

Deposition and dissolution of Li in LiN(CF₃SO₂)₂-glyme solvate ionic liquids for rechargeable Li-S batteries

Nobuyuki Serizawa^a, Kengo Shima^a, Naoki Tachikawa^a, Kazuki Yoshii^a,
Masayoshi Watanabe^b, and Yasushi Katayama^a

^a Keio University, Faculty of Science and Technology, Department of Applied Chemistry,
3-14-1 Hiyoshi, Kohoku-ku, Yokohama, Kanagawa 223-8522, Japan

^b Yokohama National University, Department of Chemistry and Biotechnology,
79-5 Tokiwadai, Hodogaya-ku, Yokohama, Kanagawa 240-8501, Japan

E-mail: serizawa@applc.keio.ac.jp

Deposition and dissolution of lithium have been investigated to realize rechargeable lithium batteries with high specific capacity and high energy density. However, the deposition of smooth Li is often difficult in conventional organic electrolytes. The solvate ionic liquids (SILs) composed of bis(trifluoromethylsulfonyl)amide (LiTFSA) and glyme (CH₃-O-(CH₂-CH₂-O)_n-CH₃) are considered the suitable electrolytes for rechargeable lithium-sulfur batteries because the low solubility of Li₂S_x leads to the better cycle stability and coulombic efficiency[1]. In the present study, deposition and dissolution of lithium were investigated in LiTFSA-tetraglyme (G4, n=4) SILs focusing on the morphology of the deposits.

Li was galvanostatically deposited on a Cu substrate in 50.0-50.0 and 54.5-45.5 mol% LiTFSA-G4 SILs. The morphology of Li deposits was observed using an optical microscope *in-situ* and a scanning electron microscope.

Fine and granular deposits were obtained homogeneously on the substrate in 50.0-50.0 mol% LiTFSA-G4 SIL, while coarse and whisker-like deposits were observed in 54.5-45.5 mol% one at low current densities (Fig. 1). The difference in the morphology of the deposits was considered related to the active Li species and/or the electric double layer structure on the anode. In 50.0-50.0 mol% SIL, Li⁺ was considered to be coordinated by G4 to form [Li(G4)]⁺ complex cation, which was accumulated homogeneously on the negatively charged electrode, resulting in formation of uniform nuclei of Li. On the other hand, Raman spectroscopy and potentiometric titration indicated [Li(TFSA)₂]⁻ formed besides [Li(G4)]⁺ in 54.5-45.5 mol% SIL. The reduction potential of anionic [Li(TFSA)₂]⁻ was found to be higher than that of [Li(G4)]⁺, leading to deposition of Li from [Li(TFSA)₂]⁻ sparsely due to inhibition of homogeneous nucleation by [Li(G4)]⁺ accumulated on the anode.

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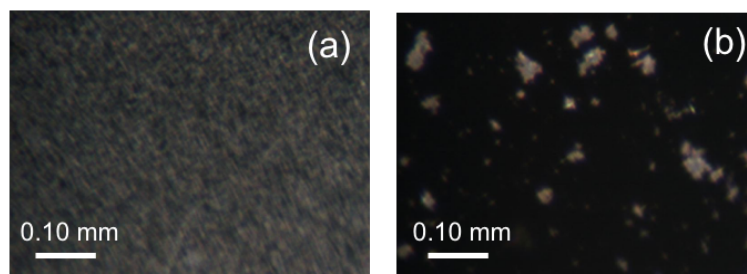


Fig. 1 Optical microscope images of the deposits obtained by galvanostatic deposition at $-10 \mu\text{A cm}^{-2}$ in (a) 50.0-50.0 and (b) 54.5-45.5 mol% LiTFSA-G4 solvate ionic liquids. Electric charge: 50 mC cm^{-2} .

References:

[1] K. Dokko, N. Tachikawa, K. Yamauchi, M. Tsuchiya, A. Yamazaki, E. Takashima, J.-W. Park, K. Ueno, S. Seki, N. Serizawa, M. Watanabe, J. Electrochem. Soc. 160 (2013) A1304-A1310.