R1414 and R1417

Investigation of discharging products (Li_2O_2) stemming from side reaction in Li-O_2 battery using various nanocatalysts

CeO_2 Nanoparticle-Guided Formation and Decomposition of Amorphous Li_2O_2 on Carbon Nanotube Cathode in a Li-O_2 Cell

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Nanosized cerium oxide (CeO_2) particles incorporated carbon nanotube (CNT) is employed as a binder-free cathode for Li-O_2 batteries. Unique film-like morphology of Li_2O_2 is formed on the discharged electrode with poorer crystallinity and crystal size comparing to typical toroidal-shaped Li_2O_2. O and Li K-edge XANES spectra are conducted to identify the chemical species present on the discharged and recharged electrodes.

Keywords: Li-O_2 battery, XANES, Lithium peroxide, Cerium oxide (ceria) nanoparticles.

背景と研究目的 (Introduction)：

Rechargeable non-aqueous lithium-oxygen (Li-O_2) batteries have been the focus of recent research due to their high theoretical energy density which is about one order of magnitude higher than those commercial Li-ion batteries.[1,2] However, the Li-O_2 battery is still under its infancy stage, as various fundamental issues need to be addressed before their practical application, including poor cycle life, low round trip efficiency, and poor rate capability.

The structure and morphology of Li_2O_2 in a Li-O_2 cell have been widely explored by their correlation to recharge potential. The bulk size and poor conductivity of Li_2O_2 toroids incur sluggish decomposition during recharge, resulting in a rapid potential rise to more than 4.2 V vs. Li/Li^+ concomitant with severe side reactions. In this study, we introduce nanoceria (CeO_2) as structural promoter onto carbon nanotube cathode (i.e. positive electrode) to alternate the structure, morphology and crystalline size of discharge product of Li_2O_2. It is known that nanosized CeO_2 nanoparticle (NP, ~5 nm) has strong affinity towards the reactive oxygen species (ROS, such as O_2, O_2^- and O_2^{2-}), which can affect the nucleation behaviors of Li_2O_2, thus the morphology. As a result, unique Li_2O_2 film is observed on discharged cathode, which has much poorer crystallinity and smaller size than typical toroidal-shaped Li_2O_2. To identify the chemical species formed during discharge and recharge in Li-O_2 cells, O and Li K-edge X-ray absorption near-edge structure (XANES) spectrum are conducted.

実験 (Experimental)：

i) Synthesis and cell fabrication

CeO_2 NPs were synthesized by thermal decomposition of cerium nitrate precursor in the presence of protecting agent of oleylamine according to the literature.[3] Subsequently, ~0.6 mg CeO_2 NPs (with an average particle size of ~5.3 nm) and CNT (1.8 – 2.0 mg) were well mixed by ultrasonication in hexane, then assembled as a binder-free porous carbon cathode by vacuum filtration. The cathode 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 $LiClO_4$ electrolyte in an Ar-filled glovebox to fabricate Li-O_2 cell.

ii) Electrochemical evaluation

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

iii) Characterisation

O and Li K-edge XANES data were collected at BL2 and BL11 lines of The SR Center, Ritsumeikan University.

<u>結果、および、考察 **(Results and Discussion)**</u> :

From the SEM image in Figure 1a, it is shown that nanosized CeO_2 particles are homogeneously distributed on CNT network (CeO_2/CNT). After the 1st discharge (1DC), unique film-like DC product is observed on the electrode more than typical toroidal-shaped Li_2O_2 (Figure 1b). This product disappears in following recharge (RC).

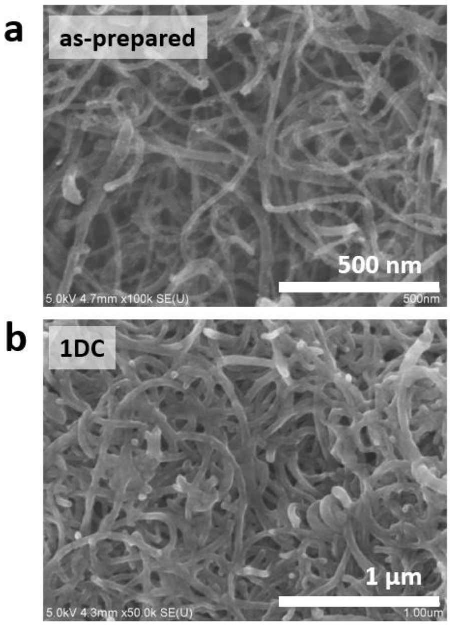

Fig. 1. SEM images of 25% CeO_2/CNT electrodes: (a) as-prepared and (b) after 1st discharge (1DC).

The 1st DC and RC potential profiles of CeO_2/CNT electrode is compared to (CeO_2-free) CNT in Figure 2, at a current density of 50 mAg^{-1} in 0.5 M $LiClO_4$/tetraglyme. Both electrodes demonstrate comparable discharge voltages at 2.63 V, whereas difference in RC potential appears. The RC potential at ~25% RC process is 3.59 V for CeO_2/CNT and 3.85 V for CNT, which demonstrates higher oxygen evolution reaction efficiency in the presence of CeO_2 NP.

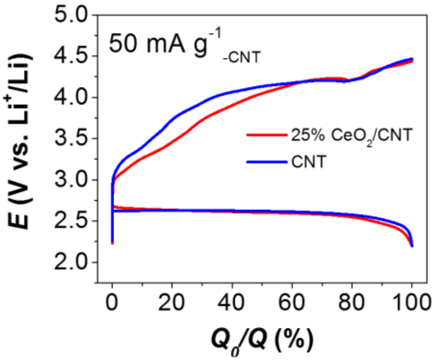

Fig. 2. The normalized potential profiles of Li-O_2 cell employing CeO_2/CNT and CNT at a current density of 50 mA $g^{-1}_{\text{-CNT}}$ in 0.5 M $LiClO_4$/tetraglyme electrolyte. The cut-off discharge voltage is 2.2 V.

To investigate chemical identification of DC and RC products on CeO_2/CNT electrode, O K-edge and Li K-edge XANES spectra are conducted. Figure 3 and 4 display the normalized O and Li K-edge XANES spectra of CeO_2/CNT in bulk sensitive partial or total fluorescence yield (PFY or TFY mode) and surface-sensitive total electron yield (TEY mode).

In Figure 3, the O K-edge spectra of as-prepared CeO_2/CNT shows three main peaks at 529.5, 532.2 and 536.6 eV, which are related to O2*p*-Ce4*f*, O2*p*-Ce5*d*-e_g and O2*p*-Ce5*d*-t_{2g} hybridization in CeO_2, respectively. An absorption peak at ~530 eV appeared after 1DC (i.e., full discharge), suggesting that the Li_2O_2 is the predominant DC product. The Li_2O_2 partially disappears at 0.5RC (~50% RC) and completely eliminated at the end of 1RC (full recharge). A small shoulder at 531.7 eV is also noticed on the TEY spectra of 1DC electrode, which corresponds to lithium carboxylates. After 0.5RC, lithium carbonate-associated absorption peak appears at 532.8 eV. These side products are apparent in the TEY mode, indicating that the degradation of electrolyte and CNT may occur on the topmost surface of electrode. After 1RC, all lithium carboxylates and lithium carbonate peaks cannot be observed, indicating full decomposition of side products. Accordingly, the CeO_2 is visible whereas the absorption peaks of O2*p*-Ce4*f* and O2*p*-Ce5*d*-e_g are largely decreased relative to that of O2*p*-Ce5*d*-t_{2g} when comparing to as-prepared electrode.

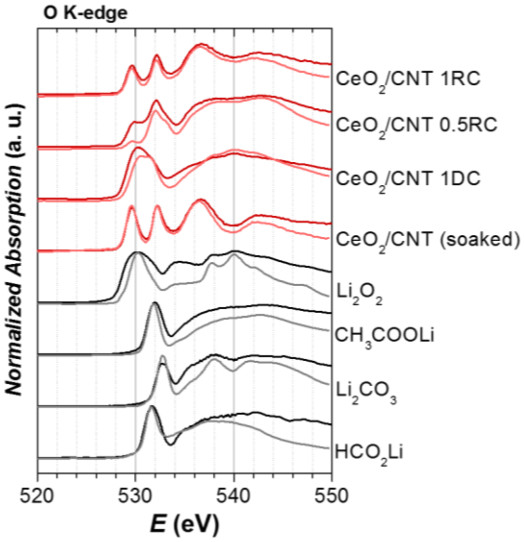

Fig. 3. The O K-edge XANES spectra of CeO_2/CNT electrodes at different DC and RC. 1DC, 0.5 RC and 1RC is the 1st full discharge, 50% recharge and full recharge, respectively. Commercial Li_2O_2, CH_3COOLi, Li_2CO_3 and HCO_2Li are employed as standard references. Black and dark red lines are PFY mode, gray and light red lines are TEY mode.

In Figure 4, the Li K-edge spectra of 1DC electrode also show peaks corresponding to Li_2O_2 at 60.7 and 62.1 eV. However, unlike the standard Li_2O_2 powder, the TEY mode of 1DC spectra has much stronger absorption at 62.1 eV, which is possibly arising from the existence of lithium carboxylates. These peaks vanish at 0.5RC, implying decomposition at local area around Li after the initial RC.

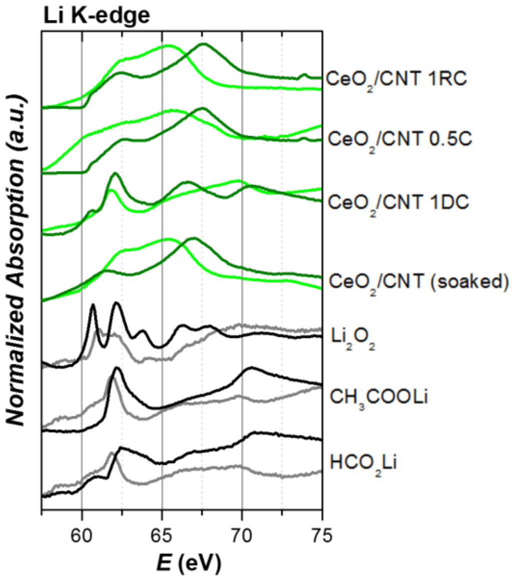

Fig. 4. The Li K-edge XANES spectra of CeO_2/CNT electrodes at different DC and RC. 1DC, 0.5 RC and 1RC is the 1st full discharge, 50% recharge and full recharge, respectively. Commercial Li_2O_2, CH_3COOLi, and HCO_2Li powders are employed as standard references. Black and dark green lines are PFY mode, gray and light green lines are TEY mode.

In summary, CeO_2/CNT composite electrode is used as the cathode in a Li-O_2 battery. The galvanostatic potential profiles show plateaus with considerably lower initial RC potential than CNT electrode. O and Li K-edge XANES were employed as the analytical tool to identify the chemical species on the DC and RC electrodes. It is found that the major DC product with film-like morphology is Li_2O_2, whereas minor side products of lithium carboxylates and carbonate are also formed. These products are decomposed after RC.

文 献 (References)

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論文・学会等発表（予定） (Articles and meetings)

Articles

[1] C. Yang, R. A. Wong, K. Yamanaka, T. Ohta and H.R Byon, *Understanding the Role of Structural Promoter in Lithium-Oxygen Battery using CeO_2 nanoparticle on CNT*. (In preparation).

Meetings

[1] Chunzhen Yang, and Hye Ryung Byon, *Structural effect of nano ceria incorporated to carbon nanotube for the formation of non-crystalline Li_2O_2 in Li-O_2 batteries*, 55th Battery Symposium Japan 2014, Electrochemical Society of Japan, Kyoto, Japan

[2] Chunzhen Yang, and Hye Ryung Byon, *CeO_2 Nanoparticle-Guided Formation and Decomposition of Amorphous Li_2O_2 on Carbon Nanotube Cathode in a Li-O_2 Cell*, 227th ECS Meeting 2015, Electrochemical Society, Chicago, USA