Effects of Sulfur Electrolyte Additives on Li-ion Batteries and X-ray Absorption Spectroscopic Studies of Solid Electrolyte Interface

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1. Introduction

Lithium ion batteries (LIBs) have been most widely used as portable power sources. However, the further improvements of LIBs are required for electric vehicles (EVs) and hybrid electric vehicles (HEVs). Many electrolyte additives have been investigated because they improve the performance of LIBs [1-3]. Solid electrolyte interfaces (SEI) are films formed on electrodes by decomposition of electrolytes and electrolyte additives. Electrolyte additives improve the feature of SEI and the performance of LIBs. In this study, the effects of an electrolyte additive of ethylene sulfite (ES) on LIBs were investigated. SEI which ES formed on the electrodes was analyzed by soft X-ray absorption spectroscopy (XAS).

2. Experimental

$LiCoO_2$/graphite cells were assembled in an argon-filled grove box. The $LiCoO_2$ electrodes were made of 90 wt% $LiCoO_2$, 5 wt% acetylene black and 5 wt% polyvinylidene difluoride (PVDF). The graphite electrodes were made of 95 wt% artificial graphite and 5 wt% PVDF. The electrolyte was a 1 M solution of $LiPF_6$ in ethylene carbonate/ethyl methyl carbonate (EC/EMC) in a 3:7 volume ratio, and ES was added at various concentrations into the electrolyte solution. $LiCoO_2$/graphite cells were cycled in the voltage range of 3.0–4.3 V at the 1 C rate.

S K-edge X-ray absorption near-edge structure (XANES) spectra of the graphite anodes were measured in the fluorescence yield (FY) and total electron yield (TEY) modes at the BL-13 of the SR Center, Ritsumeikan University. Samples of XANES measurements were collected from the $LiCoO_2$/graphite cells after the first charge and the first and 100th cycles.

3. Results and Discussion

Fig. 1 shows the discharge capacity of the cells with ES. ES of 0.5 and 1.0 vol.% improved the cycle performance of the cells. However, 2.0 and 3.0 vol.% ES degraded the cycle performance. It is shown that the cycle performance of the cells with 1.0 vol.% ES was the best among the various concentrations.

Fig. 2 shows S K-edge XANES spectra of the graphite anodes of the cells with 1.0 vol.% ES (a-c), the graphite anode after (d) and before (e) soaking in the electrolyte solution with ES and the electrolyte solution with ES (f). The solution spectrum (f) was measured using BL-10 of the SR Center [4]. Peaks around 2473 and 2482 eV in the spectrum of (e) show that the graphite anode before soaking had compounds with divalent and hexavalent sulfur. After the first charge, a peak around 2477 eV was observed and the peak around 2482 eV was broadened. The peak around 2477 eV shows that compounds with tetravalent sulfur were formed during the first charge. The broad peak around 2482 eV shows that compounds with hexavalent sulfur were probably formed on the graphite anode. It is believed that these sulfur compounds in SEI on the graphite anode improved the cycling performance of the cells.

4. References

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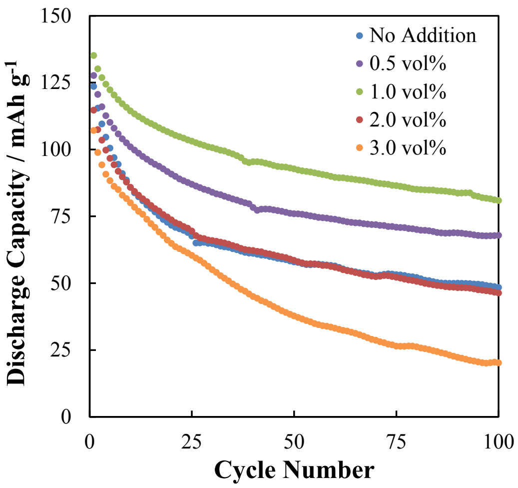

Fig. 1. The discharge capacity of the cells with ES.

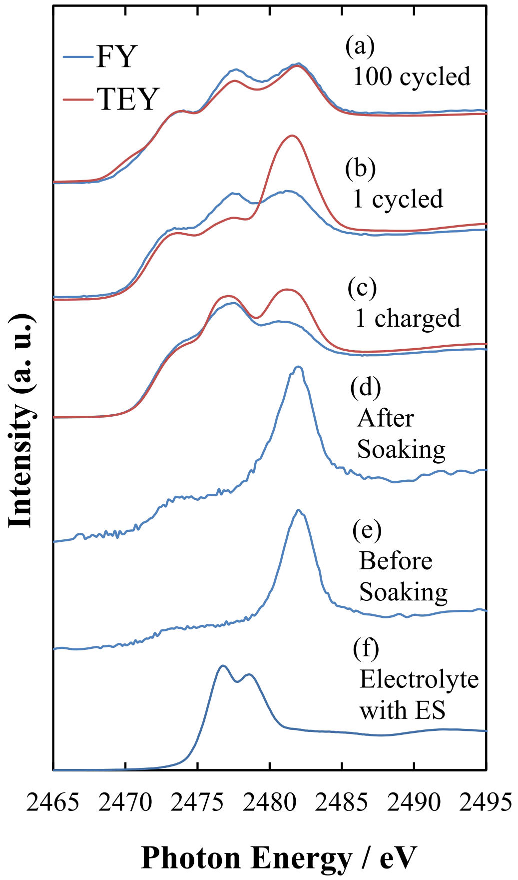

Fig. 2. S K-edge XANES spectra: (a-c) the graphite anodes of the cells with 1.0 vol.% ES, the graphite anode (d) after and (e) before soaking in the electrolyte solution with ES, and (f) the electrolyte solution with ES [4].