# Ionic Conductivity of Liquid Electrolytes for Energy Storage Devices Using Force Field Molecular Dynamics Calculations

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For energy storage devices such as a supercapacitor (also known as an electric double-layer capacitor, EDLC) and secondary batteries (*e.g.*, Li ion batteries) in electric and hybrid electric vehicles, high conductive materials are essential to charge/discharge large current in a short time[1]. The ionic conductivity of the liquid electrolytes is one of the most important factors controlling performance of the power devices. However, developing new electrolytes is difficult only by experimental techniques because of wide variety of materials selection. Reliable theoretical calculations are therefore essential for rational materials design. In the present study, ionic conductivity of ammonium and imidazolium salts based electrolytes for energy storage devices is evaluated using a force field model.

The electrolytes studied in the present study contain either propylene carbonate (PC) or gamma butyl lactone (GBL) as a solvent. Amber type force field[2] and HF/6-31G(d) RESP fitting atomic charges[3] were used for all calculations. Temperature and pressure were controlled by Nose-Hoover thermostat[4] and Anderson barostat[5], respectively. After equilibrium runs, molecular trajectories for tens of nano seconds were produced and used for estimating ionic conductivities.

Ionic conductivities of the electrolytes were derived by evaluating mutual correlation of diffusive motion of ions according to linear response theory[6]. In this method, the calculated conductivities include effect of degrees of ionization. Accordingly they can be directly compared with the experimental results by impedance measurements. In order to investigate the effect of the collective motion of ions, the conductivities at the ionic dissociation limit were also estimated using the Einstein relation.

Figure 1 shows the comparison between theoretical and experimental ionic conductivities at room temperature. The conductivities of the dissociation limit using the Einstein relation ($\lambda_{\mathrm{Ein}}$) are widely scattered. Even the hierarchy among different electrolytes is hardly reproduced. On the other hand, the hierarchy is much better reproduced when the linear response theory ($\lambda_{\mathrm{Kubo}}$) is adopted. However, the absolute value of the conductivity is underestimated by an order of magnitude. The underestimation may be ascribed to the neglect of the molecular polarization in the present force field model.

For the PC electrolytes, i.e., $Li^+BF_4^-/PC(1M)$, $Li^+PF_6^-/PC(1M)$, and

$EMI^+BF_4^-/PC(1.2M)$ , the value of $\lambda_{Kubo}$ is close to that of $\lambda_{Ein}$, whereas $\lambda_{Kubo}$ is much lower than $\lambda_{Ein}$ for GBL electrolytes such as $EMI^+BF_4^-/GBL(1.2M)$. They suggest that the ionic conditions in PC electrolytes can be approximated by the dissociation-limit model because of the strong solvation effect. On the other hand, the organic cations are weakly solvated by GBL molecules and the cation-anion interactions remain relatively strong.
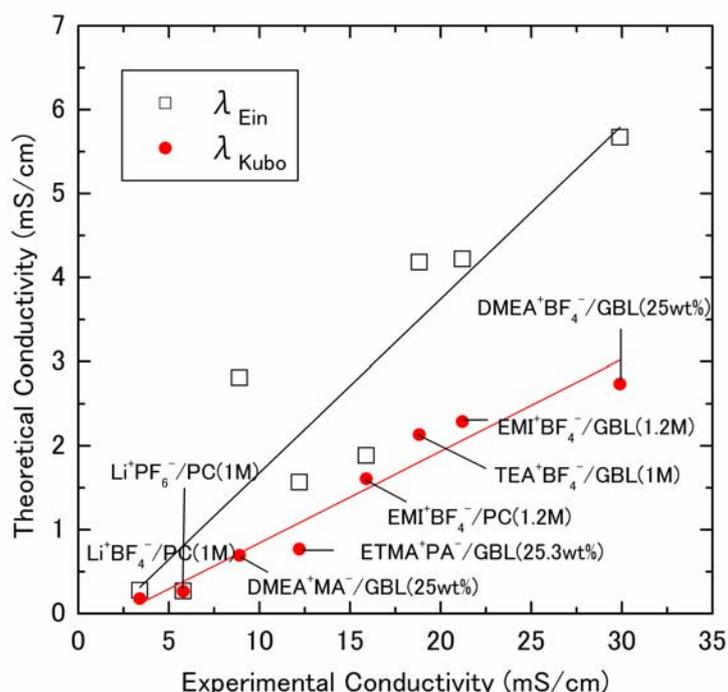


FIG. 1. Comparison of ionic conductivities of lithium, ammonium ($TEA^+$, $DMEA^+$, and $ETMA^+$) and imidazolium ($EMI^+$) salts based electrolytes by impedance measurements (Experimental) and the present molecular dynamics calculations (Theoretical). Temperature is 298K for the lithium electrolytes and 303K for the others. Solid circles are ionic conductivities evaluated by the linear response theory ( $\lambda_{Kubo}$ ). Open squares denote ionic conductivities at the dissociation limit of ions ( $\lambda_{Ein}$ ).

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