S22027

Soft X-ray Absorption Near Edge Structure Studies on Lithium Dodecyl Sulfate Effect for Distortions of $LiCoO_2$ in Aqueous Lithium-ion Batteries

Eunjin Choi[a] and Hye Ryung Byon[a]*

[a]Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST),
Daejeon 34141, Republic of Korea

e-mail: qwerfcs@kaist.ac.kr, hrbyon@kaist.ac.kr*

$LiCoO_2$ (LCO) is a representative positive electrode in lithium-ion batteries (LiBs). We utilized LCO to aqueous LiBs and found structure deformation by proton (H^+) intercalation previously, causing capacity fading. In this study, we added lithium dodecyl sulfate (LDS) to the electrolyte solution and investigated the LDS effect for LCO local structure change through slow and fast current density for cycling. The short-range-order structural irreversibility was investigated by X-ray absorption near edge structure (XANES) analysis. The LDS suppressed surface degradation of LCO at 10 C compared to the absence of LDS, revealing the protection of LCO.

Keywords: Aqueous lithium-ion batteries, $LiCoO_2$, Lithium dodecyl sulfate, XANES, O K-edge, Co L-edge

Introduction

Aqueous LiBs have been studied to lower cost and the risk of fire. However, one of the challenges is water and proton intercalation to lithium transition metal electrodes in salt-in-water, causing capacity fading and poor cyclability. Our previous study revealed that 0.5 mol/kg Li_2SO_4 suppressed the proton intercalation to LCO compared to other electrolyte salts, such as 1 mol/kg LiTFSI, $LiNO_3$, and $LiClO_4$. However, rate capability was still poor with 0.5 mol/kg Li_2SO_4[1].

In this experiment, the LDS additive was included in the aqueous electrolyte, and fast/moderate charge-discharge processes were performed. Soft XANES verified the structural stability of LCO after long-term cycles.

Experiments

LCO electrode was prepared by casting LCO slurry (LCO: Super P: poly(vinylidene fluoride) (PVdF) binder = 8:1:1 wt% in 1-methyl 2-pyrrolidine (NMP)) on the etched Ti foil, followed by drying at 80 °C in a thermal oven overnight. Ti foil was soaked in the etching solution (NH_4OH: H_2O_2 = 7:3 v/v%) for 10 min and washed with acetone and distilled water before use. The loading mass of LCO active materials was 3~5 mg cm^{-2}.

We used three-electrode cells comprised of the LCO electrode, Pt coil, and Ag/AgCl (in 3 M NaCl) as the working electrode, the counter electrode, and the reference electrode, respectively. All galvanostatic cycles were performed under an Ar-filled glovebox to prevent contamination by oxygen.

After cycles with the below conditions ((1) ~ (4)), the LCO electrodes were washed three times by soaking in DI water and dried under a vacuum at 80 °C overnight for XANES analysis.

(1) 50th cycled LCO at 0.5 C in aqueous electrolyte solution including 0.5 m Li_2SO_4 + 5 mM LDS
(2) 100th cycled LCO at 10 C in aqueous electrolyte solution including 0.5 m Li_2SO_4 + 5 mM LDS
(3) 50th cycled LCO at 0.5 C in aqueous electrolyte solution including 0.5 m Li_2SO_4
(4) 100th cycled LCO at 10 C in aqueous electrolyte solution including 0.5 m Li_2SO_4
(5) As-prepared LCO

Results and discussion

The O K-edge spectra of the cycled LCO electrodes ((1) ~ (4)) and the as-prepared LCO (5) were shown in Figure 1. As-prepared LCO showed sharp peaks at 529.6 eV, indicating the transition from O *1s* to Co^{III} *3d* and O *2p* hybridization orbital, for both total electron yield (TEY) and partial fluorescence yield (PFY) modes. In the TEY mode with ~10 nm surface depth, all cycled LCO electrodes showed a new signal at 528.5 eV, indicated as O_1, assigned to the transition from O *1s* to Co^{IV} *3d* and O *2p* hybridization orbital. It indicated distortion of the CoO_6 octahedron by the proton intercalation. The O_1 peak of the LCO cycled at 0.5 C for 50 cycles was negligible regardless of the presence and absence of LDS. For 10 C and 100 cycles, however, the O_1 intensity was different; The signal was attenuated with LDS, suggesting less structural degradation during the fast charging-discharging processes.

Figure 2 shows O K-edge spectra in the PFY mode. All electrodes exhibited the O_1 signal with comparable intensity, demonstrating distortions of LCO in the bulk structure regardless of the presence and absence of LDS. Unlike 0.5 C cases, however, the capacity difference with (~100 mAh/g after 50 cycles) and without LDS (< 30 mAh/g after 50 cycles) was significant at 10 C. Thus, this result suggested better stability of LCO with LDS at high current rate.

Figures 3-4 showed the Co L-edge spectra. We found a slight blue shift of Co L_2 and L_3 edge for all cycled electrodes in PFY modes, consistent with the bulk structural deformation in O K-edge modes with PFY mode.

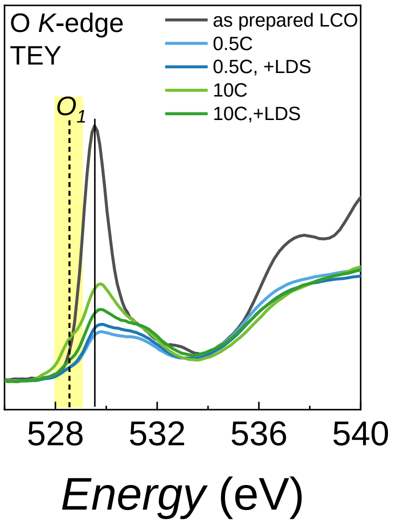

Figure 1. TEY mode of O K-edge XANES spectra.

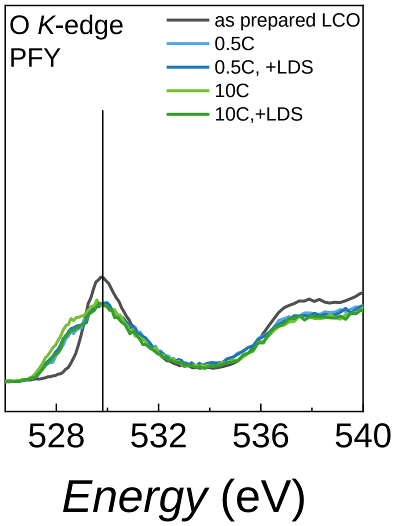

Figure 2. PFY mode of O K-edge XANES spectra.

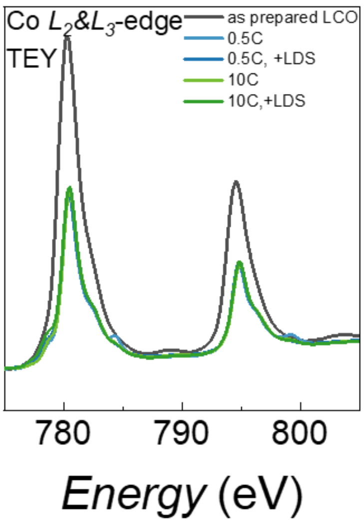

Figure- 3. TEY mode of Co L_2&L_3-edge spectra.

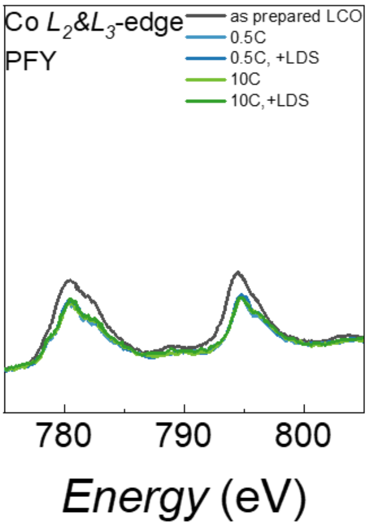

Figure 4. PFY mode of Co L_2&L_3-edge spectra.

Reference

[1] Oh, H.; Shin, S.; Choi, E.; Yamagishi, H.; Ohta, T.; Yabuuchi, N.; Jung, H.; Kim, H.; Byon, H. R. Anion-induced interfacial liquid layers on $LiCoO_2$ in salt-in-water lithium-ion batteries. JACS Au. **2023**, under revision.

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