Ion Storage in Nanoconfined Interstices Between Vertically Aligned Nanotubes in Electric Double-Layer Capacitors

Ionic liquids are considered promising electrolytes for developing electric double-layer capacitors (EDLCs) with high energy density. To identify optimal operating conditions, we performed molecular dynamics simulations of N-methyl-N-propyl pyrrolidinium bis(trifluoromethanesulfonyl)imide (mppy\textsuperscript{+} TFSI\textsuperscript{-}) ionic liquid confined in the interstices of vertically aligned carbon nanostructures mimicking the electrode structure. We modeled various surface charge densities as well as varied the distance between nanotubes in the array. Our results indicate that high-density ion storage occurs within the noninteracting double-layer region formed in the nanoconfined domain between charged nanotubes. We determined the specific arrangement of these ions relative to the nanotube surface and related the layered configuration to the molecular structure of the ions. The pitch distance of the nanotube array that enables optimal mppy\textsuperscript{+} TFSI\textsuperscript{-} storage and enhanced capacitance is determined to be 16 Å. [DOI: 10.1115/1.4037582]

Keywords: electric double-layer, capacitor, ionic liquid, molecular dynamics, carbon nanotube

1 Introduction

Energy storage devices, such as capacitors and batteries, are widely used today because of their high specific energy and power densities [1–3]. While batteries in general can achieve greater energy densities, capacitors exhibit better performance in other aspects and provide higher power density, shorter charge time, and longer life cycles [1,4,5]. Electric double-layer capacitors (EDLCs), also known as supercapacitors [6], have significantly greater energy densities than conventional capacitors and are being investigated extensively [7–11]. Recent studies indicate that EDLCs can achieve energy densities comparable to that of conventional batteries [12–14]. The most important parameter that determines the energy density of an EDLC is its capacitance, which directly depends on the double-layer formed on the available surface area of the electrode [15]. Thus, it is important to select suitable electrodes with high surface area, which facilitate the formation of a double-layer. Vertically aligned carbon nanotube (CNT)-based electrodes, which can be easily synthesized [16], are mechanically stable and have high specific surface area that enhances the storage of ions during charging or discharging, resulting in a relatively high capacitance [17–22] when used in EDLCs. Additionally, the ions are deposited both on the outer and inner wall of the nanotube, resulting in increased energy density [23,24]. Several studies have investigated the capacitance of both single-walled CNT and multiwalled CNT [25–28] based capacitors. For instance, Niu et al. [25] have reported a specific capacitance of 102 Fg\textsuperscript{-1} for multiwalled entangled CNT-based supercapacitor with an acidic electrolyte. This value, however, is low compared to that of vertically aligned single-walled CNTs that are capable of producing capacitances up to 180 Fg\textsuperscript{-1} [29].

In addition to the structure of the electrode, the other crucial component that determines the energy density is the electrolyte used in EDLCs. Studies have shown that it is possible to obtain high energy densities, comparable to that of conventional batteries, by using ionic liquid electrolytes in EDLCs [12–14]. The high energy density is achieved primarily because ionic liquids operate at wide electrochemical windows [30]. Therefore, utilizing the favorable properties of both the aligned CNT electrode and ionic liquid electrolyte can potentially accomplish improved energy densities. Some recent molecular modeling studies have investigated the double-layer formation on EDLCs using CNT electrodes and ionic liquid electrolytes [6,31–33]. For instance, Shim and Kim [31] have investigated the storage of ions inside CNTs of varying chirality and have evaluated the corresponding capacitances. Cummings and co-workers [6] performed a similar study using a single-walled CNT. The significance of the work of Cummings and co-workers was that they modeled the ion deposition pattern on the outer wall of the CNT to determine the effect of applied electrical potential and radius of the nanotubes. However, they used a CNT with closed ends, which does not take into consideration the electrostatic forces of attraction and repulsion between the ions inside and outside the CNT. Hwang and co-workers [32] investigated ion adsorption on outer wall of an infinitely long CNT. In a realistic EDLC, however, arrays of CNTs are deposited on the current collectors, which serve as electrodes. The precise architecture of these CNT arrays is dependent on the synthesis and processing conditions [34,35]. The ion storage pattern inside and around CNT arrays will affect the potential drop across the double-layer and thereby the electrode double-layer capacitance [33]. Motivated by this realistic structure of the electrode, Yang et al. [36] simulated ion storage within arrays of (5,5) CNTs with varying architecture. The study, which considered a mixed tetra-ethylammonium tetrafluoroborate ionic liquid with polycarbonate solvent as a model electrolyte, reported the effect of varying pitch between CNTs on the single electrode capacitance. The study evaluated ion storage on the nanotube surfaces with varying surface charge density of the CNTs and determined the capacitance of the EDLCs. However, it did not account for ion storage inside the nanotubes.

In recent times, N-methyl-N-propyl pyrrolidinium bis(trifluoromethanesulfonyl)imide (mppy\textsuperscript{+} TFSI\textsuperscript{-})-based ionic liquids have
been used as popular electrolytes in various energy storage devices and have shown high electrochemical stability against oxidation and reduction [30]. Therefore, in this study, we performed molecular dynamics simulations to study the ion storage and resulting capacitance for CNT arrays in presence of pure mppy+ TFSI− ionic liquid electrolyte. The objective of the study is to provide quantitative insight on the electric double-layer structure for CNT arrays with different pitches and for a range of surface charge density on the CNTs, while accounting for ions both inside and on the surface of CNTs. Therefore, we simulated the adsorption of ions on arrays of positively and negatively charged armchair CNTs, by varying the pitch between the CNTs. Based on the results, we determined the how the pitch length between two CNTs for the ions affects the structure of the electric double-layer and thereby the capacitance values. Results from the simulations provide fundamental insight that would help in maximizing the ion storage capability in CNT arrays to achieve high charge densities and capacitance in EDLCs.

2 Computational Methods

We employed classical molecular dynamics simulations to study the distribution and ordering of mppy+ and TFSI− ions around a 2 × 2 square array of CNTs. The software LAMMPS [37] was used for all simulations performed as part of this study. A nonpolarizable optimized potentials for liquid simulations force field [38,39] was used to describe atomic interactions. Partial charges for the ionic liquids were scaled down by 80% to account for the polarizability effects. Details of the force field and partial charges were selected within reasonable range corresponding to other studies [6,32]. Depending on the charge density of the CNTs, corresponding number of cations or anions are added to the system to maintain overall charge neutrality. For the sake of convenience, the simulated systems with varying surface charge densities are denoted with appropriate abbreviations as shown in Table 1. Four CNTs (8, 8), each of 10 Å diameter and 35 Å length, aligned along the z-axis, were used as the electrode, as shown in the schematic in Figs. 1(a) and 1(b). Each CNT consisted of 480 carbon atoms. The diameter of the CNTs was chosen keeping in mind the size of mppy+ and TFSI−, such that the adsorption of ions inside the CNTs could be facilitated. The simulation domain was constructed such that the aligned CNTs were periodic across the x and y-axis, thus resembling a continuous array of CNTs in those dimensions. The pitch between any two consecutive CNTs, defined by the distance between their surfaces along the x or y directions, was varied at 12 Å, 16 Å, and 20 Å. A cross-sectional view of the CNT array in the simulation domain is shown in Fig. 1(a), while Fig. 1(b) provides a three-dimensional isometric view of the simulation domain. Figure 1(c) shows the structures of the mppy+ and TFSI− ions.

The CNTs were solvated in 648 ionic liquid ions; 324 mppy+ ions and 324 TFSI− ions. This number was chosen keeping into account the minimum number of ions that can be accommodated inside and around the CNTs for the largest domain, with a pitch of 20 Å, where the “x” and “y” dimensions of the simulation domain are large. The number of ions in each domain of varying pitch was kept constant to simulate systems of identical mole fractions of nanotubes and ionic liquids. Since the x−y cross section changes depending on the pitch, the z-dimension along the axis of the nanotube is shorter for the system with the largest pitch. However, for analysis, the nanocasted region between the nanotubes is of interest, since the ordering of ions is expected to happen radially outward from the nanotube surface, as shown in Fig. 1(a).

For our analysis of the effect of surface charge on the formation of double-layer, we use four distinct charge densities on the CNTs that vary between −0.08 and +0.08 C/m². These charge densities correspond to net charges of 5 and 25 cations or anions depending on whether the CNTs are charged negative or positive. The charges were selected within reasonable range corresponding to other studies [6,32]. Depending on the charge density of the CNTs, corresponding number of cations or anions are added to the system to maintain overall charge neutrality. For the sake of convenience, the simulated systems with varying surface charge densities are denoted with appropriate abbreviations as shown in Table 1. For instance, the systems with the highest positive/negative surface charge densities on the CNTs are referred to as 25 TF/25 MP, i.e., the charge corresponding to 25 TFSI− or 25 mppy+. Table 1 shows list of the charges applied on the CNTs and the surface charge density of each CNT.

2.1 System Design

The simulation domain was constructed such that the aligned CNTs were periodic across the x–y plane, perpendicular to the axes of the CNTs, of the simulation domain is shown with emphasis on the ions that constitute the double-layer around the CNTs. The distance between the surfaces of the nanotubes is defined as the pitch and is varied at 12 Å, 16 Å, and 20 Å. (a) A three-dimensional view of the simulation domain comprising the CNTs and ionic liquid ions is shown. (c) Structures of the mppy+ ion (top) and TFSI− ion (bottom) are shown.

Table 1 Two distinct surface charge densities were assigned to the nanotubes for each pitch that was simulated. The system nomenclature is introduced along with the net charge on each atom and the corresponding surface charge density.

<table>
<thead>
<tr>
<th>System name</th>
<th>Added ions (anion/cation)</th>
<th>Net charge added per CNT (in electrons)</th>
<th>Surface charge density per CNT (C/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 TF/5 MP</td>
<td>5</td>
<td>±4.4872</td>
<td>±0.016</td>
</tr>
<tr>
<td>25 TF/25 MP</td>
<td>25</td>
<td>±22.4361</td>
<td>±0.080</td>
</tr>
</tbody>
</table>

Fig. 1  (a) A cross-sectional view of the x−y plane, perpendicular to the axes of the CNTs, of the simulation domain is shown with emphasis on the ions that constitute the double-layer around the CNTs. The distance between the surfaces of the nanotubes is defined as the pitch and is varied at 12 Å, 16 Å, and 20 Å. (b) A three-dimensional view of the simulation domain comprising the CNTs and ionic liquid ions is shown. (c) Structures of the mppy+ ion (top) and TFSI− ion (bottom) are shown.

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All systems were equilibrated in an NPT ensemble. N, the total number of ions in the simulations, was kept constant, the pressure \(P\) was set at 1 atm, and the temperature \(T\) was set at 298 K, corresponding to room temperature. The pressure and the temperature were controlled by Nosé-Hoover barostat and thermostat [41,42], respectively. Newton’s laws of motion were integrated with a time step of 1 fs. The CNT atoms were tethered to their respective initial positions, such that the pitch was always constant between the CNTs. Once equilibrated, a fixed charge density was applied on the CNTs, and corresponding number of ions were added to make the system neutral. The systems were then equilibrated once again in an NPT ensemble followed by NVT production runs, where the volume \(V\) was kept constant. Production runs were carried out for up to 15 ns, depending on the charges on the CNTs. System with lower charge densities was run for longer times to adequately sample the simulated systems.

### 3 Results and Discussion

To determine the optimal architecture of CNT arrays that enables high ion storage and high capacitance in EDLCs, we investigated the effect of varying pitch between the CNTs, which is a crucial configurational parameter. We also varied the surface charge density of CNTs to understand its effect on the nature of the electric double-layer, which ultimately determines the capacitance of CNT-based EDLCs.

#### Distribution of Ions at Varying Pitch

To understand the mechanism of ion storage in CNT-based EDLCs, it is important to determine how the densities of atoms/ions around the CNTs vary across the pitch length. As a reference system, we selected CNTs with surface charge density of \(\pm 0.080 \text{C/m}^2\), which corresponds to the systems 25 TF/25 MP. We analyzed the number density profiles of the most electronegative atom of TFSI\(^-\) and the most electropositive atom of mppy\(^+\) for varying pitches. The most electropositive atom of mppy\(^+\) is nitrogen \([\text{N(mppy}^+]\) with a partial charge of \(+0.46e\), while the most electronegative atom of TFSI\(^-\) is the nitrogen atom \([\text{N(TFSI}^-]\) that has a partial charge of \(-0.87e\). Figures 2 and 3 show the number density profiles of \(\text{N(mppy}^+)\) and \(\text{N(TFSI}^-)\), across various pitches for the systems 25 TF and 25 MP, respectively. The density profiles were evaluated across radial direction “\(R\)” from the center of the CNTs and shown for the confined interstitial domain between the nanotubes. Since the radius of each CNT is 5 Å, and no ions/atoms are observed within 2 Å from the surface of CNTs, the profiles were calculated starting at 7 Å from the center of CNTs. The profiles are averaged over the four CNTs, since the domain is symmetric over each CNT. Thus, for a pitch of 20 Å, the density was calculated till a maximum radial distance, \(R_{\text{max}} = 15 \text{Å} (5 \text{Å} + 20/2 \text{Å})\). This distance demarcates the axis of symmetry such that ions beyond this location are closer to the adjacent nanotube. Similarly, \(R_{\text{max}}\) was 13 Å and 11 Å for pitches 16 Å and 12 Å, respectively.

As seen in Figs. 2(b) and 2(c), there is a first peak in the density of \(\text{N(TFSI}^-)\) at 8.5 Å for pitches 16 Å and 20 Å. However, as seen in Fig. 2(a) for the lowest pitch of 12 Å, the first peak of \(\text{N(TFSI}^-)\) is at 9 Å. These peaks corresponding to \(\text{N(TFSI}^-)\) are followed by a peak for \(\text{N(mppy}^+)\) at 10.5 Å for pitches 16 Å and 20 Å and at 10 Å for pitch of 12 Å. Therefore, the peaks for \(\text{N(mppy}^+)\) and \(\text{N(TFSI}^-)\) are condensed and closer together for pitch 12 Å compared to the other pitches. These two peaks are again followed by a second peak for \(\text{N(TFSI}^-)\) at 11 Å for pitches 16 Å and 20 Å as seen in Figs. 2(b) and 2(c). This second peak is followed by a plateau that reaches constant number density for \(\text{N(TFSI}^-)\) at around 13 Å. This pattern indicates the presence of bulk ionic liquid domain. However, for 12 Å, the second peak of \(\text{N(TFSI}^-)\) is not followed by this plateau, indicating an incomplete transition to bulk domain.

Figure 3 shows that the first peak for \(\text{N(mppy}^+)\) forms at 10 Å for all the pitches in case of negatively charged nanotubes. This peak is followed by a second peak corresponding to \(\text{N(TFSI}^-)\) that occurs at 11 Å for pitches of 16 Å and 20 Å. However, for 12 Å pitch, the peak for \(\text{N(TFSI}^-)\) is incomplete and shared by the neighboring CNT. Overall, the peaks for \(\text{N(TFSI}^-)\) and \(\text{N(mppy}^+)\) observed in Figs. 2(a) and 3(a) for 12 Å pitch do not flatten out away from the surface of the CNT. This pattern suggests that...
while the Stern layer comprising N(TFSI\(^{-}\)) and N(mppy\(^{+}\)) ions for positively and negatively charged CNTs is completely formed, the subsequent diffuse layer interacts with the diffuse layer around neighboring CNTs. Therefore, for 12 Å pitch, the electric double-layer formed around CNT is interacting with electric double-layer around neighboring CNTs due to the smaller gap between the CNTs. Furthermore, the interacting diffuse layers can potentially lower the capacitance of the diffuse layer and ultimately reduce the overall capacitance [43]. This effect on capacitance is presented later in details. In contrast to this distribution, for 16 and 20 Å pitch, the consecutive peaks of N(TFSI\(^{-}\)) and N(mppy\(^{+}\)) in case of positively and negatively charged CNTs, as seen in Figs. 2 and 3, respectively, display a plateau region near the boundary, suggesting that a stable noninteracting diffuse layer is formed along with the Stern layer.

It is noteworthy that the distribution of negatively charged TFSI\(^{-}\) ions around positively charged CNTs, shown in Fig. 2, is significantly different from that of positively charged mppy\(^{+}\) ions around negatively charged CNTs shown in Fig. 3. A major difference is that while two distinct peaks of TFSI\(^{-}\) are seen in Fig. 2, only a single peak in the number density of mppy\(^{+}\) is seen in Fig. 3. These distinct distributions impact the structure of double-layers around positively and negatively charged CNTs. One of the reasons for the disparate distribution of the N(mppy\(^{+}\)) and N(TFSI\(^{-}\)) is the difference in the partial charges of N(mppy\(^{+}\)) (0.46 e) and N(TFSI\(^{-}\)) (−0.87 e). Additionally, the larger number of atoms in mppy\(^{+}\) causes the surface charge density of mppy\(^{+}\) to be lower than that of TFSI\(^{-}\). In Fig. 2, the N(TFSI\(^{-}\)) peak for all three pitches starts at 8 Å, the peak for 12 Å pitch is shifted to right by ~0.5 Å as compared to 16 Å and 20 Å pitch. Interacting diffuse layer for neighboring CNTs would reduce the Coulombic interactions between the N(mppy\(^{+}\)) and N(TFSI\(^{-}\)) within the diffuse layer thereby shifting the peak of N(TFSI\(^{-}\)) to a slightly higher distance. For negatively charged CNTs, the peak for N(mppy\(^{+}\)) is at a larger distance (10 Å) than the peak for N(TFSI\(^{-}\)) in positively charged CNTs. To understand why the N(mppy\(^{+}\)) peaks in negatively charged CNTs occur at a greater distance from the CNT and to explain the short N(TFSI\(^{-}\)) peak in Fig. 3, it is important to look at the density profiles of other positive atoms of mppy\(^{+}\). The molecular structure of mppy\(^{+}\), shown in Fig. 1(c), is such that N(mppy\(^{+}\)) is surrounded by other atoms so that the N atom is sterically hindered from associating with the negatively charged carbon atoms of the nanotubes. Thus, to completely understand the trend in density distribution of N(mppy\(^{+}\)), we evaluated the number density profile of hydrogen atoms of mppy\(^{+}\) [H(mppy\(^{+}\))] and compared it with that of N(mppy\(^{+}\)) for a pitch of 20 Å in case of negatively charged CNTs (25 MP). As seen in Fig. 4, a prominent peak in the density profile of H(mppy\(^{+}\)) is formed at 8.5 Å, since the H(mppy\(^{+}\)) is more accessible and always closer to the CNTs, compared to N(mppy\(^{+}\)). Additionally, since there are 18 hydrogen atoms in the mppy\(^{+}\) ions for every N atom, the height of the peak in the number density of the H atoms is much greater compared to that of the N atom. The positively charged layer of H(mppy\(^{+}\)) at 8.5 Å also leads to association with N(TFSI\(^{-}\)) that in turn leads to the short

Fig. 3 The variation of number density of nitrogen of mppy\(^{+}\) [N(mppy\(^{+}\))] and nitrogen of TFSI\(^{-}\) [N(TFSI\(^{-}\))] in the radial direction is shown for the system 25 MP. The reference distance R = 0 corresponds to the axis of the negatively charged CNTs. Three distinct pitches of (a) 12 Å, (b) 16 Å, and (c) 20 Å were analyzed, and the distributions are shown to a maximum limit R\(_{\text{max}}\) that corresponds to the axis of symmetry between two adjacent nanotubes.

Fig. 4 The variation of number density of hydrogen atom of mppy\(^{+}\) [H(mppy\(^{+}\))] and N(mppy\(^{+}\)) for the system 25 MP at a pitch of 20 Å is shown.
peak for N(TFSI\(^+\)) at 9 Å seen in Fig. 3. Therefore, the structure of electric double-layer depends on the relative proximity of the electropositive/electronegative atom of an ion to the CNT that in turn depends on its molecular structure. While in case of a linear ion, such as TFSI\(^+\) shown in Fig. 1(c), the N(TFSI\(^+\)) is not surrounded by other atoms of TFSI\(^-\) and is more accessible to adsorb on positively charged CNTs, the mppy\(^+\) cation exhibits more complex configuration with respect to the CNTs, as described above. This effect leads to the qualitative difference in the number density distribution of cations and anions seen in Figs. 2 and 3.

We observe from Figs. 2 and 3 that the heights of the first peaks for systems with pitches of 12 Å are slightly greater than that of systems with pitches of 16 Å and 20 Å. For instance, in case of 25 TF (Fig. 2), the height of the first peak of N(TFSI\(^+\)) is ~0.008 Å\(^{-3}\) for 12 Å, as compared to ~0.005 Å\(^{-3}\) for 16 Å and 20 Å. To understand why the height of the peaks changes with change in pitch, we evaluated the radial distribution function (RDF) of N(mppy\(^+\)) with respect to N(TFSI\(^+\)) in systems with surface charge density of +0.080 C/m\(^2\) (25 TF) on the CNTs. The RDFs, as shown in Fig. 5, were evaluated for ions present in the nanocoined domain between the CNTs for the whole range of pitches 12–20 Å. The first peak in the RDF is higher for the system with 12 Å (~2.2), followed by 16 Å (~2.1) and 20 Å (~1.8). The higher peaks in case of pitch of 12 Å suggest that the likelihood of finding a N(TFSI\(^+\)) around a N(mppy\(^+\)) at 4 Å is greater for a pitch of 12 Å, as compared to that for pitch of 16 Å and 20 Å. Figure 5 also indicates that N atoms of mppy\(^+\) TFSI\(^-\) are more densely packed in the confined region between the CNTs for cases with pitch of 12 Å due to interacting diffuse layers, as compared to that of 16 Å and 20 Å where no interaction with neighboring diffuse layers is observed. In bulk mppy\(^+\) TFSI\(^-\) ionic liquid [44], the height of the first peak is ~1.6 at 4 Å. Thus, it can be concluded that in the confined region the ions are more densely packed than in the bulk, even though the region within 2 Å of the nanotube surface does not have any ions. Furthermore, the packing density decreases with increase in pitch between the CNTs due to the presence of bulk ionic liquid regime, as seen in Figs. 2 and 3. In addition to the formation of double-layer, increased ion adsorption is essential to maximize the capacitance and is observed in our simulations in cases with strong N(mppy\(^+\))–N(TFSI\(^-\)) association, i.e., in cases with higher N(mppy\(^+\))–N(TFSI\(^-\)) peaks in Fig. 5.

**Effect of Varying Surface Charge Density of the Nanotubes.**

As seen from the previous plots, it is evident that a pitch of 20 Å certainly enables the formation of noninteracting double-layer. In contrast, the neighboring electric double-layer interact with each other for 12 Å pitch. A pitch of 16 Å is the limiting case where the double-layer is are almost completely noninteracting. The previous plots, however, are for a fixed surface charge density of the CNT. In a real EDLC, the surface charge density varies, and the potential drop across the double-layer and the capacitance of the electric double-layer are functions of the surface charge density on the CNTs [6]. To quantitatively compare the ion adsorption at varying surface charge densities, the number density profiles of N(TFSI\(^+\)) and N(mppy\(^+\)) for two distinct magnitudes of positive and negative surface charge densities on the CNT are presented in Figs. 6 and 7, respectively. As a representative case, the system with 20 Å pitch is selected where the double-layer formed is completely noninteracting.

The plots in Fig. 6(a) indicate that increase in the surface charge density of positively charged CNTs causes substantial increase in the height of the first peak of N(TFSI\(^+\)). However, the second peak remains almost the same. Also, the first peak shifts toward the CNT when the charge density is increased. This suggests that increasing the charge on CNTs alters the first layer of ions near the CNTs, whereas the second peak is unaffected due to noninteracting electric double-layer. In addition, while the density of N(TFSI\(^+\)) increases, the height of the peak in the number density of N(mppy\(^+\)) decreases and shifts away from the CNT surface as the positive surface charge density is increased, as seen in Fig. 6(b). Figure 6(b) further demonstrates that the peak of N(mppy\(^-\)) spreads out over a wider radial range with increase in positive charge on CNT, suggesting strong repulsion between the positively charged CNTs and N(mppy\(^+\)). The repulsion leads to a wider distribution of N(mppy\(^+\)) in the second layer for 25 TF such that the ions are less densely packed compared to that in the system 5 TF.

In case of negatively charged CNTs, it is seen from Fig. 7(a) that the density of N(TFSI\(^-\)) decreases with increase in negative surface charge density on the CNTs. Also, like the trend seen in the distribution of N(mppy\(^+\)) in positively charged CNTs, the peaks are lower and are spread out across the radial direction. Figure 7(b) indicates that the height of the peak for N(mppy\(^-\)) increases and shifts slightly toward the CNT for 25 MP. The hydrogen atoms of mppy\(^-\), however, limit the shift in peak of N(mppy\(^-\)) because of their presence near the CNT, as discussed earlier. Overall, these plots indicate that increase in negative

![Fig. 5 The RDF for N(mppy\(^+\)) (denoted as N\(^+\)) with respect to N(TFSI\(^+\)) (denoted as N\(^0\)) is shown for the system 25 TF at different pitches](image-url)
surface charge density on CNTs results in a higher number density in the layer of $N(mppy^{+})$ and shifts the first layer near the CNT, whereas the peak on the oppositely charged ion is reduced and is shifted away from the CNT. It is also observed from Figs. 6 and 7 that beyond 13 Å, no peaks for $N(TFSI^-)$ or $N(mppy^+)$ are formed for CNT array with 20 Å pitch. This observation, in conjunction with the distributions presented in Figs. 2 and 3, suggests that 16 Å is a limiting case to form fully noninteracting electric double-layer.

**Capacitance Calculations for Different Charge Densities.** To corroborate the earlier claims about lowering of capacitance due to interacting electric double-layer for CNT arrays with 12 Å pitch, we evaluated the integral capacitance values using a method employed by Yang et al. [36]. The electric double-layer integral capacitance of the single electrode can be evaluated by setting the net charge on the surface of the CNT and determining the electrostatic potential at the surface of CNT relative to that of the bulk electrolyte. The potential difference $\Delta \Phi$ is calculated using the equation below:

$$\Delta \Phi(R) = \left(\frac{-1}{2 \pi \epsilon_0}\right) \int_0^{R} Q(\lambda) \frac{d\lambda}{\lambda} = \Phi(R) - \Phi(\text{surface}) \quad (1)$$

where $Q(\lambda)$ is the charge enclosed in a cylinder of radius $\lambda$ parallel to the CNT and centered on it. The value of $\Delta \Phi$ plateaus out at large values of $R$, indicating the electrostatic potential within the bulk electrolyte with respect to CNT. The single electrode capacitance values are obtained by the total charge of CNT divided by the potential difference between CNT and bulk electrolyte. Figure 8 shows the potential difference between CNT and bulk electrolyte for CNTs with $\pm 0.08 \text{ C/m}^2$ charge density. The calculations were done for all pitches considered in the study. $-\Delta \Phi$ values are plotted for positively charged CNT for easier comparison.

The electrostatic potentials were calculated all the way till the earlier specified cutoff distances for the respective pitch lengths. These cutoff distances correspond to the symmetry line between neighboring CNTs in the array. Thus, the plots in Fig. 8 are shown till 11 Å, 13 Å, and 15 Å for pitch length of 12 Å, 16 Å, and 20 Å, respectively. It is evident from the plots that the electrostatic potential difference for 16 Å and 20 Å is lower than that for the CNT array with 12 Å pitch. Dense packing of ions due to confinement between CNTs and interacting electric double-layer leads to higher voltage that ultimately reduces the overall capacitance as indicated in Table 2. Table 2 lists the electrostatic potential relative to the surface charge on CNTs along with respective capacitances. As stated earlier, the electric double-layer becomes noninteracting at pitch distances above 16 Å, which is observed from the plateau in Fig. 8 for both 16 Å and 20 Å. The capacitance values for both these cases are nearly equal, indicating that increase in pitch beyond 16 Å does not lead to any significant increase in the capacitance values. For the CNT array with 12 Å pitch, the electrostatic potential is $\sim 2.64 \text{ V}$ which leads to a capacitance of $\sim 3.03 \mu \text{ F/cm}^2$. In comparison, for CNT arrays with pitch 16 Å and 20 Å, the calculated capacitance values are 6.2 $\mu \text{ F/cm}^2$ and 6.25 $\mu \text{ F/cm}^2$, respectively.

Table 2 shows that for a low surface charge density of $\pm 0.016 \text{ C/m}^2$, the calculated capacitance values are lower than that for surface charge density of $\pm 0.08 \text{ C/m}^2$. Moreover, since the surface charge is low, the effect of interacting double-layer does not play a significant role in reducing the overall capacitance for CNT array with 12 Å pitch. The density of ions within the double-layer is lower as compared to high surface charge, thus reducing the Coulombic interactions and ultimately weakening...
the impact of interacting electric double-layer. The increase in surface charge density leads to increase in the number of ions stored within the double-layer resulting in the increase in the capacitance. The data in Table 2 also indicate that the capacitance values increase as we increase the pitch of the CNT arrays from 12 Å to 20 Å, particularly evident for the higher surface charges. However, the capacitance tends to saturate above 16 Å, indicating 16 Å to be a limiting pitch to achieve noninteracting electric double-layer with neighboring electrodes.

4 Conclusion

Results from our simulations of adsorption of mppy \(^{+}\) and TFSI \(^{-}\) ions on charged nanotube arrays indicate that the pitch between the CNTs plays a crucial role in determining the nature of the neighboring electric double-layer. Maximum utilization of space between the CNTs, which is required to achieve maximum energy density in EDLCs, occurs in the electric double-layer region around CNTs where the density of stored ions is the greatest. This region optimally forms for a pitch of 16 Å due to the presence of noninteracting electric double-layer within 13 Å from the center of the CNTs. Ion storage in EDLCs using CNT arrays with a pitch of 16 Å would be more effective than in ones with 12 Å pitch. Our results further indicate that the molecular structures of ions play an important role in absorption around the CNTs. Therefore, the optimal EDLC architecture depends on the specific electrolyte. For ions, whose electropositive/electronegative atoms are not sterically hindered by other atoms, the double-layer would form closer to the CNT surface. To implicitly capture ion storage with change in surface charge density, we separately modeled systems with disparate surface charge densities. Our simulations demonstrate that increasing the charge on the CNT increases the number density of ions in the double-layer and shifts the layer closer to the CNT, while the number density of ions in the diffuse layer spreads over a greater radial distance. We also calculated the integral capacitance for the CNT array with varying pitches from 12 Å to 20 Å. The results obtained confirmed that the interacting double-layer lead to a reduced overall capacitance, particularly observed at higher surface charge densities. Overall, the results from this study can help identify and optimize crucial EDLC parameters such as the right pitch between the aligned CNTs in an array to maximize the overall capacitance.

Table 2: Integral capacitance values for CNT arrays with pitch of 12 Å, 16 Å, and 20 Å

<table>
<thead>
<tr>
<th>Pitch (Å)</th>
<th>Surface charge density (C/m²)</th>
<th>Average electrostatic potential ΔΦ (V)</th>
<th>Capacitance (μF/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>-0.016</td>
<td>-1.95</td>
<td>0.82</td>
</tr>
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<td></td>
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<td>0.24</td>
<td>0.71</td>
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<td></td>
<td>-0.08</td>
<td>-2.64</td>
<td>3.03</td>
</tr>
<tr>
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