Investigation of CeO$_2$ nanoparticles' redox reaction in Li-O$_2$ battery

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The effect of ceria (CeO$_2$) nanoparticle (NP) on carbon nanotube (CNT) in a lithium-oxygen (Li-O$_2$) battery is studied in this work. CeO$_2$/CNT electrodes are collected at different discharge/recharge states from Li-O$_2$ batteries and investigated by Ce L$_3$-edge XANES. The oxidation states of cerium are analyzed to determine whether the Ce$^{3+}$/Ce$^{4+}$ redox reaction plays some catalytic role for the formation and decomposition of Li$_2$O$_2$ in Li-O$_2$ battery.

**Keywords:** Li-O$_2$ battery, XANES, lithium peroxide, Cerium oxide nanoparticles.

**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. Around 0.6 mg CeO$_2$ NPs and CNT (1.8 – 2.0 mg) were well mixed by ultrasonication 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$_2$ transport in Li-O$_2$ 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 (tetrarglyme) with 0.5 M LiClO$_4$ electrolyte in an Ar-filled glovebox. The complete cell was filled with O$_2$ 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$^+/Li$. 

In the other hands, we can also consider the effect of physical adsorption of ROS at defect site, without any charge transfer. To corroborate the role of CeO$_2$ NP for the Li-O$_2$ battery, it is necessary to observe oxidation-state change of cerium using Ce L$_3$-edge XANES.

**背景と研究目的 (Introduction):**

The Li-O$_2$ batteries have been widely investigated thanks to high gravimetric energy density. However, there are several critical challenges to realize commercialization, which are high recharge overpotential and poor capacity retention. This is mainly due to poor conductivity and large particle size of discharged product of lithium peroxide (Li$_2$O$_2$) that is deposited on the carbonaceous electrode. We have explored the way to decrease in recharge overpotential using metal oxide nanoparticle (NP), which can alter Li$_2$O$_2$ structure and physical property. We have particularly focused on key mechanism for suppression of recharge potential via distinct nucleation and growth process of Li$_2$O$_2$ on the metal oxide from those on the carbon electrode. Namely, the metal oxide has higher binding energy to reactive oxidative species (ROS), such as oxygen and superoxide species, via surface redox reaction of NPs or their physicochemical affinity. For a case study, we here employed ceria (CeO$_2$) NPs to multi-walled carbon nanotube (CNT) as the positive electrode in the Li-O$_2$ cell. The CeO$_2$ has strong binding affinity to the ROS via charge transfer. The oxygen vacancy associated with Ce$^{3+}$ on the CeO$_2$ is the active site, which is abundant at smaller size (less 5 nm). As the ROS reacts with the Ce$^{3+}$ (Ce$^{3+}$ + O$_2$ ↔ Ce$^{4+}$ + O$_2$) around the oxygen vacancy, the nucleation of Li$_2$O$_2$ can primarily occur on the CeO$_2$. Therefore, the changed oxidation state on the CeO$_2$ may be important clue for nucleation of Li$_2$O$_2$, which can be attributed to altered Li$_2$O$_2$ structure and low recharge potential.
iii) Characterization

The XANES spectra were acquired at the beamline of BL-3 in the Synchrotron Radiation (SR) center of Ritsumeikan University. The electrode samples were enclosed by Al-laminated packs in the glove box. The XANES spectral measurements were conducted with a Si (220) double crystal monochromator. The FY mode was applied for different states of electrodes while the transmission mode was used for air-exposed reference samples of Ce(NO$_3$)$_3$ and CeO$_2$ powder.

結果、および、考察 (Results and Discussion):

The characterization of CeO$_2$ in Figure 1a shows uniform size of CeO$_2$ NPs (with an average particle size of ~5.3 nm), which has fluorite crystal (Figure 1c). These CeO$_2$ NPs are well incorporated onto the CNT without considerable agglomeration (Figure 1b). The mass ratio of CeO$_2$ is around 25% to total electrode mass (CeO$_2$ + CNT).

The 1st discharge (DC) and recharge (RC) potential profiles of Li-O$_2$ battery with CeO$_2$/CNT and CNT electrodes are shown in Figure 2. The DC potential shows a plateau of ~2.63 V for both electrodes. On the contrary, the initial RC potential for the CeO$_2$/CNT is lower than that for the CNT. The RC potential approaches to ~4.5 V at the end of RC for both electrodes. It is noted that the Ce$^{3+}$/Ce$^{4+}$ redox reaction takes place around 4.76 V (thermodynamic reversible potential), which indicates negligible electrochemical redox reaction of Ce$^{3+}$/Ce$^{4+}$ within the DC and RC potential range.

Figure 3 exhibits Ce L$\text{\textsubscript{3}}$-edge XANES spectra with FY mode for all electrodes. Different states of DC and RC, such as as-prepared, 0.5DC (~50% of DC), 1DC (full DC with a cut-off potential of 2.2 V), 0.25RC (~25% RC), 0.75RC (~75% RC) and 1RC (full RC) electrodes, reveal the oxidation states of cerium in CeO$_2$ NP during the battery performance. The Ce(NO$_3$)$_3$ and CeO$_2$ powders in the bottom indicate standard references of Ce$^{3+}$ and Ce$^{4+}$, respectively, which were taken with transmission mode. All CeO$_2$/CNT electrodes show similar absorption spectra with predominant doublet (as indicated by dashed red lines) of Ce$^{4+}$ at 5729 and 5736 eV. In addition, a transition shoulder at 5725 eV is also present, which arises from Ce$^{3+}$. This result reveals that the CeO$_2$ NPs are electrochemically inactive during the battery performance: there is no evidence of Ce$^{3+}$ ↔ Ce$^{4+}$ as the ROS is bound or unbound at the oxygen vacancy during DC and RC, which rules out the charge transfer effect.
Fig. 3. The normalized Ce L₃-edge XANES spectra of CeO₂/CNT electrodes with FY mode at different DC and RC states in Li-O₂ cells. Commercial Ce(NO₃)₃ and CeO₂ powders are characterized as standard references for Ce³⁺ and Ce⁴⁺, respectively, with transmission mode.

In summary, we investigated the electrochemical performance of Li-O₂ cells with CeO₂ NPs decorated on the CNT. The Ce L₃-edge XANES spectra demonstrate that CeO₂ NPs are not involved in reversible redox reaction during DC and RC. This result reveals that lower initial RC potential on the CeO₂/CNT electrode is not attributed to the charge transfer effect of Ce³⁺ on the CeO₂. Presumably, other physicochemical characteristics of CeO₂ can aid in decrease in the RC potential in Li-O₂ cells.

文献 (References)

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

Meetings
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