

Research Article

Local Ordered Structure of Propylene Carbonate in Slit-Shaped Carbon Nanopores by GCMC Simulation

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An electric double-layer capacitor (EDLC) has high potential for storing electrical energy at a high power density. It was reported that a narrow nanopore system provides higher performance of EDLCs. In such a system, propylene carbonate (PC) is generally used as a solvent in EDLCs. Hence, the structure of PC in the slit-shaped carbon nanopores should be investigated to reveal the EDLC mechanism. In this paper, grand canonical Monte Carlo simulation of PC adsorbed in nanopores was performed to elucidate molecular-level understanding of the influence of PC on the EDLC performance. PC molecules have a highly ordered structure and longer intermolecular distances in nanopores of a pore width less than 0.7 nm. Thus, the highly ordered and low-density structure formation of the adsorbed PC molecules in narrow nanopores provides a permeation path for electrolytes through nanopores, indicating high-performance EDLCs.

1. Introduction

Conventional batteries have high energy density but inadequate power density. An electric double-layer capacitor (EDLC), which is also called a supercapacitor or ultracapacitor, can store electrical energy at a high power density. In addition, EDLCs are durable, have efficient charge and discharge cycles, and contain no heavy metals, which are all advantageous features for relevant applications. Therefore, EDLCs have received much attention as environment-friendly and low-cost electrical power capacitors. However, conventional EDLCs have low energy density. Hence, EDLCs have been actively investigated to obtain both high power and energy density [1–3]. This might be achieved by using carbon materials with a large surface area and adaptable nanopore widths and ions as electrodes. As an EDLC is a liquid-solid interface system, the surface area and nanopore width strongly affect the capacity and cyclability. For this purpose, activated carbons and related materials have been fabricated [4–11].

Ionic solutions are commonly used as electrolytes. The investigation of nanopore width with respect to the effective size of the ion is essential for obtaining highly efficient capac-

itors. Chmiola et al. reported an anomalously high capacitance when the nanopore width was less than 1 nm [12]. Simon et al. also showed a relationship between the ion size and nanopore width; high capacitance is obtained similar to the size of the ion [13, 14]. The removal of the solvation shell of ions is also important, and the mobility of the ions in nanopores is significantly affected by the solvent. Therefore, the effect of the solvent is important to understand in order to elucidate the electrical mechanism of EDLCs. Furthermore, solvents strongly affect the energy and power outputs of capacitors [15]. Propylene carbonate (PC) is relatively inert and is one of the dipolar aprotic solvents commonly used for nonaqueous electrolytes. PC also has a relatively low melting point (224 K) and a high boiling point (515 K). PC molecules create an effective solvation shell around ions due to its high polarity. Thus, PC is an efficient solvent and generally used as the solvent in EDLCs. The structure of the adsorbed PC molecules in carbon nanopores is essential for study of EDLC mechanism. Grand canonical Monte Carlo (GCMC) simulation is a powerful tool to understand molecular behavior and structure in nanopores. It has been used to evaluate and estimate the unique behaviors of simple molecules such as N₂, Ar, and

CH₄ adsorbed in nanopores [16–24]. However, molecular simulation of a cyclic hydrocarbon is much more difficult because of its complexity. Thus, the structure and adsorption mechanism of PC molecules in nanopores have not been studied despite their importance. In this study, the PC structure in slit-shaped carbon nanopores with a width of 0.4–2.0 nm is evaluated by GCMC simulation.

2. Simulation Procedure

GCMC simulation was performed to obtain adsorption isotherms and the adsorbed structure of PC at 303 K. Potential parameters of a PC molecule that were reported by Soetens et al. are used here; a 13-centered model for the rigid PC structure was adopted for the calculations [25]. Intermolecular interactions were described by the sum of the Lennard-Jones interactions and electrostatic interactions between two atoms of different molecules with Ewald summation:

$$\phi_{ij}(r) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^6 \right] + \sum_i \sum_{j(\neq i)} \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}}. \quad (1)$$

Here, the Lorentz-Berthelot mixing rules were applied to obtain the interaction potential and collision size parameters. The cutoff length of the intermolecular interactions was set to 5 nm.

Activated carbons are assumed to have a plenty of slit-shaped nanopores. A slit-shaped nanopore is modeled using two semi-infinite graphite slabs that are assumed to have a neutral charge. Then, a PC molecule-graphite slab interaction is a result of the sum of the Lennard-Jones interaction between a PC molecule and carbon atoms of the graphite wall. Hence, the interaction of a PC molecule with the graphite slab was approximated by Steele 10-4-3 potential [26], which represents a molecule-graphite slab interaction as follows:

$$\begin{aligned} \phi_{sf}(z) \\ = 2\pi\sigma_{sf}^2\epsilon_{sf}\rho\Delta_C \left[\frac{2}{5} \left(\frac{\sigma_{sf}}{z} \right)^{10} - \left(\frac{\sigma_{sf}}{z} \right)^4 - \frac{\sigma_{sf}^4}{3\Delta_C(z+0.61\Delta_C)^3} \right], \end{aligned} \quad (2)$$

where z , ρ , and Δ_C are the vertical distance of the PC molecule from the graphite wall, the atomic number density of the graphite wall, and the interlayer distance of the graphene sheets, respectively. The interaction potential of a PC molecule with the slit-shaped nanopore is given by the following equation.

$$\begin{aligned} \phi_p &= \phi_{sf}(z) + \phi_{sf}(H-z), \\ H &= w + 2z_0, \\ z_0 &= 0.856\sigma_{sf}, \end{aligned} \quad (3)$$

where H is the physical width defined as the internuclear distance between the graphite pore walls and z_0 is the contact

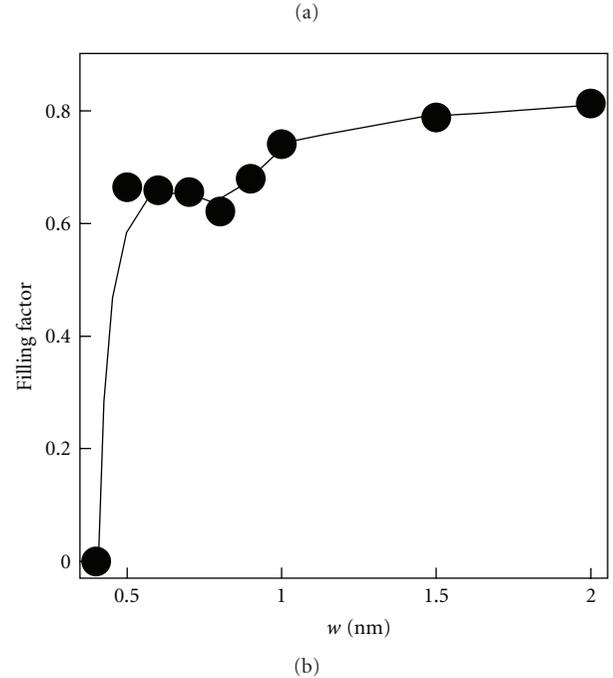
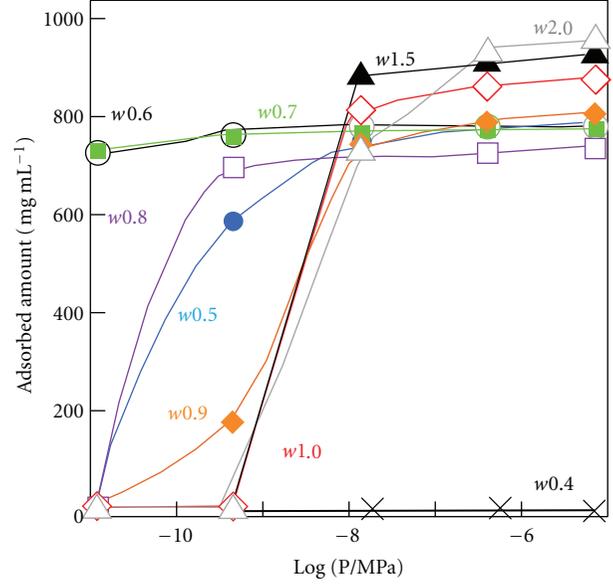


FIGURE 1: (a) Adsorption isotherms of PC in nanopores with $w = 0.4$ – 2.0 nm at 303 K and (b) fractional fillings as a function of pore width.

distance between the PC molecule and graphite pore wall. Thus, we related the physical width, H , to the experimentally determined nanopore width, w . A rectangular cell with dimensions of $10 \times 10 \times H$ nm³ was used for the simulation of PC adsorption in a nanopore. The calculation number for each equilibrium-adsorbed amount is 1×10^7 .

3. Results and Discussion

Figure 1(a) shows the adsorption isotherms of PC adsorbed in the nanopores with $w = 0.4$ – 2.0 nm. PC molecules are not

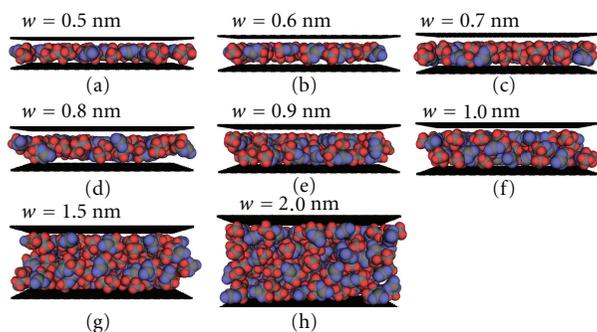
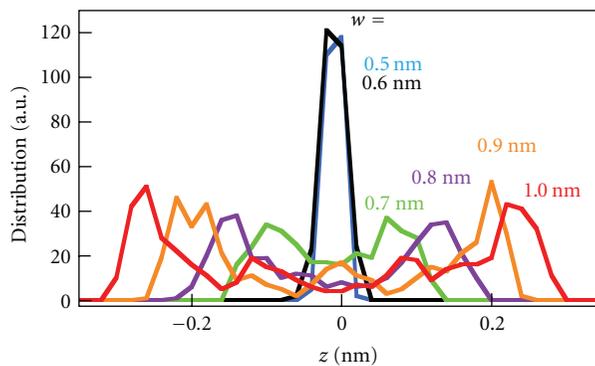


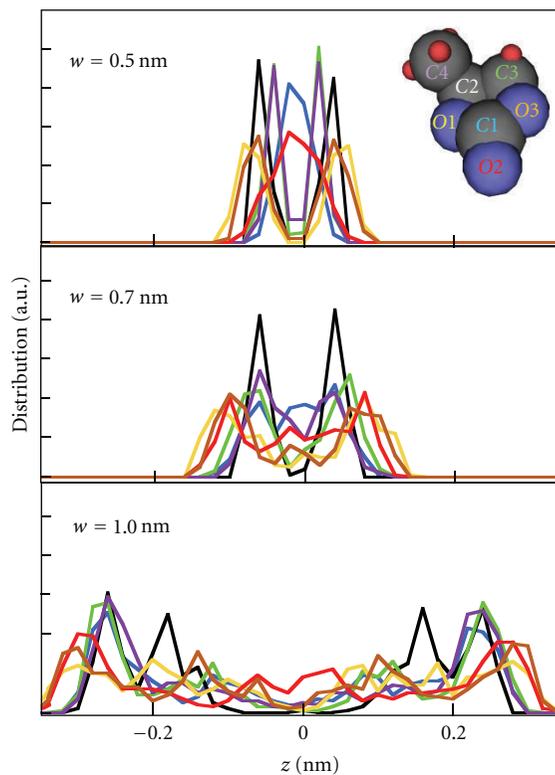
FIGURE 2: Snapshots of PC adsorbed in the nanopores at 10^{-5} MPa.

adsorbed in the case of $w = 0.4$ nm because the nanopore is narrower than the PC molecular size. In nanopore with $w = 0.5$ nm, PC molecules can be adsorbed above 10^{-10} MPa. PC molecules begin to adsorb even below 10^{-10} MPa for $w = 0.6$ and 0.7 nm, which is a result of strong interactions with the pore walls. The threshold pressure of adsorption shifts to pressures higher than 10^{-9} MPa in the nanopores larger than 0.8 nm. Thus, PC molecules are preferentially adsorbed in the nanopores of 0.6 and 0.7 nm. As the bulk density of PC is 1200 mg ml^{-1} , fractional fillings of adsorbed PC are 0.6 - 0.7 for $w = 0.5$ - 0.9 nm and 0.7 - 0.8 for $w = 1.0$ - 2.0 nm, as shown in Figure 1(b). Relatively low fractional fillings of adsorbed PC (<0.7) were observed for $w < 1.0$ nm. The lowest fractional filling was for $w = 0.8$ nm in the range of $w = 0.5$ - 2.0 nm. On the other hand, higher fractional fillings were observed for $w = 1.0$ - 2.0 nm rather than the w smaller than 1.0 nm. The lower fractional filling for the narrower nanopore widths is due to packing restriction of adsorbed PC. Figure 2 shows the snapshots of PC adsorbed in the nanopores at 9×10^{-6} MPa, which is equivalent to a saturated vapor pressure of 7×10^{-6} MPa at 303 K. Monolayer adsorptions of PC molecules roughly occurred for w less than 0.9 nm, while when $w = 0.9$ nm the adsorption is intermediate between monolayer and two layers. Two-, three-, and four-layer adsorption was obviously observed for $w = 1.0$, 1.5 , and 2.0 nm, respectively. Therefore, monolayer adsorption leads to low fractional filling.

Molecular distribution functions of PC for $w = 0.5$ - 1.0 nm in a direction perpendicular to the pore wall were calculated from the snapshots, as shown in Figure 3(a). (See Supplementary Material available online at doi:10.5402/2011/708927.) Here, we focus on the structure of adsorbed PC molecules for $w \leq 1.0$ nm because the trends of the structures for $w = 1.0$ nm and $w > 1.0$ nm are similar to each other. The PC molecules are adsorbed in the center of the nanopores for $w = 0.5$ and 0.6 nm. In contrast, the PC molecules are situated on both pore walls in nanopores larger than 0.6 nm. Figure 3(b) shows the atomic distribution functions of PC for $w = 0.5$, 0.7 , and 1.0 nm. In every nanopore, oxygen atoms are in contact with the pore walls, and, therefore, the carbon atoms are situated relatively far from the pore walls. In the case of the 0.5 nm nanopore width, all the atoms, and especially the double-bonded C



(a)



(b)

FIGURE 3: (a) Distribution functions of the molecular center of PC for $w = 0.5$ - 1.0 nm and (b) atomic distribution functions of each atom for $w = 0.5$, 0.7 , and 1.0 nm in a direction perpendicular to the pore wall at 10^{-5} MPa.

and O atoms (C1 and O2), are situated in the central part of the nanopore. Furthermore, ordered atomic structures were observed for $w = 0.5$ nm, while loose structures were observed for $w = 0.7$ and 1.0 nm.

The intermolecular distance is evaluated from the radial distribution functions of the PC molecules shown in Figure 4. PC molecules have a more ordered structure in the nanopores than in bulk liquid. The distance to the nearest neighboring molecule for the 1 nm nanopore system

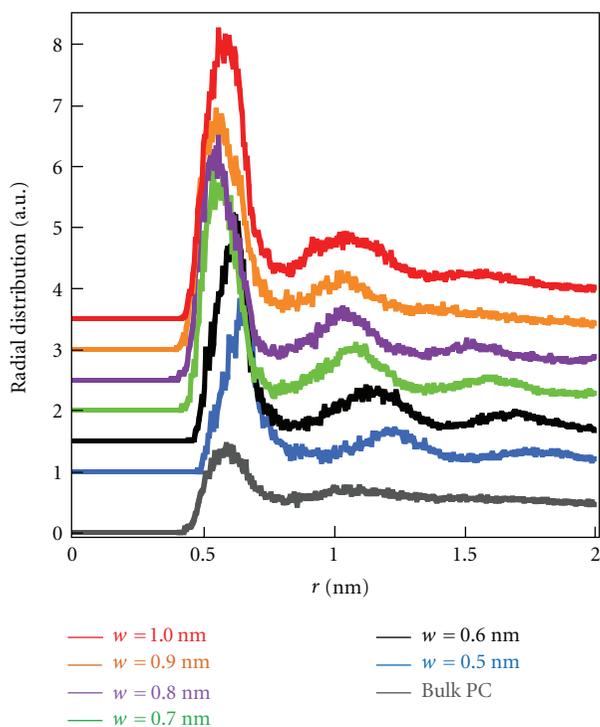


FIGURE 4: Radial distribution functions of PC for $w = 0.5\text{--}2.0$ nm.

is 0.58 nm, which is consistent with that for bulk PC. When $w = 0.7\text{--}0.9$ nm, the nearest-neighbor distance is 0.56 nm, while it is 0.63 nm for the 0.5 and 0.6 nm nanopore systems. Thus, the nearest-neighbor distance in the nanopore widths of 0.5 and 0.6 nm is greater than that for $w \geq 0.7$ nm and bulk PC. The same trends were observed for the distances to the second nearest neighbor, which were 1.2 nm for $w = 0.5$ nm and 1.1 nm for $w = 0.6$ nm. On the other hand, the distance of the second nearest neighbor was 1.0 nm for $w > 0.7$ nm. In the case of bulk PC, no obvious peak was observed. Thus, the second-nearest-neighbor distances also decreased with an increase of the nanopore width. The nanopores with $w < 0.7$ nm induce longer intermolecular distances of the PC molecules.

In this study, the structure of PC adsorbed in slit-shaped carbon nanopores is revealed by GCMC simulation. The adsorbed PC molecules form monolayers in narrower nanopores than 1.0 nm, which imposes unique electrochemical behavior and high electric capacitance according to the preceding study [12]. In the case of nanopores with $w < 0.7$ nm, we observed an ordered structure of the PC molecules in a perpendicular direction to the pore wall and longer intermolecular distances of adsorbed PC molecules. Electrolyte smoothly permeates among PC molecules owing to highly ordered and less dense structure formation of PC molecules, providing highly efficient performance of EDLCs. Further studies are necessary for a full understanding of the mechanism of EDLC by molecular simulations of electrolytes in nanopores.

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