

Investigation of NiO promoter structure in Li–O₂ battery

Misun Hong,^{a,b,c} Misaki Katayama,^d Yasuhiro Inada,^d Hye Ryung Byon^a

^aByon Initiative Research Unit (IRU), RIKEN, Japan

^bDepartment of Chemistry, Pohang University of Science and Technology (POSTECH), South Korea

^cCenter for Artificial Low Dimensional Electronic Systems, Institute for Basic Science, South Korea

^dDepartment of Applied Chemistry, College of Life Sciences, Ritsumeikan University, Japan

The stability of nickel oxide (NiO) during lithium–oxygen (Li–O₂) battery operation is demonstrated by using Ni K-edge X-ray absorption near edge structure (XANES) spectroscopy with fluorescence yield (FY) mode. We fabricate NiO plates that is dispersed in the multi-walled carbon nanotubes network (NiO/CNT) as cathode of the Li–O₂ cell. After 10-times discharge-charge cycles, stable NiO is observed in the NiO/CNT without any peak shift in XANES spectra.

Keywords: NiO, Li–O₂ battery, Ni K-edge XANES.

背景と研究目的: The nonaqueous Li–O₂ battery has been received great attention by virtue of its superior theoretical energy density. However, the current Li–O₂ battery has suffered from poor cycle-ability arising from parasitic side reactions by decomposition of carbon cathodes and aprotic organic electrolytes.[1] In particular, appearance and accumulation of side products such as lithium carbonate (Li₂CO₃) and lithium carboxylates (RCO₂Li, R is the alkyl or hydrogen) is crucial drawback to prevent long-term operation of the Li–O₂ battery.[2],[3]

Here we have used NiO nanoplates incorporation into CNT as a cathode for Li–O₂ cell to sustain stable and long-term discharge-charge cycling. By using Ni K-edge XANES spectroscopy, we have demonstrated stable oxidation state of NiO during 10 cycles.

実験: NiO was prepared via hydrothermal method in the presence of CNT, which formed homogeneously dispersed NiO in the CNT network.

1. Synthesis of NiO/CNT composite

(1) Ni(NO₃)₂•6H₂O of 0.05 M and urea of 0.25 M were dissolved in a mixture of deionized (DI) water and ethanol (1:4 v/v) along with CNT of ~1.5 mg mL⁻¹.

(2) The mixture was transferred to a Teflon-lined autoclave and heated at 80 °C for 14 h.

(3) After cooling down, the suspension was filtered and washed by DI water and ethanol to remove residual reagents.

(4) The dried powder was calcined at 400 °C (ramping rate of 2 °C min⁻¹) for 3 h under Ar flow of 50 sccm.

2. Fabrication of Li–O₂ cells

(1) The NiO/CNT powder was dispersed in ethanol by tip sonication.

(2) The suspension was filtered through glass fiber paper and detached to be free-standing after drying.

(3) The NiO/CNT cathode was assembled into a Li–O₂ cell along with lithium metal anode, 0.5 M LiN(SO₂CF₃)₂ in tetraglyme, and two separator sheets of Celgard and glass fiber.

3. Sample preparation and measurement of XANES for cycled NiO/CNT cathodes

(1) Galvanostatic discharge-charge was conducted repetitively in the Li–O₂ cell at 0.1 mA cm⁻².

(2) After 1st, 5th, and 10th discharge (*n*DC, *n* is the cycling number) and charge (*n*RC) process, the cell were disassembled, washed with acetonitrile, and dried at 60 °C under vacuum—total six cycled cathodes.

(3) The XANES spectra were acquired at the beamline of BL-3 in the Synchrotron Radiation (SR) center of Ritsumeikan University. The cathode samples were prepared by attachment to glass slides and enclosed by Al-laminated packs in the glove box. The XANES spectral measurements were conducted with a Si (220) double crystal monochromator and a step scan of 0.35 eV. The FY mode was applied for the cycled cathodes while the transmission mode was used for air-exposed reference samples of Ni foil, Ni(OH)₂ and NiO powder which we prepared.

結果、および、考察: The nanometer-scaled rock salt crystalline NiO plates were homogeneously mixed with entangled CNTs as shown in microscopic images (Figure 1a–b) and corresponding selected area electron diffraction (SAED) (yellow arrows in Figure 1c). The NiO/CNT cathodes contain 40 wt% NiO measured by thermal gravimetric analysis.

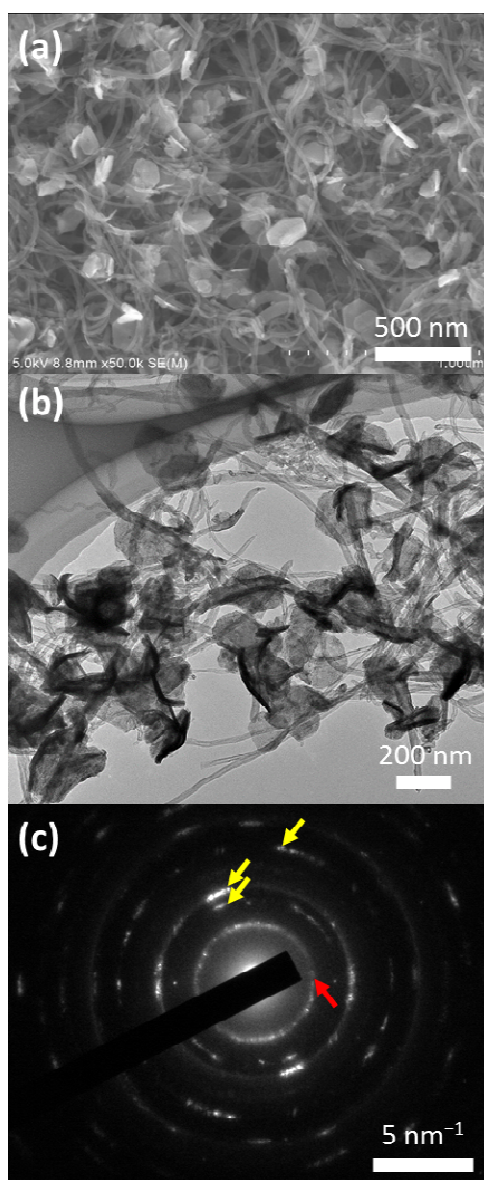


Figure 1. (a) SEM image and (b) TEM image of NiO/CNT. (c) SAED (Selected area electron diffraction) of NiO/CNT cathode film. The red arrow and yellow arrows indicate CNT and NiO, respectively.

The Li–O₂ cells with NiO/CNT cathodes showed high capacity retention and cycle-ability (data are not shown here). This is probably owing to the NiO role to promote elimination of side products such as lithium carbonate/carboxylates during recharge.

During 10-times discharge–recharge cycles in the Li–O₂ cells, the NiO plates in the NiO/CNT cathodes were chemically and structurally stable. The oxidation state of NiO after discharge or charge cycles was investigated using Ni K-edge XANES spectroscopy with the bulk sensitive FY mode. Figure 2 shows reference material spectra of Ni (blue, Ni⁰), NiO (red, Ni²⁺) and Ni(OH)₂ (orange, Ni²⁺), as-prepared NiO/CNT cathode

(green) and the cycled NiO/CNT cathodes after 1st-cycled discharge (1DC), 1st-cycled recharge (1RC), 5DC, 5RC, 10DC and 10RC (black, from bottom to top). The XANES spectra of the cycled NiO/CNT cathodes show an intense white line at ~8346 eV with a half-height energy of ~8340 eV, which are identical to the as-prepared NiO/CNT and NiO reference.

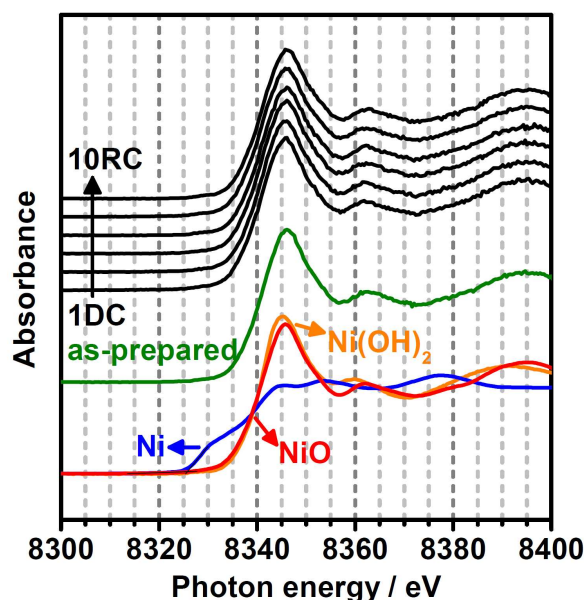


Figure 2. Ni K-edge XANES spectra for as-prepared, 1DC/RC, 5DC/RC and 10DC/RC NiO/CNT cathodes (from bottom to top, black) with the FY mode, and Ni metal (Ni⁰), NiO (Ni²⁺) and Ni(OH)₂ (Ni²⁺) reference powders obtained with the transmission mode.

In conclusion, the NiO plates used for the cathodes in the Li–O₂ cells were stably preserved without chemical and structural change. We expect that stable NiO can retain the Li–O₂ cell performance with improved cycle-ability.

文 献

- [1] Li, F.; Zhang, T.; Zhou, H. *Energy Environ. Sci.* **2013**, *6*, 1125–1141.
- [2] Peng, Z.; Freunberger, S. A.; Chen, Y.; Bruce, P. G. *Science* **2012**, *337*, 563–566.
- [3] Sharon, D.; Etacheri, V.; Garsuch, A.; Afri, M.; Frimer, A. A.; Aurbach, D. *J. Phys. Chem. Lett.* **2013**, *4*, 127–131.