**Ionic Liquid’s Structural Variations inside Nano-slit by Molecular Dynamic Simulations**

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**Highlights**

* the [Emim][DCA] IL behave differently both in the charged and uncharged graphene interface.
* The number density of anion near the interface is always greater than the cation when the pore size is 0.8 nm in both charged and uncharged systems.
* imidazolium rings prefer to lie parallel to the graphene surface in narrow silt pore.
* imidazolium rings gradually tends to be perpendicular to the surface as the pore width increases.

**1. Introduction**

Exploring ionic liquids (ILs) / graphene charged interface is importance in the energy collection and storage devices, because the structural properties and transportation of ILs at the interface have great influence on the performance of energy collection and storage devices. Unfortunately, it is still challenging to directly detect the interface properties of nanoconfined ILs by experimental methods. Therefore, we present a molecular dynamics(MD) simulation study of 1-ethyl-3-methylimidazolium dicyanamide ([Emim][DCA]) ionic liquid confined by two charged graphene planar surfaces with different pore widths. Graphene surfaces with positive and negative charges can be imagined as positive and negative electrodes of capacitors, respectively.

**2. Methods**

MD simulation for [EMIM][DCA]-graphene system were carried out using the LAMMPS software. Ionic liquids ([EMIM][DCA]) were confined to two parallel interfaces of graphene, respectively. Four different slit pore sizes were considered with 3.6、2.4、1.6、0.8nm，separately. Graphene sheets were modeled as rigid entities along all the considered simulations. The box size for the xy plane was reach to 49.12×48.22 Å2, as a consequence, it can accommodate enough ion pairs to obtain dependable statistically significant results. According to previous reports, all the four systems have a comparable IL density to the bulk value.[1] Therefore, 270、190、130 and 65 [EMIM][DCA] ion pairs were randomly placed in the two-dimensional graphene slits with the pore size of 3.6, 2.4, 1.6, and 0.8nm, respectively. The force field parameter for [EMIM][DCA] ions was obtained from literature.[2,3] The Lennard-Jones (L-J) parameter and partial atomic charges used for graphene in this work were taken from literature.[4]

**3. Results and discussion**

We find that the [Emim][DCA] IL behave differently both in the charged and uncharged graphene interface. The number density profiles of [Emim][DCA] IL along the direction perpendicular to the graphene wall indicates that the anion DCA- peak intensity is always greater than the cation Emim+ when the pore size is 0.8 nm in both charged and uncharged systems. The 3D orientation analysis of cations and anions close to the graphene surface indicates that imidazolium rings prefer to lie parallel to the graphene surface, and imidazolium rings gradually tends to be perpendicular to the surface as the pore width increases. Finally, their diffusion coefficients exhibit anomalies in negatively charged pores.



**Figure 1.**   The [probability distribution](http://dict.cnki.net/javascript:showjdsw('jd_t','j_')) of [angle orientation](http://dict.cnki.net/javascript:showjdsw('jd_t','j_')) in a silt pore with charge density of 2.29 e/nm2 (pore size= 0.8 nm).

**4. Conclusions**

The research work aimed at interface nanostructures is helpful for the design of electrode materials. From the results of simulation we found pore size is important for the Ionic Liquid’s Structural Variations and diffusion coefficient inside Nano-slit, which are critical to the performance of energy collection and storage devices such as electrochemical capacitance.

**References**

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