Investigation of discharging product structure in Li-O₂ battery using metal oxide catalyst

Eda Yilmaz[a], Chihiro Yogi[b], Keisuke Yamanaka[b], Toshiaki Ohta[b], Hye Ryung Byon[a]

[a] 理化学研究所 Byon 国際主幹研究ユニット，[b] 立命館大学 SR センター
[a] Byon Initiative Research Unit, RIKEN, [b] The SR Center, Ritsumeikan University

We report chemical identification of discharge and recharge products of lithium–oxygen (Li–O₂) cell with ruthenium oxide nanoparticles (RuO₂ NPs) dispersed on multi-walled carbon nanotubes (MWCNTs) electrode. O and Li K-edge XANES measurements reveal that a main discharge product is lithium peroxide (Li₂O₂) with tiny quantity of lithium hydroxide (LiOH) and lithium carbonate (Li₂CO₃), which completely disappear after recharge.

Keywords: Lithium-oxygen battery, Ruthenium oxide Nanoparticle, Carbon nanotube, XANES.

背景と研究目的(**Introduction**)：Li–O₂ battery has been developed to provide high specific-energy-density ($\sim$3 kWh kg$^{-1}_{cell}$), applied for various portable electronics and electric vehicles in the future. [1,2] However, the current Li–O₂ battery being developed suffers from huge energy–loss consumed unnecessarily due to the difficulty of decomposition of insulating Li₂O₂ on recharge (Li₂O₂(s) → 2Li⁺ + O₂(g) + 2e⁻). [3,4] In addition, byproducts parasitically formed from degradation of non–aqueous electrolytes have required further energy to be decomposed on recharge.

In this study, we employ in RuO₂ NPs dispersed on MWCNTs (RuO₂/MWCNT) electrode to suppress the energy-loss in the Li–O₂ battery. With electrochemical performance testing, we address chemical identification of products after discharge and recharge by XANES with the FY and TEY modes, which provide bulk and surface-sensitive chemical information, respectively. The XANES spectra reveal the main discharge product of Li₂O₂ that completely disappear after recharge.

実験(**Experimental**)：
(*1*) *Electrochemical Performance*
The Li–O₂ cell was composed of lithium metal, separator and the RuO₂/MWCNT or the MWCNT with tetraethylene glycol dimethyl ether (tetraglyme, <5 ppm of H₂O measured by Karl Fischer titration) containing 0.5 M of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). The completely assembled cell containing an O₂ tank (40 mL of volume capacity) was purged with O₂ gas. Electrochemical examinations of the complete Li-O₂ cells using a galvanostatic method were performed using a battery cycler (WBCS3000, WonATech). The specific capacity was estimated from the mass of carbon (equal to the mass of MWCNT) and the current rate was set on the basis of the geometric area of cathode (1.13 cm²). All examined Li–O₂ cells performed at a current rate of 0.1 mA cm⁻² and potentials were referred to Li/Li⁺.

(*2*) *Characterizations*
After discharge or recharge, the cathodes were then washed with a super-dehydrated acetonitrile and dried in a vacuum oven without exposing the cathode to air. The completely dried cathode samples were conveyed using a hermetic vessel. TEM images were attained from a JEOL JEM–2100F with 200 kV accelerating voltage. XANES spectral measurements with the FY and TEY modes were performed at BL2 for O and Li K–edge and BL10 for Ru L₃–edge in the SR center of Ritsumeikan University. All samples and references of Li₂O₂ (99% purity), LiOH (98% purity), Li₂CO₃ (99% purity) and RuO₂ were loaded in an Ar-filled glove box and directly transferred into the chamber for XANES measurements without air exposure by using a custom-made hermetic vacuum vessel.

結果、および、考察(**Results and discussion**)：
The RuO₂/MWCNT composites have uniformly distributed RuO₂ NPs with an averaged particle size of $\sim$1.7 nm over the MWCNT surface (transmission electron microscopy (TEM) in **Fig. 1a**). The crystalline RuO₂ NPs as shown in the TEM image were assigned to a rutile structure. The Ru L₃–edge XANES spectrum of the RuO₂ NPs obtained with the FY mode showed an intense white-line at $\sim$2836.5 eV, which was
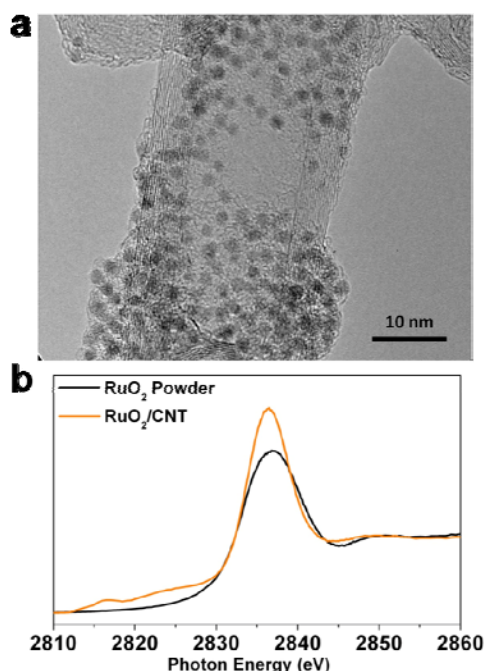
consistent with the spectrum of RuO_2 powder (**Fig. 1b**).

Fig. 1 Characterization of RuO_2/MWCNT **(a)** TEM image of RuO_2/MWCNT and **(b)** Ru L_3-edge XANES spectra of RuO_2/MWCNT (orange) and reference of RuO_2 powder (black) with FY mode.

Binder-free RuO_2/MWCNT (~32 wt% RuO_2) and MWCNT (without RuO_2 NPs) films, made by vacuum–filtration method, were used as a cathode in the Li–O_2 cells. **Fig. 2** shows discharge/charge profiles of the Li–O_2 cells with the RuO_2/MWCNT and MWCNT cathodes at a current rate of 0.1 mA cm^{-2}. The Li–O_2 cells with RuO_2/MWCNT and MWCNT cathodes delivered 1500 and 1550 mAh g$^{-1}_{carbon}$ of specific capacities, respectively. The averaged recharge potentials are 3.6 V for the RuO_2/MWCNT and 4.0 V for the MWCNT cathodes. The decreased over-potential with RuO_2, determined by the different potential from the thermodynamically reversible potential (2.96 V vs. Li/Li$^+$) of Li–O_2 electrochemical reaction, results in ~70% electrical efficiencies. This is greatly efficient compared to the use of MWCNT cathode that allows only ~55%.
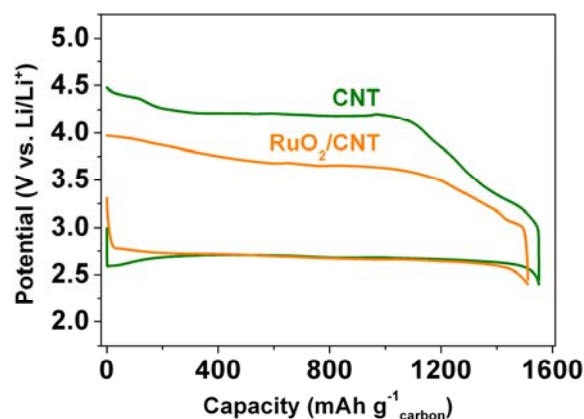

Fig. 2. Electrochemical performance with RuO_2/MWCNT (orange) and MWCNT (green) cathodes at a current rate of 0.1 mA cm^{-2} and a discharge cut-off potential of 2.4 V (referenced to Li$^+$/Li) using 0.5 M of LiTFSI in tetraglyme.

To demonstrate that the potential profiles in **Fig. 2** arise from the ideal Li–O_2 electrochemical reaction, which produces Li_2O_2 discharge product, XANES measurements were performed with the RuO_2/MWCNT and MWCNT cathodes. **Fig. 3** presents O and Li K–edge XANES spectra of as-prepared (soaked in the electrolyte, washed and dried), 1st discharged (DC), 1st recharged (RC) cathodes and reference powders of Li_2O_2, Li_2CO_3, LiOH and RuO_2 with the FY mode. The FY mode provides bulk-sensitive chemical information. The O K–edge spectra of the as–prepared cathodes showed a π* (C=O) transition peak at 531.3 eV with a σ* (C–O) transition band at higher photon energy from the MWCNT.[5] The split peaks at 528.9 and 531.7 eV from the RuO_2 NPs in the RuO_2/MWCNT arise from O 2p–Ru 4d hybridization. After first discharge (DC), the Li_2O_2-associated peaks clearly appeared for both cathodes; at 530.3 eV in O K–edge and at 60.6 and 62.1 eV in Li K–edge spectra.[6] Consequently, the Li_2O_2 was the predominant discharge product for both RuO_2/MWCNT and MWCNT. The Li_2O_2 peaks totally disappeared in the subsequent recharge (RC). After the first recharge, the relative peak–intensity of π* (C=O) transition from MWCNT visibly increased, which indicated an increasing extent of C=O species from the MWCNTs. In addition, a shoulder newly emerged at 532.8 eV arising from Li_2CO_3 was observed in the MWCNT RC.[6]
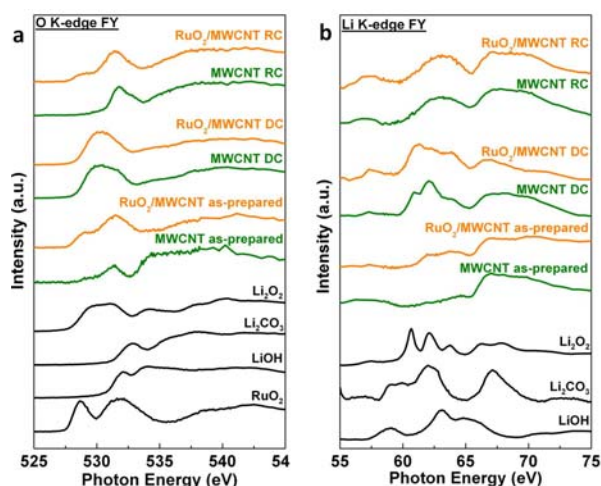
Fig. 3 XANES spectra with the FY mode of RuO$_2$/MWCNT (orange) and MWCNT (green) cathodes as–prepared, 1st discharged (DC) and 1st recharged (RC) with references (black) of Li$_2$O$_2$, Li$_2$CO$_3$, LiOH and RuO$_2$ in (a) O K–edge and (b) Li K–edge spectra.

The chemical identification of the products could be further investigated using the TEY mode (**Fig. 4**). TEY spectra provide details of surface sensitive information on the cathode sample due to a shallow escape depth as ~10 nm for O K–edge and less 1 nm for Li K–edge. In the O K–edge, the spectra patterns were almost identical to those with the FY mode in **Fig. 3**, presenting appearance and disappearance of Li$_2$O$_2$ after DC and RC, respectively, in both cathodes. More interestingly, in the Li K–edge TEY spectra, the discharged products in RuO$_2$/MWCNT and MWCNT cathodes were somewhat different. The MWCNT DC showed sharp Li$_2$O$_2$ peaks at ~60.8 and 61.8 eV referred to the reference powder of Li$_2$O$_2$ and no significant evidence in the presence of other LiOH and Li$_2$CO$_3$. In contrast with the MWCNT DC, the RuO$_2$/MWCNT DC provided ambiguous and broad TEY spectra that could be interpreted as the superposition of the spectra from Li$_2$O$_2$, LiOH and Li$_2$CO$_3$. This suggested that the topmost surface in the RuO$_2$/MWCNT DC was covered with miscellaneous Li compounds. The reason for these byproducts deposited on the topmost surface of the RuO$_2$/MWCNT DC albeit with tiny quantity was not clearly understood, but possibly due to the presence water strongly adsorbed on the RuO$_2$ NP surface. After first recharge, the presence of Li$_2$CO$_3$ on the RuO$_2$/MWCNT was apparently observed by the shoulder at ~532.8 eV in the RuO$_2$/MWCNT RC. The Li K–edge TEY spectra, providing the most top surface information, clearly revealed the presence of Li$_2$CO$_3$ in both RuO$_2$/MWCNT and MWCNT cathodes after first recharge. Both RC

cathodes showed a Li$_2$CO$_3$–associated peak incorporated with a lithium salt peak at ~531.5 eV, probably arising from the electrolyte as evidenced by that in the as-prepared cathodes. The formation of Li$_2$CO$_3$ has been inevitably observed in other reports also due to the degraded tetraglyme electrolyte, yet the predominant product was Li$_2$O$_2$ in both cathodes as evidenced from the FY spectra. [7]

In summary, XANES spectra revealed that the main discharge product in Li–O$_2$ cells using both RuO$_2$/MWCNT and MWCNT cathodes was Li$_2$O$_2$, which was completely decomposed after recharge. This chemical analysis demonstrated that the ideal Li–O$_2$ electrochemical reaction occurred for the first cycle with and without RuO$_2$ nanoparticles that increased electrical efficiency up to 70% in the Li–O$_2$ cells.
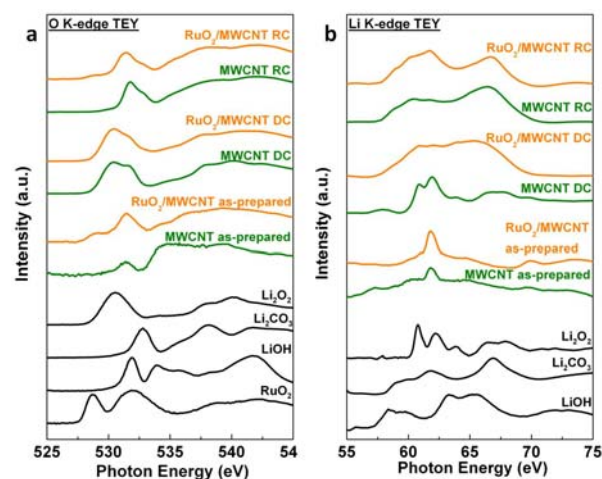

Fig. 4 XANES spectra with the TEY mode of RuO$_2$/MWCNT (orange) and MWCNT (green) cathodes as–prepared, 1st–discharged (DC) and 1st–recharged (1–RC) with references (black) of Li$_2$O$_2$, Li$_2$CO$_3$, LiOH and RuO$_2$ in (a) O K–edge and (b) Li K–edge spectra obtained.

文　献(**references**)
(1) G. Girishkumar, B. McCloskey, A. C. Luntz, S. Swanson and W. Wilcke, *J. Phys. Chem. Lett.* **2010**, 1, 2193.
2) P. G. Bruce, S. A. Freunberger, L. J. Hardwick and J.-M. Tarascon, *Nat Mater* **2012**, 11, 19.
(3) J. S. Hummelshoj, J. Blomqvist, S. Datta, T. Vegge, J. Rossmeisl, K. S. Thygesen, A. C. Luntz, K. W. Jacobsen and J. K. Norskov, *J. Chem. Phys.* **2012,** 132, 071101.
(4) B. D. McCloskey, R. Scheffler, A. Speidel, G. Girishkumar and A. C. Luntz, *J. Phys. Chem. C*, **2012,** 116, 23897.
(5) S. Banerjee, T. Hemraj-Benny, M. Balasubramanian, D. A. Fischer, J. A. Misewich and S. S. Wong, *Chem. Commun.* **2004**, 772.

(6) R. Qiao, Y.-D. Chuang, S. Yan and W. Yang, *PLoS ONE* **2012**, **7**, e49182.
(7) S. A. Freunberger, Y. Chen, N. E. Drewett, L. J. Hardwick, F. Barde and P. G. Bruce, *Angew. Chem. Int. Ed.* **2011**, 50, 8609.

論文・学会等発表（予定）
(Articles and meetings)
Article
[1] E. Yilmaz, C. Yogi, K. Yamanaka, T. Ohta and H. R. Byon, 2013, submitted.
Meetings
[1] E. Yilmaz and H. R. Byon, The 53rd Battery Symposium in Japan. (Oral Presentation)
[2] E. Yilmaz and H. R. Byon, The 93rd Annual Meeting of Chemical Society of Japan. (Oral Presentation)
[3] E. Yilmaz and H. R. Byon, 224th ECS Meeting. (Submitted)