

(Form: No.5)

## Experiment Report for Prefectural Beamline

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### **XPS analysis of Li-O<sub>2</sub> electrochemical reaction product for Li-O<sub>2</sub> battery**

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#### **1 . Summary** (Note: Please include conclusions)

We report Li-O<sub>2</sub> electrochemical reaction products for reduction and oxidation with respect to potential, and for 5-times cycles on nanoporous gold electrode. Synchrotron X-ray photoelectron spectroscopy (XPS) data reveals a main product of Li<sub>2</sub>O<sub>2</sub> during reduction, which is completely decomposed after oxidation while new side products such as Li<sub>2</sub>CO<sub>3</sub> and lithium carboxylates are also produced. After 5 cycles, significant side-products are also observed.

#### **2 . Purpose of experiment and background**

The Li-O<sub>2</sub> battery is received great attention to apply for long-range-driving electric vehicles in the near future owing to its high specific energy density ( $\sim 3 \text{ kWh kg}^{-1}_{\text{cell}}$ ), which is more than 10 times higher than lithium ion battery. The Li-O<sub>2</sub> battery can be operated by O<sub>2</sub> gas reduction and oxidation reactions, which produce insoluble Li<sub>2</sub>O<sub>2</sub> ( $2\text{Li}^+ + \text{O}_2(\text{g}) + 2\text{e}^- \rightarrow \text{Li}_2\text{O}_2(\text{s})$ ) and decomposition of Li<sub>2</sub>O<sub>2</sub> ( $\text{Li}_2\text{O}_2(\text{s}) \rightarrow 2\text{Li}^+ + \text{O}_2(\text{g}) + 2\text{e}^-$ ), respectively. However, this Li-O<sub>2</sub> electrochemical reaction is accompanied by parasitic reactions as aprotic organic electrolyte and carbon electrode react with superoxide radical (O<sub>2</sub><sup>-</sup>) as the reduced form of O<sub>2</sub> gas, which results in side products such as Li<sub>2</sub>CO<sub>3</sub> and lithium carboxylates. Accordingly, one of the significant challenges in the Li-O<sub>2</sub> battery is to suppress the parasitic side reactions by using of superoxide-tolerated electrolyte and carbon-free electrode.

Here we investigate the reduction and oxidation products of Li-O<sub>2</sub> reaction using nanoporous

gold (NPG) electrode and tetraethylene glycol dimethyl ether (tetraglyme) electrolyte using synchrotron XPS at BL12 of SAGA-LS. The combination of carbon-free electrode and electrolyte is expected to produce less side products while acting as a platform to form and decompose the predominant  $\text{Li}_2\text{O}_2$  after reduction and oxidation. In particular, because the products formed on the NPG have very small quantity, light X-ray source of XPS can aid in identifying the chemical information of thin product film.

### 3. Experimental (Note: Description of sample, method of experiment and analysis, etc.)

We prepared following 5 NPG samples via potential-controlled cyclic voltammetry (CV) with a metallic Li as the counter and reference electrodes (table). The clean NPG electrodes were swept in 0.5 M LiTFSI (lithium bis(trifluoromethanesulfonyl)imide) in  $\text{O}_2$ -saturated tetraglyme for oxygen reduction reaction (ORR) at 2.4 V and 2.0 V and for oxygen evolution reaction (OER) at 3.8 V and 4.5 V, separately, at a sweeping rate of  $1 \text{ mV s}^{-1}$ . The NPG electrodes were then washed out using dimethyl carbonate in an Ar-filled glove box and dried in vacuum chamber at  $60 \text{ }^\circ\text{C}$  for 6 h.

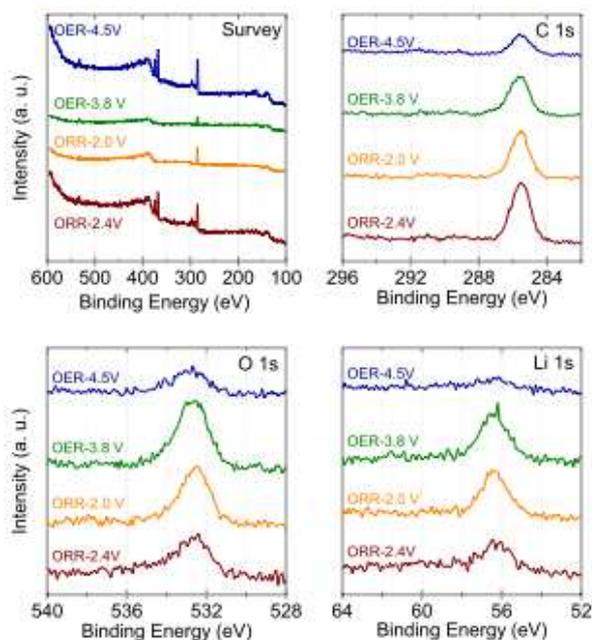
No.	Sample name	Description	Preparation
1	NPG @OCV	Soaking into electrolyte	Potential controlled electrochemical sweep, washing with anhydrous dimethyl carbonate (DMC) in an Ar-filled glove box, followed by drying in vacuum chamber at $60 \text{ }^\circ\text{C}$ for 6 h without air exposure.
2	NPG@2.4V	Shallow reduction	
3	NPG@2.0V	Deep reduction	
4	NPG@3.8V	Shallow oxidation	
5	NPG@4.5V	Deep oxidation	

All samples were transferred to XPS chamber using hermetic Ar-filled transfer vessels to avoid air exposure. The synchrotron XPS measurements were performed using a photon energy of 650 eV and a base pressure of  $10^{-8}$  Pa. Considering the escape depth of the photoelectron, the excitation energy was selected to measure surface sensitive spectra, which allows us to obtain top thinner surface information on the NPG electrodes. The XPS peaks were calibrated by Au  $4f_{5/2}$  and Ag  $3d_{3/2}$  and  $3d_{5/2}$  peaks from the as-prepared NPG. The peak intensity was normalized as referring to the injection current ( $I_0$ ). The pass energy is 117.4 eV for survey and 23.5 eV for Li, O, and C 1s binding energy (BE) region. The scanning numbers are 100 times for Li 1s, 75 times for O 1s and 10 times for C 1s region with a time step for 50 ms.

### 4. Results and Discussions

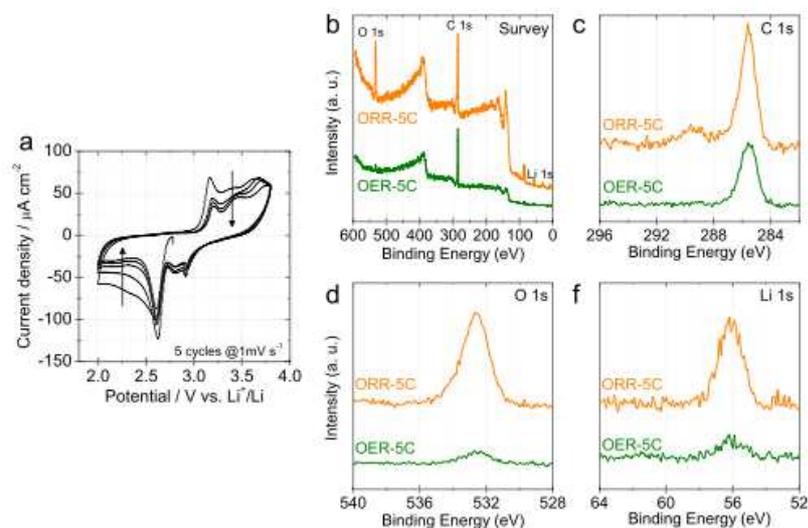
To investigate products during the Li- $\text{O}_2$  electrochemical reaction, four NPG electrodes were prepared at different reduction and oxidation stages: ORR at 2.4 (ORR-2.4V), 2.0 V (ORR-2.0V) and OER at 3.8 V (OER-3.8V), 4.5 V (OER-4.5V). Figure 1 shows synchrotron XPS spectra of survey, C 1s, O 1s, and Li 1s. The survey spectra demonstrate the decreasing Au  $4f_{7/2}$ ,  $4f_{5/2}$  (84, 88 eV) and Ag  $3d_{5/2}$ ,  $3d_{3/2}$  peak intensities (368, 374 eV) upon the ORR, which totally disappear at 2.0 V due to deposition of Li- $\text{O}_2$  reduction product on the NPG. On the contrary, the Au and Ag peaks increase upon the OER as the oxidation (decomposition) occurs. In the C 1s BE region, all NPG electrodes have identical carbon-related peaks (285.5 eV) deconvoluted to  $\text{sp}^3$  hybridized carbon (285.2 eV) and C-O (286.1 eV). These peaks may arise from the tetraglyme residue physically adsorbed. The O and Li 1s spectra reveal the predominant Li- $\text{O}_2$  product of  $\text{Li}_2\text{O}_2$ . The O 1s and Li 1s peak at 532.4 and 56.3 eV, respectively, for the ORR-2.4V and ORR-2.0V correspond to those on the  $\text{Li}_2\text{O}_2$

powder measured under the same condition (proposal no. 1310119R). Along with the  $\text{Li}_2\text{O}_2$ , the small tails over 533.5 eV in asymmetric O 1s peaks on the ORR NPG electrodes demonstrate the presence of  $\text{Li}_2\text{CO}_3$  (proposal no. 1310119R) despite its insignificant quantity. The  $\text{Li}_2\text{O}_2$  is completely decomposed after the oxidation as revealed by negligible Li 1s peak for the OER-4.5V. However, there is still significant carboxylate and carbonate peaks (289.1 and 291.6 eV) in the C 1s BE region and a long tail of  $\text{Li}_2\text{CO}_3$  (over 533.5 eV) in the O 1s BE region. These  $\text{Li}_2\text{CO}_3$  and lithium carboxylates presumably arise from the oxidized tetraglyme over 4 V.



**Figure 1.** XPS spectra of NPG electrodes with different reduction (ORR) and oxidation (OER) stages in survey, C 1s, O 1s, and Li 1s BE regions.

Over 5 time cycles, the side products, i.e.,  $\text{Li}_2\text{CO}_3$  and lithium carboxylates, are more significant. Figure 2 shows CV curves of 5 cycled NPG electrode and the corresponding XPS spectra. The ORR and OER peaks in the CV curves decrease during 5 cycles due to the deposition of products, which cannot be decomposed completely. The XPS spectra of the 5-cycled ORR (ORR-5C) reveal largely increasing C, O, and Li 1s peaks in comparison with those of the 1st-cycled result (Figure 1). In particular, the additional peak at 289 eV in the C 1s BE region and the broad peak in the O 1s BE region demonstrate notable side products in addition to the  $\text{Li}_2\text{O}_2$ . After the OER at 4.5 V (OER-5C), all peak intensities decrease due to decomposition of products at high oxidation potential while the small side products still remain.



**Figure 2.** CV (left panel) and XPS in survey, C 1s, O 1s, and Li 1s BE regions for 5 times-cycled NPG.

## 5. Future issues

None

## 6. References

- (1) R. Wen, M. Hong and H. R. Byon, *J. Am. Chem. Soc.*, **2013**, *135*, 10870–10876.
- (2) D. M. Itkis, D. A. Semenenko, E. Y. Kataev, A. I. Belova, V. S. Neudachina, A. P. Sirotnina, M. Hävecker, D. Teschner, A. Knop-Gericke, P. Dudin, A. Barinov, E. A. Goodilin, Y. Shao-Horn and L. V. Yashina, *Nano Lett.*, **2013**, *13*, 4697–4701.
- (3) S. Kundu, Y. Wang, W. Xia and M. Muhler, *J. Phys. Chem. C*, **2008**, *112*, 16869–16878

## 7. Publications, patents (Note: Typical deliverables related to this proposal.)

**Publication:** Rui Wen and Hye Ryung Byon, “In situ monitoring of the Li-O<sub>2</sub> electrochemical reaction on nanoporous gold using electrochemical AFM”, *Chemical Communications*, **2014**, *50*, 2628-2631.

## 8. Keywords (Note: 2-3 words about samples and experimental methods.)

Li-O<sub>2</sub> battery, nanoporous gold, XPS

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