

(De)Lithiation Mechanism of Se-based Lithium Batteries  
Determined by In-situ Synchrotron X-ray Probes

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Abstract

Increasing demand for advanced energy storage system used in electric vehicles has greatly accelerated the development of high energy density storage system. New electrode material or new battery system development is a key to achieve the goal of new high energy storage system with energy densities five times or more greater. In 2012, we reported that selenium could serve as cathode material for rechargeable lithium and sodium batteries.<sup>1</sup> However, the cell performances are unsatisfactory, the underlying mechanism are not well understood as well. Recently, we adopted an ether-based electrolyte in the Li/SeS<sub>x</sub> cell; the results demonstrate that the cell performance is significantly improved in terms of voltage profile and Coulombic efficiency.<sup>2</sup> The voltage profiles of these cells indicate that complete lithiation of selenium to Li<sub>2</sub>Se is occurring through the formation of intermediate phases, i.e., Li<sub>2</sub>Se<sub>n</sub> (n≥4). This behavior differs from the single-phase transition in carbonate-based electrolyte, as reported earlier.<sup>1</sup> These results clearly suggest that cell performance highly depends on the nature of the electrolyte.

In order to better understand the relationship between the formation of the intermediate phases and voltage profile of the cells with the ether-based electrolyte, we performed an in-depth study by different characterization techniques, including high-energy X-ray diffraction (HEXRD) and X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS) and electrochemical impedance spectroscopy (EIS). In situ HEXRD patterns show that Se and SeS<sub>2</sub> cathodes material was reduced into Li<sub>2</sub>Se/Li<sub>2</sub>S by the end of discharge, Se is recovered and SeS<sub>2</sub> is decomposed into Se and S by the end of charge. While the in situ XANES results suggest the formation of polyselenides, since XANES allowed us to track the evolution of the Se valence state for both crystalline and noncrystalline phases, including amorphous and electrolyte-dissolved phases in the (de)lithiation process. The existence of lithium polyselenides is further confirmed by solubility test. On the basis of these results, a mechanism for the (de)lithiation process is proposed, where Se is reduced to the polyselenides, Li<sub>2</sub>Se<sub>n</sub> (n≥4), Li<sub>2</sub>Se<sub>2</sub>, and Li<sub>2</sub>Se sequentially during the lithiation, and Li<sub>2</sub>Se is oxidized to Se through Li<sub>2</sub>Se<sub>n</sub> (n≥4) during the delithiation. In addition, X-ray photoelectron spectroscopy and electrochemical impedance spectroscopy demonstrated the reversibility of the Li/Se system in ether-based electrolyte and the presence of side products in the carbonate-based electrolytes. These results demonstrated the advantages of ether-based electrolyte over carbonate-based electrolyte as well as the importance of

electrolyte on the performance and mechanism of battery system.

Reference

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