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Investigation of CeO₂ nanoparticles' redox reaction in Li-O₂ battery

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The effect of ceria (CeO₂) nanoparticle (NP) on carbon nanotube (CNT) in a lithium-oxygen (Li-O₂) battery is studied in this work. CeO₂/CNT electrodes are collected at different discharge/recharge states from Li-O₂ batteries and investigated by Ce L₃-edge XANES. The oxidation states of cerium are analyzed to determine whether the Ce³⁺/Ce⁴⁺ redox reaction plays some catalytic role for the formation and decomposition of Li₂O₂ in Li-O₂ battery.

Keywords: Li-O₂ battery, XANES, lithium peroxide, Cerium oxide nanoparticles.

背景と研究目的 (Introduction) :

The Li-O₂ 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 (Li₂O₂) that is deposited on the carbonaceous electrode.^{1,2} We have explored the way to decrease in recharge overpotential using metal oxide nanoparticle (NP), which can alter Li₂O₂ structure and physical property.³ We have particularly focused on key mechanism for suppression of recharge potential via distinct nucleation and growth process of Li₂O₂ 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 (CeO₂) NPs to multi-walled carbon nanotube (CNT) as the positive electrode in the Li-O₂ cell. The CeO₂ has strong binding affinity to the ROS via charge transfer.⁴ The oxygen vacancy associated with Ce³⁺ on the CeO₂ is the active site, which is abundant at smaller size (less 5 nm). As the ROS reacts with the Ce³⁺ (Ce³⁺ + O₂ ↔ Ce⁴⁺ + O₂⁻) around the oxygen vacancy, the nucleation of Li₂O₂ can primarily occur on the CeO₂. Therefore, the changed oxidation state on the CeO₂ may be important clue for nucleation of Li₂O₂, which can be attributed to altered Li₂O₂ structure and low recharge potential. On the other

hands, we can also consider the effect of physical adsorption of ROS at defect site, without any charge transfer.⁵ To corroborate the role of CeO₂ NP for the Li-O₂ battery, it is necessary to observe oxidation-state change of cerium using Ce L₃-edge XANES.

実験 (Experimental) :

i) Synthesis and cell fabrication

CeO₂ NPs were synthesized by thermal decomposition of cerium nitrate precursor in the presence of protecting agent of oleylamine according to the literature.⁶ Around 0.6 mg CeO₂ NPs and CNT (1.8 – 2.0 mg) were well mixed by ultra-sonication 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 O₂ transport in Li-O₂ 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 (tetraglyme) with 0.5 M LiClO₄ electrolyte in an Ar-filled glovebox. The complete cell was filled with O₂ 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.

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 $\text{Ce}(\text{NO}_3)_3$ 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 ($\text{CeO}_2 + \text{CNT}$).

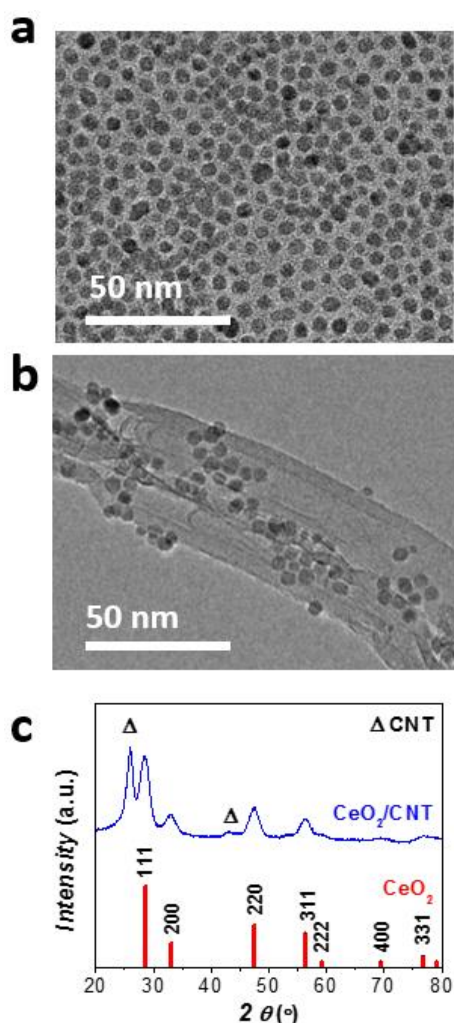


Fig. 1. Characterization of CeO_2 NPs and CeO_2/CNT electrode: TEM images of (a) CeO_2 NPs and (b) as-prepared CeO_2/CNT . (c) XRD pattern of fluorite CeO_2 on the CNT.

The 1st discharge (DC) and recharge (RC) potential profiles of Li-O₂ 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 $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox reaction takes place around 4.76 V (thermodynamic reversible potential), which indicates negligible electrochemical redox reaction of $\text{Ce}^{3+}/\text{Ce}^{4+}$ within the DC and RC potential range.

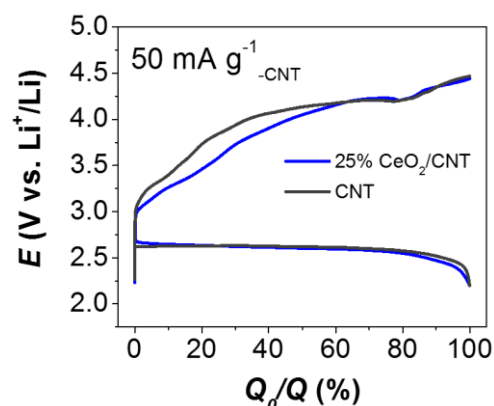


Fig. 2. Normalized galvanostatic DC and RC profile of Li-O₂ cell with CeO_2/CNT electrode in $\text{LiClO}_4/\text{tetraglyme}$ electrolyte. A current density of $50 \text{ mA g}^{-1}_{\text{CNT}}$ and a cut-off discharge voltage is 2.2 V.

Figure 3 exhibits Ce L₃-edge XANES spectra with FY mode for all electrodes. Different states of DC and RC, such as as-prepared, 0.5DC ($\sim 50\%$ of DC), 1DC (full DC with a cut-off potential of 2.2 V), 0.25RC ($\sim 25\%$ RC), 0.75RC ($\sim 75\%$ RC) and 1RC (full RC) electrodes, reveal the oxidation states of cerium in CeO_2 NP during the battery performance. The $\text{Ce}(\text{NO}_3)_3$ 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 $\text{Ce}^{3+} \leftrightarrow \text{Ce}^{4+}$ as the ROS is bound or unbound at the oxygen vacancy during DC and RC, which rules out the charge transfer effect.

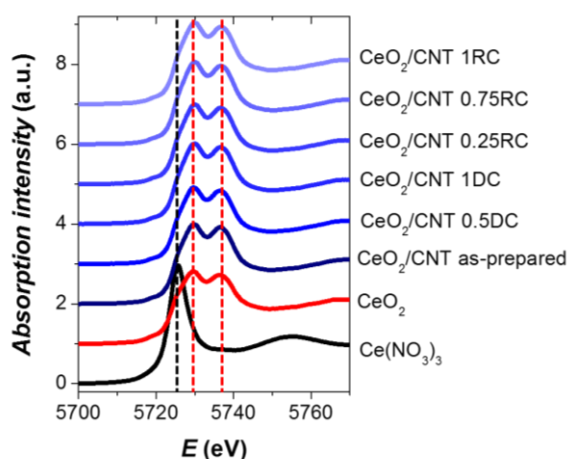


Fig. 3. The normalized Ce L₃-edge XANES spectra of CeO₂/CNT electrodes with FY mode at different DC and RC states in Li-O₂ cells. Commercial Ce(NO₃)₃ and CeO₂ powders are characterized as standard references for Ce³⁺ and Ce⁴⁺, respectively, with transmission mode.

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)

- [1] J. Christensen *et al.*, J. Electrochem. Soc., 2012, 159, R1-R30.
- [2] R. Black *et al.*, Adv. Energy Mater., 2012, 2, 801-815.
- [3] E. Yilmaz *et al.*, Nano Lett. 2013, 13, 4679-4684.
- [4] S. S. Lee *et al.*, ACS Nano, 2013, 7, 9693-9703.
- [5] J. Xu *et al.*, Chem. Comm., 2010, 46, 1887-1889.
- [6] S. Lee *et al.*, ACS Nano, 2013, 7, 9693-9703.

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 CeO₂ 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 Li₂O₂ in Li-O₂ batteries, 55th Battery Symposium Japan 2014, Electrochemical Society of Japan, Kyoto, Japan

[2] Chunzhen Yang, and Hye Ryung Byon, *CeO₂ Nanoparticle-Guided Formation and Decomposition of Amorphous Li₂O₂ on Carbon Nanotube Cathode in a Li-O₂ Cell*, 227th ECS Meeting 2015, Electrochemical Society, Chicago, USA