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Soft X-ray Absorption Spectroscopy of Copper Electrode after Lithium Metal Plating and Stripping

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Rechargeable batteries using lithium metal anode are expected to be candidate as next generation high energy density batteries. Theoretical capacity of lithium metal anode is 3860 mAhg^{-1} which is ten times higher than the conventionally used graphite anodes. However, dendrite formation during charge reaction is a serious issue, which causes short circuit between lithium metal anode and cathode, resulting battery explosion. To prevent the dendrite formation, the formation of functionalized surface film at lithium metal is important. The surface film at lithium-ion battery anodes is a key factor in their efficiency and durability [1]. Despite numerous analyses of the surface film on lithium metal anode, comprehensive understanding has not yet been achieved. Furthermore, the reactions of lithium plating and stripping become particularly complex at elevated temperatures around 60°C. The battery charge-discharge at such an elevated temperature is necessary for the real battery operation without temperature managing. In this study, we examine the lithium plating and stripping at 60°C using copper current collectors with different electrolytes. The surface film on the copper after the lithium plating and stripping was analyzed by soft X-ray absorption spectroscopy (XAS).

Two-electrode flat cells were assembled using copper foil as the working electrode, Li metal as the counter electrode, and a glass fiber filter as the separator. The electrolyte used was either 1.0 M LiPF6 in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) at a 3:7 v/v ratio, or 1.0 M lithium bis(fluorosulfonyl)imide (LiFSI) in propylene carbonate (PC). Cyclic voltammetry (CV) was performed in the range of −0.1 V to 0.1 V for 10 cycles at a sweep rate of 1.0 mV s^{-1} at 60°C. Soft XAS measurements were performed at the SR center of Ritsumeikan University. The cycled copper electrodes were transferred to the measurement chamber without air-exposing. F K-edge XAS were measured by the fluorescence and the total electron yield modes.

Coulombic efficiency of Li plating and stripping using LiPF$_6$ electrolyte showed a decrease for the CV cycles. On the other hand, the cell using LiFSI electrolyte did not show the decrease despite of the lower initial efficiency. To investigate the difference of the Coulombic efficiency, the surface state after lithium plating and stripping for 1 and 10 cycles was studied by F K-edge XAS. Figure 1 shows the F K-edge X-ray absorption near edge structure (XANES) of the copper electrodes using LiPF$_6$ or LiFSI electrolytes. After one cycle with the LiPF$_6$ electrolyte, the structure resembles that of LiF. This shape drastically changes after the CV cycles, indicating the disappearance of the LiF surface layer. The decrease in LiF can affect the Coulombic efficiency. For the cell using the LiFSI electrolyte, two different components, attributed to LiF and an SO$_2$F-containing component, are detected after one cycle. After ten cycles, the LiF component becomes the main phase, which can act as a stable surface film. The presence of LiF influences the Li plating and stripping efficiency.

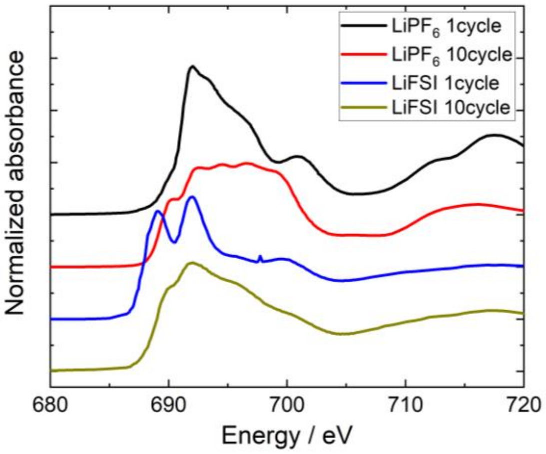

Fig. 1 F K-edge X-ray absorption near edge structure of copper electrode using LiPF$_6$ or LiFSI electrolytes after CV cycles.

References

[1] Y. Zhang, T. Zuo, J. Popovic, K. Lim, Y. Yin, J. Maier, and Y. Guo, *Mater. Today*, **2020**, *33*, 56.