simulations used throughout this study.

**Evaluation of self-diffusion coefficient.** To study self-diffusion of ions inside nanopores, we setup MD systems which consist of a single pore only (and the ions in it), with periodic boundary conditions in all directions. We tuned the number of cations and anions to match the desired total and charge densities inside the pore. Since pore walls are modeled as equipotential surface, they form a Faraday cage around ions, and electroneutrality is automatically satisfied. The diffusion coefficient of ions was computed
using the Einstein-Helfand relation [96]; the ion trajectories were obtained from at least 5 ns equilibrium runs.

5.2. Charging of Nanopores Pre-wetted by Ionic Liquids

5.2.1. Charging Dynamics from MD simulations

Because of the symmetry of the negative and the positive electrode pores and the cations and anions in the model, hereafter we describe only the charging of the negative electrode pore. We first examine the charging of electrode pores with width of 0.66 nm after a voltage of 3 V is imposed impulsively between the negative and positive electrode pores. Figure 47 (a), (b) and (d) shows that, between the time voltage is imposed \( t = 0 \) and \( t \approx 1 \) ns, the influx of cations into the pore is slightly larger than the outflux of anions from the pore, and this leads to a moderate over-filling of the pore. At \( t = 1 \) ns, the net charge inside the pore already reaches \( \sim 98\% \) of its equilibrium value. At \( t > 1 \) ns, a small amount of cations and anions are continuously removed from the pore, and this produces a weak de-filling of the pore. This de-filling process is much slower than the charging at \( t < 1 \) ns, and its contribution to charging of the pore is very limited. The observations that charging is accompanied by overfilling till a pore is almost fully charged and overfilling is followed by a slow de-filling and very limited charging closely resemble those predicted by mean-field theory simulations [66]. In light of these similarities, we hypothesize that the charging of pores considered here observes an effective diffusion equation \( \partial_t c = D_{\text{eff}} \partial^2 c \) as suggested by the previous continuum simulations. We then fit the evolution of the net
charge inside the pore to the following analytical solution of this effective diffusion equation in the system under impulsive charging condition.

$$\frac{Q}{Q_\infty} \approx 4\left(\frac{D_{eff}}{\pi H^2}\right)^{1/2} \sqrt{t}$$

(5.1)

showing that the charging observes a square root scaling at short times, and

$$\frac{Q}{Q_\infty} \approx 1 - \frac{8}{\pi} e^{-t/\tau}$$

(5.2)

showing that the charging observes an exponential saturation scaling at long times. Here $Q$ is the net charge inside the pore during charging process, $Q_\infty$ is the net charge inside pore when final equilibrium is achieved, $H$ is the pore length, and $\tau$ is the relaxation time given by $\tau = H^2/\pi^2 D_{eff}$. Figure 47(c) and 47(d) show that the early stage of charging (72-288 ps) in the 0.66 nm wide pore observes a square root scaling law with $D_{eff} = 7.17 \pm 0.88 \times 10^{-8}$ m$^2$/s and the late stage of charging (288-828 ps) observes an exponential scaling law with $D_{eff} = 5.91 \pm 0.71 \times 10^{-8}$ m$^2$/s.

We next examine the charging of electrode pores with width of 0.53nm under impulsively applied voltages. As shown in Figure 47 (a), (b), and (c), charging of this pore is first accompanied by overfilling ( $t < 0.14$ ns) and then by defilling, which is qualitatively similar to those found in wide pores ($W = 0.66$ nm). However, in this narrower pore ($W = 0.53$ nm), the overfilling is weaker and defilling is much stronger and contributes significantly to charging of the pore. These differences are similar to those observed for equilibrium charge storage in pores with different sizes and originate from the stronger screening of electrostatic ion-ion interactions by pore walls in narrower pores,
which favors removal of co-ions and demixing of counter-ions and co-ions at moderate electrode voltages rather than swapping of counter-ions and co-ions and overfilling of the pores. Similar to that for the 0.66 nm wide pore, Figure 47 (c) and (d) confirms that the charging in this narrower pore also observes an effective diffusion equation. The effective diffusion coefficient of space charge in the pore is found to be $D_{eff} = 3.09 \pm 0.39 \times 10^{-8}$ m$^2$/s during the initial stage of charging (80 - 323 ps) and $D_{eff} = 0.4 \pm 0.08 \times 10^{-8}$ m$^2$/s during the late stage of charging (1800 - 6000 ps) (cf. Figure 47 (d)).

![Figure 47](image)

**Figure 47.** Charging of ionophilic pores of length 12.09 nm obtained from MD simulations. A voltage of 3 V is imposed impulsively between the negative and positive electrodes at $t = 0$. The average cation and anion densities are shown in panel (a) and the total pore occupancy in (b). The evolution of the net charge inside the pores exhibits a diffusive behavior: the initial stage of charging follows a square-root law (c) and the late stage of charging follows an exponential saturation law (d).
5.2.2. Ion diffusion in charged nanopores.

A limitation of the mean-field theory is that $D_\pm$ is taken as constant despite that $\rho_\Sigma$ and $\rho_+ / \rho_-$ inside pore vary temporally and spatially during charging. Most existing works on transport of RTILs focus on RTILs in bulk or confined in mesopores at the PZC state[69,97], and little are known about the dynamics of RTILs in charged micropores, which is relevant to the charging of narrow pores considered here. To fill this gap, we perform MD analysis of the equilibrium self-diffusion of ions ($D_\pm$) in pores considered above with different total density ($\rho_\Sigma$) and charge ($c$) density. For other parameters kept fixed, the $D_\pm$ turns a complicated function of $\rho_\Sigma$ and $c$. To compute the equilibrium cation and anion densities (thus $\rho_\Sigma$ and $c$), separate simulations are conducted inside nanopores at applied voltages ranging from 0 to 6 V. From these simulations, we determined the total ion density $\rho_\Sigma$ corresponding to each net charge density $c$ under equilibrium conditions, and the results are shown in Figure 48a.

Figure 48(a) shows the relation between $\rho_\Sigma$ and $c$ at 3V impulsive charging and equilibrium state. We find that the average total ion density during charging, $\bar{\rho}_\Sigma(t)$, does not drop below the equilibrium density, $\rho_\Sigma^{(equ)}(c)$, at the same degree of charging, i.e.~for $c = \bar{c}(t)$. Therefore, as shown in Figure 48(b), we calculate (see Methods Section 5.2) the in-plane self-diffusion coefficient along the equilibrium state, as a limiting case, and compare it with $D_\pm$ along the average $\bar{\rho}_\Sigma(c)$, at $c = \bar{c}(t)$ corresponding to the impulsive charging at 3 V. We focus on the diffusion coefficient of cations ($D_+$) and note that $D_-$ shows similar behavior as shown later.
The ion diffusion coefficient varies non-monotonically with the charge density inside the pores: When the pore is neutral, ion's self-diffusion is nearly two orders of magnitude slower than in bulk; as the charge inside the pore increases, ion's self-diffusion accelerates and can become ten times faster than in bulk; it slows down only when the pore become highly charged ($c \geq 2.6 \text{ e/nm}^2$).

**Figure 48.** Ion self-diffusion during charging of ionophilic pore. (a) A map showing the average total ($\rho_\Sigma$) and charge ($c$) densities during ‘impulsive’ charging (solid line) and in equilibrium (dash double dot line); the dash-dot line corresponds to an ionophobic pore (cf. Figure 52). The average total and charge densities during charging lie within the shaded (blue) area. (b) Cation's self-diffusion coefficient along the equilibrium path and along $\rho_\Sigma (c)$ corresponding to the impulsive charging at 3 V. The diffusion coefficient is expressed in terms of the diffusion coefficient of a neutral bulk system ($D_{\text{bulk}}$). For the 3 V charging, the data only up to 6 ns is shown. Blue and orange spheres in the inset denote the cations and anions, respectively. The pore size is 0.53 nm in (a) and (b).

Similar non-monotonically variation of self-diffusion of ions are observed in anion in 0.53 nm and cation and anion in 0.66 nm pore. Figure 49 shows how the self-diffusion of ions in the 0.53 nm wide slit pore vary as a function of the ion charge density ($c$) along the equilibrium path and for the total ion density, $\rho_\Sigma (c)$, corresponding to the impulsive charging at 3 V (cf. Figure 48(a)). In Figure 50 we compare the self-diffusion coefficient
Figure 49. Variation of the self-diffusion coefficients ($D_{\pm}$) of ions in a 0.53 nm wide pore. The pore carries a net charge density ($c$). In panel (a), the total ion density at each $c$ is set to the equilibrium value. In panel (b), the ion density at each $c = \bar{c}(t)$ is set to the average $\bar{\rho}_z(t)$ corresponding to the impulsive charging at 3 V (see Figure 48(a)).

Figure 50. Variation of the self-diffusion coefficients ($D_{\pm}$) of ions in 0.66 nm (dash lines) and 0.53 nm (solid lines) pores. The self-diffusion increases with increasing pore width in most cases. The total ion density is fixed at that at the PZC.
in 0.66 nm and 0.53 nm wide pores. Here we consider a constant total ion density at the PZC. It can be found that such behavior of self-diffusion of ions exists no matter certain ions and pore width.

To ascertain that the key features of $D_\pm$ revealed in Figure 48 and Figure 49 are universal characteristics of the ion diffusion under conditions relevant for charging of nanopores, rather than artifacts of the simplicity of the RTIL models adopted here, we studied the self-diffusion of [BMIM][PF$_6$] confined in narrow nanopores. The force fields developed in ref. [98] are used for modeling the RTILs. These force fields have been used to accurately predict the transport properties of bulk RTILs [98] and the enhanced specific capacitance in microporous carbon electrodes with realistic structures.[99] The center-to-center width of the slit pore was 1.0 nm, which is similar to that found in carbide derived carbons synthesized from crystalline TiC using chlorination temperatures of 1200°C.[100] Visualization shows that BMIM$^+$ and PF$_6^-$ ions effectively form a single ion layer when confined inside this pore. To study ions' self-diffusion coefficients at different charge densities $c$, the total ion density inside nanopores is varied along the equilibrium path (we do not examine the situations in which $\rho_\Sigma$ is fixed: The size of cation and anion in this RTIL are different, consequently $\rho_\Sigma$ inside the pore is not constant under most charging conditions). Figure 51 shows how the self-diffusion of ions in the pore vary as a function of the ion charge density $c$ when the pore wall is positively charged. We observe that the variation of counter-ion's (PF$_6^-$ ion) self-diffusion coefficient with the charge density shows essentially the same feature as those shown in Figure 48(b). For example, $D_\pm$ varies non-
monotonically with charge density, and can be more than one order of magnitude higher than its bulk value.

**Figure 51.** Variation of the self-diffusion coefficients ($D_\pm$) of real RTILs in a 1.0 nm pore. The total ion density at each $c$ is set based on the $\rho_\Sigma - c$ relation under equilibrium charging conditions. $D_\pm$ of BMIM$^+$ and PF$_6^-$ ions in bulk at $T = 400$ K and $P = 1$ atm are shown as red and blue dashed lines, respectively.

The non-monotonic variation of ion’s self-diffusion coefficient found here for different ions, pore size and real force field, originates from the different structure of RTILs inside a pore as the pore becomes charged. At PZC, cations and anions form a two-dimensional lattice with each ion forming pairs with its neighboring ions with the opposite charge (see Figure 48(b) inset), and this hinders ion diffusion since the movement of one ion disrupts such lattice for all its surrounding ions.[101] As more counter-ions (here cations) are introduced, such a lattice gradually disappears and the ions diffuse more easily.
Such accelerated self-diffusion has also been observed near charged planar surfaces[69], but the effect is moderate. However, when the pore is highly charged, cations inside the pore will form a quasi-Wigner crystal with a small number of anions inside the pore behaving like impurities. Under such condition, moving one cation will again disrupt the ionic lattice involving many counter-ions and consequently ion’s self-diffusion is small.

The above results on ion diffusion in charged pores suggest that, to accelerate the charging of narrow pores by optimizing selection of RTILs, one should examine the diffusion of ions inside charged pores rather than simply extrapolating such information from ion diffusion in bulk RTILs. The fact that the structure of RTIL inside narrow pore depends strongly on the net charge in the pore and confinement by pore walls suggest that strategies different from optimizing ion diffusion in bulk state must be adopted. While this renders the design of RTILs more complex, it also opens up exciting opportunities for tailoring RTILs for specific pores and degree of charging.

*Comparison of $D_{\text{eff}}$ and $D_{\text{self}}$.* An essential prediction of the mean-field theory for charging of sub-nanometer pores using RTILs is that the effective diffusion coefficient of charge, $D_{\text{eff}}$, is much larger than the self-diffusion coefficient of ions and the difference between $D_{\text{eff}}$ and $D_{\pm}$ become smaller in wider pores. Here we examine the ratio of effective and self-diffusion coefficient. Evaluation of $D_{\text{eff}}/D_{\pm}$ is complicated by the fact that the self-diffusion coefficient, $D_{\pm}$, varies with RTIL density and charge (i.e., $\rho_\Sigma$ and $c$), both of which vary along the pore length and in time. During charging, the net charge in the pore entrance region (defined as within two ion diameters from the edge of the vertical
walls in Figure 44) increases with time and is higher than that in pore interior, while RTIL density does not vary greatly along the pore at most time instants. Based on the results shown in Figure 50 and the fact that the charge in the pore entrance never exceeds 3.0 e/nm$^2$ in the systems studied here, the self-diffusion coefficients obtained under condition corresponding to the RTIL density and charge in the pore entrance region at $t = t_b$ (in innermost region of the pore at $t = t_a$) are the highest (lowest) self-diffusion coefficients of ions in time window $t = t_a \rightarrow t_b$. To obtain a conservative estimation of $D_{eff}/D_\pm$, we take the highest value of $D$ at relevant conditions in most cases.

In the 0.66 nm wide pore, a $D_{eff}$ of $7.17 \pm 0.88 \times 10^{-8}$ m$^2$/s was obtained during the initial stage of charging (72-288 ps) when a voltage of 3 V was impulsively applied. The average $\rho_\Sigma$ and $c$ in the pore entrance region at 288 ps is $4.59 \#$/nm$^2$ and $1.75$ e/nm$^2$, respectively. Using separate simulations, the self-diffusion coefficients of cations and anions under this condition are found to be $2.48 \times 10^{-9}$ and $2.20 \times 10^{-9}$ m$^2$/s, respectively. Therefore, $D_{eff}/D_\pm \approx 30$ for the initial stage of charging. In the same pore, a $D_{eff}$ of $5.91 \pm 0.71 \times 10^{-8}$ m$^2$/s is obtained during the late stage of charging (288-828 ps). The average $\rho_\Sigma$ and $c$ in the pore entrance region at 828 ps is $4.68 \#$/nm$^2$ and $1.86$ e/nm$^2$, respectively. The self-diffusion coefficients of cations and anions under this condition are found to be $1.77 \times 10^{-9}$ and $2.00 \times 10^{-9}$ m$^2$/s, respectively. Therefore, $D_{eff}/D_\pm \approx 30$ for the late stage of charging.

The $D_{eff}$ of space charge inside the pore studied here is ~30 times larger than the self-diffusion coefficient of cations and anions. Such a significant enhancement of charge
transport compared to ion diffusion is consistent with the prediction of the continuum simulations, and is caused by the electric migration of ions as explained earlier. The fact that the charging observed in MD simulations can be fitted well to the solution of the effective diffusion equation confirms that charging of narrow pores with RTILs is a diffusive process. Furthermore, the fact that $D_{\text{eff}}/D \gg 1$, a key prediction of the MFT simulation, is confirmed by the above MD simulations indicates, under the conditions examined here, the essential physics of charging narrow pores with RTILs are incorporated in the mean-field theory model.

In the 0.53 nm wide pore, a $D_{\text{eff}}$ of $3.09 \pm 0.39 \times 10^{-8} \text{ m}^2/\text{s}$ was obtained during the initial stage of charging (80-323 ps) when a voltage of 3 V was impulsively applied. The average $\rho_{\Sigma}$ and $c$ in the pore entrance region at 323 ps is 3.80 #/nm$^2$ and 1.91 e/nm$^2$, respectively. The self-diffusion coefficients of cations and anions under this condition are found to be $3.20 \times 10^{-9}$ and $2.85 \times 10^{-9}$ m$^2$/s, respectively. Therefore, $D_{\text{eff}}/D_{\pm} \approx 10$ for the initial stage of charging. In the same pore, a $D_{\text{eff}}$ of $0.4 \pm 0.08 \times 10^{-8} \text{ m}^2/\text{s}$ was obtained during the late (1800-6000 ps) stage of charging. The average $\rho_{\Sigma}$ and $c$ in the pore entrance region at 6000 ps is 2.95 #/nm$^2$ and 2.52 e/nm$^2$, respectively. The self-diffusion coefficients of cations and anions under this condition are found to be $1.07 \times 10^{-8}$ and $7.36 \times 10^{-9}$ m$^2$/s, respectively. Therefore, the lower limit of $D_{\text{eff}}/D_{\pm}$ is $\approx 0.5$ for the late stage of charging. Using the average $\rho_{\Sigma}$ and $c$ in the innermost region of the pore at 1800 ps ($\rho_{\Sigma} = 3.6$ #/nm$^2$ and $c = 1.95$ e/nm$^2$), the self-diffusion coefficients of cations and anions under this condition are found to be $3.50 \times 10^{-9}$ and $3.25 \times 10^{-9}$ m$^2$/s,
respectively. Therefore, the upper limit of $D_{\text{eff}}/D_{\pm}$ is estimated to be $\approx 1$ for the late stage of charging.

Hence, $D_{\text{eff}}$ of the space charge inside a 0.53nm-wide pore is $\approx 20$ times larger than the self-diffusion coefficient of cations and anions inside the same pore, as compared to a factor of $\approx 30$ larger in the 0.66nm-wide pore studied above. The weaker enhancement of $D_{\text{eff}}$ of space charge over the diffusion coefficient of ions in narrower pore is consistent with the prediction by MFT simulations. During the late stage of charging, the fact that $D_{\text{eff}}$ is on the same order of magnitude as $D_{\pm}$ and only anion (co-ion) removal contributes to charging suggests that the charging at $t > 1.8$ ns is contributed mainly by the outflux of anion due to diffusion instead of by electric migration. The limited contribution of electric migration to charging is also supported by the fact that cations (counter-ions) actually leave the pore at $t > 1.8$ ns. To understand this, note that, if the outflux of anions from pore driven by electric field inside pore is significant, then this electric field must induce large influx of cations into the pore. The limited contribution of electric migration to charging can be understood as follows. At $t > 1.8$ ns, the number of cations inside the pore is much larger that of anions. Consequently, regardless of where an anion is located along the pore, its vicinity is packed densely with cations but depleted of anions. This, along with the fact that an ion interacts strongly only with its closest neighbors due to screening of electrostatic interactions by metallic pore walls, has two effects: anion removal is favored over anion-cation swapping for charging the pore and the electrical potential experienced by anions along pore length direction is rather uniform. The MFT simulations predict that, against that observed in MD simulations, in the entire process of charging 0.53 nm-wide pores,
$D_{\text{eff}}/D_{\pm} \gg 1$ and counter-ion/co-ion swapping (rather than co-ion removal) dominates charging. Such a disagreement likely stems from the mean-field model of ions’ electrostatic energy inside nanopores, which becomes inaccurate when the ratio of counter-ion to co-ion inside nanopore is large.

The various self-diffusion coefficients described above, along with the self-diffusion coefficient of bulk RTILs, are summarized in Table 4. The self-diffusion coefficients vary with density, hence we take the maximum. The effective diffusion coefficients at different stages of charging inside ionophilic pores are also shown. For comparison, the diffusion coefficient of a bulk system is $2.32 \times 10^{-9} \text{ m}^2/\text{s}$.

**Table 4.** Comparison of diffusion coefficient for different systems.

<table>
<thead>
<tr>
<th>Charging regime</th>
<th>Square-root</th>
<th>Exponential saturation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D_{\pm}^{\text{max}}$</td>
<td>$D_{\pm}^{\text{max}}$</td>
</tr>
<tr>
<td>Diff. coeff., $10^{-9}$ m²/s</td>
<td>$D_{\pm}^{\text{max}}$</td>
<td>$D_{\pm}^{\text{max}}$</td>
</tr>
<tr>
<td>0.53 nm pore</td>
<td>3.2</td>
<td>2.85</td>
</tr>
<tr>
<td>0.66 nm pore</td>
<td>2.48</td>
<td>2.0</td>
</tr>
</tbody>
</table>

**5.3. Accelerating Charging by Ionophobicity**

**5.3.1. Charging of Ionophobic pores with smooth walls**

The above results suggest that when the number of counter-ions inside a pore is much larger than that of co-ions, further charging is achieved mainly by diffusion-driven co-ion removal till most co-ions are removed, and this leads to a much slower charging than the electric ion migration-dominated charging. Therefore, to achieve fast charging, it is useful to adopt wide pores, which helps enhance the electric migration of ions inside.
pore (cf.[89]) and increase the number of co-ions inside pore so that charging is not dominated by diffusion-driven co-ion removal. Increasing the width of a pore, however, may reduce its capacitance and energy density[53,87]. Here we examine the possibility of accelerating charging by making the surface of nanopore ionophobic. Ionophobic pore can be achieved, for instance, by using mixtures[102] of different RTILs or by adding surfactants[103].

Figure 52 compares the charging of this ionophobic pore with that of the same pore that is wetted by RTILs at PZC. Clearly, charging is much faster in the ionophobic pore, e.g., 90% of full charging corresponding to an applied voltage of 3 V is reached at 0.48 ns in the ionophobic pore compared to 5.0 ns in the ionophilic pore. Visualization of the charging process inside the ionophobic pore showed that charging initially proceeds in a front-like fashion with ions quickly spread throughout the pore and distribute rather uniformly along the pore length direction. This is followed by a continuous insertion of counter-ions into the pore and the ion-ion spacing gradually reduces. A 6 ns charging trajectory of ionophobic pore is provided in ref. [89].
The fast charging is mainly caused by the fast diffusion of ions inside the pore. Specifically, at the early stage of charging when the ion density is low inside the pore, ion-ion separation is much larger than ion-wall separation and the diffusion of ions is limited by its collision with the wall. The diffusion coefficient of ion is very large under this condition and approaches the Knudsen limit (cf. Figure 52). As more counter-ions enter the pore, the diffusion of counter-ions gradually becomes Fickican like and the diffusion coefficient reduces. However, before the diffusion coefficient is reduced to very low values, the pore already approaches fully charged state. For example, when the mean ion density inside pore reaches 3.42 #/nm$^2$, the pore is already charged to 91% and the diffusion coefficient of counter-ion inside pore at this state is $7.02 \times 10^{-9}$ m$^2$/s, which is much lower.
higher than that in ionophilic pores with the same size. It is worth noting that the capacitance of the ionophobic pore considered here is 2% smaller than that of the ionophilic pore. This suggests that accelerating charging is not achieved at the expense of charge storage capacity.

5.3.2. Charging of ionophobic pores with imperfect walls

So far we have focused on ‘smooth’ walls, but local defects are ubiquitous in practical electrode materials and may slow down molecular transport significantly, as, e.g., in case of fluid transport in carbon nanotubes[40]. To assess the effect of surface defects on charging, we performed simulations where the pore-wall atoms protrude into the pore center and locally impede the ion transport. Although charging of the pore with defects is slower (Figure 52(a)), the defects do not seem to affect the charging dynamics qualitatively, and in particular its acceleration in ionophobic pores. A 6 ns charging trajectory of ionophilic pore with imperfect walls is provided in ref. [89].

5.4. Conclusions

In summary, MD simulations show that the charging of pores with width comparable to ion diameter using RTILs follows an effective diffusion law. The observations from MD simulation are in line with MFT-based continuum simulations. The fact that such charging, which is complicated by issues such as strong ion crowding and extreme confinement, follows a simple diffusion law is both remarkable and of practical importance. In particular, it can greatly simplify the development of electrode-scale
homogenization models for charging, and thus opening doors for device-level optimization of ECs.

Self-diffusion coefficient of ions show interesting relation with the charge density and the total density of ions. The self-diffusion coefficient varies during charging over a few orders of magnitude, and can exceed a few times the ion diffusion in the bulk (under similar conditions). This suggests that fast charging can in principle be achieved if an ionic liquid is optimized specifically for selected porous materials and the required degree of charging.

We have found that charging is usually accompanied by overfilling of the pores, and the effective diffusion of charge is much faster than the diffusion of ions due to presence of electric ion migrations. When the charging is dominated by de-filling or co-ion removal, charging becomes much slower because the charging is dominated by ion diffusion. While such slow charging can be avoided by using wider pores, adopting ionophobic pores that are not wetted by RTILs at PZC can also greatly accelerate charging without notably sacrificing the charge storage capacity of the nanopore. These insights can be useful for designing or selecting nanopores and RTILs to accelerate the charging of nanoporous electrodes and/or to achieve optimal balance between the energy density and power density of ECs based on nanoporous electrodes and RTILs.
CHAPTER 6

Conclusions

With extraordinary long service life and high power output, electrochemical capacitors are ideal energy storage device for application, such as regenerative breaking. Electrochemical capacitors can also be applied in many high profile areas, such as regulating the power grid and powering the electric vehicles if energy density of ECs improves without sacrificing their high power output.

The recent surge of development over ECs is partially fueled by breakthroughs in engineering electrode and electrolyte materials. In particular, porous electrodes featuring sub-nanometer pores and the use of room-temperature ionic liquids, are emerging as promising material candidates for next generation electrochemical capacitors. Given that these materials span an extremely large design parameter space, rational design and selection of these materials for electrochemical capacitors are essential for exploring their potential to the fullest extent. Such rational design and selection, however, is impeded by the limited understanding of the charge storage mechanisms in these materials, in large part because classical electrical double layer theories are not applicable for these novel materials.

In this dissertation, atomistic simulations were used to gain insights into the mechanisms of charge storage in electrochemical capacitors. The focus were on the thermodynamics and dynamics of the charge storage using sub-nanometer pores and room-
temperature ionic liquids, which governs the maximal energy density and power density of electrochemical capacitors respectively.

For the thermodynamics of charge storage, firstly investigation was conducted to examine how the size of nanopores affects their capacitance. The key findings are as follows.

1. Simulation results showed that the capacitance of slit-shaped nanopores in contact with room-temperature ionic liquid exhibits a U-shaped scaling behavior in pores with width from 0.75 to 1.26 nm. The left branch of the capacitance scaling curve directly corresponds to the anomalous capacitance increase reported in previous experimental studies. The right branch of the curve indirectly agrees with experimental findings that so far have received little attention. The overall U shape scaling behavior provides insights on why there have been difficulties in experimentally observing the pore width dependent capacitance by some research groups.

2. A new mechanistic model was developed for nanopore capacitance to rationalize the observed scaling behaviors. Analysis based on this model indicates that ion solvation structure in nanopores and its response to pore electrification play a critical role in capacitance controlling. This insight lays a theoretical basis for optimizing pore capacitance via manipulation of ion solvation inside nanopores by tailoring the chemical details of ion pairs for a given pore, e.g., pore size.

3. Moreover, there exists significant potential drop between the pore center and bulk electrolytes at equilibrium state. Such an observation contradicts one of the most
fundamental assumptions in the classical transmission line model for electrochemical capacitors. These results suggest that the transmission line model breaks down in pores studied here, and a capacitor regime qualitatively different from that in wide pores emerges. Specifically, although the charge on the pore wall are balanced by ions enclosed between the pore wall and the pore central plane, there exists a significant potential drop between the pore center and the bulk electrolyte, which has no analogy in classical capacitors. Consequently, although the pore walls and the EDLs together can still be viewed as capacitors, they can no longer be described by the classical transmission line model.

Next, research was conducted to investigate how the electrode voltage, one of the most important operating conditions of electrochemical capacitors, affects the thermodynamics of charge storage in sub-nanometer pores. The key findings are as follows:

1. The study showed that charge storage in sub-nanometer pores follow a distinct voltage dependent behavior. Specifically, at low voltages, charge storage is achieved by swapping co-ions in the pore with counter ions in the bulk electrolyte. As voltage increases, further charge storage in due mainly to the removal of co-ions from the pore, leading to a capacitance increase. The capacitance eventually reaches a maximum when all co-ions are expelled from pore. At even higher electrode voltages, additional charge storage is realized by counter-ion insertion into the pore, accompanied by a reduction of capacitance.

2. The change of charge storage mode from ions swapping to co-ion removal is caused by the asymmetry in size of the counter-ions and co-ions and by the fact that, at
high potential, the counter-ion/counter-ion repulsion dominates the system’s energy. It follows that removal of co-ions is more effective in reducing this energy than insertion of counter-ions. The capacitance increases because, at higher potential, the stabilization of co-ions inside the pore by the ionic charges inside the pore per unit surface charge on the pore wall becomes weaker, which is in turn caused by the short-ranged nature of the electrostatic interactions in sub-nanometer pores. At even higher electrode voltages, additional charge storage is realized by counter-ion insertion into the pore and the capacitance reduces due to entropic effects. These results illustrate that the charge storage in sub-nanometer pores exhibits rich behaviors as the voltage changes. The various trends depend on the specific nature of ionic liquids (e.g., cation/anion size asymmetry) and the generic features of sub-nanometer pores (e.g., strongly screened electrostatic interaction between ions).

Finally, investigation was performed to explore the charging dynamics of sub-nanometer pores connected with ionic liquids reservoirs. The key finds are as follows:

1. The charging of nanopores with width comparable to ion size follows an effective diffusion law, in apparent agreement with the predictions by both the classical transmission line model and the phenomenological mean field theory proposed by some researchers most recently. While the agreement with the mean-field theory is physical, the agreement with the transmission-line model is by ‘coincidence’. In particular, the effective diffusion coefficient inferred from the simulations and the mean-field model expresses the collective behavior of ions due to inter-ion
interactions rather than the double layer capacitance and the bulk electrolyte of ionic liquids as in the transmission line model. The fact that the charging of sub-nanometer pores by ionic liquids, which is complicated due to issues such as strong ion crowding and extreme confinement, follows a simple diffusion law is both remarkable and of practical importance. In particular, it can greatly simplify the development of electrode-scale homogenization models for charging, and thus open new avenues for device-level optimization of ECs.

2. The self-diffusion coefficients of ions changes with charge density and the total ion density. During charging, they vary over a few orders of magnitude during charging, and can exceed the ion diffusion in the bulk (under similar conditions) several times. This suggests that fast charging can in principle be achieved if an ionic liquid is optimized specifically for selected porous materials and the required degree of charging.

3. Charging of ionophilic pores is usually accompanied by overfilling of the pores, and the effective diffusion of charge is much faster than the diffusion of ions due to presence of electric ion migrations. When charging is dominated by de-filling or co-ion removal, charging becomes much slower because it is dominated by ion diffusion. While such slow charging can be avoided by using wider pores, or adopting ionophobic pores that are not wetted by ionic liquids at the potential of zero charge can also greatly accelerate charging without notably sacrificing the charge storage capacity of the nanopores.
4. Overall, the studies indicated that electrodes with sub-nanometer pores and room temperature ionic liquids can potential enable the development of electrochemical capacitors with concurrently high power and energy densities.

These insights gained from these studies can be useful when designing or selecting nanopores and ionic liquids to accelerate the charging of nanoporous electrodes and/or to achieve optimal balance between energy density and power density of electrochemical capacitors based on nanoporous electrodes and ionic liquids.
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