Li Ionic Liquids Consisting of Novel Asymmetric Li Imide Salts

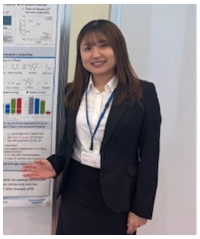
Yuna Matsuyama,[a] Frederik Philippi,[a] Taku Sudoh,[a] Hossain Md. Sharif,[a] Saki Sawayama,[b] Kenta Fujii,[b] Seiji Tsuzuki,[a] and Kazuhide Ueno[a,*]

[a] *Department of Chemistry and Life Science, Yokohama National University, Yokohama, Japan*
[b]*Graduate School of Sciences and Technology for Innovation, Yamaguchi University, Yamaguchi, Japan*
**Corresponding author's e-mail address ueno-kazuhide-rc@ynu.ac.jp*

Towards even higher performance for Li secondary batteries, previous research has predominantly focused on enhancing the ionic conductivity of the electrolyte. It is now clear that the Li ion transference number is equally important for further improving battery performance in automotive applications[1]. To achieve a high Li-ion transference number in liquid electrolytes, considerable interest has emerged in utilizing molten Li salts[2] (melting point, $T_m \geq 100$ °C) and Li ionic liquids (T_m < 100 °C). As these systems consist only of Li ions and counter anions, without the presence of solvent molecules that cause concentration polarization, it has been reported that Li ions are the dominant transport species under anion-blocking conditions, resulting in a high Li ion transference number. [3] However, most Li salts possess high T_m and low ionic conductivity due to the high viscosity of the system, rendering them unsuitable for battery integration. Therefore, Li salts with lower T_m and viscosities are required. This study presents new asymmetric Li imide salts in which a flexible oligoether side chain is introduced to further lower the melting point of the Li salt. The aim was to create a lithium ionic liquid that would combine high ionic conductivity with a high Li ion transference number. We synthesized two novel Li imide salts: Li(3-(2-methoxyethoxy)propyl)((trifluoromethyl)sulfonyl)amide (Li[PMEA]) and Li(2-(2-methoxyethoxy)ethyl)((trifluoromethyl)sulfonyl) amide (Li[TfN2O2O1]), having both trifluoromethanesulfonyl and ether groups. Investigation of the thermophysical properties of the synthesized Li salts showed that the melting points of both Li[PMEA] and Li[TfN2O2O1] were around 100 °C, in particular Li[TfN2O2O1] was confirmed to be a Li ionic liquid. The melting entropy (ΔS_f) of Li[TfN2O2O1] with the flexible ether group was found to be relatively high value of 47 [J mol^{-1}K^{-1}]. Given the relationship between melting point and melting entropy, $T_m = \Delta H_f / \Delta S_f$, the lower T_m of Li[TfN2O2O1] was attributable to the high ΔS_f. Additionally, we studied the structure of the molten state of these lithium salts through molecular dynamics (MD) simulations and investigated its correlation with their electrochemical stability and ion transport properties.

References

1. Diederichsen, K. M. et al., *ACS Energy Lett*. **2017**, 2, 11, 2563–2575.
2. Kubota, K. et al., *J. Phys. Chem. C.* **2013**, 117, 37, 18829–18836.
3. Shigenobu, K. et al., *Phys. Chem. Chem. Phys.* **2023**, 25, 6970-6978.



Yuna Matsuyama is a master's course student at Department of Chemistry and Life Science, Yokohama National University, Japan. Her research interests include synthesis and characterization of ionic liquids as an electrolyte of Li ion batteries. She has received awards for oral presentation prize (The 91th ECSJ Annual Meeting, 2024), and *Chemical Communications* prize (14th Ionic Liquid Conference Japan, 2024). *e-mail address matsuyama-yuna-km@ynu.jp*