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Elucidation of catalyst role in the lithium-oxygen battery

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We report chemical identification of discharge and recharge products of lithium–oxygen (Li–O_2) cell using Au, Pt, Pd, Ru, Co_3O_4 and NiO nanoparticles on carbon nanotube (CNT) electrode. O and Li K-edge XANES measurements reveal that lithium peroxide (Li_2O_2) is the main product during discharge, which is decomposed during recharge. In addition, some side products such as lithium carboxylates and lithium carbonate (Li_2CO_3) are also emerged.

Keywords: Catalyst, Metal and metal oxide nanoparticles, Lithium-oxygen battery, Carbon nanotube, XANES.

背景と研究目的**(Introduction)**：Despite high theoretical capacity, a Li-O_2 battery has suffered from huge oxidation potential polarization on carbonaceous positive electrode for recharge (RC, >4.2 V vs. Li/Li^{+}), due to sluggish decomposition of non-conductive discharge (DC) product, lithium peroxide ($Li_2O_2 \leftrightarrow 2Li^+ + O_2 + 2e^-$)[1]. Such high potential triggers side reactions such as degradation of electrolyte and carbonaceous electrode, which results in poor cycle-ability[1]. To mitigate this problem during oxygen evolution reaction (OER), solid-state metal or metal oxide nanoparticles (NPs), which are expected to serve as catalyst-like role, were introduced to the electrode[2]. However, the specific role of these NPs in the Li-O_2 battery is little known due to complication from accompanying parasitic side reactions[3]. In addition, reasonable comparison of these NPs' activities is not feasible under different performance conditions when various reports were referred.[2] Therefore, to gain a reasonable assessment of their activities and an understanding of their role, it is necessary to examine Li-O_2 batteries with metal and metal oxide NPs under the same condition and analyze their reaction processes in detail. Here we present diagnosis of the true role of these NPs, such as platinum (Pt), gold (Au), palladium (Pd), ruthenium (Ru), cobalt oxide (Co_3O_4) and nickel oxide (NiO), for OER in Li-O_2 batteries under

very similar condition and analysis of DC and RC products using XANES spectroscopy.

実験**(Experimental)**：
(1) Composite electrode synthesis: The Au, Pt, Pd, Ru, Co_3O_4 and NiO NPs were synthesized using wet chemistry. Thereafter, stabilizing agents were thoroughly washed out. The metal and metal oxide NPs were then incorporated with multi-walled carbon nanotubes (CNTs) following by preparation of binder-free electrode using vacuum-filtration technique. The CNTs serve as a 3-D framework with abundant voids (more than 100 nm), which are suitable to O_2 gas transport in the Li-O_2 cell. We designed that all NPs account for ~40 wt% for the electrode weight (NP + CNT). The mass of CNT (~1.2 mg) is comparable for all electrodes to reasonably compare NPs' role in the Li-O_2 cells. The size of synthesized NP is as follows: Au (~9 nm), Pt (~3.5 nm), Pd (~3.5 nm), Ru (~1.5 nm), Co_3O_4 (~10 nm) and NiO (~2.5 nm).
(2) Galvanostatic tests: The Li-O_2 cells were assembled with metallic Li as the negative electrode, CNT with various metal/metal oxide NPs as the positive electrode and 0.5M LiTFSI/tetraglyme as the electrolyte solvent in an Ar-filled glove box. Galvanostatic DC and RC were performed after filling of O_2 gas and maintaining the open circuit potential for 3 h.

The tests were examined at a current rate of 0.06 mA using a battery cycler (WonATech WBCS3000) in a constant-temperature chamber (25 °C, Yamada). A cut-off DC potential was 2.2 V and the RC was examined to the equivalent capacity of the corresponding DC. All potentials were referred to Li^+/Li.

(3) Characterizations: After DC and RC, the $Li-O_2$ cells were disassembled inside the Ar-filled glovebox and the electrodes were directly transferred to XANES chamber using a hermetic vessel and without exposing to air. The XANES spectral measurements were performed for O and Li K–edge at BL2 and BL11 at the SR center of Ritsumeikan University.

結果、および、考察(Results and discussion)：

Fig. 1 shows the 1st cycled galvanostatic curves with CNT (red), Au/CNT (blue), Pt/CNT (orange), Pd/CNT (green), Ru/CNT (grey), Co_3O_4 (violet) and NiO/CNT (dark yellow) in 0.5 M LiTFSI/tetraglyme electrolyte. All electrodes have similar discharge (DC) potential to ~2.7 V, which suggests negligible effect of metal/metal oxide NPs for DC. The DC capacities are different from electrodes: The Pt, Ru and NiO on the CNT electrodes have lower capacity than metal/metal oxide-free CNT (~1900 mAh/g$_{-CNT}$) whereas the $Li-O_2$ cells with Co_3O_4, Pd and Au deliver greater capacity (over 2000 mAh/g$_{-CNT}$). The reason for the different capacity with respect to the metal and metal oxide NPs is not very clear. In contrast to the comparable DC potential, different RC potentials appear. Referring to the potential of CNT (~4.4 V) at the end of RC, Ru (3.95 V), Co_3O_4 (4.07 V), Pd (4.14 V), Pd (4.15 V), NiO (4.15 V) and Au (4.37 V) have lower potentials. It seemingly shows that the metal/metal oxide lowers the RC potential, i.e., enhanced OER from the DC-RC profiles.
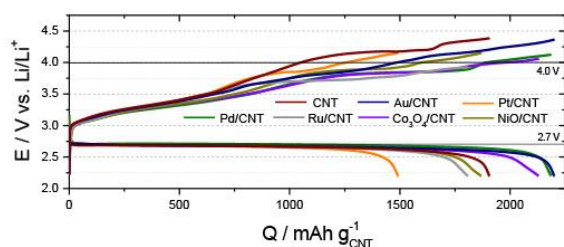

Fig. 1. Electrochemical performance of various electrodes in 0.5 M LiTFSI/tetraglyme at a current rate of 0.06 mA and cut-off potential of 2.2 V for DC in O_2 atmosphere. The electrodes are CNT (red), Au/CNT (blue), Pt/CNT (orange), Pd/CNT (green), Ru/CNT (grey), Co_3O_4 (violet) and NiO/CNT (dark yellow).

To investigate true role of metal and metal oxide, XANES spectroscopy with Li and O K-edge were performed. If these NPs can trigger more unintended reactions instead of catalytic role, which can drop the RC potential, the side products are predominant compared to Li_2O_2. **Figs. 2–4** displays O and Li K-edges XANES spectra. **Fig. 2** shows O K-edge of DC electrodes (after full discharged electrode) with bulk-sensitive PFY and surface-sensitive PEY modes. It is very clear that all electrodes have main $\sigma^*(O-O)$ peak of Li_2O_2 at ~530 eV in PFY mode, demonstrating predominant $Li-O_2$ electrochemical reaction. Interestingly, the NiO electrode has an apparent shoulder at ~531.5 eV, which corresponds to the peaks from lithium carboxylates ($LiCO_2H$ and $LiCO_2CH_3$). This can be further corroborated by the result from PEY mode. The PEY spectra reveal formation of lithium carboxylates-like side products at surface for almost all electrodes. In particular, NiO, Ru and Au electrodes have greater side products on the surface compared to Li_2O_2. This is presumably due to decomposition of electrolyte at the Li_2O_2 surface.
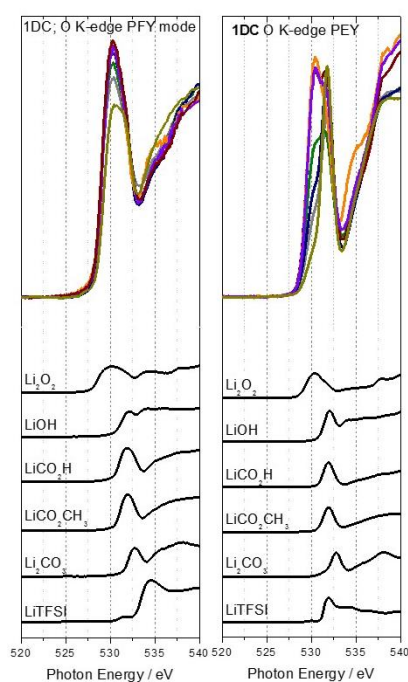

Fig. 2. O K-edge XANES spectra of DC electrodes with PFY and PEY mode. The bottom spectra are reference powders of Li_2O_2, LiOH, $LiCO_2H$, $LiCO_2CH_3$, Li_2CO_3, and LiTFSI.

Fig. 3 displays O K-edge spectra after RC (fully recharge). It is obvious that the Li_2O_2-related peak completely disappear as it was decomposed. The black graph and dashed area indicate the standard reference of 'as-prepared' CNT electrode. It is ideal that all electrodes return to

its original form (like as-prepared CNT) without any degradation. However, we could find the trace of side products. There is a pronounced shoulder at ~532 eV for CNT, Ru, Co_3O_4 and NiO, which arises from lithium carboxylates. For the Co_3O_4, the Li_2CO_3-associated peak at ~533 eV is also apparent. The Pt and Pd have relatively low side product-related peak. In addition, the Au/CNT has even lower peak at ~531.5 eV than the as-prepared CNT, of which specific reason is not clearly revealed at the current stage. It is noted that the Co_3O_4 and Ru show pre-edge absorption peak at ~527.5 eV, which result from Co_3O_4 itself and RuO_2 (outer layer of Ru), respectively. All other electrodes have similar pre-edge to the as-prepared CNT.
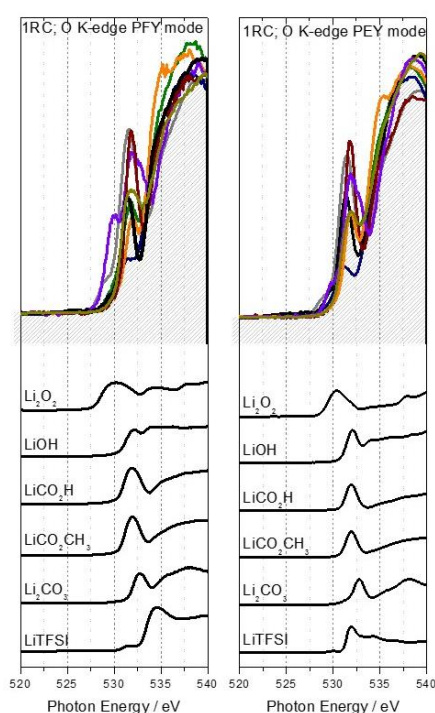

Fig. 3. O K-edge XANES spectra of 1RC electrodes with PFY and PEY mode. The black graph and dashed-line area indicate the reference of as-prepared CNT.

The Li K-edge spectra for DC and RC with TFY mode in **Fig. 4** are in good agreement with the O K-edge results. After DC, all electrodes have two main peaks of 60.5 and 62 eV. For the Pd, Ru and NiO on the CNT, the second peak of ~62 eV is intense, which is likely due to additional side products of lithium carboxylates and LiF obtaining by decomposition of LiTFSI salt. After RC, all Li_2O_2 peaks disappear. In addition, we cannot find any side-product peak possibly due to lower sensitivity of Li K-edge relative to O K-edge XANES.
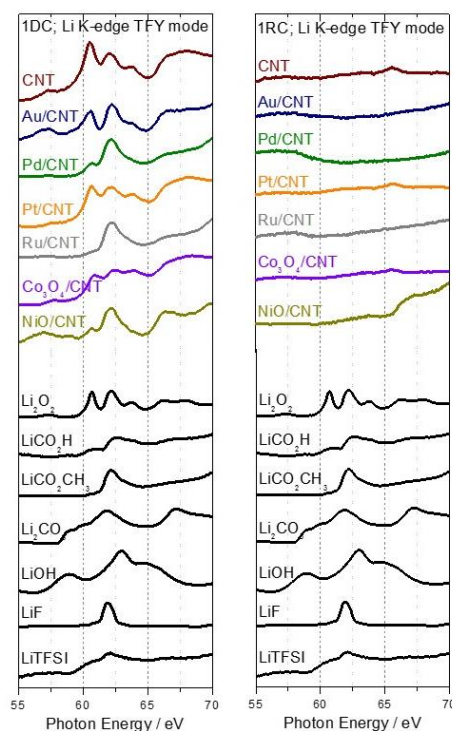

Fig. 4. Li K-edge XANES spectra of DC and RC electrodes with TFY mode. The bottom spectra are reference powders of Li_2O_2, $LiCO_2H$, $LiCO_2CH_3$, Li_2CO_3, LiOH, LiF and LiTFSI.

In summary, we study DC and RC products on positive electrodes with various metal and metal oxide NPs in $Li-O_2$ cells after the first cycle. The XANES spectra demonstrate that the main DC product is Li_2O_2 for all electrodes, which is also completely decomposed after 1RC. All electrodes cover with thin side products such as HCO_2Li and CH_3CO_2Li after 1DC, which is likely to form chemical reaction at the interface of Li_2O_2/electrolyte. Therefore, the formation of these side products cannot be taken into account of metal/metal oxide NPs' effect. After 1RC, such lithium carboxylate-related products are observed for all electrodes, which are particularly intense for CNT, Ru and Co_3O_4. The Li_2CO_3 is also found from the Co_3O_4 electrode. This suggests that (1) the Ru and Co_3O_4 electrodes remain much side products due to low RC potential, which is not as much as high to decompose insulating side products or (2) they can trigger further unintended reactions compared to other metal/metal oxide NPs. The pronounced side products on the metal/metal oxide-free CNT can be understood from the highest RC potential, which enhances degradation of electrolyte and CNT. The study of XANES spectra correlated with DC-RC galvanostatic profiles reveal the effect of metal/metal oxide NPs for RC.

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