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XANES investigation of side products in Na-O₂ battery

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We report chemical identification of discharge and recharge products of non-aqueous sodium–oxygen (Na–O₂) cell. O, C and Na K-edge XANES measurements reveal that side products are formed.

Keywords: Sodium-oxygen battery, Carbon nanotube, XANES.

背景と研究目的(Introduction) : Metal-oxygen (or metal-air) batteries have been considered as one of promising energy storages to fulfill the increasing demand on high energy density system for applications from portable electronic devices to electric vehicles. Among the metal-oxygen batteries, the non-aqueous sodium-oxygen (Na-O₂) battery is particularly attractive because of its expected low cost and its reasonably high specific energy (~1.1 kWh/kg, which is almost twice of lithium-ion batteries). In addition, the first demonstration of Na-O₂ battery revealed moderate overpotential for both discharge and charge ^[1] unlike the lithium-oxygen (Li-O₂) battery suffering from huge overpotential for charge ^[2]

However, there is little knowledge for Na-O₂ electrochemistry, which is associated with low Coulombic efficiency and poor cycle life in the Na-O₂ battery. ^[1, 3-4]

In this work, in order to gain an understanding about the electrochemical processes involved in Na-O₂, we performed chemical identification of products after discharge and recharge by XANES. The spectra show that several side products are formed which reveals that, despite low overpotentials, side reactions related to electrolyte are possibly also involved in Na-O₂ batteries.

実験(Experimental) :

Galvanostatic tests: The Na-O₂ cells were assembled with metallic Na disk (diameter ≈ 12 mm) as the anode, carbon nanotube (CNT) as the positive electrode and 0.5 M sodium triflate (NaOTf) in diglyme as the electrolyte. The O₂ gas was then filled with the Na-O₂ cells at atmosphere. Galvanostatic discharge and recharge examinations were conducted in a potential range of 1.8–4.3 V at a current rate of 60 mA.g⁻¹ using a battery cyler

(WonATech WBCS3000) after maintaining the open circuit potential for 3 h. The cell was kept at room temperature during the measurements using a constant temperature incubator. All potentials were referred to Na/Na⁺.

Characterizations: After discharge and recharge, the cells were disassembled inside glovebox and the CNT electrodes were conveyed using a custom-made hermetic vessel for XANES spectral measurements for O, C and Na K-edge, performed at BL2 in the SR center of Ritsumeikan University. All samples and references of Na₂O₂, Na₂O, NaOH, Na₂CO₃, CH₃CO₂Na, HCO₂Na and NaOTf 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 The Na-O₂ cells discharge(DC)-recharge(RC) profile is discharge and charge plateau at 2.15 V and 2.35 V, respectively. This demonstrates moderate discharge and charge overpotential in a range of 0.08~0.12 V. SEM observations (inset **Fig. 1**) revealed that cubic products with micrometer size are formed on the CNT and completely decomposed during charge. X-ray diffraction (XRD) demonstrates that the primary discharge product is sodium superoxide crystal (NaO₂). The NaO₂ can be formed at a thermodynamic potential of 2.27 V (Na⁺ + 1e⁻ + O₂ ↔ NaO₂ (E⁰ = 2.27 V vs Na/Na⁺)).

Cyclability tests revealed that full charged cycles (voltage. 4.0 V) lead to very poor cyclability with severe capacity fading (cell failure after 4-5 cycles). However when voltage cut-off is applied for charge (2.6 V or 3.25 V), the performance was remarkably improved, with more than 20 cycles

Online electrochemical mass spectroscopy (OEMS) analysis confirms the 1e⁻ process for both discharge

and charge (up to 80%), where the O₂ gas evolution is predominant. Over 80% charge, the potential drastically increases up to 4.0 V and H₂ and CO₂ start evolving.

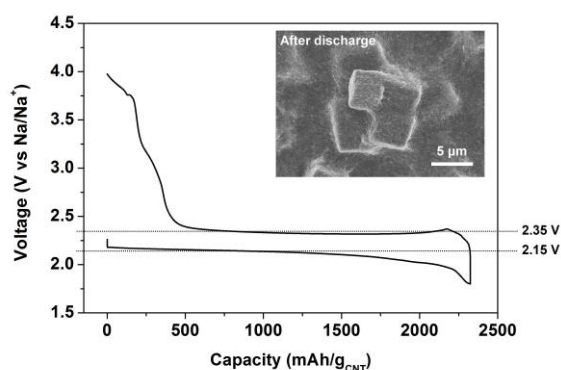


Fig. 1. Galvanostatic discharge-charge curves at room temperature and at a current rate of 60 mA/g. Inset: SEM image of discharge product.

In **Fig. 2**, in the O K-edge spectra, we cannot confirm the presence of NaO₂, since it is not available commercially. However, after 1DC we observed that the peak initially present in the pristine electrode at 531.3 eV is slightly increased and shift to 531.6 eV. This peak is decreased after 1RC. This might be related to the formation and decomposition of NaO₂. Besides, we can clearly see a new peak at 533 eV after three cycling, 3DC and 3RC. By comparing with reference spectra and FTIR data (not shown here), this peak is probably related to Na₂CO₃. The C K-edge spectra show the appearance and disappearance of a clear peak at 288.5 eV after 1DC and 1RC, respectively, while the peak remains after 3DC and 3RC. A small peak at around 284 eV also appears after 1DC, 1RC, 3DC and 3RC. The assignment of these peaks is difficult from the current data. For future work, further analysis using X-ray photoelectron spectroscopy is needed. In summary, XANES spectra reveal that Na₂CO₃ and unknown side products are formed beside NaO₂. This implies that parasitic side reactions occurred during charge and discharge, which drastically affect the cyclability of NaO₂ cells.

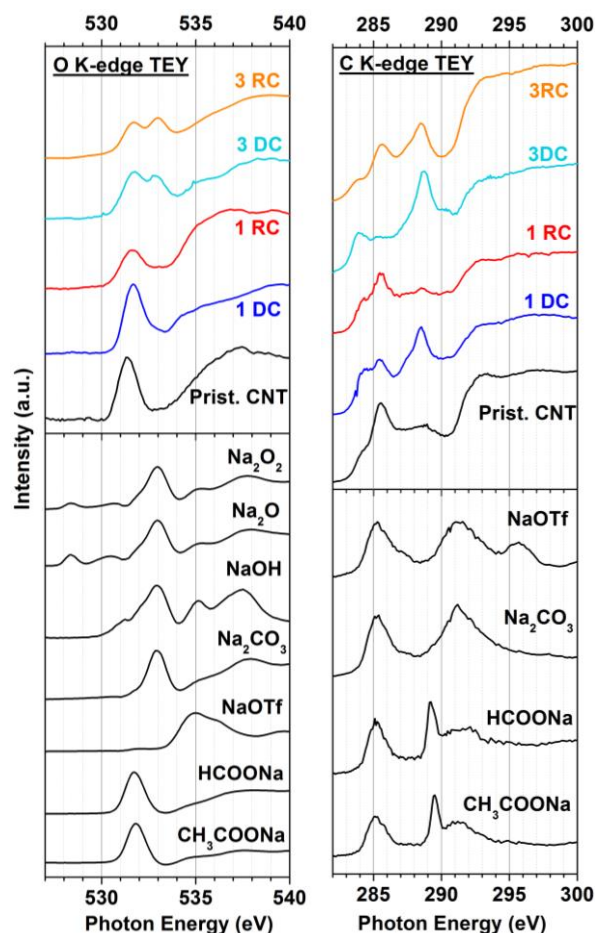


Fig. 2. O K-edge XANES spectra (left) and C K-edge XANES spectra (right) using TEY mode of as-prepared (black), 1st discharged (1DC, blue), 1st recharged (1RC, red), 3rd discharged (3DC, light blue) and 3rd recharged (3RC, orange) CNT electrode (discharge cut-off at 1000 mAh/g) and reference powders of Na₂O₂, Na₂O, NaOH, Na₂CO₃, NaOTf, HCO₂Na and CH₃CO₂Na

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論文・学会等発表 (予定) (Articles and meetings)

N. Bonnet-Mercier and H. R. Byon, 66th Annual Meeting of the International Society of Electrochemistry in Taiwan (Oral Presentation)