S25002

リチウム空気電池の放電生成物の構造解析と副生成物の定量分析

Structure analysis and byproduct quantification of discharge products in Li−O_2 battery

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Abstract

Discharged products in lithium air batteries at different (dis)charging states were examined to elucidate their forming/decomposing reaction mechanism. X-ray absorption fine structure (XAFS) spectra of partially/fully (dis)charged samples on the carbon paper cathode were obtained at SR center BL-11 at Ristumeikan University. XAFS spectra showed that Li_2O_2 are electrochemically formed with byproducts of $LiRCO_2$ and Li_2CO_3 during discharging. PEY and PFY spectra showed that these byproducts formed not only near-surface but also inside of the discharge product toroid. By LCA analysis on the PEY spectra from the carbon paper cathode after fully-charged in fluorinated amide electrolyte (DETFA-50), less byproducts remained on the cathode surface in consistent our SEM/EDX observation. This result suggests that decomposition of the discharged products including insulating byproducts are affected by additives in amide electrolytes.

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

Background

Li-O_2 battery is a promising next-generation energy storage systems because of its high theoretical energy density. Its application is hindered by low cycle performances, which possibly originates from formation of less-decomposable discharge products, including insulating carbonate byproducts. 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 identify and quantify phases formed during (dis)charging.

Experiment

Cathode samples were prepared in the electrochemical cell. Li foil (25 mm diameter and 400 μm thickness). 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; *N*,*N*-dimethylacetamide (DMA) and DETFA-50 (50 vol.% *N*,*N*-diethyl-2,2,2- trifluoroacetamide (DETFA) + 50 vol.% DMA). The electrochemical cell employed in this study is previously described elsewhere [1].

Results and Discussion：

Figures 1 shows the XAFS spectra of O in DMA and DETFA. XAFS 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. In addition to Li_2O_2, $LiRCO_2$ and Li_2CO_3 peaks were observed at ~532 and ~533 eV as byproducts. These phases are consistent with our previous analysis using Fourier transform infrared spectrometer (FT-IR).

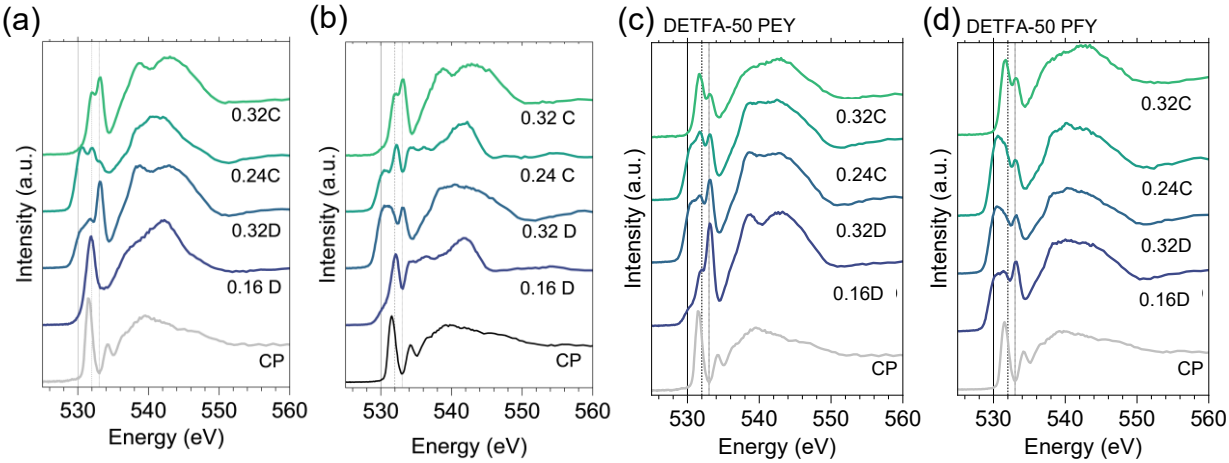

Fig. 1. Spectra of O K-edge XAFS at different (dis)charging states in (a) DMA by PEY, (b) DMA by PFY, (c) DETFA-50 PEY, and (d) DETFA-50 by PFY. The samples were (dis)charged to 0.16, 0.24, and 0.32 mAh cm^{-2} at a constant current of 0.1 mA cm^{-2}. D and C denote discharge and charge.

Fig. 2 shows the results of linear combination analysis (LCA) for the CP samples discharged to 0.32 mAh cm^{-2} and subsequently charged to 0.32 mAh cm^{-2} at a constant current of 0.1 mA cm^{-2}. The LCA was performed using reference spectra from CP and standard powders of Li_2CO_3, CH_3COOLi, and CF_3COOLi. The fittings for the DMA and DETFA-50 samples resulted in R-factors of 0.0216 and 0.0218, respectively. In the CP sample fully charged in DMA, the spectrum was composed mainly by the byproducts, where the byproduct proportions of ~90% in DMA. On the contrary, the remaining byproducts in the CP sample fully-charged in DETFA-50 was ~50%. This indicates that the insulating byproducts remained on the CP surface even after the full charging, while Li_2O_2 were electrochemically decomposed. Notably, the remaining byproducts were less in DETFA-50 electrolyte. These results are fully consistent with our SEM/EDS and FT-IR results, in which sub-micron byproduct particles remained on the CP after being fully charged in DMA. These results may imply facilitated decomposability of discharge products in DETFA-50. Effect of fluorinated electrolytes on decomposability and possible link to structures of discharge products will be further investigated in our future study.

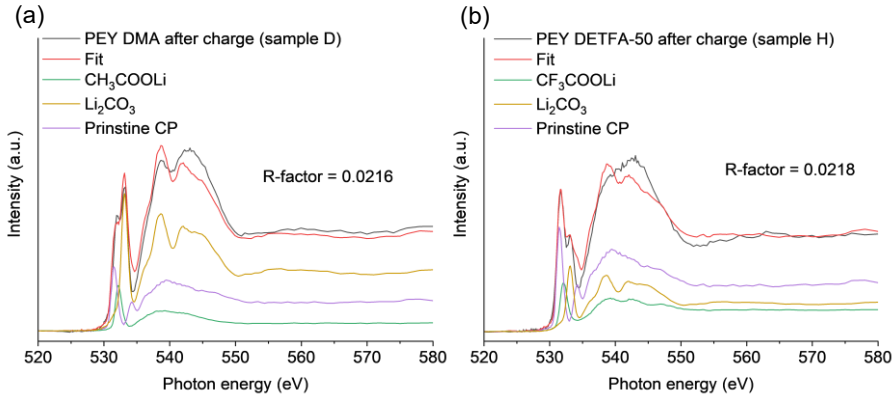

Fig. 2. Fittings by LCA on the PEY spectra from cathode samples fully-charged in (a) DMA and (b) DETFA-50.

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.