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Surface protection of $LiCoO_2$ positive electrode in aqueous lithium-ion batteries

Hyunjeong Oh[a], Hirona Yamagishi[b], Keisuke Yamanaka[b], Toshiaki Ohta[b], Hye Ryung Byon[a*]

[a] Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro,
Yuseong-gu, Daejeon 34141, Republic of Korea
[b] Synchrotron Radiation (SR) Center, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan
*e-mail: ohj2010@kaist.ac.kr, hrbyon@kaist.ac.kr

We have investigated cycling stability of lithium cobalt oxide ($LiCoO_2$) as the positive electrode in aqueous electrolyte solution and tried to protect the $LiCoO_2$ surface from the adverse effect of water. First, we attempted to form artificial coating layer of LITHion to minimize direct contact of water to $LiCoO_2$ surface while allowing for Li^+ ion transport. However the access of hydrated lithium ion through a coating layer eventually provided non-trivial quantity of water. Therefore LITHion coating gave a delay of capacity fading while distortion of CoO_6 layer of $LiCoO_2$ arising from water became severe for cycling. Alternatively, we tried to make a solution-phase protection layer using inner Helmholtz layer of SO_4^{2-} in Li_2SO_4 electrolyte solution. In the absence of any artificial layer, the aqueous lithium-ion cells showed highly improved capacity retention with 0.5 m Li_2SO_4(aq) (~100% even after 30 cycles) relative to that with 1 m LiTFSI(aq) (~30% capacity retention for the same cycling number). The O K-edge X-ray absorption near-edge structure (XANES) spectra revealed dramatic alleviation of CoO_6 distortion and negligible side products with Li_2SO_4 electrolyte solution.

Keywords: Aqueous lithium-ion battery, $LiCoO_2$, XANES

背景と研究目的 (Introduction)：

Recently, aqueous electrolyte for rechargeable lithium batteries (ARLB) have received a lot of attention owing to the safety and cost issues[1]. Non-flammable and low cost of water could solve the catching fire problems of battery system. However, the positive electrode of lithium transition metal oxides has shown poor cycling stability in the aqueous media than the ones in the non-aqueous ones. For that reasons, especially in case of layered structured $LiCoO_2$ (LCO) Xia group suggested preferential proton (H^+) insertion into layered-structure of LCO at low pH. The irreversible insertion of H^+ blocked the pathway of Li^+ movement while this issue was relatively suppressed in alkaline solution[2]. Yushin group demonstrated the adverse effect of water at the surface of LCO which resulted in a larger increase in ionic and electronic resistances[3].

In this research, we tried to find methods to protect the surface of LCO from undesired reactions arising from water at neutral pH. First we tried to design an artificial coating layer of the LCO surface using LITHion (Lithiated nafion). The structure of LITHion is shown in **Figure 1(a)**, when the layer deposited on the surface. The large hydrophobic domain can minimize the water poisoning effect while the separating narrow routes of SO_3^- allow for Li^+ ion transport. In addition, we also investigated anionic inner Helmholtz layer from SO_4^{2-} by using Li_2SO_4 solution, which remarkably could protect the LCO surface even in the absence of any artificial coating layer. Along with electrochemical performance tests, we have studied the surface and bulk structures of LCO electrodes using X-ray absorption near-edge structure (XANES) spectroscopy in PEY (partial electron yield) and PFY (partial fluorescence yield) to shed light on the effect of protecting layers.

実験 (Experimental)：

i) Electrode preparation

(1) Commercial $LiCoO_2$ (Sigma 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 to make slurry, which was casted on the carbon paper (Toray, TGP-H-90) using doctor blade method in an argon-filled glove box. The electrode dried at 60 °C in vacuum overnight.

(2) Preparation of LITHion-coated LCO

10 wt% LITHion solution in isopropyl alcohol

(Ion power) was diluted 40 times by N,N-dimethylforamide (DMF, Sigma aldrich). The LCO electrodes were soaked in this solution for 9 hours, followed by drying at 80 °C for 4 h and subsequent drying at 100 °C for 2 h in a vacuum oven.

ii) Electrochemical test

Galvanostatic charge and discharge examinations were conducted using battery testers (Biologic) and an Ar-filled glove box to avoid the adverse effect of O_2 gas[4]. The LCO electrode (area: 0.826 cm^2) was used as the working electrode (WE), and Pt coil was used as the counter electrode (CE). Ag/AgCl (3 M NaCl) was used as the reference electrode (RE) and the potential range was set to –0.2 ~ + 0.8 V vs Ag/AgCl. Two aqueous electrolyte solutions including 1 m lithium bis(trifluoromethane sulfonyl)imide (LiTFSI, Kishida) and 0.5 m Lithium sulfate (Li_2SO_4, Alfa aesar) were used as the aqueous electrolyte solutions.

iii) Characterizations

The cycled LCO electrodes in LiTFSI solution were washed with 1,2-dimethoxyane (DME) while H_2O was used as the washing solution when LCO cycled in Li_2SO_4 solution. All samples dried at 60 °C in vacuum overnight and were directly transferred into the measurement chamber using a custom-made hermetically sealed vessel. 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.

結果、および、考察 (Results and Discussion) :

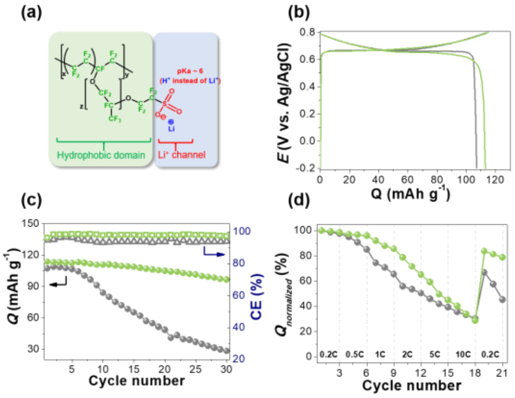

Figure 1. Galvanostatic examinations of bare LCO (gray) and LITHion@LCO (green) in 1 m LiTFSI solution (a) Structure of LITHion. (b) 1st galvanostatic charge and discharge curves (b) Comparison of cyclability and columbic efficiency during 30 cycles with 0.5 C current density. (d) Rate capability result.

LITHion was coated on LCO with several nanometer of thickness. The first galvanostatic charge and discharge curves of LITHion coated LCO (LITHion@LCO) was compared with bare LCO in **Figure 1(b)**. Electrochemical reaction of LITHion@LCO are identical to that of pristine LCO, showing similar lithiation/delithiation potential plateaus at 0.67 V vs Ag/AgCl and no additional plateaus. However, for 30 cycles, the capacity retentions from two electrodes are notably different. **Figure 1(c)** showing cyclability of LCO in 1 m LiTFSI aqueous solution reveals ~85% capacity retention from LITHion coating and ~20% from bare LCO. Higher columbic efficiency for LITHion@LCO also supported reversible Li^+ ion (de)lithiation. However, **Figure 1(d)** demonstrates poor rate capability in high current density of 10 C even with LITHion coating and unstable capacity retention once the current density increased.

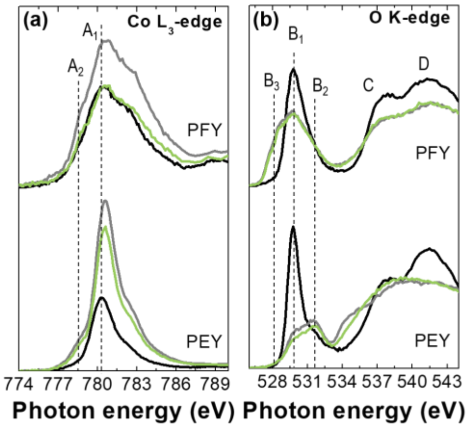

Figure 2. XANES spectra of as-prepared LCO (black), 30th cycled LITHion coated LCO (green), and 30th cycled bare LCO (gray) with 1 m LiTFSI aqueous solution (pH ~7). PFY mode (top) and PEY (bottom) of (a) cobalt L_3-edge and (b) oxygen K-edge region

To investigate the structural degradation of LCO from aqueous electrolyte, we analyzed the local structure change of LCO using XANES spectroscopy. **Figure 2** shows Co L_3-edge and O K-edge regions of LCO electrodes in PEY and PFY modes. The Co L_3-edge spectrum for the as-prepared pristine LCO shows the Co 2p to 3d transition peak indicated as indicated by A_1 at 780.3 eV, which slightly shifts positively in both PEY and PFY mode after 30th cycle (**Figure 2(a)**). It indicates the delihitated Li^+ ions are not totally lithiated again for cycling, which is consistent with the result of remaining Co^{4+} in LCO[5,6]. Concomitantly, the new peak of A_2 that is related to Co^{2+} appears at the surface of PEY mode. The reason for the formation of Co^{2+} is understood for the reduction of Co^{3+} at the space charge region of LCO surface [3, 7].

For the O K-edge region in **Figure 2(b)**, the Co 3d-O 2p hybridization peak at ~530 eV is assigned to B_1. 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 C and D. After 30th cycles, the XANES spectra are totally different from PEY and PFY modes. At the surface from the PEY mode, the B_2 peaks of 521.8 eV associated with the partial oxidation of oxygen ($O^{-2+\delta}$) are enhanced for both LiTHion coated and bare LCO electrode surface. This peak results from the interfacial reaction between LCO and electrolyte solution. On the other hand, at the bulk region from the PFY mode, the pre-edge B_3 peak of 529.9 eV significantly emerges for both electrodes. It indicates the distortion of CoO_6 octahedral structure[8, 9] as the delithiation occurs. Namely, the distortion of CoO_6 octahedral structure irreversibly takes place due to less lithiation process for cycling.

Unfortunately, although LITHion coating on LCO shows enhanced cyclability, distortion of CoO_6 local structure and surface degradation are analogous to those of bare LCO electrode in 1 m LiTFSI aqueous solution. Therefore we conclude that LITHion is not capable of preventing the water poisoning efficiently although it can delay it in some extent. Presumably, the hydrated Li^+ ion ($Li(H_2O)_4^+$) itself can approach LCO electrode through the SO_3^- channel in the LITHion layer, and the remaining water after dehydration of Li^+ for lithiation process destructs LCO structure.

Alternatively, we designed the new concept of solution-phase protection layer using surface adsorption-favorable anions. It was reported that high concentration of anion ($TFSI^-$) in water-in-salt electrolyte made a dense inner Helmholtz layer at the surface of positively charged electrode and prevented the access of water.[10,11] The molecular dynamic (MD) simulation revealed that the oxygen atoms of $TFSI^-$ were attractive to the positively charged surface[12]. However when the anion concentration is lower and competes with much higher concentration of water in a typical electrolyte solution, the oxygen atoms linked with a bulky CF_3 group in $TFSI^-$ may not be easily exposed toward electrode surface. Therefore, the water has a high chance to accommodate the electrode surface and induces the water-poisoning result for LCO. Therefore, we tried to find the new anion which has high affinity to adsorb on the positive electrode surface compared to water. The tetrahedral structure of SO_4^{2-} anion contains four oxygen atoms at the vertexes, which can directly approach to electrode surface without any hinderance. Its smaller size and resonance structures are also attractive to form stable and solution-phase protection layer.

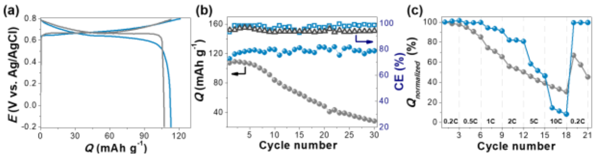

Figure 3. Galvanostatic electrochemical test of pristine LCO in 1 m LiTFSI solution (gray) and 0.5 m Li_2SO_4 solution (light green) (a) 1st galvanostatic charge and discharge curves (b) Comparison of cyclability and Columbic efficiency during 30 cycles with 0.5 C current density. (c) Rate capability test

Figure 3 shows galvanostatic charge and discharge curves with 0.5 m Li_2SO_4 solution, which are similar to the one with 1 m LiTFSI solution. In addition, the cell with 0.5 m Li_2SO_4 solution shows superior cyclability and rate capability. The capacity retention maintained 100% even after 30th cycles (**Figure 3(b)**). For rate capability test, although capacity drop is increased with increasing current density, the capacity retention is much improved without any destruction even after fast cycling (**Figure 3(c)**).

The structure change of LCO was also investigated from XANES. With 5 m Li_2SO_4 solution, the shift of A_1 peak is suppressed as shown in Co L_3-edge region (**Figure 4(a)**). In addition, emergence of B_2 and B_3 peaks in O K-edge spectra is significantly alleviated, indicating less CoO_6 distortion caused by the protection of LCO surface from SO_4^{2-} ions. Therefore, the SO_4^{2-} anion (0.5 m) could make less damage of LCO structure and lower side reaction compared to $TFSI^-$ anion (1 m). This stable LCO structure is consistent with reversible lithiation/delithiation process for cycling.

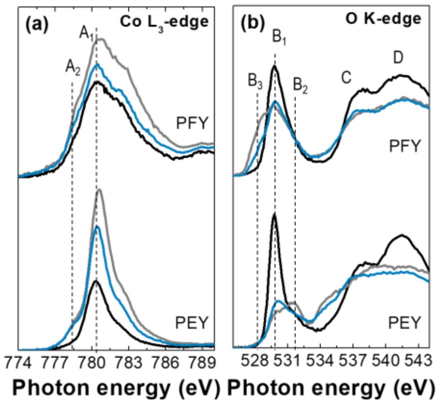

Figure 4. XANES spectra of pristine LCO (black), 30 cycled LCO with 1 m LiTFSI (gray) and 30 cycled LCO with 0.5 m Li_2SO_4 (blue). (a) PEY (bottom) and PFY mode (top) of cobalt L_3-edge spectra (b) oxygen K-edge spectra

In summary, we studied surface protection methods for $LiCoO_2$ positive electrode, (1) LITHion coating and (2) *in-situ* formation of solution-phase SO_4^{2-} anion layer. The LITHion could not efficiently prevent water poisoning and it resulted in severe structural distortion in both bulk and surface region. The alternative method using SO_4^{2-} anion in the electrolyte solution could much more suppress CoO_6 distortion and enhance reversible lithiation/delithiation process. It may be attributed to high adsorption affinity of SO_4^{2-} anion to $LiCoO_2$ electrode and hindering the access of water.

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論文・学会等発表（予定）(Articles and meetings)

Meetings

[1] Hyunjeong Oh, Hirona Yamagishi, Keisuke Yamanaka, Toshiaki Ohta and Hye Ryung Byon, *Degradation mechanism of $LiCoO_2$ in aqueous lithium-ion batteries*, Korean society of industrial and engineering chemistry 2018 Spring, Daegu, Republic of Korea

[2] Hyunjeong Oh, Hirona Yamagishi, Keisuke Yamanaka, Toshiaki Ohta and Hye Ryung Byon, *Study of the degradation mechanism of $LiCoO_2$ layered-structure positive electrode in aqueous lithium-ion batteries*, The 19th international meeting on lithium batteries, Tokyo, Japan

[3] Hyunjeong Oh, Hirona Yamagishi, Keisuke Yamanaka, Toshiaki Ohta Hirona Yamagishi, Keisuke Yamanaka, Toshiaki Ohta and Hye Ryung Byon, *Understanding interfacial reaction of layered $LiCoO_2$ positive electrode in aqueous lithium-ion batteries*, International Battery Associate, San Diego, USA.