Spatial-Decomposition Analysis of Electrical Conductivity in Ternary Mixtures of Ionic Liquid

Lukman Hakim [1*], Nobuyuki Matubayasi [2]

[1]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Brawijaya University, Indonesia
[2]Graduate School of Engineering Science, Osaka University, Japan

[*]Email: lukman.chemist@ub.ac.id

Ionic liquids (ILs) have attracted considerable interest for secondary batteries' electrolytes owing to their unique properties such as low flammability, high thermal and chemical stabilities, wide liquid-temperature range, and broad electrochemical window. In a highly concentrated ionic system, such as IL, the formation and decay of ion aggregates occur constantly and the correlated motion becomes influential on the transport properties. Therefore, a molecular-level understanding of the correlated dynamics of ions in IL is essential to drive a rational design toward an effective IL-based electrolyte for a high-performance secondary battery. Herein, all-atom analyses are conducted through molecular dynamics simulations to bridge the macroscopically observable electrical conductivity with the molecular pictures of the correlated motion of ion pairs. Although the Green-Kubo formula is an exact expression to describe electrical conductivity in the time domain, the formula does not include any reference to the space domain that naturally arises when the concept of ion pair is introduced. In this work, an intuitively appealing picture of ion pairs in the space domain is incorporated into the cross-correlation functions between the velocities of two distinct ions according to their separation distance by introducing a conditional average. The spatially decomposed cross-correlation function then provides a quantitative picture of the strength of the velocity correlation of two ions at time t when they are initially separated by a distance r. The analysis is applied to ternary mixtures consisting of IL and sodium salt that is relevant to the electrolyte for a sodium-ion battery.

Keywords: ionic liquid, electrical conductivity, spatial decomposition, MD/DFT

References

1. Hakim, L., Ishii, Y., & Matubayasi, N. (2021) *J. Phys. Chem. B*, **125** (13), 3374–3385.
2. Hakim, L., Ishii, Y., Matsumoto, K., Hagiwara, R., Ohara, K., Umebayashi, Y., & Matubayasi, N. (2020) *J. Phys. Chem. B*, **124** (33), 7291–7305.