様式３

R1432

Investigation of nanocatalyst effect of carbon cathode in Li-O_2 battery

-XANES Analysis of Discharge Products with Mesoporous Carbon Electrode-

Arghya Dutta[a], 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, Wako, Saitama 351-0198 Japan
[b] SR Center, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan

Here we report a mesoporous carbon as the positive electrode in a nonaqueous Li-O_2 battery. Application of O, Li and C K-edge XANES spectra identifies the chemical species present in the discharge product and explains the nature of recharge curve of this carbon electrode.

Keywords: Li-O_2 battery, XANES, lithium peroxide, mesoporous carbon

背景と研究目的 (Introduction)：

Research on non-aqueous lithium-oxygen (Li-O_2) battery has drawn considerable attention, in recent time, because of its potential to deliver high energy density, which is suitable for possible application in electric vehicles.[1] However the great promise of this battery system is still hindered from practical use due to high polarization, low rate capability, poor cycle life etc.[2] The main reason behind high charge overpotential in Li-O_2 battery is thought to be poor ionic and electronic conductivities of solid Li_2O_2 that is the principal discharge product. The high charge overpotential is always associated with electrolyte and carbon decomposition leading to parasitic discharge products in addition to Li_2O_2.[3] It is thus essential to identify the discharge products chemically to properly understand the chemistry of this kind of battery.

In this study, we have used a mesoporous carbon as the positive electrode in Li-O_2 battery, and employed XANES as the primary analytical tool for chemical identification of discharge products.

実験 (Experimental)：

i) Synthesis and cell fabrication[4]

The mesoporous carbon was synthesized by using mesoporous silica SBA-15 as the hard template. Phenol and formalin were used as the carbon precursors. In a typical synthesis procedure, a mixture of phenol and formalin in a particular ratio was dissolved in de-ionized water and infiltrated inside SBA-15 silica. The composite material was then dried and carbonized at high temperature under Ar atmosphere. Finally the silica template was removed by washing with 10% HF solution. The electrodes were prepared by spreading an ink of the mesoporous carbon over commercial carbon paper and punched into discs with 12 mm diameter.

ii) Electrochemical evaluation

Galvanostatic charge/discharge cycles of the mesoporous carbon electrodes were carried out by using a battery cycler (WBCS3000, WonATech, Korea). The mesoporous carbon was used as the positive electrode and metallic lithium as the negative electrode. 0.5 M LiTFSI in tetraethylene glycol dimethyl ether (TEGDME) was used as the electrolyte. The applied current density and capacity were calculated based on the mass of the mesoporous carbon.

iii) Characterization

Pore structure of the mesoporous carbon was confirmed by using JEOL (JEM-1230) transmission electron microscope (TEM) with 80 keV accelerating voltage. XANES data of the discharged and recharged electrodes were collected by using beam line 11 (BL-11) at SR Center, Ritsumeikan University, for Li, C and O K-edge.

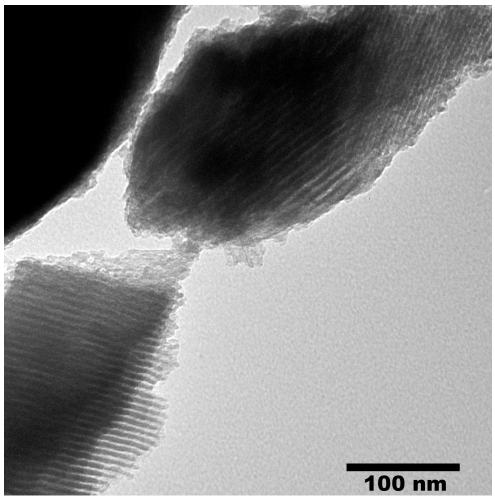

Figure 1. TEM image of mesoporous carbon

結果、および、考察 (Results and Discussion) :
From the TEM image in Figure 1 it is seen that the carbon material has ordered mesoporous structure. In Figure 2, the 1st cycle discharge/charge profile of the mesoporous carbon has been shown at a current density of 50 mAg^{-1}.

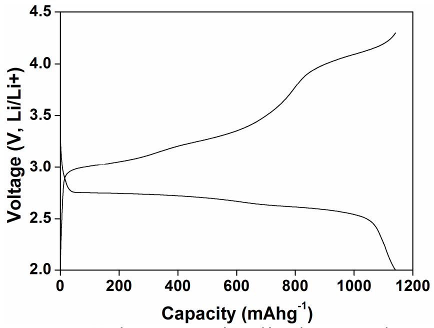

Figure 2. Galvanostatic discharge-charge profile of mesoporous carbon

It is known from previous reports that the major discharge product is Li_2O_2 in a nonaqueous lithium-oxygen battery with glyme-based electrolytes.[5] The equilibrium potential for reversible formation and decomposition of Li_2O_2 is 2.96 V (vs Li/Li^+). The galvanostatic recharge curve of the mesoporous carbon shows two distinct plateaus and gradual increase in overpotential is evident throughout the recharge process. Interestingly, the first potential plateau is greatly lower than that from other carbonaceous electrodes,[6] which implies the role of catalytic effect on the mesoporous carbon. To understand the reason for two different potential plateaus, it is essential to identify the chemical species involved during discharge and recharge. XANES, for this reason, was employed as an analytical tool for this purpose.
Figures 3-5 display O, Li and C K-edges XANES spectra of different discharged and recharged electrodes of mesoporous carbon along with the reference spectra of standard Li_2O_2, Li_2CO_3, HCO_2Li, CH_3CO_2Li, Li_2O, LiOH.
The O K-edge spectrum of 1st discharge (1DC) electrode in Figure 3 clearly shows Li_2O_2 as the major discharge product with a small shoulder peak at 532 eV corresponding to HCO_2Li. The spectrum of 75% RC electrode shows that the intensity of the peak at 530.3 eV is diminished indicating decomposition of Li_2O_2. At the same time a new peak at 532.8 eV is emerged arising from Li_2CO_3 while the HCO_2Li-related peak at 532 eV is more prominent. After 1st recharge (1RC) there is no peak of Li_2O_2 and Li_2CO_3, but HCO_2Li associated peak is present.

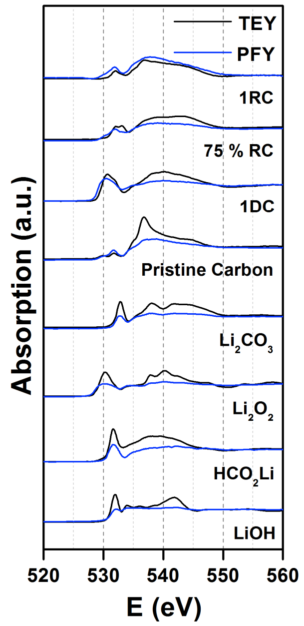

Figure 3. O K-edge XANES spectra in TEY (black) and PFY (blue) modes. 1DC, 75% RC and 1RC indicate mesoporous carbon electrodes after full discharge (DC), 75% recharge (RC) and full RC, respectively. The standard references are LiOH, HCO_2Li, Li_2O_2, Li_2CO_3 and as-prepared mesoporous carbon (indicated as Pristine Carbon).

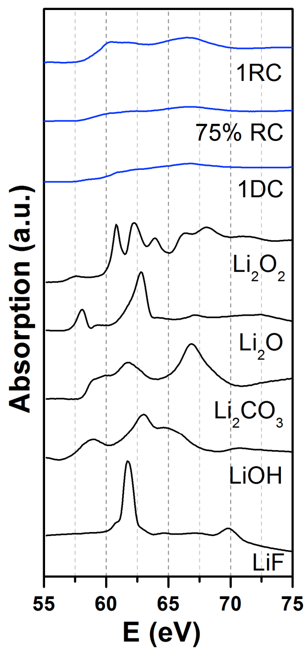

Figure 4. Li K-edge XANES spectra (TEY) of mesoporous carbon electrodes

The Li K-edge spectra of the electrodes in Figure

4 are not very conclusive. But from the spectrum of 1RC electrode, there is indication of some undecomposed Li_2CO_3. Similarly the C K-edge spectra of 75% RC and 1RC electrodes in Figure 5 show a small peak at 291 eV for Li_2CO_3.
Therefore, it is clearly evidenced by XANES spectra of different discharged/recharged electrodes that the major discharge product in this mesoporous carbon electrode is Li_2O_2 and it is completely decomposed during the course of recharge. In addition to Li_2O_2, there is also formation of some parasitic discharge products in the form of lithium-carboxylate (HCO_2Li). On the other hand, Li_2CO_3 is formed during recharge and at the end of 100% RC there is accumulation of both Li_2CO_3 and HCO_2Li. It is believed that the first plateau with a low voltage, during recharge, corresponds to decomposition of Li_2O_2 and high potential plateau at the end of recharge is possibly due to decomposition of the parasitic side products.

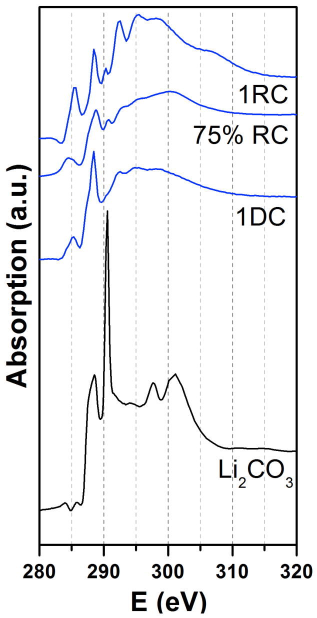

Figure 5. C K-edge XANES spectra (TEY) of mesoporous carbon electrodes

In summary, a mesoporous carbon is used as the positive electrode in a Li-O_2 battery. The galvanostatic recharge profile shows to plateaus with considerably low overpotential up to 75% of recharge. XANES was employed as the analytical tool to identify the chemical species present in the discharged/recharged electrodes. It was found that the decomposition of Li_2O_2 occurred at relatively low recharge potential, whereas, the increase in potential at the end is due to parasitic side products.

文　献 (References)

[1] Bruce, P. G.; Freunberger, S. A.; Hardwick, L. J.; Tarascon, J. M. *Nature Mater*. **2012**, *11*, 19
[2] Christensen, J.; Albertus, P.; Sanchez-Carrera, R. S.; Lohmann, T.; Kozinsky, B.; Liedtke, R.; Ahmed, J.; Kojic, A. *J. Electrochem. Soc*. **2012**, *159*, R1
[3] Ottakam Thotiyl, M. M.; Freunberger, S. A.; Peng, Z.; Bruce, P. G. *J. Am. Chem. Soc*. **2013**, *135*, 494
[4] Jun, S.; Joo, S. H.; Ryoo, R.; Kruk, M.; Jaroniec, M.; Liu, Z.; Oshuna, T.; Terasaki, O. *J. Am. Chem. Soc*. **2000**, *122*, 10712.
[5] McCloskey, B. D.; Sche, R.; Speidel, A.; Girishkumar, G.; Luntz, A. C. *J. Phys. Chem. C* **2012**, *116*, 23897
[6] Ding, N.; Chien, S. W.; Hor, T. S. A.; Lum, R.; Zong, Y.; Liu, Z. *J. Mater. Chem. A*, **2014**, *2*, 12433

論文・学会等発表（予定）(Articles and meetings)

Articles

[1] *Low recharge potential on a mesoporous carbon cathode: Effect of Li_2O_2 morphology*
Arghya Dutta, and Hye Ryung Byon (Under preparation)

Meetings

[1] *Discharge Product Inside Porous Carbon Cathode: Pore Confinement Effect On Li-O_2 Battery Performance*

Arghya Dutta, and Hye Ryung Byon

55th Battery Symposium Japan 2014, Electrochemical Society of Japan, Kyoto, Japan

[2] *Mesoporous Carbon Cathode in a Li-O_2 battery: Effect on Li_2O_2 product Morphology and Recharge Potential*

Arghya Dutta, and Hye Ryung Byon

227th ECS Meeting 2015, Electrochemical Society, Chicago, USA