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

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We report chemical identification of discharge and recharge products of lithium–oxygen (Li–O\textsubscript{2}) cell with ruthenium oxide nanoparticles (RuO\textsubscript{2} 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 (Li\textsubscript{2}O\textsubscript{2}) with tiny quantity of lithium hydroxide (LiOH) and lithium carbonate (Li\textsubscript{2}CO\textsubscript{3}), which completely disappear after recharge.

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

実験(Experimental):

(1) Electrochemical Performance
The Li–O\textsubscript{2} cell was composed of lithium metal, separator and the RuO\textsubscript{2}/MWCNT or the MWCNT with tetraethylene glycol dimethyl ether (tetraglyme, <5 ppm of H\textsubscript{2}O measured by Karl Fischer titration) containing 0.5 M of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). The completely assembled cell containing an O\textsubscript{2} tank (40 mL of volume capacity) was purged with O\textsubscript{2} gas. Electrochemical examinations of the complete Li-O\textsubscript{2} cells using a galvanostatic method were performed using a battery cycler (WBGS3000, 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 cm\textsuperscript{2}). All examined Li–O\textsubscript{2} cells performed at a current rate of 0.1 mA cm\textsuperscript{-2} and potentials were referred to Li/Li\textsuperscript{+}.

(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 L\textsubscript{3}–edge in the SR center of Ritsumeikan University. All samples and references of Li\textsubscript{2}O\textsubscript{2} (99% purity), LiOH (98% purity), Li\textsubscript{2}CO\textsubscript{3} (99% purity) and RuO\textsubscript{2} 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.
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.](image)

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$^{-1\text{carbon}}$ 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.](image)

To demonstrate that the potential profiles in Fig. 2 arise from the ideal Li–O$_2$ electrochemical reaction, which produces Li$_2$O$_2$ 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$_2$O$_2$, Li$_2$CO$_3$, 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 $\pi^*$ (C=O) transition peak at 531.3 eV with a $\sigma^*$ (C–O) transition band at higher photon energy from the MWCNT. 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$_2$O$_2$-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. Consequently, the Li$_2$O$_2$ was the predominant discharge product for both RuO$_2$/MWCNT and MWCNT. The Li$_2$O$_2$ peaks totally disappeared in the subsequent recharge (RC). After the first recharge, the relative peak–intensity of $\pi^*$ (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$_2$CO$_3$ was observed in the MWCNT RC.
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.

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.

論文・学会等発表（予定）
(Articles and meetings)
Article
Meetings
[3] E. Yilmaz and H. R. Byon, 224th ECS Meeting. (Submitted)