

Understanding degradation mechanism of positive electrode LiCoO_2 in aqueous lithium-ion batteries

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In this work, we investigated LiCoO_2 's electrochemical oxygen evolution reaction (OER) property with various alkali metal hydroxide as electrolyte. CsOH, KOH, NaOH, and LiOH were used for electrolyte to compare the activity of the catalyst. With same concentration of 0.1 M, larger alkali metal cation exhibits higher OER activity of LiCoO_2 . The overpotential with LiOH was 80 mV larger than CsOH at current density of 10 mA cm^{-2} . To obtain deep understanding, precise structural analysis of ex-situ XANES analysis were employed to oxygen K edge.

Keywords: Oxygen evolution reaction, LiCoO_2 , XANES

背景と研究目的 (Introduction) :

For past several decades, human societies generate desired power by combustion of fossil fuels to satisfy energy demands in several industries and transports. Consequently, the concentration of greenhouse gas, the product of combustion, has increased in the atmosphere, and made severe climate change. In response, the intelligentsia attempted to develop clean and renewable energy conversion and storage system. One such technology is hydrogen fuel cell, the electricity generation of which is absolutely pollutant free.

To achieve sustainability, not only electricity generation, but also the hydrogen feeding to fuel cell should be eco-friendly. One of the most promising and efficient hydrogen productions is an electrochemical process of water splitting cell. On electrodes surface, hydrogen and oxygen are evolved from each side of cathode and anode. Here, oxygen evolution reaction (OER) is much slower than hydrogen evolution reaction (HER) due to sluggish OER kinetic of consuming 4 electrons per one dioxygen molecule. As a result, OER requires much more potential energy to reach sufficient production rate. It becomes a bottle neck step of water splitting process.

In this present work, LiCoO_2 's

electrochemical OER property was investigated in-depth with different size of alkali metal cation in electrolyte. CsOH, KOH, NaOH, and LiOH were used for electrolyte to compare the activity of the catalyst. With same concentration of 0.1 M, larger alkali metal cation exhibits higher OER activity of LiCoO_2 . The overpotential with LiOH was 80 mV larger than CsOH at current density of 10 mA cm^{-2} . To obtain deeper insight, precise soft X-ray ex-situ XANES was employed to understand the local electronic structure of oxygen.

実験 (Experimental) :

1) Electrochemical Measurement

To make electrode, weight ratio between LiCoO_2 , carbon black, and PVdF was kept about 80:10:10 with total mass of 500 mg. And 540 mg of N-Methyl-2-pyrrolidone was added to mixture. The mixture underwent Thinky operation (20 min, 1100 rpm) to get black slurry. The slurry was spread on restricted area of small size of gas diffusion layer. After applying, the electrode dried at 80°C oven for 4 h, followed by drying at 80°C vacuum for 12 h. For electrochemical cell, platinum (Pt) wire was used as counter electrode, and Hg/HgO (1 M NaOH) was selected as reference electrode. Cesium hydroxide monohydrate, potassium

hydroxide, sodium hydroxide, and lithium hydroxide monohydrate were used with distilled water in concentration of 0.1 mol L⁻¹ as electrolyte. Potential of measurement was calibrated in reversible hydrogen electrode (RHE) by following equation: $E \text{ vs. RHE} = E \text{ vs. Hg/HgO(1M NaOH)} + 0.0592 \times \text{pH}$. Oxygen evolution polarization curve was obtained by averaging of cathodic and anodic scan of interested region of cyclic voltammetry (CV) with 1 mV s⁻¹ scan rate. All electrochemical measurements were conducted under argon (Ar) gas bubbling condition.

3) XANES Characterization

The LiCoO₂ electrodes were washed with distilled water and dried in vacuum condition. 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) :

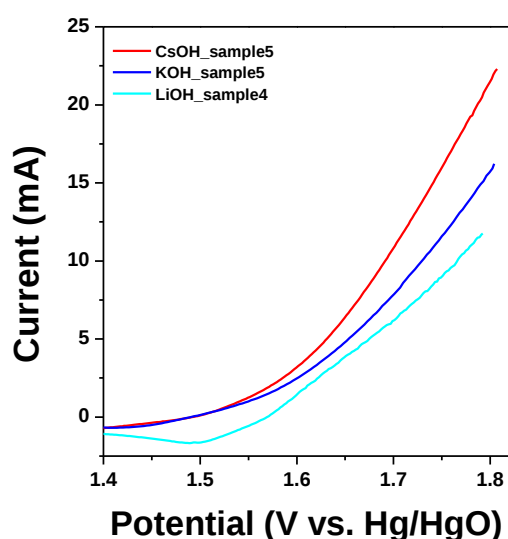


Figure 1. Polarization curves of LiCoO₂ with different alkali metal cation. (red: CsOH, blue: KOH, cyan: LiOH)

To compare the OER activity of LiCoO₂, each polarization curve was obtained by averaging anodic and cathodic scan of CV with 1 mV s⁻¹ of scan rate (Figure 1). As result, CsOH shows the best performance followed by KOH and LiOH electrolytes. Overpotential of CsOH case was 80 mV less than LiOH case. To understand origin of activity difference, we decided to study local

electronic structure of LiCoO₂.

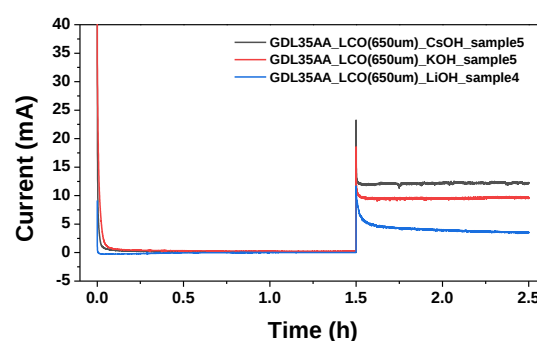


Figure 2. Chronoamperometric result at 0.6V and 0.8 V vs. Hg/HgO of LiCoO₂ electrode at different electrolyte. (black: CsOH, red: KOH, blue: LiOH)

For XANES analysis, larger geometric area electrodes, where LiCoO₂ was deposited on gas diffusion layer were exposed for *i-t* experiment. Initially the potential was kept at 0.6 V for 1.5 h and rise to 0.8 V vs. Hg/HgO for 1 h. Figure 2, shows different activity of LiCoO₂ at each electrolyte. The trend of OER currents coincides with polarization curve of Figure 1. After obtain *i-t* curve, the samples dried at vacuum and oxygen K edge and cobalt L edge XANES were measured.

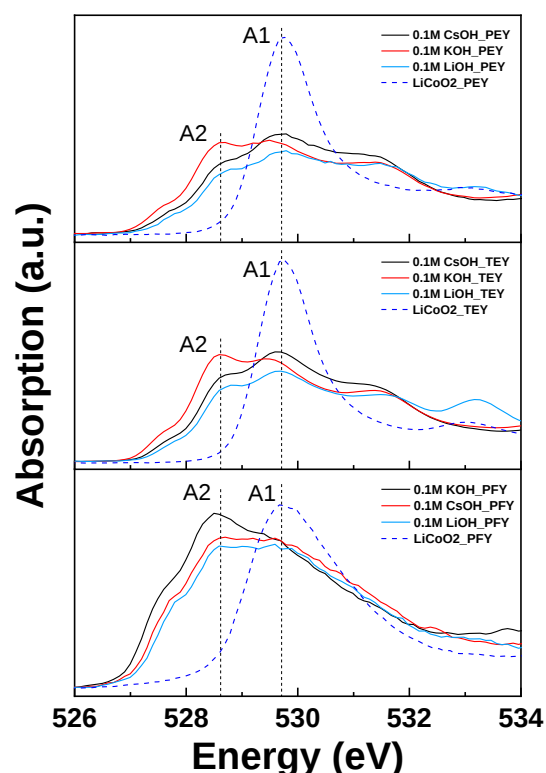


Figure 3. O K edge of LiCoO₂ after OER reaction. Top layer: PEY, middle layer: TEY,

bottom layer: PFY, solid black: CsOH, solid red: KOH, solid cyan: LiOH, dash blue: pristine LiCoO₂.

Figure 3 shows oxygen K edge spectra of XANES. The A1 peak is associated with O 1s → Co 3d-O 2p hybridized state transition from LiCoO₂ and the A2 peak related to distortion of CoO₆ that is the unit structure of LiCoO₂. The LiCoO₂ operating with KOH have the most distorted CoO₆ for both surface and bulk structures as Li⁺ is irreversibly delithiated. This sample ordering according to distortion structure of CoO₆ is not consistent with the OER activity (Figures 1-2). Instead, the intensity of A1 peak might be key to correlate with active sites for OER.

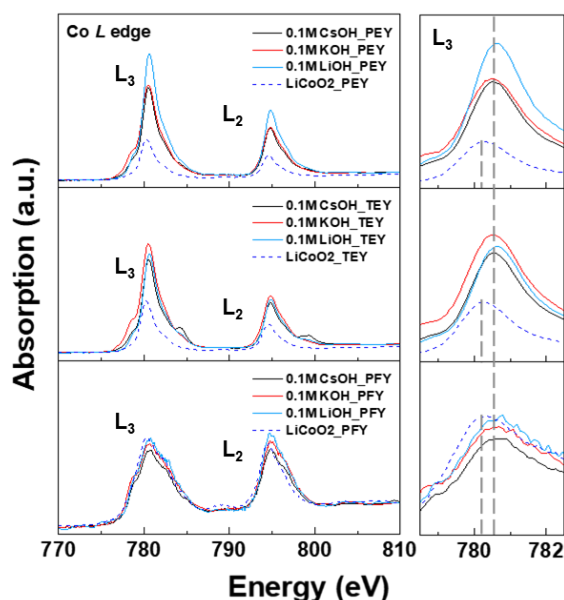


Figure 4. Co L edge of LiCoO₂ after OER reaction. Top layer: PEY, middle layer: TEY, bottom layer: PFY, solid black: CsOH, solid red: KOH, solid cyan: LiOH, dash blue: pristine LiCoO₂.

In addition, cobalt L edge structure was investigated, and the result is shown at Figure 4. All samples after OER reaction show higher oxidation state compared with pristine LiCoO₂ at L₃ spectra. The L₃ peaks shift positively for all samples, indicating the presence of Co⁴⁺ from delithiation. Interestingly, the peak of LiOH sample is the most positive among those from CsOH and KOH samples. This result is not consistent with the result from in-situ cobalt K edge hard X-ray XANES obtain from PAL 8C beam line. Possibly this discrepancy arises from different in-situ and ex-situ condition and

sample treatments. The samples for ex-situ measurement were prepared through washing and drying process, which might alter the LiCoO₂ structure.

In summary, we investigated the local structure of LiCoO₂ that performed OER at 0.6 and 0.8 V with different electrolyte solutions, 0.1 M LiOH, KOH and CsOH. The significant distortion of CoO₆ was observed for all samples. The electrodes working with CsOH had the most intense Co 3d-O 2p hybridized state, which could be correlated with the highest OER performance from CsOH electrolyte solution. In addition, all samples have the shifting L₃ peaks indicating the presence of Co⁴⁺. For more accurate comparison and finding true active sites for OER, further experiments are needed.

文献 (References)

論文・学会等発表 (予定) (Articles and meetings)

None.