

## Investigation of discharging product structure in Li-O<sub>2</sub> battery

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The introduction of perfluorinated moieties as a covalently-bonded component of a multiwalled carbon nanotube electrode has been shown to improve performance in the Li-O<sub>2</sub> battery. XANES measurements were employed to determine the chemical speciation of the thin layer of discharge products formed on this structured electrode.

**Keywords:** Li-O<sub>2</sub> battery, XANES, lithium peroxide, fluorinated

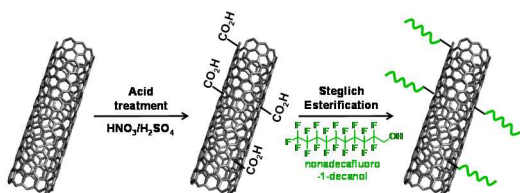
### 背景と研究目的 (Introduction) :

The non-aqueous lithium-oxygen (Li-O<sub>2</sub>) secondary battery is of great interest due to a high theoretical specific energy, suitable for possible application in electric vehicles. However, the great promise of this battery system has as yet not been realized due to several key challenges (high polarization, poor rate capability and passivation of the cathode) that are currently the focus of intensive research.<sup>1,2</sup> Earlier reports have indicated that fluorinated moieties, as a component of the aprotic medium or cathode, may improve capacity, and enhance rate capability.<sup>3,4</sup> In this study, we synthesized a fluorine-containing cathode, and employed XANES as the primary analytical tool for identification of chemical speciation in the discharge products.

### 実験 (Experimental) :

#### i) Synthesis and cell fabrication

Multi-walled carbon nanotube (MWCNT) sidewalls were modified as shown in Fig. 1. The modified MWCNTs (with a grafted fluorinated chain) were then assembled as a binder-free porous carbon cathode (1.8 – 2.0 mg) by vacuum filtration. The cathodes was rigorously dried under vacuum, and assembled with a metallic lithium anode, glass fiber separator and tetraethylene glycol dimethyl ether (tetraglyme) with 0.5 M LiTFSI (LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>) electrolyte in an Ar filled glovebox to form the Li-O<sub>2</sub> cell.



**Fig. 1.** Synthesis of F-grafted MWCNTs by two-step procedure

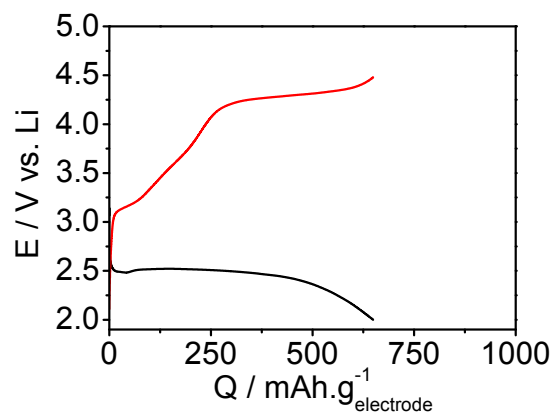
#### ii) Electrochemical evaluation

Galvanostatic discharge/charge was performed using a battery cycler (WBCS3000, WonATech, Korea). The applied current (mA.g<sup>-1</sup>) and calculated capacity (mAh.g<sup>-1</sup>) were calculated based on the total cathode mass (including covalently bonded perfluorinated chains).

#### iii) Characterisation

XANES data 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) :



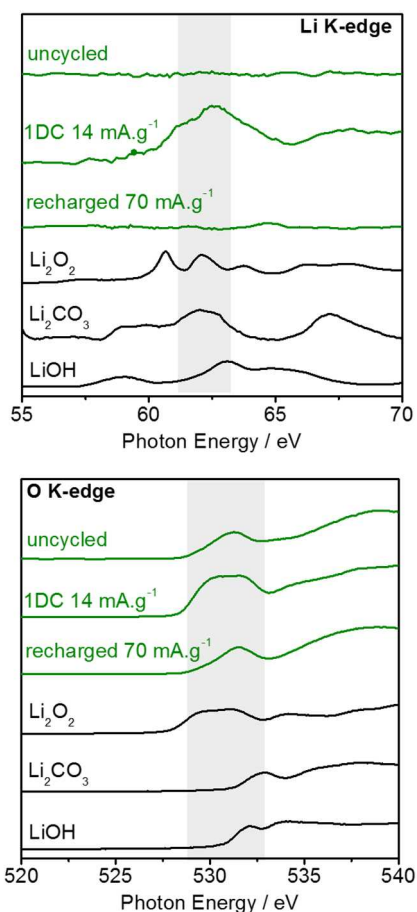
**Fig. 2.** Galvanostatic discharge and charge performance of the modified electrode at 70 mA.g<sup>-1</sup>. The MWCNT films grafted with fluorinated chains were used for the cathodes and were subjected to galvanostatic cycling. Fig. 2 shows the first discharge and subsequent recharge for the cell in an oxygen environment. Due to the relatively thin layer of discharge products formed during the cell discharge, analyses by conventional methods (i.e. X-ray diffraction and FTIR) were not successful. Consequently, XANES was employed to fully characterise the solid discharge products, as shown in Fig. 3. From these measurements, it could be determined that lithium peroxide (Li<sub>2</sub>O<sub>2</sub>), the expected electrochemical product, was indeed

formed during the discharge, and was absent after recharge. The contribution of possible side products, namely lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) and lithium hydroxide ( $\text{LiOH}$ ) was deemed to be negligible. Further work is needed to investigate the cycling performance of the cathodes, and the chemical speciation of the discharge products after further cycling. Furthermore, F K-edge and C K-edge measurements indicated the possibility of instability of the cathode, further work is required to clarify this.

*a surface modifier in the non-aqueous lithium-oxygen battery, in preparation.*

#### **Meetings**

[1] M.L. Thomas and H.R. Byon, "Surface modification of a porous carbon cathode for the lithium-oxygen battery: the role of grafted fluorinated moieties", Battery Symposium in Japan (Osaka, Japan), 7-9 October 2013.



**Fig. 3.** XANES spectra (FY mode) of uncycled, 1<sup>st</sup> discharge (1DC) at 14 mA.g<sup>-1</sup> and recharged (at 70 mA.g<sup>-1</sup>) modified electrodes.

#### **文献 (References)**

- [1] J. Christensen *et al.*, J. Electrochem. Soc., 2012, 159, R1-R30.
- [2] R. Black *et al.*, Adv. Energy Mater., 2012, 2, 801-815.
- [3] C. Tran *et al.*, Carbon, 2011, 49, 1266-1271.
- [4] S. Zhang *et al.*, J. Power Sources, 2011, 196, 3906-3910.

#### **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*