



# Computer simulation study of differential capacitance and charging mechanism in graphene supercapacitors: Effects of cyano-group in ionic liquids

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## ABSTRACT

Molecular dynamics simulation is employed to study graphene supercapacitors. Four different ionic liquids are considered as an electrolyte, each of which is combination of the same cation 1-ethyl-3-methylimidazolium([emim]<sup>+</sup>), and different, cyano-containing anions, thiocyanate ([SCN]<sup>-</sup>), dicyanamide ([N(CN)<sub>2</sub>]<sup>-</sup>), tricyanomethanide ([C(CN)<sub>3</sub>]<sup>-</sup>), and tetracyanoborate ([B(CN)<sub>4</sub>]<sup>-</sup>), respectively. In particular we investigate how electric double layer structure and electrical properties are affected by the structure of cyano containing anions. Cations and anions make alternating structure near charged electrode. Differential capacitances in four ionic liquids are found to have a maximum value at negative potential. The maximum capacitances are comparable to each other, but the corresponding potential shifts to the negative side as more cyano groups are attached to the anion. Starting from the interfacial layer, the effects of the further ionic layers on differential capacitance are systematically investigated. Comparing charges of the electrode and those of ionic layers, we find that differential capacitance behavior mainly stems from the ion exchange between electric double layer and bulk region. The ion exchange behaviors are decomposed into cation and anion contributions. The differential charging mechanisms of the system are strongly dependent on the electric potential. The maximum capacitances are consequence of rapid desorption of respective anions.

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## 1. Introduction

Electric double layer capacitors (EDLCs) are promising devices used for energy storage due to their high capacitance, which can be achieved by a distinctive interfacial structure, electric double layer (EDL) formed at the electrode. Ions in electrolyte of EDLCs, where ionic liquids (ILs) as well as aqueous electrolytes are commonly used, in contrast to dielectric materials, screen the electrode charges completely at sub-nanometer length scale to form a prominent EDL, with which the electrode can store more charges [1,2]. The structure of EDL thus crucially affects the capacitance, with a change of the stored charges in response to the external electric potential [3–5].

Much research on EDLCs has been dedicated to understanding of the dependence of differential capacitance (DC) on electrode

potential. To explain DC behaviors, different theoretical approaches have been made. Bell-shaped [5–10] and camel-shaped [8–17] curves are explained by a mean field theory with “lattice saturation effect” [3,4,18,19] in which capacitance decreases as the electrode potential increases because electric double layer is thickened. As ion concentration increases, two maxima in camel-shaped DC get closer and eventually merge into single maximum of bell-shaped curve which is located at potential of zero charge (PZC). Monte Carlo simulation studies provide an alternative explanation of camel-shaped DC based on a coarse-grained model of ILs with neutral chain [8,20]. Neutral beads form “latent voids” near PZC. Maxima of DC at an intermediate potential are generated by replacement of latent voids by charged beads. In addition, the self-consistent mean field models explain the camel-shaped DC curve with the dependence of permittivity on the distance from the electrode surface [9,11].

Experimental studies of EDLCs have reported varied shapes of DC curves, even for the cases with the same set of electrolyte and electrode material. For the imidazolium-based ionic liquids, the

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camel-shaped DC curves were observed at glassy carbon electrode [13], but U-shaped curves were found in the case of glassy carbon [21], highly oriented pyrolytic graphite (HOPG) [22], and graphene electrodes [23]. ILs with 1-ethyl-3-methylimidazolium cation with different anions show camel-shaped curves [24]. On the other hand, bell-shaped [7] and U-shaped [25] curves were reported for 1-butyl-3-methylimidazolium tetrafluoroborate at the gold electrode.

To elucidate the microscopic picture of capacitance behavior of the system, both experimental [26–29] and simulation [10,30–33] studies have paid attention to charging mechanism of ions. Various mechanisms have been reported, namely anion-dominated [29–31,33], cation-dominated [32,33], counterion-dominated [10], and equally-contributed [26,27]. The charging mechanisms of the systems have even been found to be a function of electric potential [10,28–33]. In spite of the great number of investigations of IL-electrode interfacial systems [5–17,21–23,25–36], relation between charging mechanism and differential capacitance is still unclear.

Ionic liquids are engineered ionic materials which stay in the liquid phase at ambient temperatures, and are commonly employed as electrolytes in EDLCs due to their high ion conductivity and electrochemical stability [1–3,37]. Rather recently developed and alternative to conventional electrolytes, ILs have unique properties such as non-volatility, non-flammability, solubility of both polar and nonpolar solutes, and easy recycling. Another remarkable feature of ILs is their enormous diversity generated by combinations of different cations and anions [37]. Often composed of organic ions, such combinations have been expanded by chemical tuning of ion structures [38,39].

Among the variety of ILs, the cyano-based have unique properties and have attracted different kinds of applications. Some liquids were suggested as possible solvent material for extractive distillation due to their high selectivity and reasonable solubility such as tetracyanoborate([B(CN)<sub>4</sub>]<sup>−</sup>)-based ILs and 1-ethyl-3-methylimidazolium dicyanamide ([emim]<sup>+</sup>[N(CN)<sub>2</sub>]<sup>−</sup>) for aromatic/nonaromatic and ethanol/water separation, respectively [40]. 1-butyl-3-methylimidazolium thiocyanate ([bmim]<sup>+</sup>[SCN]<sup>−</sup>) and 1-butyl-3-methylimidazolium tricyanomethanide ([bmim]<sup>+</sup>[C(CN)<sub>3</sub>]<sup>−</sup>) were used as extracting solvents as they have high solubility of carbohydrates and sugar alcohols [41]. 1-ethyl-3-methylimidazolium thiocyanate ([emim]<sup>+</sup>[SCN]<sup>−</sup>) was employed as a local probe molecule in 2D-IR experiments because it does not affect structure and dynamics when it is mixed with other ILs [42]. High solubility of carbon dioxide was utilized in CO<sub>2</sub> capturing [43,44]. Dicyanamide([N(CN)<sub>2</sub>]<sup>−</sup>)-based ILs have low viscosity and were applied in electrodeposition of metals [45]. Due to high conductivity and low viscosity, cyano-based ILs have been widely applied in dye-sensitized solar cells [46–48] as well as EDLCs [49].

Understanding the charging mechanism is very important when one utilizes ILs as energy storage material for EDLCs. The charging mechanism has been examined by counting the number of ions in the pore of electrode materials [26–29,32]. It was demonstrated that the effect of further ionic layers and the ion exchange behavior therein is required to be considered to explain the molecular origin of the DC behavior [5,10]. One of the attempts was to evaluate the charge of ionic layers with fixed thickness out of a number of trials [10]. The optimal thickness, however, was determined in an *ad hoc* manner, and little microscopic insight could be obtained from the result. To overcome this issue, we previously found that the DC behavior can be explained with the interfacial layer in which ions are most actively accumulated [5]. Nevertheless, it was not so straightforward to explain the saturation of DC at further potentials, which was predicted in mean field theory with “lattice saturation effect” [3,4,18,19].

The purpose of the present study is to investigate charging mechanism of EDLC with ILs and its molecular origin by decomposing it into contribution of each ionic species. This paper extends our previous study [5], where the cations were varied with different alkyl chain lengths, by systematically considering the effect of anions with charged functional groups. We examine the effect of cyano functional group of anion on electric double layer structure, differential capacitance and charging mechanism at graphene electrode, employing ILs with 1-ethyl-3-methylimidazolium ([emim]<sup>+</sup>) cation. Anions contain one to four cyano groups, which are thiocyanate ([SCN]<sup>−</sup>), dicyanamide ([N(CN)<sub>2</sub>]<sup>−</sup>), tricyanomethanide ([C(CN)<sub>3</sub>]<sup>−</sup>), and tetracyanoborate ([B(CN)<sub>4</sub>]<sup>−</sup>), respectively.

The present paper is organized as follows. Section 2 provides a brief description of the model system and simulation method. In Section 3, electric double layer structure, differential capacitance and charging mechanism of EDLC systems are analyzed to investigate their dependence on number of CN-groups. Conclusions are given in Section 4.

## 2. Models and methods

Four different cyano-based ILs are employed as dielectric material in this comparative study, namely 1-ethyl-3-methylimidazolium thiocyanate ([emim]<sup>+</sup>[SCN]<sup>−</sup>), 1-ethyl-3-methylimidazolium dicyanamide ([emim]<sup>+</sup>[N(CN)<sub>2</sub>]<sup>−</sup>), 1-ethyl-3-methylimidazolium tricyanomethanide ([emim]<sup>+</sup>[C(CN)<sub>3</sub>]<sup>−</sup>), and 1-ethyl-3-methylimidazolium tetracyanoborate ([emim]<sup>+</sup>[B(CN)<sub>4</sub>]<sup>−</sup>), respectively. A total of 1024 ion pairs are confined between basal plains of graphene electrodes for each system [Fig. 1]. Each electrode consists of a rigid single graphene sheet of 1792 sp<sup>2</sup>-hybridized carbon atoms [50], with dimensions 68.6 × 67.9 Å<sup>2</sup>. We employed a Cartesian coordinate system where graphene electrodes spanned xy-plane and are located at z = ±z<sub>0</sub>. Electrode separation d(= 2z<sub>0</sub>) was determined by NPT ensemble simulation and fixed during NVT simulations. The respective values are 60.5, 65.3, 75.3 and 84.5 Å for [emim]<sup>+</sup>[SCN]<sup>−</sup>, [emim]<sup>+</sup>[N(CN)<sub>2</sub>]<sup>−</sup>, [emim]<sup>+</sup>[C(CN)<sub>3</sub>]<sup>−</sup> and [emim]<sup>+</sup>[B(CN)<sub>4</sub>]<sup>−</sup>. [emim]<sup>+</sup> cation was modeled with flexible all-atom force fields [51,52]. Anion models are taken from previous study of bulk ILs [53]. The parameters are compiled in supporting information of Ref [52] and [53]. Total electrode charge Q<sub>e</sub> was varied from 0 to ±34 e with an increment of 2 e, which reproduced the same charge density increment as Ref [5].

GROMACS program was employed for the whole simulation process [54]. The equation of motion was integrated using velocity Verlet algorithm with a time step of 1 fs. Coulomb interaction was computed by Particle Mesh Ewald Summation with correction for slab geometry [55]. The vacuum regions are introduced both above and beneath the capacitor such that the whole simulation cell spans −3z<sub>0</sub> < z < 3z<sub>0</sub>. Five independent trajectories were sampled. We equilibrated the system for 25 ns with simulated annealing from 500 K to 350 K. 10 ns production runs were then conducted with Nosé-Hoover thermostat at 350 K.

## 3. Results and discussion

### 3.1. Interfacial structure

We first investigate the structure of ILs near graphene electrode. Number density distribution n<sub>α</sub>(z) of the ionic species α is integrated from local, center of mass distribution of ions n<sub>α</sub>(x', y', z),

$$n_{\alpha}(z) = A_0^{-1} \int_{-x_0}^{x_0} \int_{-y_0}^{y_0} dx' dy' n_{\alpha}(x', y', z); A_0 = 4x_0 y_0 \quad (1)$$

with the electrode surface area A<sub>0</sub>. The average ion densities n<sub>α</sub>(z)

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