

Structure analysis of polysulfide intermediates in lithium sulfur battery during discharge by soft X-ray absorption fine structure

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Sulfur is a promising cathode material for the lithium based battery because of its advantages such as eco-friendness, 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 liquid (SIL)¹ 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 depth of discharge were performed in two types of lithium-sulfur batteries using electrolytes with different polysulfide solubility.

Fig. 1 shows S K-edge XANES spectra and its difference of sulfur active material of lithium sulfur battery using (a) (1M LiTFSI in 1,3-dioxolane (DOL)/1,2-dimethoxyethane (DME) 1:1 (v/v)) electrolyte and (b) with polysulfide insoluble SIL electrolyte (Li(G3)TFSI/hydrofluoroether (HFE) 1:4 (v/v)) at various depth of this charge. DOL/DME and G3 were used as polysulfide soluble electrolyte and polysulfide insoluble electrolyte, respectively. Solid S₈ in each electrolyte decreased with increase in depth of discharge (DOD). However, formation of polysulfide was different. The polysulfide formation using DOL/DME was measured, and that using G3 was not measured from the K-edge spectra. It is revealed that the chemical state of polysulfide depended on the electrolyte, and the difference between reaction in the electrolyte depended on the chemical state.

References

- (1) K. Dokko et al., *J. Electrochem. Soc.*, **160** (8), A1304-A1310 (2013).
- (2) N. Nakamura et al., *J Power Sources*, **274**, 1263-1266 (2015).

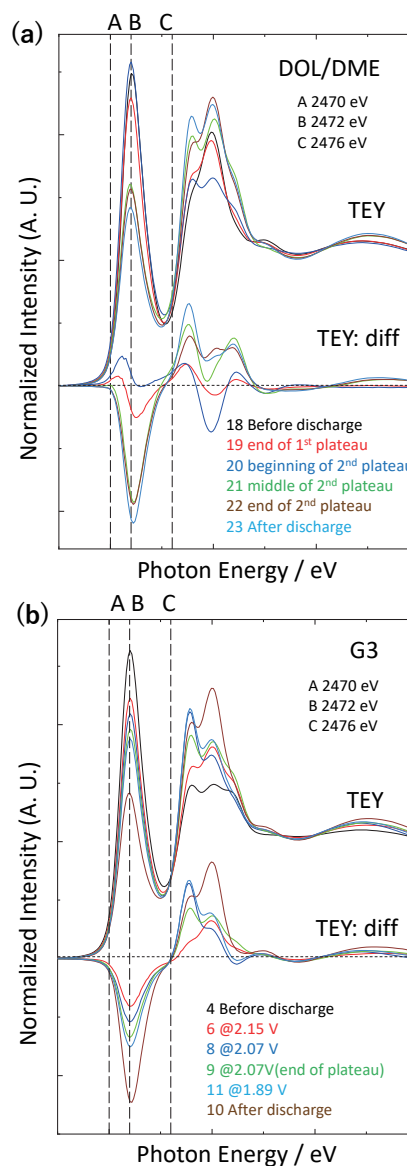


Fig. 1 Observed S K-edge XANES spectra and its difference of sulfur active material of lithium sulfur battery using (a) DOL/DME electrolyte and (b) glyme-Li⁺ solvent ionic liquid electrolyte (G3) at various depth of this charge.