

XANES investigation of side products in Li-O₂ battery using solid polymer electrolyte

Nadege Bonnet-Mercier^a, Chihiro Yogi^b, 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 Synchrotron Radiation Center, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan

We report chemical identification of discharge and recharge products of lithium–oxygen (Li–O₂) cell using a solid polymer electrolyte combined with a multi-walled carbon nanotubes electrode. O, C and Li K-edge XANES measurements reveal that products are mixtures of lithium hydroxide (LiOH), lithium carboxylates, lithium peroxide (Li₂O₂) and lithium carbonate (Li₂CO₃).

Keywords: Lithium-oxygen battery, Solid polymer electrolyte, Carbon nanotube, XANES.

背景と研究目的(Introduction): Non-aqueous Li-O₂ batteries have received considerable attention because of their remarkably higher theoretical specific energy density than other Li-ion batteries.^[1] However, one of the great challenges for practical applications is low stability of liquid-type non-aqueous electrolyte by superoxide radical attack. To improve chemical and physical stability of electrolyte, solid-state Li ion conductive materials using polymer or ceramic have been extensively studied.^[2] In particular, solid polymer electrolyte (SPE)^[3] has been the promising medium for Li batteries, for example poly(ethylene oxide) (PEO) with Li salt complex (PEO-based SPE) which has exhibited wide electrochemical window, appreciable stability and reasonable solvation ability for alkali metal salts. In this work, we performed chemical identification of products using a PEO-based SPE incorporated with carbon nanotubes (CNT) electrode after discharge and recharge by XANES. The spectra show that a main discharge product is not the expected Li₂O₂ but a mixture of Li based compounds stemming from side reaction due to SPE decomposition.

実験(Experimental) :

(1) Composite electrode synthesis: The homogeneous, flexible and semi-transparent PEO-based SPE was prepared by a solvent-free procedure using ball-milling and hot-press techniques. The SPE was then merged with the free-standing CNT film by using the same hot-press technique, which resulted in a two-phase membrane having the SPE and the

CNT/SPE. In the CNT/SPE phase, the conductive network of CNT film was coated by the thin PEO-based SPE, which maintained the CNT film pores required for the smooth O₂ gas transport and accommodation of discharge products.

(2) Galvanostatic tests: The Li-O₂ cells were assembled with metallic Li disk (diameter ≈ 12 mm, Honjo) as the anode, CNT/SPE as the cathode/electrolyte. The O₂ gas was then filled with the Li-O₂ cells at atmosphere. Galvanostatic discharge and recharge examinations were conducted in a potential range of 2.0–4.5 V at a current rate of 0.05 mA.cm⁻² using a battery cycler (WonATech WBCS3000) after maintaining the open circuit potential for 3 h. The temperature was kept at 55°C during the measurements using a constant temperature chamber (Isuzu seisakusho). All potentials were referred to Li+/Li.

(2) Characterizations: After discharge and recharge, the cells were disassembled inside glovebox and the CNT/SPE electrodes were conveyed using a custom-made hermetic vessel for XANES spectral measurements for O, C and Li K-edge, performed at BL2 in the SR center of Ritsumeikan University. All samples and references of Li₂O₂ (99% purity), LiOH (98% purity), Li₂CO₃ (99% purity) CH₃CO₂Li (98% purity) and HCO₂Li·H₂O (98% purity) and PEO were loaded directly transferred into the chamber for XANES measurements without air exposure.

結果、および、考察(Results and discussion) :

Fig. 1 shows galvanostatic the 1st cycled discharge-recharge profile at 55°C. The Li-O₂ cell delivers a capacity of ~300 mAh.g⁻¹ at an

average discharge potential of 2.65 V. The recharge potential reaches to ~ 4.5 V at the end of recharge. The capacity of the SPE-employed Li-O₂ cell is lower than the cell with typical liquid-type electrolyte. This is probably due to low conductivity of SPE.

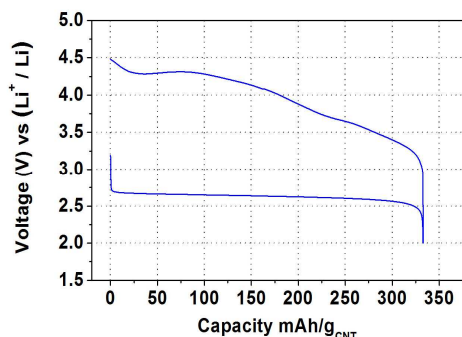


Fig. 1. Electrochemical performance using CNT/SPE composite electrode at $0.05 \text{ mA}\cdot\text{cm}^{-2}$ and 55°C in O₂ atmosphere

Figs. 2–4 display O, Li and C K-edges XANES spectra of as-prepared (black), 1st discharged (1DC, pink) and 1st recharged (1RC, green) CNT/SPE with the TEY mode. The bottom spectra indicate reference powders of LiOH, Li₂O₂, Li₂CO₃, HCO₂Li, CH₃CO₂Li and PEO.

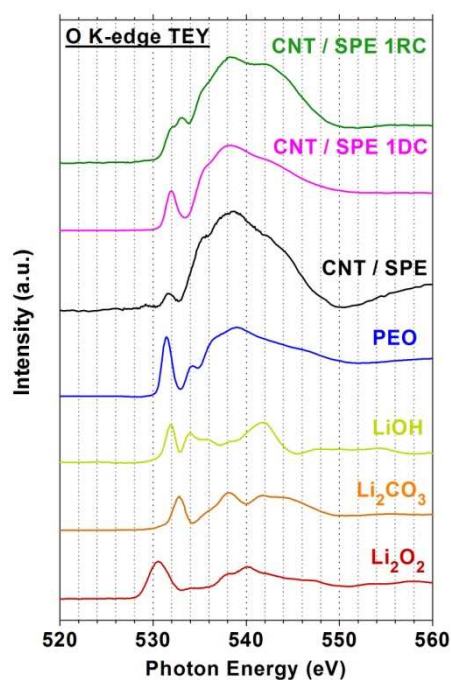


Fig. 2. O K-edge XANES spectra using TEY mode of as-prepared, 1DC, 1RC CNT/SPE and references of PEO, Li₂O₂, Li₂CO₃ and LiOH

The O K-edge spectrum of as-prepared CNT/SPE in **Fig. 2** exhibits ether-correlated peak at 531.5 eV arising from the PEO. At the end of 1DC, such a PEO peak is silence probably due to deposition of discharge product but the new peak

attributed to LiOH at 532 eV is shown. After the 1st recharge, the Li₂CO₃-related peak at 533 eV newly appears in addition to the LiOH peak.

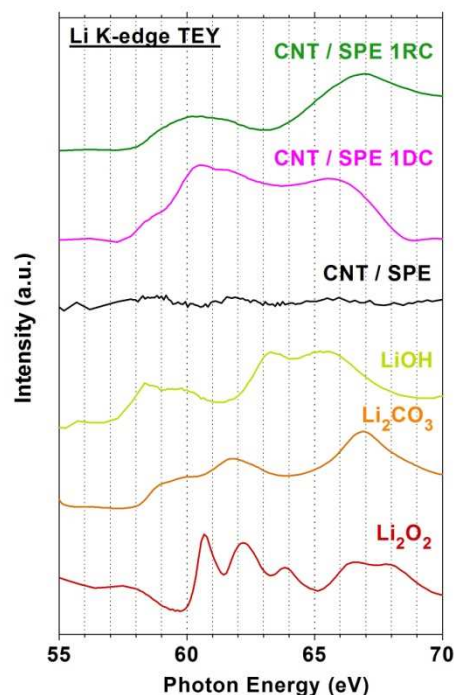


Fig. 3. Li K-edge XANES spectra using TEY mode of as-prepared, 1DC, 1RC CNT/SPE and references of Li₂O₂, Li₂CO₃ and LiOH

The Li K-edge spectra in **Fig. 3** corroborate the O K-edge results. The edge of 1DC CNT/SPE at ~ 57.5 eV arises from the LiOH and that of 1RC at ~ 58 eV is associated to the Li₂CO₃. Interestingly, a sharp peak and broad shoulder at 60–62 eV for the 1DC CNT/SPE are observed, which is not be shown from the LiOH spectrum. It is attributed to the Li₂O₂, as the ideal Li–O₂ reaction product. Consequently, the Li K-edge spectra determine the discharge products to LiOH and Li₂O₂ that probably distributed on the surface.

The C K-edge spectra in **Fig.4** demonstrate additional formation of lithium carboxylates such as formate (HCO₂Li) and acetate (CH₃CO₂Li) for the 1DC and 1RC CNT/SPE as evidenced by appearance of a sharp peak at 288.5 eV. A predominant peak at 285.5 eV for the as-prepared CNT/SPE decreases after 1DC and 1RC caused by deposition of Li compounds.

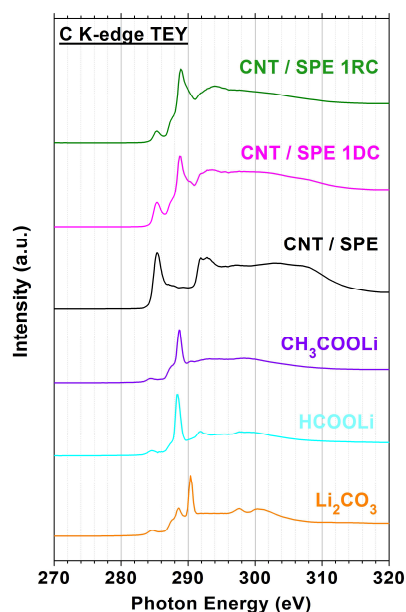


Fig. 3. C K-edge XANES spectra using TEY mode of as-prepared, 1DC, 1RC CNT/SPE and references of Li_2CO_3 , HCO_2Li and $\text{CH}_3\text{CO}_2\text{Li}$.

In summary, XANES spectra reveal that the main discharge product in Li–O₂ cells using SPE is a mixture of Li compounds such as LiOH, HCO_2Li and $\text{CH}_3\text{CO}_2\text{Li}$, which are accumulated in addition to the Li_2CO_3 formed during recharge. This result implies acute parasitic side reaction for the SPE-employed Li–O₂ cell, and also instability of ether-based electrolyte even for liquid type.

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論文・学会等発表（予定）(Articles and meetings)

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