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The effect of different organic solvents on sodium ion storage in carbon nanopores

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In this study fully atomistic grand canonical Monte Carlo (GCMC) simulations have been employed to study the behaviour of electrolyte salt (NaPF_6) and different non-aqueous (organic) solvents in carbon nanopores, to reveal the structure and storage mechanism. Organic solutions of Na^+ and PF_6^- ions at 1 M concentrations were considered, based on the conditions in operational sodium ion batteries and supercapacitors. Three organic solvents with different properties are selected: ethylene carbonate (EC), propylene carbonate (PC), ethyl methyl carbonate (EMC). The effects of solvents, pore size and surface charge were quantified by calculating the radial distribution functions and ionic density profiles. It is shown that the organic solvent properties and nanopore confinement can affect the structure of the organic electrolyte solution. For the pore size range (1-5 nm) investigated in this paper, the surface charge used in this study, can alter the sodium ions but not the solvent structure inside the pore.

Introduction

The sodium (Na) ion battery (NIB) [1] has emerged as a candidate for medium- and large-scale stationary energy storage devices, and it has been proposed as a low cost alternative to the lithium ion battery (LIB). This is mainly because sodium is available in great abundance and at low cost: natural sodium is over 1000 times more abundant than lithium [2, 3]. Another application of sodium is in sodium ion-based supercapacitors where sodium ions are stored in nanoporous materials. A promising electrode material for sodium ion based batteries and supercapacitors is nanoporous hard carbon [4, 5], which presents highly disordered structure and larger interlayer distance than that of graphite. Different models such as the slit pore model are often used [6, 7] to design the hard carbon materials with desirable porous structure. The spatial confinement in hard carbon can affect the solvation of ions and ultimately the specific capacitance [8, 9].

The electrolyte is equally important as a good electrolyte can provide good conductivity and diffusion of ions, greatly reduce side reactions and provide stable performance [10]. The electrolyte is often a mixture of salts and organic solvents for non-aqueous systems. The properties of organic solvents affect their interactions with the salt ions and the solid electrode materials, and ultimately the performance and stability of the electrochemical devices. These properties include: (i) polarity (a good solvent should have a dielectric constant $\epsilon > 15$, in order to solvate the salt ions and limit ion pairing.), (ii) viscosity (low viscosity to improve the Na^+ mobility), (iii) chemical stability (i.e. remaining inert to the charged surfaces of the cathode and the anode during cell operation), (iv)

low melting point and high boiling point to remain liquid at a wide range of temperatures and (v) safety (i.e. nontoxic, and economical) [10]. An appropriate solvent often possesses a combination of the above properties. For the applications of Na ion based electrochemical devices, the interactions of Na^+ ions with a number of organic solvents have been studied in a recent paper [11]. The highest free solvation energy $\Delta G(\text{sol})$ values for the interaction of Na^+ ions with ethylene carbonate (EC), vinylene carbonate (VC), propylene carbonate (PC), butylene carbonate (BC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC) solvents were recently computed [11, 12]. The interactions of the organic solvents with electrode materials are, nonetheless, not fully understood.

A number of first-principle density functional theory (DFT) calculations [13, 14] did study the interactions of Na^+ ions with carbon electrode materials, in which the adsorption energies and electronic properties for the adsorption of Na^+ ions onto graphene and graphene oxide [15] were calculated. This type of simulation is limited owing to its computational expense and the neglect of the organic solvents. Thus, to reduce the computational demand, a one-dimensional (1D) pore model was implemented using classical density functional theory (CDFT) simulations [8, 9]. It has been shown that there is a specific orientation of the solvent molecules forming alternating layers of counter-ions and co-ions near a strongly charged surface, which can lead to capacitance oscillations [16, 17]. Although it could provide some useful insight, such a simplified 1D pore model cannot capture the detailed molecular structure of the organic solvents.

Molecular simulation is a powerful computational technique to investigate further the behaviour of organic electrolytes in carbon nanopores [18]. Very recently it was shown, using atomistic molecular dynamics (MD) simulations, that both nanopore width and surface charge alter the density profiles of Na^+ ions and the

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solvent molecules inside the pores [19]. Both MD and nuclear magnetic resonance (NMR) experiments reveal an amount of ions inside nanopores in the absence of an applied potential (neutral nanopores) [20]. The nanopore confinement affects the movement of the ions in and out the nanopores and, in particular, decreases the self-diffusion coefficients of ions by more than 2 orders of magnitude in comparison to the neat electrolyte [21]. In another study, the structures and stability of tetraethylammonium (Et_4N^+) and tetrafluoroborate (BF_4^-) ions in PC solution in carbon nanopores (of widths 0.5–2 nm) were examined using grand canonical Monte Carlo (GCMC) simulations [22, 23]. Specifically for the case of carbon nanopores of width $w=0.7$ nm, an ordered structure of the PC molecules, which are vertically aligned, and interact with Et_4N^+ and BF_4^- ions [24] was observed. The solvation of Et_4N^+ and BF_4^- ions was found to be much weaker than that of small inorganic ions in aqueous solutions [25] owing to the large size, charge delocalisation and irregular shape of the cations [25]. In addition, the structure of quaternary ammonium $\text{Et}_4\text{N}^+\text{BF}_4^-$ salt solution in PC solvent in slit shaped carbon nanopores was researched [26]. In such a system, PC molecules form a double-layer-like structure by including Et_4N^+ and BF_4^- ions [26]. In an atomistic study of electrochemical capacitors, formed by carbon nanotubes (CNTs) immersed into organic electrolytes of 1M Et_4N^+ and BF_4^- PC solution, it was found that under high electrode charge density, organic ions are contact-adsorbed on the CNT surfaces.

In this paper we use GCMC fully atomistic simulations to study the coupled effects of nanoporous hard carbon and different organic solvents on sodium ion storage. Unlike other GCMC simulations [28], in our study the solvent molecules and atoms are represented explicitly. The paper reports the structure of Na^+ , PF_6^- ions and solvents inside carbon nanopores of various sizes and at different surface charges. The rest of this paper is organised as follows: In Section 2, the simulation methodology and details are given. In Section 3.1, we discuss the radial distribution function of ions and EC, PC, and EMC solutions in neutral and charged carbon nanopores in comparison to their structure in the bulk solution. Subsequently in Section 3.2, we study the density distribution of the ions and solvent along the nanopore direction. Finally in Section 4, conclusions are presented.

Simulation Methodology

Nanoporous hard carbons often presents flat carbon fragments, as has been seen by high resolution transmission electron microscopy [5]. The flat carbon pattern can be modelled effectively by a slit pore model, which has been widely used in molecular simulation studies of physical and chemical processes in nanoporous carbons. The slit pore model offers the space for designing the hard carbon materials with desirable porous structure and is adopted for the investigations in this paper. The unit cell size for the slit pore is $5.165 \times 5.112 \times (w+1.34)$ nm³, where w is the pore width. The unit cell consists of four parallel graphene sheets, two placed at the top and the other two at the bottom of the unit cell [29, 30]. The interlayer distance between the two graphene sheets at the top is 0.335 nm [31, 32]. The same interlayer distance is used for the two graphene sheets at the bottom. Here the nanopore width w is defined as the distance between the top inner-most graphene sheet and the bottom inner-most graphene sheet. The interlayer distance between two graphene sheets was 0.335 nm [31, 32].

GCMC simulations were performed in neutral and partially charged carbon nanopores at 303 K, and were programmed in house. Grand canonical ensemble was adopted for three solvents, ethylene carbonate (EC), propylene carbonate (PC), ethyl methyl carbonate (EMC) (see Figure 2), while canonical ensemble were adopted for Na^+ and PF_6^- ions. The numbers of Na^+ and PF_6^- ions, together with the number of organic solvent molecules, are given in Table 1 for neutral carbon pores and in Table 2 (supplementary information) for charged carbon pores. The numbers in neutral carbon pores are determined so that NaPF_6 concentration is 1M. In charged nanopores, there are more Na^+ ions to keep the whole system neutral. For organic solvents, three equivalent trials of creation, deletion, and movement with rotation were conducted in the GCMC simulations and three cycles of data were averaged for every 2×10^6 steps. Bulk organic electrolytes were also calculated for comparison. The unit cell size in the bulk was $4 \times 4 \times 4$ nm³.

We used a combination of Lennard-Jones and point charge potentials. The potential parameters of Na^+ [33] and PF_6^- [34] ions were as follows: $\sigma_{\text{Na}} = 0.25300$ nm, $\epsilon_{\text{Na}} = 0.06184$ kJ mol⁻¹, $q_{\text{Na}}/e = +1.0$ C, $\sigma_{\text{P}} = 0.37418$ nm, $\epsilon_{\text{P}} = 0.8368$ kJ mol⁻¹, $q_{\text{P}}/e = +0.7562$ C, $\sigma_{\text{F}} = 0.31181$ nm, $\epsilon_{\text{F}} = 0.2552$ kJ mol⁻¹, and $q_{\text{F}}/e = -0.2927$ C. The potential parameters of EC, EMC, and PC are taken from the reference [35], and their molecular numbers are given in Tables I and II in the supplementary information. The potential parameters of carbon atom were $\sigma_{\text{C}} = 0.340$ nm, $\epsilon_{\text{Na}} = 0.2328$ kJ mol⁻¹ [36] and, $q_{\text{Na}}/e = 0.0$ for the neutral carbons and -0.01556 C for the partially charged carbons. In the case of charged nanopores, our model does not allow polarization of the electrode by the electrolyte. A constant, uniform charge is assigned to each carbon atom. Such constant charge simulations provide a fair description of the structure of a liquid at the electrode surface and thus of the capacitance. Intermolecular interactions were calculated using Lennard-Jones and Coulomb potentials. The cross interactions between two kinds of molecular species were calculated on the basis of the Lorentz-Berthelot mixing rules. Ewald summation was imposed in all three directions for accurate calculation of the Coulomb interactions of partial charges.

Figure 1: Snapshots of slit nanopore (of 5 nm) model, containing Na^+ (blue), PF_6^- ions (olive) and a) EC, b) EMC, c) PC molecules between neutral graphene layers.

Figure 2: a) EC, b) PC, and c) EMC solvent molecules. Red: Oxygen, Grey: Carbon, White: Hydrogen. Carbonyl oxygen is the negative pole. Carbons C₁ and C₂ constitute the positive poles.

Results and discussion

Structure within neutral and charged nanopores.

In order to obtain information about the structure inside the nanopores the radial distribution function (RDF) $g(r)$ is calculated. In general, the $g_{AB}(r)$ between two particles A and B is defined by:

$$g_{AB}(r) = \frac{V}{4\pi r^2} \sum_i^{N_A} \sum_j^{N_B} P(r)$$

where V is the volume, N_A and N_B are the number of atoms A and B, respectively, and $P(r)$ is the probability to find a B atom at a distance r from an A atom.

Figure 3 shows the radial distribution functions (RDFs) of Na^+ , PF_6^- , and EC, in different neutral and charged nanopores. The EC solvent has a high dielectric constant (89.78) [37, 38], a viscosity 1.95 cP at 27 °C [11], and a high dipole moment (4.9D). The Na^+ transport number: $t^+ = \frac{D_+}{D_+ + D_-}$, in EC, where D_+ is the diffusion coefficient of Na^+ and D_- is the diffusion coefficient of PF_6^- in EC is 0.49 [11], which is high for sodium ion batteries. The nearest neighbour distances of Na^+ -EC, PF_6^- -EC, and EC-EC in all the carbon nanopores investigated were 0.47, 0.49, and 0.52 nm, respectively, which were very similar to those in the bulk. Decreasing the nanopore width down to 1 nm does not change the nearest neighbour distances. This confirms the strong interactions of EC molecules with the salt ions and that the

Figure 3: Radial distribution functions: i) EC-EC (cyan line), ii) Na-EC (black line), iii) PF_6^- -EC (blue line), and iv) Na- PF_6 (red line). Solid and dotted lines are for neutral and charged nanopores respectively.

Figure 4: Radial distribution functions: i) PC-PC (cyan line), ii) Na-PC (black line), iii) PF_6^- -PC (blue line), and iv) Na- PF_6 (red line). Solid and dotted lines are for neutral and charged nanopores respectively.

nanopores of 3–5 nm do not show strong pore confinement effect. In the nanopores of 1, 2 nm, a shoulder peak of EC – EC distribution appears around 0.6 nm, suggesting weakened EC-EC interactions by space restriction in such narrow nanopores. For each pore size studied here, there is a qualitatively similar ordering structure of Na^+ , PF_6^- and EC, between neutral and charged pores, as can be seen in Figure 3. However, as the nanopore width w decreases, there is a larger discrepancy in the PF_6^- -EC RDFs since the concentration of PF_6^- decreases in charged smaller nanopores.

For the Na^+ – EC RDFs, a stronger discrepancy between neutral and charged pore appears only for the nanopores width of 1 nm, where a more ordered structure was observed. Interestingly, the Na^+ – PF_6^- structure does not depend on the pore confinement (for 3–5 nm pores) in neutral nanopores, as it is instead controlled by the ion pairing and solvation in the EC solvent. The Na^+ – PF_6^- pairing is stronger in the bulk solution than in the nanopores as can be seen by the decrease of the amplitude of the nearest-neighbour peak in Figure 3. The PF_6^- – EC structure shows a peak independent of the nanopore width, and then approaches its bulk value. Overall the nearest neighbour distances of RDFs appear on the same distances for neutral and charged nanopores.

Figure 4 shows the radial distribution functions (RDFs) of Na^+ , PF_6^- and PC in different neutral and charged nanopores. PC solvent has a higher viscosity (2.53 cP at 25 °C [10]) than the EC solvent (1.9 cP at 25 °C [10]). In addition, it has a high dielectric constant of 64.92 [37, 38] and a high dipole moment (4.94D) similar to EC. The nearest neighbour distances of Na^+ -PC, PF_6^- -PC, and PC-PC in the carbon nanopores investigated (2 – 5 nm) were 0.52, 0.49, and 0.54 nm, respectively, which were very similar to those in the bulk. Note that these nearest neighbour distances in the PC solvent are bigger than in the EC solvent, meaning that the interactions with PC solvent are slightly weaker than with EC solvent. The decrease of the nanopore width to 1 nm does not change the nearest neighbour distances (except for the PF_6^- -PC), however a more ordered structure was observed for Na^+ – PC and PF_6^- -PC RDFs. In addition, a stronger discrepancy between neutral and charged pore appears for Na^+ – PC RDF. To compare, the experimental nearest neighbour distance of PC-PC molecules in the bulk was reported to be 0.53–0.54 nm [24], which is in good agreement with our results, indicating the reliability of our simulations. The reported experimental value for the nearest neighbour distance of the PC-PC molecules in the nanopores was reported to be 0.48 nm, which is different from our results, owing to the extreme confinement (narrow slit pores of width $w < 1$ nm).

From Figure 4 can be seen that as the nanopore width w decreases, there is a larger discrepancy on Na^+ – PC and PF_6^- – PC RDFs between charged and neutral nanopores. The bulk radial distributions of PF_6^- – PC were broad but the distribution in pores have relatively sharp peaks. The Na^+ – PF_6^- ordering and correlation is decreased in carbon nanopores in comparison to that in bulk solution. Na^+ – PF_6^- ion pairs were observed in nanopores. In Figure 4, the Na^+ and PF_6^- RDFs in PC are shown to have higher intensity peaks compared to the Na^+ , PF_6^- RDFs in EC solvent. The Na^+ - PF_6^- interactions in the EC solvent appear to be weaker (as shown by the smaller intensity peaks) compared to the Na^+ – PF_6^- interactions in PC. This is owing to the better solvation of EC with Na^+ , PF_6^- than in PC solvent. The Na^+ – PF_6^- ion pair formation in EC was not observed much. Overall, the nearest neighbour distances of RDFs appear on the same distances for neutral and charged nanopores. The solvation of Na^+ in the PC solvent is weaker than the Na^+ – EC solvation, in agreement with the study by Kamath et al. [11, 12], since the peaks of Na^+ -PC distributions were broader than the peaks of Na^+ -EC distributions. The PF_6^- – PC RDF shows a similar peak to that in PF_6^- – EC, which has a higher intensity in the smaller nanopores.

Figure 5 shows the radial distribution functions (RDFs) of Na^+ , PF_6^- , and EMC, in different neutral and charged nanopores. The EMC solvent has a low dielectric constant (2.93) [39] and a low dipole moment in contrast to the EC and PC solvents. However, EMC viscosity is low (0.65 cP at 25 °C [10]) thus leading to Na^+ transport number of 0.44 [11] same to that in PC solvent, and lower than that in EC solvent (0.49). This is a high transport number, acceptable for operation in sodium ion batteries [40]. The nearest neighbour distances of Na^+ -EMC, PF_6^- -EMC, and EMC-EMC in the carbon nanopores were 0.3, 0.61, and 0.6 nm, respectively, which were very similar to those in the bulk. Compared to the results in Figures

3 and 4, the nearest neighbour distance of Na^+ -EMC is shorter than that of Na^+ -EC and Na^+ -PC. For the range of pore size (1 – 5 nm) investigated in this paper, the change of the nanopore width does not alter the nearest neighbour distances.

It can be seen, from Figure 5, that there is a qualitatively similar ordered structure of Na^+ -EMC, PF_6^- -EMC and EMC-EMC between neutral and charged nanopores. In addition, it can be seen that as

Figure 5: Radial distribution functions: i) EMC-EMC (cyan line), ii) Na-EMC (black line), iii) PF_6^- -EMC (blue line), iv) Na^+ - PF_6^- (red line). Solid and dotted lines are for neutral and charged nanopores respectively.

Figure 6: Density distribution along the z direction: i) Carbons of EC (cyan line), ii) Carbonyl oxygen of EC, iii) Na^+ (black line), iv) PF_6^- (blue line), v) Na^+ - PF_6^- (red line). Solid and dotted lines are for neutral and charged nanopores respectively.

the nanopore width w decreases, there is a stronger ordering in the Na^+ -EMC RDF and a larger discrepancy in charged and neutral

Figure 7: Density distribution along the z direction: i) Carbons of PC (cyan line), ii) Carbonyl oxygen of PC, iii) Na^+ (black line), iv) PF_6^- (blue line), v) Na^+ - PF_6^- (red line). Solid and dotted lines are for neutral and charged nanopores respectively.

nanopores, indicating that small nanopores and the surface charge can alter the Na^+ -EMC interactions. Also an ordered structure of the PF_6^- -EMC RDF is observed, with the decrease of the nanopore width. For the EMC-EMC RDFs, owing to its low polarity, no obvious ordered structure is observed, indicating a much weaker correlation than the EC-EC (Figure 3) and PC-PC (Figure 4) interactions. As shown in Figure 5, the Na^+ - PF_6^- structure depends on the charged nanopore surface.

The Na^+ - PF_6^- pairing is weaker in the bulk solution than in a small nanopore of 1, 2 nm, as can be seen from the nearest neighbour peak in Figure 5. This is opposite to the behaviour that appears in high polar solvents such as EC and PC. This is because the ions pairing becomes stronger when the ions are dissolved in a low polarity solvent. In bigger nanopores ($w = 3$ -5 nm), the solvation of Na^+ in the EMC solvent becomes stronger in agreement with the EC and PC solvents (see Figure in supplemental information). The higher Na^+ -EMC and Na^+ - PF_6^- RDF peaks in Figure 5 (compared to Figure 3 and Figure 4) suggest that the correlation between electrolyte ions and EMC is stronger in EMC solutions, than in EC or PC solutions, in agreement with experiments [40]. This is due to the higher accessibility of Na^+ to EMC, whereas EC, PC solvents have a ring structure that is hard for Na^+ to access. The PF_6^- -EMC RDF shows little ordering, which is pronounced for the smaller nanopores, similar to the structures in EC and PC solvents (see also Figure 2 in supplementary information).

Density distribution within neutral and charged nanopores

In Figures 6 and 7 the density distribution of EC and PC solutions confined in nanopores is depicted. The EC and PC solvents shows strong layering. Adsorbed structures of the carbons and carbonyl oxygens of EC and PC molecules on the nanopore walls can be clearly observed from the density distributions in Figures 6 and 7. EC and PC molecules mostly formed double, triple or multiple layers in nanopores of widths 2, 3, 4, and 5 nm, respectively. In particular, the carbons of the EC (or PC), which constitute the positive pole of EC (or PC), and the carbonyl oxygen, which constitutes the negative pole, are adsorbed on the carbon nanopore surfaces owing to the strong vdW attraction between the solvent and the carbon walls. A higher density distribution is observed for both the positive and negative poles of EC (or PC) near the wall surfaces than further away from them, but still there is larger density of positive poles near the walls. The density distribution is more uniform for the largest nanopore (5 nm) studied. The carbons and carbonyl oxygen of the EC and PC molecules are nearer to the pore wall than the Na^+ and PF_6^- ions for the nanopore width of 2 nm. The Na^+ ions are not adsorbed (condensed) on the nanopore walls; instead, they are dissolved in the EC (or PC) solvent. This behaviour is contrary to the theoretical predictions by Jiang et. al. [8, 9], where the counterions are condensed to the walls of the pore. Similar layering of the solvent density profile appears in the ionic liquid (TEA^+ , BF_4^-)/acetonitrile (ACN) [41] or (BMIM^+ , BF_4^-)/ACN mixtures (near the interfacial region) [42]. In such ionic liquid solutions, most of the cations are observed near the negatively charged surface, which is in contrary to our results where the Na^+ ions are displaced by the solvent, further from the charged surface. The difference is because our electrolyte system is asymmetric with smaller Na^+ cations in comparison to bigger PF_6^- anions. The asymmetry of the ions can have an effect on the structure of the ions near the electrode surface. In these atomistic simulations of the ionic liquids [41,42] (the cation and anion are of similar size), the density of counterions (TEA^+ or BMIM^+) are higher near the electrode surface, and more pronounced than the solvent density. This phenomenon observed by the atomistic simulations are in qualitative agreement with the theoretical model by Jiang et. al. [8, 9] when the systems have the cations and anions of similar sizes.

A similar alternating layers structure was observed for Na^+ and PF_6^- ions. The distances from a pore wall were mostly independent of nanopore width for 3–5 nm and were 0.2, 0.2, and 0.25 nm for Na^+ , PF_6^- , and PC, respectively. The charged nanopore does not seem to significantly alter the density distribution of the positive PC poles and the Na^+ and PF_6^- ions.

Figure 8: Density distribution along the z direction: i) Carbons of EMC (cyan line), ii) Carbonyl oxygen of EMC, iii) Na^+ (black line), iv) PF_6^- (blue line), v) $\text{Na}^+ \text{PF}_6^-$ (red line). Solid and dotted lines are for neutral and charged nanopores respectively.

Moreover, the nanopore size does not affect the trend of the density profiles of the PC solvent and ions. Thus, the distribution of PC near the nanopore walls seems to be responsible, in part, for the accumulation of Na^+ ions near the nanopore centre for both neutral

and charged nanopores. A similar behaviour also appears for the EC solution (results shown in supplemental information), which has a high dipole moment similar to the PC solvent. In particular, in a one-dimensional charged pore model of 4 nm width, studied by classical density functional theory (CDFT) [9], it was shown that the opposite charge (to the surface) pole of a dipole solvent is adsorbed to the nanopore walls [8]. Next to the pole of the dipole, the counterions are accumulated [8]. In that one-pore model there are no counterions present in the centre of the nanopore [8]. This behaviour is opposite to that presented in our atomistic simulation work where the counterions (Na^+ ions) are distributed uniformly further from the nanopore walls towards the centre of the nanopore. For a smaller nanopore size of 1.5 nm width [8] or 2.5 nm width [9], the opposite charge (to the surface) pole of the solvent is adsorbed mainly on the nanopore walls but a smaller density also appears in the centre of the nanopore. In those smaller nanopore widths the counterions distribution is found next to the opposite charge (to the surface) pole of the dipole, close to the nanopore walls [9]. Instead, our simulation results, in Figure 6, show that most of Na^+ ions (counterions) are distributed further than nanopore walls towards the nanopore centre.

In Figure 8 the density distribution of EMC solutions confined in the nanopores is depicted. A layer of carbons of the EMC molecules appears very near to the pore wall whereas most of the carbonyl oxygens are further from the pore wall. This is different compared to the case with a high polarity solvent such as PC and EC. Carbon rings in EC and PC have relatively strong interaction with carbon walls. On the other hand, EMC has weak interaction with carbon walls. Therefore, EMC could freely move in nanopores, while EC and PC rings were parallelly adsorbed on carbon surfaces. The density distribution of EMC carbons and carbonyl oxygens with nanopore width of 5 nm is uniform, whereas the ordering near the graphene walls becomes more explicit at a nanopore width of 2 nm.

In addition, Na^+ and PF_6^- ions were based mainly in the centre of the nanopore. The nanopore width does not affect the trend of the density profiles of the ions. Furthermore, the charged nanopore does not seem to significantly alter the density distribution of the EMC solvent and ions. It only enhances the layering of the positive pole (carbons) and the negative pole (carbonyl oxygen). Similar behaviour was observed for a higher charge distribution of $-50e$ (results shown in supplemental information). The Na^+ ions are not adsorbed (condensed) near the charged walls of the pore (the same behaviour appears for a higher charge distribution of $-50e$: results shown in the supplementary information). According to the data presented in Figures 6, 7, 8 the polarity of the solvent does not dramatically alter the density distribution of solvent atoms and electrolyte ions, in contrast to the work of Jiang et al. [8], where a small decrease of the dipole moment (from 2.55 Debye to 1.7 Debye) of the solvent significantly alters the density distribution of the poles of the solvent and the ions, especially for nanopores of size 1.5 – 2.5 nm. According to Zhang et al. [42], an increase of solvent polarity weakens the accumulation of counterions next to the electrode surface owing to the screening of electrode charges and the relatively lower ionic desolvation. This is contrast to results from a one dimensional pore model [8] where the counterion concentration is increased near the walls [8]. Wide pores (larger than 2 nm diameter) often appear in cylindrical shape. We would expect that Na^+ would be solvated, in all the solvents considering our results for slit-pore models. In particular for negatively charged cylindrical mesopores, a cylindrical compact layer of Na^+ ions will be

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formed [43, 44] along the pore wall. By increasing the radius of the cylindrical nanopore, more Na^+ will diffuse into the pore centre, due to the decrease of the confinement effect. Compared to slit pores, we would expect to observe a stronger correlation between Na^+ ions and the pore wall in cylindrical nanopores. For charged cylindrical nanopores, we would expect a stronger Na^+ - solvent correlation, than the slit pores, due to formation of the Na^+ cylindrical layer.

Conclusions

In summary, we have reported GCMC results obtained for Na^+ and PF_6^- ions in EC, PC and, EMC bulk solutions and confined in slit-shaped carbon nanopores with different neutral and charged pore sizes. The slit pore widths considered were 1-5 nm. It can be concluded that the use of a linear solvent such as EMC provides a different structure to cyclic solvents such as EC and PC on the Na^+ structure. The nearest neighbour distances of the organic electrolyte solution were not altered by the nanopore confinement for the range of pore sizes studied. In addition, the low polarity of the EMC solvent alters the salt ion pairing. Moreover, the carbonyl oxygen (negative pole) and carbon (positive pole) density distributions very close to the nanopore wall are different for the EMC and PC (or EC) solvents. In a one pore model studied by CDFT, a small change (decrease) in solvent polarity rather overestimates the density distribution of the poles of the solvent and salt ions, in comparison to our atomistic simulation data. The counterion condensation on the charged nanopore walls, which was observed in CDFT, does not appear in our data. Instead, the ions prefer to be further from the charged nanopore wall, forming an alternating layering structure. The fully atomistic description presented here combined with GCMC simulations is an effective methodology to study and achieve a better understanding of organic electrolyte solutions confined in carbon nanopores. An alternative method is to apply a constant potential to electrode surfaces with arbitrary geometries where the charges can vary depending on the local geometry [45]. However, such approach is very computationally expensive and would increase an order of magnitude the computational cost [46]. Using such a molecular simulation methodology, we can easily tune to carbons of different physical and chemical properties or different organic solvents to extrapolate ion storage, diffusion [47] and, capacity under charge/ discharge cycles [48] and under operating conditions.

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