Understanding degradation mechanism of positive electrode LiCoO₂ in aqueous lithium-ion batteries

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We have investigated cycling stability of lithium cobalt oxide (LiCoO₂) as the positive electrode in aqueous electrolyte solution. The LiCoO₂ cycled in 1 m LiTFSI/H₂O shows significant capacity fading, and X-ray absorption near-edge structure (XANES) spectrum reveals severe CoO₆ distortion in the bulk structure of LiCoO₂ at pH ~6.8. This structural degradation along with capacity fading may be attributed to the H₂O effect that hinders lithiation process.

Keywords: Aqueous lithium-ion battery, LiCoO2, XANES

Introduction

In recent, much attention has been paid to aqueous electrolyte solution used for rechargeable lithium batteries (ARLB), aiming to reduce the battery cost and catch fire. However, the positive electrode of lithium transition metal oxides has shown poorer cycling stability in the aqueous media than the one in the non-aqueous ones. To understand the main cause for severe capacity fading during cycles, much endeavor has been attempted. Xia group suggested preferential proton (H⁺) insertion into layered-structure of positive electrodes such as LiCoO₂ and LiNi_{1/3}Co_{1/3}Mn_{1/3} at low pH. The irreversible insertion of H⁺ blocked the pathway of Li⁺ movement while this issue was relatively suppressed at alkaline solution¹. Yushin group demonstrated the adverse effect of water at the surface of positive electrodes such as LiCoO₂ and LiFePO₄, which resulted in a larger increase in ionic and electronic resistances^{2,3}. Despite several reports, however, there is still a lack of the detailed degradation behavior and mechanism in particular for the almost neutral pH of aqueous electrolyte solution. Here, we have studied the surface and bulk characteristics of LiCoO2 electrode cycled in aqueous and non-aqueous electrolyte solutions using X-ray absorption near-edge structure (XANES) spectroscopy.

Experimental

i) *Electrode preparation*

Commercial LiCoO₂ (Aldrich) powder was mixed to Super P as the conducting agent and polyvinylidene fluoride (PVDF, Kynar) as the binder with 8:1:1 weight ratio. N-methyl pyrrolidine (NMP) was used as solvent for this mixture, and the resulting slurry was casted on the titanium foil (Welcos, thickness (t) ~20 μ m) using doctor blade method in an argon-filled glove box. The titanium foil was pretreated with piranha etchant (3:7 volume ratio of NH4OH (Fluka) and H₂O₂ (Aldrich)) to reduce contact resistance with the electrode film. The electrode dried at 60 °C in vacuum overnight.

ii) Electrochemical test

Galvanostatic charge and discharge experiment was conducted with three different electrolyte conditions using potentiotstat (Biologic). All tests were conducted in the Ar-filled glove box to avoid the adverse effect of O_2 gas⁴. The prepared LiCoO₂ electrode (area: 0.32 cm²) was used as the working electrode (WE).

(1) Aqueous electrolyte conditions: Two aqueous electrolyte solutions including 1 m lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) were prepared at pH ~6.8 and ~10. Pt coil was used as the counter electrode (CE). For the aqueous solution with pH ~6.8, Ag/AgCl (3 M NaCl) was used as the reference electrode (RE) and the potential range was set to $-0.2 \sim + 0.8$ V vs Ag/AgCl. In the basic condition prepared by the addition of LiOH, Hg/HgO (1 M NaOH) was used as the RE and cycled in the potential range of $-0.131 \sim +0.869$ V vs Hg/HgO.

(2) Non-aqueous electrolyte condition: The similar three-electrode set was prepared, but Li metals on Ni wire were used for both RE and CE and 1 m LiTFSI in EC/DMC/DEC (1:2:1 volume

ratio of ethylene carbonate/dimethyl carbonate/diethyl carbonate) was prepared for the electrolyte solution. The galvanostatic cycle was conducted between $3.05 \sim 4.05$ V vs Li/Li⁺.

iii) Characterization

The LiCoO₂ electrodes were washed with 1.2-dimethoxyane (DME) and dried at 60 °C in vacuum overnight after cycling. The measurements of O K-edge and Co L-edge spectra using XANES spectroscopy were performed at BL-11 of the SR center in Ritsumeikan University. All LiCoO2 electrode samples and references were loaded in an Ar-filled glovebox and directly transferred into the measurement chamber using a custom-made hermetically sealed vessel.

Results and Discussion

Galvanostatic charge and discharge curves with different electrolyte solutions are shown in **Figure 1**. The lithiation/delithiation potential plateau from LiCoO₂ appears at 0.67 V vs Ag/AgCl in pH ~6.8 aqueous solution, similar to 0.74 V vs Hg/HgO at pH ~ 10 and 3.92 V vs Li/Li⁺ in the non-aqueous electrolyte solution, EC/DMC/DEC. However, the stability of LiCoO₂ electrode is significantly different from three electrolyte solutions. The capacity from both aqueous solutions is continuously reduced during 5 cycles, which is distinguished from the stable retention from the non-aqueous electrolyte cell.



Figure 1. Galvanostatic charge and discharge curve of $LiCoO_2$ with different electrolyte conditions (a) 1 m LiTFSI in H₂O (pH ~6.8), (b) 1m LiTFSI in 0.1 mM LiOH (aq) (pH ~10), (c) 1 m LiTFSI in EC/DMC/DEC (d) Comparison of Columbic efficiency and capacity retention of aqueous and non-aqueous electrolytes during 5 cycles.

The unique cycling profiles from the basic aqueous solution in **Figure 1(b)** may arise from

oxygen evolution reaction (OER) because the delithiated $LiCoO_2$ can act as the OER catalyst⁵.

To shed light on the degradation mechanism of $LiCoO_2$ in the aqueous solutions, we investigated local-structure change of $LiCoO_2$ using XANES spectroscopy.



Figure 2. XANES spectra of $LiCoO_2$ cycled from different electrolyte conditions. (a,b) PEY mode of (a) oxygen K-edge spectra and (b) cobalt L-edge spectra and (c,d) PFY mode of (c) oxygen K-edge spectra and (d) cobalt L-edge spectra

Figure 2(a)–(b) shows local structure of LiCoO₂ in PEY (partial electron yield) mode after 1st and 5th cycles. For the O K-edge region in Figure 2(a), the Co 3d-O 2p hybridization peak at ~530 $eV(A_1)$ is revealed from the as-prepared LiCoO₂. In addition, the O 1s transition to the hybridized states of O 2p and Co 4sp appears to the broad peaks over 535 eV, which are indicated as B and C. After 1st charge, new peaks emerge at 531.8 eV (A₂) and 529.9 eV (A₃) for all conditions. The pre-edge peak of A₃ indicates the distortion of CoO_6 octahedral structure^{6,7} as the delithiation occurs. However, the A₃ peak disappears in the following 1st discharge, implying the reversible structure change with respect to Li+ lithiation/delithiation. The A₂ peak corresponds to the partial oxidation of oxygen $(O^{-2+\delta})$ that may result from the charge compensation for the delithiation. However, the presence of A₂ after 1st discharge and 5th cycles implies the occurrence of possible side reaction of the LiCoO₂ surface with the electrolyte solutions. The significant increase in A_2 peak relative to A_1 is revealed after 5 cycles for all three electrolyte conditions in O K-edge PEY mode. The Co L-edge spectrum for the as-prepared LiCoO2 shows the Co 2p to 3d transition peak B_1 at 780.3 eV (Figure 2(b)). This peak shifts towards the high energy region to ~0.33 eV after charge and moves back to the original photon energy after discharge, which is attributed to the oxidation of Co3+ and the reduction of Co⁴⁺, corresponding to delithiation and lithiation, respectively^{8,9}. Concomitantly, the new peak (B₂) related to Co^{2+} appears at lower energy region. The reason for the formation of Co2+ is understood for unintended side reaction with the electrolyte media. In particular, the significant increase in peak B₂ in PEY mode with non-aqueous electrolyte solution indicates the inclusion of Co²⁺ for cathode electrolyte interphase (CEI) that contributes to high stability of LiCoO₂ and capacity retention during cycling.

By comparison, the PFY (partial fluorescence vield) mode spectra for O K-edge and Co L-edge regions in Figure 2(c)-(d) show bulk behaviors of LiCoO₂. Unlike the negligible change of bulk Co L-edge spectra for cycling (Figure 2(d)), the A3 peak in O K-edge spectra becomes intense in particular after cycling in aqueous electrolyte solution at pH ~ 6.8 (Figure 2(c)). Namely, the distortion of CoO_6 octahedral structure irreversibly takes place in contrast with the reversible behavior at the surface. This result indicates the less lithiation occurring in the bulk structure of LiCoO₂, which is distinct from far more moderate change at pH ~10.0 and the non-aqueous electrolyte solution. Possibly, the presence of OH- in the aqueous solution at pH ~10 and the CEI layer of $LiCoO_2$ surface in the non-aqueous electrolyte solution prevent the irreversible lithiation/delithiation process. The ones can consider the role of higher H⁺ concentration at pH ~6.8 than the one at pH ~10, where the insertion of H⁺ incurs the irreversible lithiation¹. However, the concentration of H^+ (1.5 x 10^{-7} M) is far lower than the concentration of H₂O (~55 M) and Li⁺ (~1 m). Thus, we propose the predominant effect of H₂O that thickly hydrates Li⁺ and and also forms a blocking layer on the surface of LiCoO₂. The lithiation process however is likely to suppression when OH⁻ is adsorbed on the surface of LiCoO₂.

In summary, we conducted galvanostatic charge and discharge tests in three different aqueous and non-aqueous electrolyte solutions to investigate the degradation mechanism of LiCoO₂. The correlation between electrochemical performances and XANES analyses revealed that the capacity fading at pH ~6.8 aqueous medium arose from the irreversible local structure change at the inner side of bulk electrode, possibly due to the adverse H₂O effect. Despite capacity loss, the negligible change of bulk LiCoO₂ structure at pH ~10.0 implied more reversible lithiation /delithiation process in the presence of large amount of OH⁻ while the capacity fading was continuous due to OER. In contrast, the CEI layer formed in non-aqueous electrolyte solution protected LiCoO₂ and retained the capacity during cycling.

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Articles and meetings

Meetings

[1] Hyunjeong Oh, and Hye Ryung Byon, *Degradation mechanism of LiCoO₂ in aqueous lithium-ion batteries*, Korean society of industrial and engineering chemistry 2018 Spring, Daegu, Republic of Korea