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## Investigation of Li<sub>2</sub>O<sub>2</sub> Film Growth on Carbon Nanotube Electrodes with CeO<sub>2</sub> Nanoparticles

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Unexpected Li<sub>2</sub>O<sub>2</sub> film growth with thicknesses of ~60 nm is observed on a 3-D carbon nanotube (CNT) electrode incorporated with cerium dioxide (ceria) nanoparticles (CeO<sub>2</sub> NPs) in Li-O<sub>2</sub> battery. CeO<sub>2</sub>/CNT electrodes are collected at different discharge/recharge states from Li-O<sub>2</sub> batteries and investigated by C, Li, and O K-edge XANES. Bulk Li<sub>2</sub>O<sub>2</sub> film is decomposed together with formation/decomposition of side products.

**Keywords:** Li-O<sub>2</sub> battery, XANES, lithium peroxide, Cerium oxide nanoparticles.

### 背景と研究目的 (Introduction) :

The rechargeable Li-O<sub>2</sub> battery has been intensively studied due to its promising potential for providing superior energy density.<sup>1</sup> However, the actual performance with respect to capacity and round-trip efficiency has significantly underperformed at the current stage,<sup>1-3</sup> which is closely associated with the nucleation, growth and decomposition processes of Li<sub>2</sub>O<sub>2</sub>.

It is generally believed that lithium peroxide (Li<sub>2</sub>O<sub>2</sub>) electrochemically forms thin films with thicknesses less than 10 nm resulting in capacity restrictions due to limitations in charge transport. However, we observed unexpected Li<sub>2</sub>O<sub>2</sub> film growth with thicknesses of up to ~60 nm on a 3-D carbon nanotube (CNT) electrode incorporated with cerium dioxide (ceria) nanoparticles (CeO<sub>2</sub> NPs).<sup>4</sup> The CeO<sub>2</sub> NPs favor Li<sub>2</sub>O<sub>2</sub> surface nucleation owing to their strong binding towards reactive oxygen species (e.g., O<sub>2</sub> and LiO<sub>2</sub>). The subsequent film growth results in thicknesses of ~40 nm (a cut-off potential of 2.2 V vs Li/Li<sup>+</sup>), which further increases up to ~60 nm with the addition of trace amounts of H<sub>2</sub>O which enhances the solution free energy. To understand the growth and decomposition mechanisms of Li<sub>2</sub>O<sub>2</sub>, it is necessary to analyze the surface and bulk properties of these film-like Li<sub>2</sub>O<sub>2</sub>. Therefore, CeO<sub>2</sub>/CNT electrodes are collected at different discharge/recharge states from Li-O<sub>2</sub> batteries and investigated by C, Li, and O K-edge XANES.

### 実験 (Experimental) :

#### *i) Synthesis and cell fabrication*

CeO<sub>2</sub> NPs were synthesized by thermal decomposition of cerium nitrate precursor in the presence of protecting agent of oleylamine according to the literature.<sup>5</sup> Around 0.6 mg CeO<sub>2</sub> NPs and CNT (1.8 – 2.0 mg) were well mixed by ultra-sonication in hexane, then made binder-free positive electrode via vacuum filtration. The electrode consisting of 3-D framework of CNTs has many voids (more than 100 nm of size), which is appropriate for O<sub>2</sub> transport in Li-O<sub>2</sub> battery. The positive electrode was annealed at 350 °C in Ar gas and rigorously dried under vacuum, which was then assembled with metallic lithium as the negative electrode, glass fiber separator and tetraethylene glycol dimethyl ether (tetraglyme) with 0.5 M LiClO<sub>4</sub> electrolyte in an Ar-filled glovebox. The complete cell was filled with O<sub>2</sub> gas at atmosphere.

#### *ii) Electrochemical evaluation*

Galvanostatic discharge/charge was performed using a battery cycler (WBCS3000, WonATech, Korea) at 25 °C. The applied current (mA/g) is based on the CNT mass. All potentials were referred to Li<sup>+</sup>/Li.

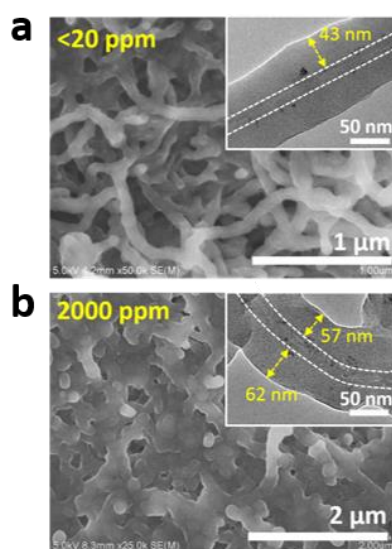
#### *iii) Characterization*

XANES experiments were performed at the SR center in Ritsumeikan University. C, O and Li K-edge XANES spectra were obtained at BL-02 and BL-11, where all electrode samples and references were loaded in a glove box and directly transferred into the measurement

chamber using a custom-made hermetically sealed vessel.

### 結果、および、考察 (Results and Discussion) :

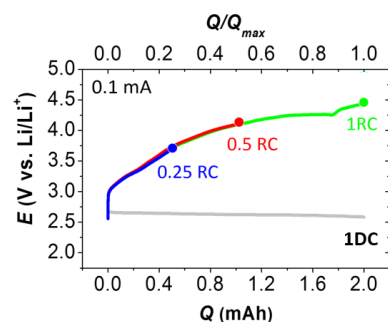
In Li-O<sub>2</sub> battery, the nucleation and growth of Li<sub>2</sub>O<sub>2</sub> occurs during discharge (DC) through oxygen reduction reaction (ORR, O<sub>2</sub>\* + e<sup>-</sup> + Li<sup>+</sup> → LiO<sub>2</sub>\*, the asterisk mark (\*) denotes adsorption on the surface) and a second step via either electrochemical reduction process (LiO<sub>2</sub>\* + e<sup>-</sup> + Li<sup>+</sup> → Li<sub>2</sub>O<sub>2</sub>(s)) or disproportionation (2LiO<sub>2</sub>(sol) → Li<sub>2</sub>O<sub>2</sub>(s) + O<sub>2</sub>).<sup>2,3</sup> The diffusion of superoxide species (LiO<sub>2</sub>\*) on electrode surface leads to the predominant surface nucleation and Li<sub>2</sub>O<sub>2</sub> film growth (indicated as surface-mediated growth). Morphology of the fully discharged Li<sub>2</sub>O<sub>2</sub> product formed on CeO<sub>2</sub>/CNT electrode is characterized by SEM and TEM (Figure 1). A thick film-like Li<sub>2</sub>O<sub>2</sub> (thickness ~ 40 nm) is observed on CeO<sub>2</sub>/CNT electrode when using the dry electrolyte (0.5 M LiClO<sub>4</sub> in tetraglyme, with H<sub>2</sub>O content < 20 ppm). With the presence of 2000 ppm of H<sub>2</sub>O in the electrolyte, the film thickness increased to ~60 nm. Results demonstrate the contribution of increased LiO<sub>2</sub>(sol).



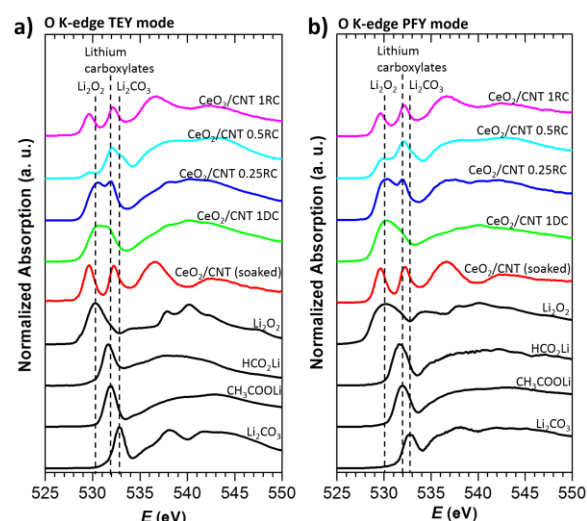
**Figure 1.** SEM and TEM (inset) images of CeO<sub>2</sub>/CNT electrode surfaces after full discharge (DC) with (a) dry tetraglyme and (b) 2000 ppm of H<sub>2</sub>O. The white dashed line in TEM image is a guide to indicate the CNT surface.

Galvanostatic discharge/charge profiles with a limited discharge capacity of 2 mAh is shown in Figure 2. The discharge of CeO<sub>2</sub>/CNT electrode in Li-O<sub>2</sub> cell shows a stable potential plateaus at ~2.63 V (vs. Li/Li<sup>+</sup>), whereas recharge of Li<sub>2</sub>O<sub>2</sub> thick films required a high overpotential (over

4.0V). CeO<sub>2</sub>/CNT electrodes at 1DC (100% discharge, 2.0 mAh), 0.25RC (25% recharge) 0.5RC and 1RC are collected from Li-O<sub>2</sub> cells and characterized by O K-edge.



**Figure 2.** Galvanostatic discharge (DC)/recharge (RC) curves at a current density of 0.1 mA with a limited DC capacity of 2.0 mAh using CeO<sub>2</sub>/CNT electrode as cathode in Li-O<sub>2</sub> battery. The water content in the electrolyte is < 20 ppm.



**Figure 3.** O K-edge XANES spectra of soaked (as prepared and soaked in the tetraglyme electrolyte), 1DC (Q = 2.0 mAh), 0.25RC, 0.5RC and 1RC CeO<sub>2</sub>/CNT electrodes with (a) surface-sensitive total electron yield (TEY) mode and (b) bulk-sensitive partial fluorescence yield (PFY) mode. The reference spectra are Li<sub>2</sub>O<sub>2</sub>, HCO<sub>2</sub>Li, CH<sub>3</sub>COOLi and Li<sub>2</sub>CO<sub>3</sub>. The galvanostatic conditions are shown in Figure 2.

O K-edge XANES spectra of as-prepared CeO<sub>2</sub>/CNT electrode exhibits three main peaks related to O2p-Ce4f (529.5 eV), O2p-Ce5d-e<sub>g</sub> (532.2 eV) and O2p-Ce5d-t<sub>2g</sub> (536.6 eV) hybridization in CeO<sub>2</sub> NPs (Figure 3).<sup>6</sup> After 1DC, σ\* (O-O) absorption peak of Li<sub>2</sub>O<sub>2</sub> is predominant at ~530 eV,<sup>7,8</sup> which is partially diminished at 0.25RC and 0.5RC suggesting Li<sub>2</sub>O<sub>2</sub> decomposition, as demonstrated by appearance of CeO<sub>2</sub>-related peaks such as the O2p-Ce5d-e<sub>g</sub> and O2p-Ce4f, and completely

disappear after 1RC. Along with the primary product of  $\text{Li}_2\text{O}_2$ , side products are also observed. The IDC spectrum with the TEY mode reveals a shoulder corresponding to lithium carboxylates ( $\text{HCO}_2\text{Li}$  and  $\text{CH}_3\text{COOLi}$ ) at 531.7-532 eV. After 0.25RC, an absorption peak at ~532 eV is significant, which is attributed to both lithium carboxylates and  $\text{CeO}_2$  ( $\text{O}2p\text{-Ce}5d\text{-}e_g$ ). After 0.5RC, lithium carboxylates are more pronounced than the  $\text{Li}_2\text{O}_2$  being decomposed. Besides, there is an additional small shoulder related to  $\pi^*$  ( $\text{C}=\text{O}$ ) absorption of lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) appears at 532.8 eV<sup>8</sup> with the TEY mode. These side products result from degradation of electrolyte solution and CNT.<sup>9,10</sup> After 1RC, the side product peaks disappear almost completely and the three main peaks from  $\text{CeO}_2$  are visible.

In summary, we investigated the electrochemical performance of  $\text{Li-O}_2$  cells with  $\text{CeO}_2$  NPs decorated on the CNT. An unexpected film product is observed on the discharged electrode, with thickness of ~ 40 nm, and increased to ~ 60 nm when enhancing the solvation of  $\text{LiO}_2$  by addition of  $\text{H}_2\text{O}$  in the electrolyte. Through the analysis of O K-edge XANES spectra, the discharge product is mainly  $\text{Li}_2\text{O}_2$ , with trace amount of carbonaceous side product on the surface. The recharge process is accompanied with further formation and decomposition of side products, which are mainly lithium carbonate and lithium carboxylates.

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### 論文・学会等発表（予定）(Articles and meetings)

#### Articles

- [1] Yang, C.; Wong, R. A.; Hong, M.; Yamanaka,

K.; Ohta, T.; Byon, H. R. *Nano Lett* **2016**, *16*, 2969.

#### Meetings

[1] Chunzhen Yang, and Hye Ryung Byon, *Structural effect of nano ceria incorporated to carbon nanotube for the formation of non-crystalline  $\text{Li}_2\text{O}_2$  in  $\text{Li-O}_2$  batteries*, 55th Battery Symposium Japan 2014, Electrochemical Society of Japan, Kyoto, Japan

[2] Chunzhen Yang, and Hye Ryung Byon,  *$\text{CeO}_2$  Nanoparticle-Guided Formation and Decomposition of Amorphous  $\text{Li}_2\text{O}_2$  on Carbon Nanotube Cathode in a  $\text{Li-O}_2$  Cell*, 227th ECS Meeting 2015, Electrochemical Society, Chicago, USA