

Structure Analysis of Polysulfide Intermediates in Lithium Sulfur Battery during Discharge by Soft X-ray Absorption Fine Structure II

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Sulfur is a promising cathode material for the lithium based battery because of its advantages such as eco-friendliness, abundance in nature, and high theoretical capacity of 1675 mAh g⁻¹. However, sulfur cathodes are not without their own intrinsic problems such as low ionic and electronic conductivity, large volumetric expansion upon lithiation from S₈ to Li₂S, and the dissolution of so-called polysulfide intermediates (Li₂S_x where x represents a value between 4 and 8). In previous studies, glyme-Li⁺ solvent ionic liquid¹⁾ and polypyrrole film containing ionic liquid²⁾ were proposed to mitigate dissolution of polysulfide. Meanwhile, dependence of sulfur cathode's reaction mechanism on polysulfide solubility of electrolyte is still unclear. To investigate the relationship between the chemical state and the dissolution of polysulfide intermediates, S K-edge XANES measurements at various depths of discharge (DOD) were performed in two types of lithium-sulfur batteries using electrolytes with different polysulfide solubility.

Fig. 1 shows S K-edge XANES spectra and their differences of sulfur active material of lithium sulfur battery using (a) DOL/DME electrolyte, (b) G3 electrolyte and (c) sulfolane (SL) electrolyte at various DOD. DOL/DME, G3 and SL were used as polysulfide soluble electrolyte, polysulfide slightly soluble electrolyte and polysulfide insoluble electrolyte, respectively. Solid S₈ in each electrolyte decreased with increase in DOD. On the other hand, the behavior of formation of Li₂S was different. The Li₂S formation using DOL/DME was at lower DOD than those using G3 and SL from the S K-edge spectra. Furthermore, formation of polysulfide using G3 was observed from the S K-edge spectra. However, that using DOL/DME and SL was slightly observed from S K-edge spectra. It is revealed that the chemical state of polysulfide at the same DOD depended on the electrolyte, and that the difference between the chemical states during discharge process depended on the difference of lithiation reaction in each electrolyte.

References

- (1) K. Dokko et al., *J. Electrochem. Soc.*, **160** (8), A1304-A1310 (2013).
- (2) N. Nakamura et al., *J Power Sources*, **274**,

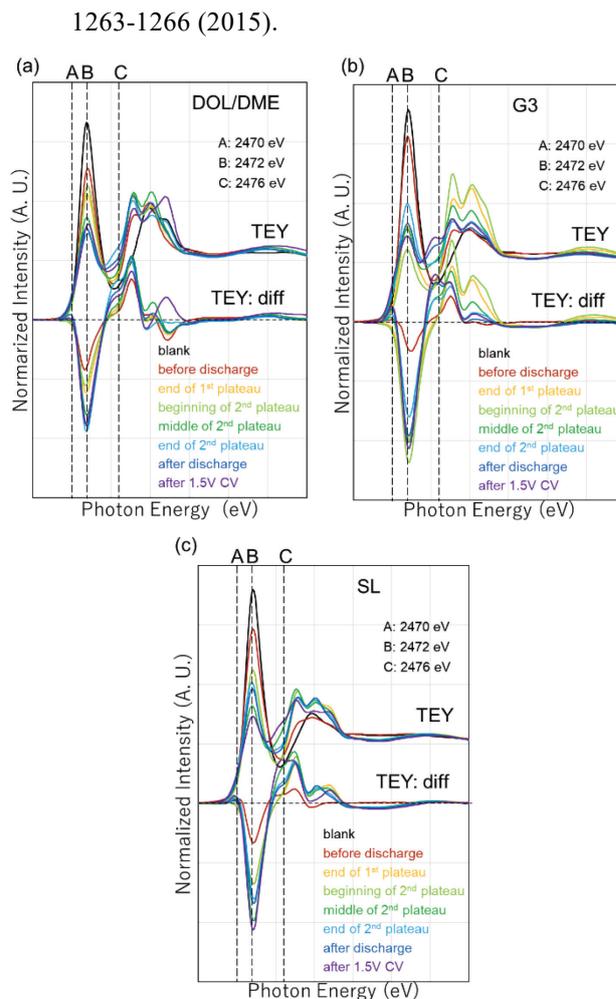


Fig. 1 Observed S K-edge XANES spectra and their differences of sulfur active materials of lithium sulfur battery using (a) polysulfide soluble electrolyte (1M LiTFSI in 1,3-dioxolane (DOL)/1,2-dimethoxyethane (DME) 1:1 (v/v)), (b) polysulfide slightly soluble electrolyte (Li(G3)TFSI/hydrofluoroether (HFE) 1:4 (mol/mol)) and (c) polysulfide insoluble electrolyte (Li(SL)₂TFSI/HFE 3:2 (mol/mol)) at various depths of discharge.