

Effects of ethylene sulfite as an electrolyte additive on the rate capability of lithium ion batteries

**Shota Kikuzaki¹, Chihiro Yogi², Kei Mitsuhashi², Tomoe Sanada¹,
Kazuo Kojima¹, Misaki Katayama¹, Yasuhiro Inada¹, Toshiaki Ohta²**

1) *Department of Applied Chemistry, College of Life Sciences, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu, Shiga 525-8577, Japan*

2) *SR Center, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu, Shiga 525-8577, Japan*

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). A solid electrolyte interface (SEI) is a film formed on the electrodes by degradation of both electrolyte and electrolyte additives [1]. Electrolyte additives improve SEI properties, leading to improvement in the performance of LIBs. Many electrolyte additives have been studied. Among them, ethylene sulfite (ES) has been known to improve the cycle performance [2,3]. However, ES has not been reported to improve the rate characteristics. In this study, we found that the ES additive improved the rate characteristics and studied the cause using X-ray absorption near-edge structure (XANES) measurements.

2. Experimental

LiCoO₂/graphite cells were assembled in an argon-filled glove box. The LiCoO₂ electrodes were composed of LiCoO₂, acetylene black, and polyvinylidene difluoride (PVDF) with a mass ratio of 100:5:3. The graphite electrodes were composed of spherulitic graphite, graphite and PVDF with a mass ratio of 85:15:7.5. The electrolyte was a 1 M solution of LiPF₆, where a solvent was ethylene carbonate/ethyl methyl carbonate (EC/EMC) with a 3:7 volume ratio, and 0.3 vol% ES was added into this electrolyte solution. An aging process was performed for 1 cycle at a 0.1-C rate. After the aging process, LiCoO₂/graphite cells were cycled in the voltage range of 3.0–4.2 V at the 1-, 2- and 4-C rates.

S K-edge XANES spectra of the LiCoO₂ electrodes were measured with the fluorescence yield (FY) and total electron yield (TEY) modes at BL-13 of the SR Center, Ritsumeikan University. Samples for XANES measurements were collected from the LiCoO₂/graphite cells.

3. Results and Discussion

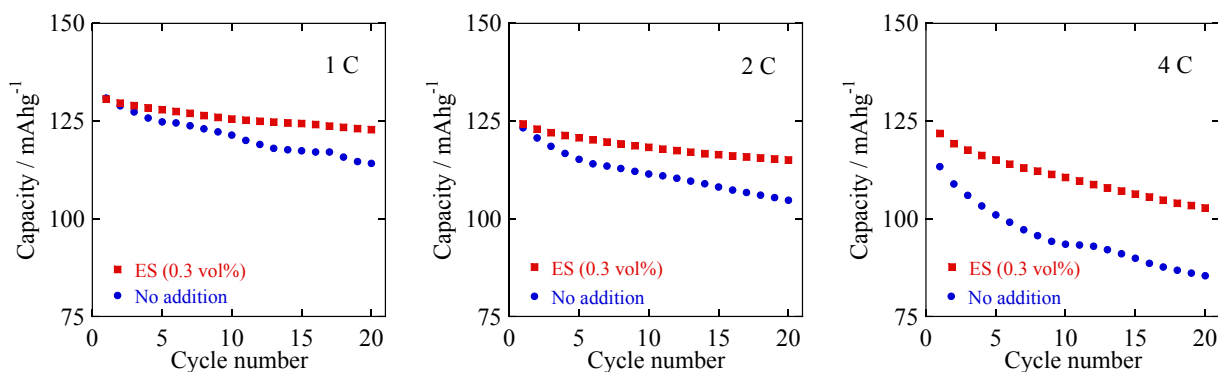


Fig. 1. The capacity of the cells with ES at the 1-, 2- and 4-C rates.

Fig. 1 shows the capacity versus cycle number for the LiCoO₂/graphite cells with 0.3 vol% ES in the electrolyte. ES suppressed greatly the capacity fade of the cells at the 4-C rate, and improved the rate capability of the cells. Compared to the cells without ES, the ES-containing cells showed much better capacity retention at the 4-C rate.

Fig. 2 shows S K-edge XANES spectra of the LiCoO₂ cathodes of the cells with 0.3 vol% ES. A peak around 2482 eV in the spectrum of the pristine LiCoO₂ cathode shows that the LiCoO₂ cathode before the first charge has some compounds with hexavalent sulfur. After the aging charge, a peak around 2472 eV was observed, indicating some compounds with divalent sulfur were formed on the LiCoO₂ cathode during the aging charge. It is believed that the compounds with divalent sulfur in SEI on the LiCoO₂ cathode reduced the interface resistance of the cathode to improve the rate capability of the cells.

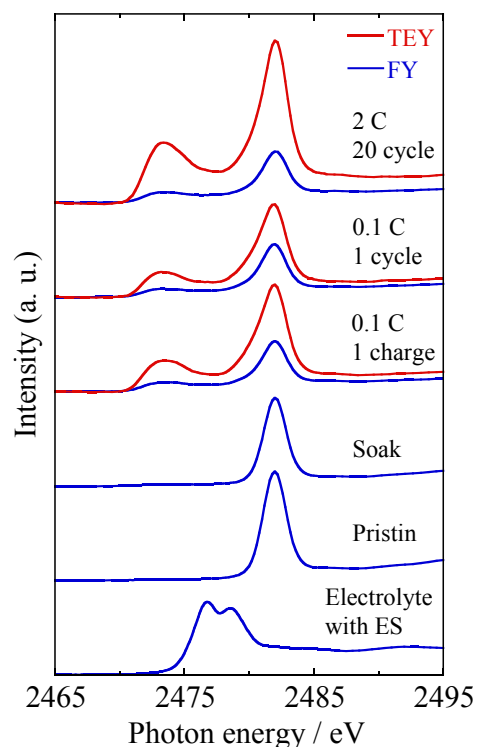


Fig. 2. S K-edge XANES spectra of the LiCoO₂ cathodes of the cells.

References

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