S24018

超軟 X 線 XAFS によるリチウム空気電池の放電生成物の構造解析

Local structure analysis of discharge products in lithium air battery by ultra soft X-ray absorption fine structure

Do Duy Khiem,[a] Keisuke Mukai[a]

[a] National Institute for Fusion Science, National Institute for Fusion Science, 322-6 Oroshi-cho, Toki, Gifu 509-5292, Japan

e-mail: mukai.keisuke@nifs.ac.jp

Abstract

Discharged products in lithium air batteries working under different electrolytes were examined to estimate their performance and elucidate the reaction mechanism. X-ray absorption fine structure (XAFS) of the fully discharged samples on the carbon cathode were investigated at SR center BL-11 at Ristumeikan University. As a result, the formation of Li_2O_2 and byproducts was observed. In addition, working under DETFA electrolytes showed a higher intensity of the Li_2O_2 peaks, while G4 and DMA electrolytes indicated weak peaks and different spectra shapes. The structures of discharge products in various electrolytes will be further investigated to understand the reaction mechanisms and to control formations of decomposable discharge products.

Keywords: Lithium, Li K-XANES, O K-XANES, byproduct

Background

In the field of clean energy, particularly in renewable energy sources, Li-O_2 air-battery is a promising alternative energy storage that surpasses the Li-ion battery in terms of energy density. One of the technical challenges, the formation of non-reversible discharge products and electrolyte degradation mitigated the reverse charging, leading to poor cycle stability. To understand the reaction mechanism, the chemical phases of Li-related products formed during operation in different electrolytes must be clarified. In this study, we have employed XAFS to evaluate the Li compounds after discharging in various electrolytes.

Experiment

Li foil (25 mm diameter, 100 or 400 μm thick, Honjo Metal) was used as a negative electrode, while carbon paper (CP, 20 mm diameter, TGP-H-060, Toray) was used as a positive electrode. The CP was prepared by immersing pristine CP in hot acid (H_2SO_3:HNO_3 = 3:1) for 2 h. A glass-fiber filter (GF/A, 22 mm diameter, Whatman) was used as the separator after it was dried under a vacuum at 110 °C overnight. Dehydrated DMA (Wako) was used as the solvent for the electrolyte. $LiNO_3$ (Kishida, Japan) was used as the salt. The electrolytes were prepared by stirring the salt and solvent overnight. Discharge products were formed on the CP in three different electrolytes; namely tetraglyme (G4, Japan Advanced Chemicals), *N*,*N*-dimethylacetamide (DMA), and 50 vol % *N*,*N*-diethyl-2,2,2- trifluoroacetamide (DETFA) + 50 vol % DMA (50:50). The electrochemical cell employed in this study is previously described elsewhere [1]. Also, spectra of Li_2O, Li_2CO_3, and LiOH powders on Cd plates were obtained as references. The XAFS spectrum of Li_2O_2 peak is taken from the previous measurement at SR center [2].

Results and Discussion：

Figures 1 and 2 show the XANES spectra of O and Li K-edge in different electrolytes and references. XANES O K-edge spectra acquired peaks at approximately 530 eV for all samples, corresponding to the σ*(O-O) absorption peak of Li_2O_2. However, these were convoluted peaks attributed to the formation of byproducts (Li-carboxylates) [2]. The convolution caused a broadened peak, as observed at 530-532 eV.

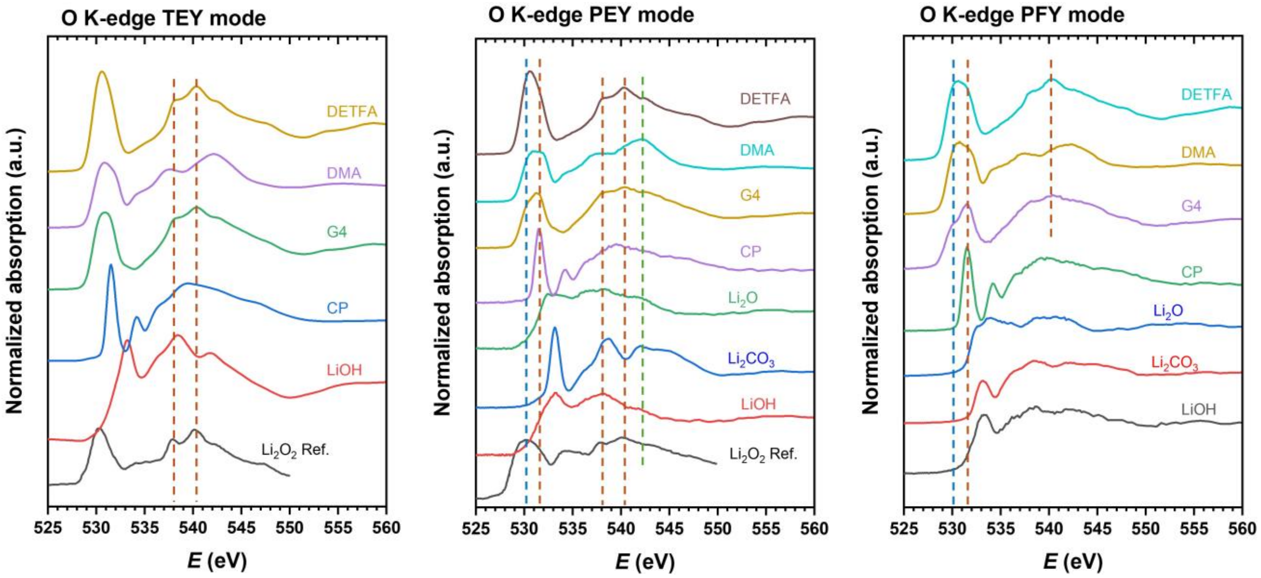

Fig. 1. Spectra of O K-edge XANES in different electrolytes and reference samples

Although the σ^*(O-O) peak of Li_2O_2 at ~538 eV was observed in the DMA sample, the additional peak at ~540 eV remained unclear. In addition, the spectral shape above 530 eV differed significantly from those of the DETFA and G4 samples. The appearance of peaks at ~542 eV could be attributed to Li_2CO_3 based on comparison with the reference spectra. However, the conclusion was ambiguous due to uncertainties related to sample condition or intrinsic product. Therefore, a reacquisition of the data is planned to clarify the peaks spectra. In the G4 sample, the absorption peak of Li_2O_2 was predominant at ~530 eV, whereas the other peaks were weak under both PEF and PFY modes. Consequently, the DEFTA samples exhibited a significantly higher intensity of the Li_2O_2 peaks. For the O K-edge under TEF mode, spectra of Li_2O and Li_2CO_3 were affected by surface charging effects, leading to improper measurement.

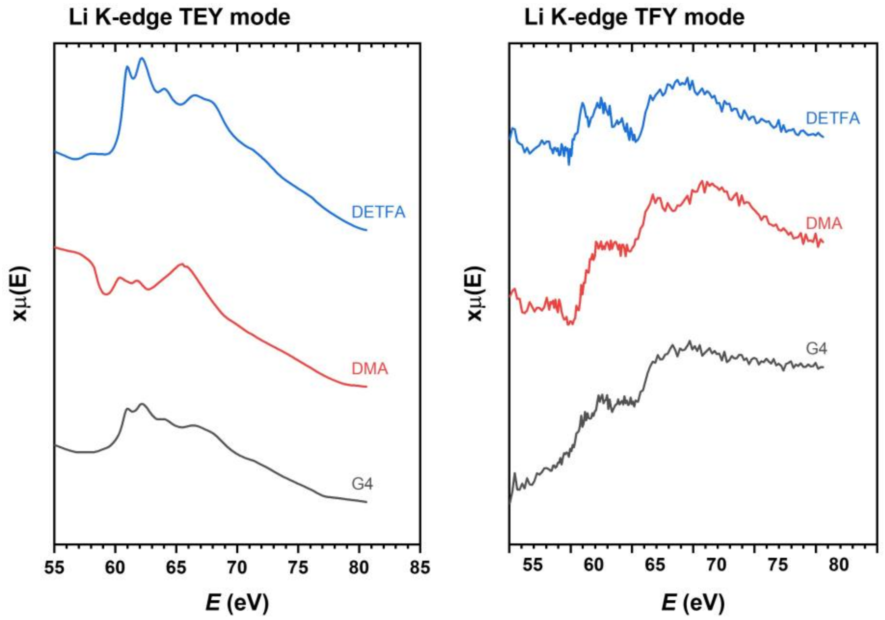

Fig. 2. Spectra of Li K-edges XANES in different electrolytes and reference samples

As shown in Fig. 2, despite measuring the reference samples, the absorption spectrum of Li K-edge has a weak intensity. In addition, the background was complex, leading to data acquisition being unsuitable for analysis. Therefore, the normalized data has not been exhibited in this report. Theoretical calculations as well as additional XAFS measurements will be performed in our future study to understand the structure of the discharge products formed in the electrolytes.

References

[1] Morimoto, K.; Kusumoto, T.; Nishioka, K.; Kamiya, K.; Mukouyama, Y.; Nakanishi, S. Dynamic Changes in Charge Transfer Resistances during Cycling of Aprotic Li−O2 Batteries. ACS Appl. Mater. Interfaces 2020, 12 (38), 42803−42810.

[2] C. Yang, H. R. Byon, K. Yamanaka, Toshiaki Ohta, RS1503, Synchrotron Radiation (SR) Center, Ritsumeikan University.