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リチウム空気電池の放電生成物の構造解析と副生成物分析
Structural analysis of discharge and by-product products of lithium-air batteries

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Abstract

In this study, we analyzed the structures of discharged products and byproducts from Li-O_2 batteries in DMA and DETFA-50 electrolytes using X-ray absorption fine structure (XAFS) at beamline 11 (BL-11) at the Synchrotron Radiation Center, Ritsumeikan University. Samples were synthesized at 50%, 75%, and 100% charge/discharge levels, and full-charge recycling for up to 30 cycles for each electrolyte. In the DMA electrolyte, byproducts were dominant in TEY and PEY modes, but high-intensity Li_2O_2 peaks appeared in PFY modes, suggesting that Li_2O_2 particles were covered by byproducts. In DETFA-50, the results show electrochemical decomposition of both Li_2O_2 and the electrolyte during charge/discharge.

Keywords: Li-O_2 battery, O K-XANES, Li K-XANES, byproduct

Background

Li-air batteries are a promising alternative to Li-ion batteries in clean energy applications due to their higher energy density. However, irreversible discharge products and electrolyte degradation hinder reverse charging and reduce cycle stability.

To clarify the reaction mechanism, we analyzed the chemical phases of Li-related products formed in DMA and DETFA-50 electrolytes. The charge and discharge process was examined under various conditions: 50%, 75%, and 100%, and with full charge recycling up to 30 cycles. X-ray absorption fine structure (XAFS) analysis enabled the identification and evaluation of Li_2O_2 formation and byproducts, including Li_2CO_3, lithium carboxylates (CF_3COOLi, CH_3COOLi), and LiOH.

Experiment

N,*N*-dimethylacetamide (DMA, Wako) and *N*,*N*-diethyl-2,2,2- trifluoroacetamide (DETFA, Wako) were used as electrolyte solvents. They were synthesized by stirring overnight in $LiNO_3$ salt (Kishida, Japan), forming $LiNO_3$/DMA and $LiNO_3$/DETFA-50 electrolytes. In particular, the $LiNO_3$/DETFA-50 electrolyte was synthesized by mixing 50 vol% DMA and 50 vol% DETFA. A Li-O_2 battery cell was principally assembled with a negative electrode of Li foil (25 mm diameter, 100 or 400 μm thick, Honjo Metal), a positive electrode of carbon paper (CP, 20 mm diameter, TGP-H-060, Toray), and electrolytes. It was then mounted with a full-oxygen cylinder and cell components to form a compact battery cell [1]. Subsequently, battery cells were tested in an electrochemical system under various conditions, including 50%, 75%, and 100% charge/discharge levels, and at full charge up to 30 cycles for each electrolyte. The CP electrodes were removed for characterizations to examine the charged and discharged products and by-products. The XAFS spectra of Li_2O, Li_2CO_3, CH_3COOLi, CF_3COOLi, and LiOH standard powders were acquired as references. The Li_2O_2 spectrum was taken from the previous measurement at the SR center [2]. The experiment was conducted at the Synchrotron Radiation Center (Ritsumeikan University) on beamline BL-11 for XAFS.

Results and Discussion：

Figures 1 and **2** show the XANES spectra of the O and Li K-edges in DMA and DETFA-50 electrolytes at charge and discharge levels of 50%, 75%, and 100%, with standard powders as references. The samples showed peaks corresponding to byproducts at approximately 532 eV and 539 eV (lithium carboxylates), LiOH at 533.5 eV, and Li_2CO_3 at 539 eV and 533.5 eV. In the DMA electrolyte, the σ*(O-O) absorption peak

of Li_2O_2 was detected at approximately 530 eV for samples at 75% charge, 100% charge, and 75% discharge using the O K-edge PFY mode. For the TEY and PEY modes, the Li_2O_2 peaks had weak intensity, except for the 75% discharge sample. This indicates that Li_2O_2 was covered by the byproducts.

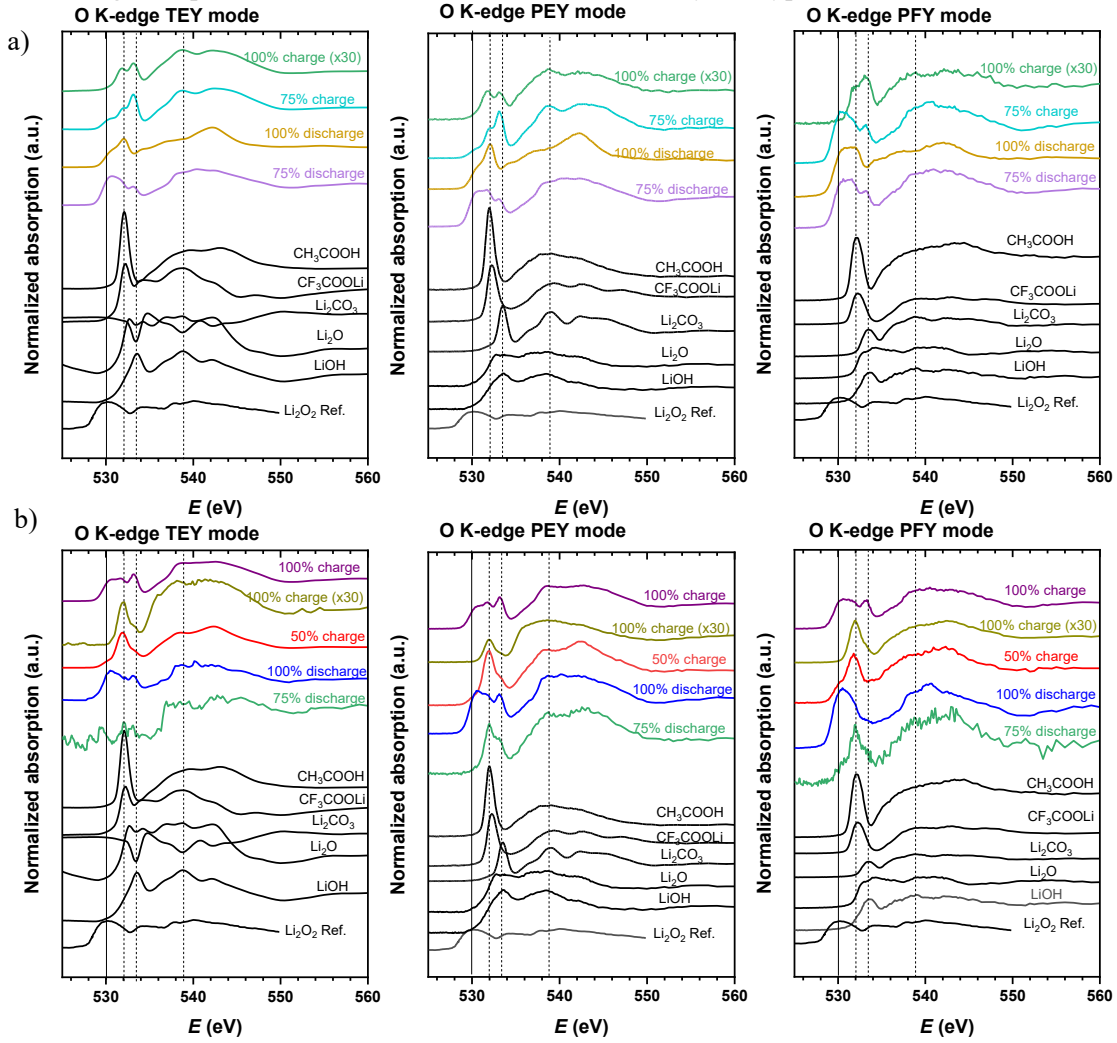

Figure 1. Spectra of O K-edge XANES in a) DMA and b) DETFA-50 electrolytes and reference samples

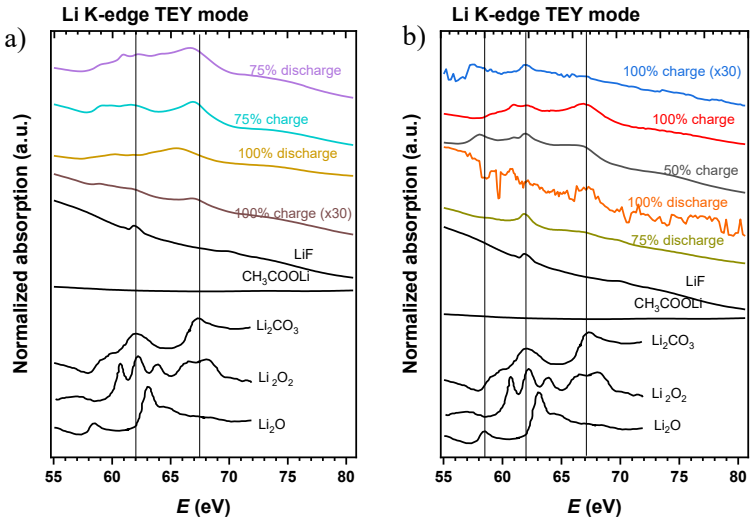

Figure 2. Spectra of Li K-edge XANES in a) DMA and b) DETFA-50 electrolytes and reference samples [3]

In the DETFA-50 electrolyte, samples at 50% charge and 75% discharge were dominated by lithium carboxylates, with no Li_2O_2 peak. These results revealed that Li_2O_2 underwent electrochemical

decomposition. By contrast, Li_2O_2 peaks were observed at 100% discharge using all TEY, PEY, and PEY modes.

The samples fully charged up to 30 cycles were primarily byproducts in both the DMA and DETFA-50 electrolytes. In particular, the LiF peak at 62 eV appeared at 50% charge, 75% discharge, and 100% charge (30 cycles) in the DETFA-50 electrolyte, as shown in **Fig. 2b**. These results indicate that the DETFA-50 electrolyte decomposed during the charge/discharge process.

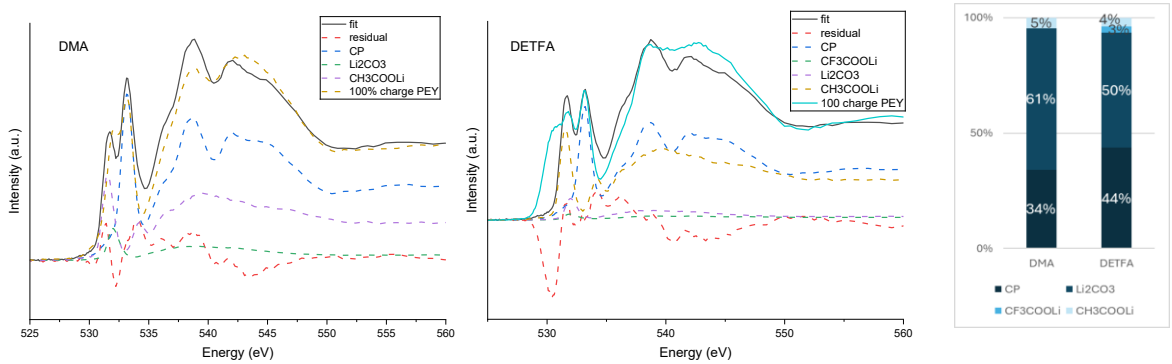

Figure 3. Linear combination fitting for 100% charge samples in DMA and DETFA-50

The concentrations of byproducts were determined by using linear combination fitting, as shown in **Fig. 3**. The spectra of CF_3COOLi, CH_3COOLi, Li_2CO_3, and pristine CP were used as references. Li_2CO_3 was the primary byproduct, accounting for 61% in the DMA electrolyte and 50% in the DETFA-50 electrolyte, while CF_3COOLi and CH_3COOLi accounted for less than 7% in these samples. These results revealed that byproducts, as an insulating layer, remained on the CP surface even in the fully charged process.

References

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