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Effect of pore size and surface charge on Na ion storage in carbon nanopores

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Na ion batteries (NIBs) are considered as a promising low cost and sustainable energy storage technology. To better design nanoporous carbons as anode materials for NIBs, molecular dynamics simulations have been employed to study the behavior of Na^+ ions (as well as PF_6^- ions) confined within carbon nanopores, in the presence of non aqueous (organic) solvent. The effects of pore size and surface charge density were quantified by calculating ionic density profiles and concentration within the pores. Carbon slit pores of widths 0.72-10 nm were considered. The carbon surfaces were charged with densities ranging from 0 (neutral pores), $-0.8e/nm^2$, $-1.2e/nm^2$, $-2e/nm^2$. Organic solutions of Na^+ and PF_6^- at 1M concentrations were considered at operating sodium ion batteries conditions. As the surface charge density increases, more Na^+ ions enter the pores. In all pores, when the surface is highly charged the Na^+ ions move toward the negatively charged graphene surfaces because of counterion condensation effects. In some instances our results reveal the formation of multiple layers of adsorbed Na^+ inside the pores. Both nanopore width and surface charge alter the density profiles of ions and solvent inside the pores.

1 Introduction

Electrochemical energy storage devices play an important role in the transition to low carbon society. The sodium (Na) ion battery (NIB) technology¹ has reemerged as a candidate for medium and large-scale stationary energy storage applications²⁻⁴, and it has been proposed as an alternative to the lithium ion battery (LIB). Unlike lithium, sodium is available in great abundance and at low cost: natural sodium is over 1000 times more abundant than lithium⁵. Due to the above reason, the NIB technology has attracted world-wide research interest in recent years and has seen rapid development, particularly in new electrode materials^{3,6}. A number of new cathode materials have been proposed with high operating voltage, such as layered oxides, tunnel-type oxides, Olivine $NaMPO_4$ (M= Fe, Mn, etc), pyrophosphates and mixed polyanions, NASICON $Na_xM_2(PO_4)_3$, etc^{3,7}. Compared to cathode⁸, the research on anode materials^{9,10,11} is limited. Carbon based materials is the largest category of anode materials for NIBs and is still considered as the best, due to its natural abundance, low cost and relatively good storage capacity^{12,13}. The widely used carbon materials for NIBs are hard carbons^{12,14-16}, so-called non-graphitic carbon, due to its highly disordered structure and large interlayer distance¹². Recent development has seen the use of nano cellular carbon foam¹⁷, carbon micro-spheres¹⁸, electron-spun carbon nano-fibers^{11,14}, hollow

carbon nanowires^{15,19} and carbon nanobubbles²⁰, which involve complicated preparation processes and even expensive and toxic chemicals (e.g. ionic liquids, HF). Despite the existing research, there lacks a fundamental understanding of the effects of carbon structural properties (i.e. surface area, porosity and pore size, pore chemistry) on the electrochemical performance (i.e. storage capacity and dynamics). There is therefore a need to develop research in this area, to enable break-through development in NIB technology.

Simulations at the atomic/molecular level²¹⁻²⁴ can be used to easily tune to carbons of different physical and chemical properties, and link to performance indicators. Molecular simulations have been successfully used to design materials for Li-ion batteries¹², and provided valuable insights in Li-ion intercalation into graphite²⁵. Molecular simulation studies in the context of carbon materials for NIB applications are mainly found with Na ion adsorption on graphene. Using first-principle density functional theory (DFT) calculations, the adsorption energies and electronic properties for the adsorption of Na onto graphene and graphene oxide²⁰ were calculated. The adsorption of Na^+ ions on graphene oxide-epoxide was found to be stronger than the adsorption of Na^+ on pristine graphene however resulted in the generation of NaOH²⁰ as by-product. Different types of graphene such as doped with B^{26,27} or N^{26,28} or with defects^{26,29} can exhibit differences in adsorption energy, electronic structure and Na storage than those in pristine graphene. It was proposed that boron-doped graphene can be a promising anode candidate for

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Na-ion batteries²⁷. This has been confirmed by experimental research. The reported DFT simulations are useful but limited as: (1) graphene can not represent hard carbons which have disordered and porous structure, (2) organic solvent molecules and electrolyte salt ions are not included in the simulations.

It is believed that organic solvents and electrolyte salts affect largely the electrochemical performance and the stability of electrode materials. Several organic solvents have been considered (or borrowed from LIB applications) for NIB applications. These include: ethylene carbonate (EC), vinylene carbonate (VC), propylene carbonate (PC), butylene carbonate (BC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC) solvents, due to their good polarity, low viscosity, ability to remain in liquid state at a wide range of temperatures (characterized by low melting point and high boiling point), safety and economical affordability. The salt used can have a profound effects on the battery performance. Both NaPF_6 and NaClO_4 ^{30,31} have been used as salts in NIBs, although the latter has intrinsic safety concerns. Kamath et al. recently studied the interaction energy between organic solvent molecules and NaClO_4 salt using molecular dynamics (MD) simulations. EC:DMC and EC:EMC solvent mixtures were found to be top electrolyte candidates³², as they present the highest free solvation energy.

In this paper, we report for the first time an atomistic modeling study consisting of a slit carbon pore (representing hard porous carbons), organic solvent molecules and electrolyte salt ions, with the aim to mimic the real system when porous carbons are used as anode materials in NIBs. We investigate the Na^+ , PF_6^- electrolyte³³ (which is the appropriate one for NIBs and LIBs) structure inside slit carbon nanopores^{34–39}, with the presence of EC organic solvent molecules. The rest of this paper is organized as follows. In Section 2, the simulation methodology and details are given. In Section 3.1, we discuss first the density and structure of EC solutions in neutral graphene pores and subsequently in Section 3.2 the density and structure of ions and EC molecules are presented as a function of the graphene charge density. Finally in section 4, conclusions are presented.

2 Simulation methodology

The most widely used model for nanoporous carbon is a slit pore model, which is based on the observation of the presence of flat carbon fragments using the high resolution TEM⁴⁰. The slabs below and above the slit-shaped nanopore volume consist of three and four graphene sheets, respectively, and each sheet is separated by 0.335 nm^{41,42}. A schematic of the simulation box is reported in Figure 1. In this paper we simulate both neutral and charged nanopores. The nanopore width w is defined as the distance between the center of masses (of the carbon atoms) of the two innermost graphene layers. In our study widths of 0.72, 0.74, 0.76, 0.85, 1.02, 1.14, 1.36, 2.38, 3.06 and 10 nm were considered. In the case of charged nanopores, the two inner most graphene sheets on the two slabs are assigned negative charges of $-20\text{e}(-0.8\text{e}/\text{nm}^2)$, $-30\text{e}(-1.2\text{e}/\text{nm}^2)$, $-50\text{e}(-2\text{e}/\text{nm}^2)$. The graphene layers are of (10,10) armchair type and of area $5 \times 5 \text{ nm}^2$.

In this study we use the molecular dynamics method^{43–45}. The classical Newton equation that governs the motion of the par-

Fig. 1 Slit pore model, containing Na^+ ions (blue), PF_6^- ions (olive) and EC molecules between neutral graphene layers. The EC molecule is shown explicitly.

ticles is⁴⁶

$$m_i \frac{d\mathbf{v}_i}{dt} = -\nabla V_i \quad (1)$$

where V_i is the potential acting experienced by particle i and m_i is its mass. Carbon atoms in the graphene sheets are held stationary^{47–49} and modeled as Lennard–Jones spheres, with $\sigma_C = 0.34 \text{ nm}$ and $\epsilon_C/k_B = 28$ ⁵⁰. For the ions the potential is the sum of Lennard-Jones (LJ) V_{ij}^{LJ} , acting along the line between the centers of mass of two particles force⁵¹, and Coulomb potentials, and is given by:

$$V_i = V_{ij}^{LJ} + V_{ij}^{ele} = 4\epsilon_{ij} \left(\frac{\sigma_{ij}^{12}}{r_{ij}^{12}} - \frac{\sigma_{ij}^6}{r_{ij}^6} \right) + \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} \quad (2)$$

where ϵ_{ij} is the interaction energy between atom i and atom j , q the charge of the atom, and ϵ_0 vacuum permittivity. The 12 – 6 LJ parameters for dissimilar interactions were determined using Lorentz–Berthelot mixing rules: $\epsilon_{ij} = (\epsilon_i \epsilon_j)^{1/2}$, $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ ⁵¹. For the solvent molecules the potential V_i given by a sum of three terms:

$$V_i = \sum_{j \neq i} (V_{ij}^{LJ} + V_{ij}^{ele} + V_{ij}^{torsion} + V_{ij}^{angle}) \quad (3)$$

where V_{ij}^{angle} is the bending potential between three consecutive atoms, and $V_{ij}^{torsion}$ is the dihedral potential in the EC molecules. The force field of the EC molecules has been taken from Ref.⁵². The simulated density of the EC solution at 323 K and 1 bar was 1.312 g/cm^3 , whereas the experimental value was 1.322 g/cm^3 at 313 K^{53,54}. The parameters for Na^+ and PF_6^- have been taken from References^{55,56} respectively. The simulations were performed in an electrolyte concentration of 1M. Left and right of the nanopore model (Figure 1), equilibrated bulk electrolyte solutions (1M) at 323 K were added. Before any MD simulation starts, the salt ions and EC molecules are only in the bulk phase, not in the pore volume. In total 114 number of each Na^+ and PF_6^- ions, and 1500 EC molecules (for the large 10 nm pore, 198 of each Na^+ and PF_6^- ions, and 2600 EC molecules were used). Then NPT ensemble simulations were performed at 1 bar pressure at 323 K, for 1 ns, to allow the salt ions and EC molecules to come into the pore volume. During that NPT simulations only the volume in the x dimension fluctuates, whereas the y and z dimensions remain constant. The y dimension is 5 nm, whereas as the z dimen-

sion depends on the nanopore width w . To set the temperature and pressure, in NPT simulations, the velocity rescale thermostat⁵⁷ and Berendsen barostat⁴⁴ were used with time constants $\tau = 0.5$ ps and $\tau_p = 0.5$ ps, respectively. Then, the NVT ensemble was used at 323 K for 30 ns. The results were calculated over the last 25 ns of the NVT simulations, where the coordinates of atoms were saved every 2 ps. In the NVT simulations the Nose-Hoover thermostat⁵¹ was used with $\tau = 1$ ps. All the bonds in the EC molecules are kept constant to their equilibrium value⁵² through the LINCS algorithm⁴⁴. The cut off for the non-bonded (Lennard-Jones) interaction was set to 0.9 nm. A long range dispersion corrections for Energy and Pressure was applied⁵⁸. Also, the particle mesh Ewald method (PME)⁵⁹ has been used to treat the long range electrostatics with a Fourier-spacing of 0.1 nm and an order of interpolation 6. The equations of motion (Eq. (1)) were integrated using the velocity verlet algorithm⁶⁰ with a time step of 1 fs.

3 Results and Discussion

3.1 Density distribution within neutral pores

We begin by discussing small nanopores of zero charge density, below 0.85 nm slit width ($w < 0.85$ nm). When the graphene surface charge density is zero the electrolyte (Na^+ , PF_6^-) ions concentration inside narrow sub nanometer ($w < 0.85$ nm) pores is zero, indicating that the Na^+ (and similarly the PF_6^-) ions reside in the bulk organic solution. The EC solvent has a high dielectric constant^{61–63}, which means that the electrolyte (Na^+ , PF_6^-) ions are dissolved into the bulk solution. Our results suggest that the electrolyte ions can be found within larger, simulated, neutral pores bigger than 0.85 nm, as depicted in Figure 2.

Fig. 2 Density profile of Na^+ ions along z direction of slit pore model (Fig. 1) for different slit pore widths: i) 1.02 nm (circles), iii) 2.38 nm (squares), iii) 3.06 nm (diamonds), iv) 10 nm (stars).

In particular, for a narrow nanopore of 1.02 nm width there is one layer (the same behavior appears for nanopores of 0.85, 1.14 nm width—results not shown), of low amplitude, of Na^+ (Figure 2) and PF_6^- (Figure 3) formed in the center of the nanopore,

Fig. 3 Density profile of PF_6^- ions along z direction of slit pore model (Fig. 1) for different slit pore widths: i) 1.02 nm (circles), iii) 2.38 nm (squares), iii) 3.06 nm (diamonds), iv) 10 nm (stars).

however for wider nanopores such as of 2.38, 3.06 nm two and four ions layer can be formed respectively, close to the graphene surfaces, due to the van der Waals interaction. For the largest slit nanopore studied, $w = 10$ nm, there is no obvious layering in the center of the pore, but close to the graphene surfaces (results not shown), similarly to the narrow pores. There is a similar behavior in the density profiles of PF_6^- ions inside the pores (Figure 3) to those of Na^+ ions in Figure 2 (and PF_6^- ions in Figure 3) in all pores considered, are not perfectly symmetric due to the small number of electrolytes ions within the nanopores.

Figure 4 depicts the density profile of carbonyl oxygens ($=O$), as a way to trace the structure of EC molecules inside neutral nanopores of different slit pore widths. Even in sub nanometer

Fig. 4 Density profile of carbonyl oxygen $=O$ atoms along z direction of slit pore model (Fig. 1) for different slit pore widths: i) 0.76 nm (stars), ii) 1.02 nm (circles), iii) 2.38 nm (squares), iv) 3.06 nm (diamonds).

pores (such $w = 0.72 - 0.76$), EC molecules can enter inside such neutral nanopores, forming one layer of EC molecules between the graphene surfaces (results not shown for slit pore widths $0.72 - 0.74$ nm). By increasing the nanopore width to 1.02 nm two layers of EC molecules are squeezed inside the nanopores, where the single layer of Na^+ ions is dissolved. For narrow neutral nanopores of $0.72 - 1$ nm width, few EC molecules can enter the nanopores, and most of them remain in the bulk solution. Thus the Na^+ ions preferentially, and due to the high polarity of EC molecules, reside in the bulk solution region. By further increasing the nanopore width, well-defined layering of EC molecules in the nanopores appears, which is more pronounced near the graphene surfaces due to the short range van der Waals interaction.

3.2 Density distribution within charged pores

3.2.1 Distribution of Na^+ and PF_6^- ions

In this section we investigate the density distribution of the electrolyte ions (Na^+ , PF_6^-) inside carbon nanopores which are negatively charged. The two most inner graphene layers are smoothly charged with charges $-20e(-0.8e/nm^2)$, $-30e(-1.2e/nm^2)$, $-50e(-2e/nm^2)$. Figure 5 summarizes the effect of pore size and surface charge on the number of Na^+ ions coming into the nanopores. For the same pore width, we can see the increase of the number of Na^+ ions inside the pores, with the increase of the surface charge. This is true for all the cases of nanopore width. Also it can be seen the increase of Na^+ ions inside the pores with the slit pore width for $w > \approx 1$ nm at a constant surface charge. The number of EC molecules in the pores also increases with the increase of the pore width, as shown in the inset of Figure 5. However, the pore surface charge seems to have negligible effect on the number of EC molecules; a high surface charge of $-2e/nm^2$ gives almost the same number of EC molecules compared to a neutral surface.

Fig. 5 Number of Na^+ ions inside nanopores: i) surface charge: $-2e/nm^2$ (circles), ii) surface charge: $-1.2e/nm^2$ (squares), iii) surface charge: $-0.8e/nm^2$ (diamonds), iv) neutral surface (upper triangles). Inset: Number of EC molecules inside nanopores. Filled symbols are for Na^+ ions and open symbols for EC molecules.

The impact of the surface charge on the Na^+ ions number density (number of Na^+ ions/ V_{pore} , where $V_{pore} = 5 \times 5(w - \sigma_c)$ is

the nanopore volume) is pronounced for narrow nanopores, especially at high surface charge, as can be seen in Figure 6. For example, for a nanopore of 1 nm with surface charge of $-2e/nm^2$, the number density of Na^+ ions is more than 5 times that of a neutral surface. In particular at high surface charge ($-1.2, -2e/nm^2$) the Na^+ ions density decreases with the slit pore width, however it still remains larger than the bulk value, even for large nanopores (of $w = 10$ nm), qualitatively similar to theoretical predictions⁶⁴. This happens because of accumulation of Na^+ ions near the negatively charged inner most graphene layers due to counterion condensation. The electrostatic attraction between the charged surface and Na^+ ions is the driving force that leads them inside the nanopores. Instead, in neutral nanopores, we can see that the Na^+ ions density increases with the slit pore width. The Na^+ ions density inside narrow neutral nanopores ($1.02 - 2$ nm) is lower than that in the bulk solution (0.6022 nm⁻³) as can be seen in Figure 6). This suggests that in the case of such neutral nanopores ($1.02 - 2$ nm) the electrolytes preferentially reside in the bulk EC solution, due to the large absolute Gibbs free solvation energy of Na^+ ions in EC solvent⁶⁵.

Fig. 6 Number density of Na^+ ions inside nanopores: i) surface charge: $-2e/nm^2$ (circles), ii) surface charge: $-1.2e/nm^2$ (squares), iii) surface charge: $-0.8e/nm^2$ (diamonds), iv) neutral surface (upper triangles). Dashed line shows the Na^+ ion number density in the bulk solution. Solid lines has been added to guide the eye. The volume of a nanopore is: $V_{pore} = 5 \times 5(w - \sigma_c)$ nm³.

Figure 7 shows the density profiles of Na^+ ions as a function of graphene surface charge density. It is shown that with surface charges applied on the two inner most graphene sheets, Na^+ ions enter into the sub nanometer pores; as the graphene surface charge increases, more Na^+ ions can be seen in the sub nanometer pores. The surface charge affects the Na^+ density profile inside the nanopores. In particular, for sub nanometer pores ($w = 0.76$ nm), at high surface charges ($-1.2e/nm^2, -2e/nm^2$) two layers of Na^+ ions are formed, whereas at low surface charge ($-0.8e/nm^2$) one layer of Na^+ is formed. The same behavior appears in sub nanometer pores of $0.72 - 0.74$ nm (results not shown). However PF_6^- ions cannot enter such narrow pores, due to its size.

For larger nanopores such as of $1.02, 1.36, 1.7$ nm width,

Fig. 7 Density profile of Na^+ ions along z direction of narrow slit pore models (Fig. 1) of width (a) $w = 0.76$ nm, (b) $w = 1.02$ nm, (c) $w = 1.36$ nm, (d) $w = 1.7$ nm, (e) $w = 2.38$ nm, (f) $w = 3.06$ nm) for different surface charge: i) surface charge: $-2\text{e}/\text{nm}^2$ (circles), ii) surface charge: $-1.2\text{e}/\text{nm}^2$ (squares), iii) surface charge: $-0.8\text{e}/\text{nm}^2$ (diamonds) iv) neutral surface (stars).

the confined Na^+ ions yield more, well-defined, density layers (Figures 7b-d). The intensity of the Na^+ and EC density layers at contact with the graphene surfaces increases as the charge density of the graphene layers increases. As the surface charge density increases, the pore-ion electrostatic interaction becomes more and more favorable. Thus, at a high surface charge density studied ($-2\text{e}/\text{nm}^2$), the Na^+ ions move toward the negatively charged graphene surfaces because the electrostatic attraction becomes dominant, leading to adsorption of Na^+ ions onto pore surfaces, as is depicted in the Figures 7b-f. In particular for all the nanopores at highest surface charge density ($-2\text{e}/\text{nm}^2$), a thin layer of Na^+ ions is adsorbed onto the surfaces, as depicted in Figures 7a-d. In that case, Na^+ ions are strongly bound on the negatively charged graphene layer due to counterion condensation effect^{66,67}. It can be seen that as the charge density decreases in nanopores of 1.36, 1.7 nm width, Na^+ ions tend to move away from the graphene surface. In this case, the Na^+ ions are not adsorbed to the graphene surface, rather they prefer to be to-

wards the center of the pore, and its density profile depends on the nanopore width (Figures 7c-f). This occurs because the ions prefer to be solvated to EC solvent molecules, which have high dielectric constant unless the surface is so highly charged that electrostatic interactions can overcome the energetic barriers. In all nanopores we observe a pronounced layering of the Na^+ ions with increasing surface charge. Such behavior of layered ions structure inside a charged surface has not been reported for any organic electrolyte inside a slit pore. In an one-dimensional pore model (of 1.5 nm width), with no atomistic detail considered, there was shown that in an organic electrolyte with a strong polar solvent, such as EC, the density of counterions next to the charged surface is higher than the density of counterions in the center of the nanopore⁶⁸. However that is an opposite behavior to what we observe using atomistic modeling, where the density of Na^+ is much higher in the center than that of the contact layers (Figure 7c,d).

However, the density behavior of PF_6^- ions is opposite to that

Fig. 8 Density profile of PF_6^- ions along z direction of narrow slit pore models (Fig. 1) of width (a) $w = 1.7$ nm, (b) $w = 2.38$ nm, (c) $w = 3.06$ nm for different surface charge: i) surface charge: $-2e/nm^2$ (circles), ii) surface charge: $-1.2e/nm^2$ (squares), iii) surface charge: $-0.8e/nm^2$ (diamonds) iv) neutral surface (stars).

of Na^+ ions, due to its similar charge with the graphene surfaces as is shown in Figure 8 (slit pores of $w = 1.7, 2.38$ and 3.06 nm). PF_6^- ions cannot enter the charged nanopores unless the width is equal or larger than 1.7 nm. That is due to electrostatic repulsion the PF_6^- ions feel from the negatively charged graphene layers. There is clear evidence since, in particular for the nanopore of 1.7 nm width, only if is a surface charge of $-0.8e/nm^2$ or $-1.2e/nm^2$, can PF_6^- ions enter the nanopore. By increasing surface charge less PF_6^- ions can enter into the nanopores.

3.2.2 Density distribution of EC solvent within pores

In this section we investigate the density distribution of the EC molecules inside negatively charged carbon nanopores in comparison to neutral nanopores.

Figure 9 shows the density profiles, along z direction, of carbonyl oxygens ($=O$) and carbons (excluding the carbonyl carbons) of EC molecules for both high surface charge ($-2e/nm^2$) and neutral surface (shown in the inset figures). For sub nanometer pores, one layer of EC molecules (as is shown from the density profile of carbonyl oxygens ($=O$) in Figure 9a) is formed inside that narrow pore which is not affected by the surface charge density. Figure 9a also shows that the density profiles of both carbons and carbonyl oxygens of EC molecules overlap, and present one peak at the center of the pore. This indicates that the EC molecules lay flat in the center of the pore, parallel to the pore surfaces (i.e. the two inner most graphene layers). The density profiles of carbons (excluding the carbonyl ones) and carbonyl oxygens ($=O$) of EC molecules within larger nanopores (such as of 1.02 – 3.06 nm width) are shown in Figure 9b–e. Our results show that more EC molecules can enter such pores than the sub nanometer ones (see also Figure 5). In particular for a charged nanopore of width 1.02 nm, the EC profile shows a two layering density profile, similar to the Na^+ ions density profile for charged surface ($-2e/nm^2$), unlike the one layer formation in pores of width below 1 nm. In addition in neutral nanopores two

distinct layers of carbonyl oxygens are formed (inset of Fig9b). It is clearly shown that, in the case of larger negatively charged pores ($w = 1.36$ – 3.06 nm), more EC molecules enter the pores, forming a structure of more than two layers. The reconfiguration effect of EC molecules becomes more obvious. The most carbons of EC molecules (positively charged) approach the surface and the carbonyl oxygens (negatively charged) are oriented away, aligned against the negatively charged pore surface, pointing towards the center of the pore. For comparison, in pores of the same size with neutral pore surfaces, less carbons (compared to the charged pores) are close to the internal pore surfaces, and the carbonyl oxygens are not oriented away to the graphene layers (see inset Figures 9d,e). The above results show that both pore size and surface charge can alter the configurations of EC molecules in nanopores. The second phenomenon is due to the adsorption of Na^+ ions onto the highly charged surfaces ($-2e/nm^2$). At a high negative surface charge, Na^+ ions quickly moved on the negatively charged pore surface and are adsorbed onto the graphene surfaces. As the Na^+ ions adsorb, they affect the EC molecules structure. In particular, for nanopores of 1.36 – 3.06 nm width, at surface charge of $-2e/nm^2$, layers of adsorbed Na^+ ions near the two negatively charged graphenes are accumulated as observed in Figure 7. This results in less available adsorption sites for carbonyl oxygens onto the graphene surfaces. Therefore more carbonyl oxygens ($=O$) are found inside the nanopore, than in contact with the graphene layers, as depicted by the higher intensity of the carbonyl oxygen peaks in the center of the nanopore (Figures 9c,e). This picture rather changes for lowest surface charge ($-0.8e/nm^2$), where the carbonyl oxygen peaks inside the nanopores are almost of the same height with that of neutral case. Nevertheless, the pore surface charge does impact the configuration and structure of EC molecules in nanopores.

Our results reveal that charging the nanopores has also a pronounced effect on the molecular structure of confined EC, which changes compared to that of neutral pores (inset of Figure 9)

Fig. 9 Density profile of carbonyl oxygens ($=O$), carbons (excluding carbonyl carbons) of EC along z direction of slit pores of widths (a) $w = 0.76$ nm, (b) $w = 1.02$ nm, (c) $w = 1.36$ nm, (d) $w = 1.7$ nm, (e) $w = 3.06$ nm: i) carbonyl oxygens (diamonds), ii) carbons (squares). Inset: Density profiles in neutral nanopores. The number density of carbons is normalized by two.

because of two phenomena, both related to the graphene surface charge density. Moreover, the molecular structure of EC molecules in the nanopores is the inter-play between pore size and the pore surface charge. In fact, the anisotropic orientation of EC within charged pores yield significant changes in the charge density profile, as pointed out by others^{68,69}.

4 Conclusions

In summary, we have reported molecular dynamic simulation results obtained for Na^+ and PF_6^- ions in ethylene carbonate solution confined in slit-shaped carbon pores, at different pore sizes and surface charge densities. The slit pore widths considered were 0.72–10 nm. The results are quantified in terms of concentration of ions within the nanopores and explained on the basis of the structure of the confined solutions as observed from the number of confined EC molecules, Na^+ and PF_6^- ions, and density profiles across the nanopore width. At low surface charge densities (small applied potentials) the ions prefer to remain in the bulk. As the surface charge density increases, the Na^+ ions enter the pores. The distribution of EC within small pores seems responsi-

ble, in part, for the accumulation of Na^+ ions near the pore center for neutral pores. However at high electrostatic surface charge, Na^+ are adsorbed on the graphene layers. We showed that the Na^+ ion concentration profile, inside the nanopores, depends not only on electrostatic surface charge but also on nanopore width. Using such molecular simulation methodology we can easily tune to carbons of different physical and chemical properties or different organic solvents to extrapolate Na^+ ion storage, diffusion, capacity under charge and discharge cycle and under operating conditions. Despite limitations in the procedures implemented herein (e.g., the electrodes simulated are of limited size, and realistic descriptions of the carbonaceous nanopores typically used for electrodes are not implemented), the detailed description presented is important for achieving a better understanding of Na ion batteries which it could not be attained using simulation or theoretical models⁶⁸ that overlook the presence of EC solvent molecules.

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