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Further investigation of discharging product structure in Li-O_2 battery

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XANES measurements were employed to characterise the discharge product for a Li-O_2 battery employing a chemically-modified carbon nanotube electrode. From those spectra, the main discharge product (lithium fluoride) could be identified, along with side products formed during cycling, and lithium fluoride, as an important byproduct. The role of a perfluorinated chain on the electrode was elucidated, and a potential stability issue identified.

Keywords: Li-O_2 battery, XANES, lithium peroxide, lithium fluoride, fluorinated

背景と研究目的 (Introduction) :

The reversible electrochemical reaction of lithium and oxygen hold great promise for implementation in electric vehicles. The non-aqueous system provides the greatest promise in terms of theoretical energy density.[1,2] Although first reported in 1996,[3] the development of this battery technology has been hindered by a number of key challenges.

In our earlier investigations, we observed the typical discharge product (lithium peroxide) when using a fluorinated component covalently attached to the carbon cathode material (in this case, carbon nanotubes).[4] Further study of this system is necessary to determine the role of fluorine, and here we report an XAS investigation.

実験 (Experimental) :

i) Synthesis and cell fabrication

Electrodes comprised of multi-walled carbon nanotubes (MWCNTs), with sidewalls modified with a perfluorinated chain, were synthesized and characterized as previously described.[4]

ii) Electrochemical evaluation

Galvanostatic discharge/charge was performed using a battery cycler (WBCS3000, WonATech, Korea). The applied current (mA.g^{-1}) was calculated based on the total cathode mass (including covalently bonded perfluorinated chains).

iii) Characterisation

XANES spectra were collected at BL2 of The SR Center, Ritsumeikan University, for Li, F, C and O K-edge.

結果、および、考察 (Results and Discussion) :

We undertook additional analysis to identify the principle chemical species present during cycling.

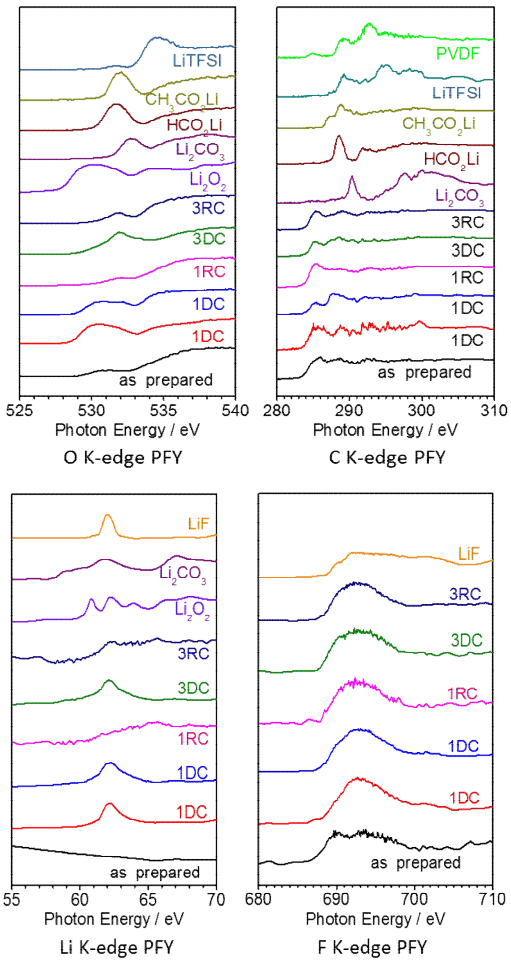

Fig. 1. XANES spectra from modified electrodes (current density 14 mA.g^{-1}) and standards for comparison.

As evident in the O K-edge spectra shown in Fig

1. (top left), the principle product after the first discharge (1DC) is lithium peroxide. However, after the third discharge (3DC), and subsequently the third recharge (3RC), the presence of side products such as lithium acetate (CH_3CO_2Li) and lithium formate (HCO_2Li) is noted. These products are further observed in the C K-edge spectra (Fig 1. top right).
Moreover, the Li K-edge and F K-edge spectra identify the presence of lithium fluoride (LiF) in the electrodes. It is clear that this is a side product formed initially during the first discharge, and is present thereafter.

In summary, we have demonstrated the use of a perfluorinated modification on a carbon cathode in the Li-O_2 battery. The stability of the C-F bond is questionable, as evident from our XANES measurements, which has important implications for other work being carried out with Li-O_2 batteries, where perfluorinated binders are often employed.
Moreover, with the aid of the XANES analysis, we have been able to determine the chemical nature of the discharge products, a key finding that will allow us to propose a mechanism for the enhanced performance when these modified electrodes are employed.

文　献 (References)

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論文・学会等発表（予定）(Articles and meetings)

Articles

[1]M.L. Thomas and H.R Byon, *Role of fluorine as a surface modifier in the non-aqueous lithium-oxygen battery*, in preparation.

Meetings

[1] M.L. Thomas, K. Yamanaka, T. Ohta, and H. R. Byon, "*Role of Grafted Perfluorinated Moieties on Porous Carbon Cathode for the Li-O_2 Battery*", Electrochemical Conference on Energy & the Enviroment (Shanghai, China), 13-16 March 2014. (Oral Presentation)