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XAFS Analysis for Electrochemical Reduction/Oxidation Processes of ZnO Nanoparticles Supported on Active Carbon

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1. Introduction

As a next-generation rechargeable battery, a redox system that utilizes a conversion reaction of MO_x/M (M: metal element) is being widely studied. In the case of the NiO/Ni system, there are some issues that must be overcome, such as the poor rate property and the low cycle performance.1) In addition, the ZnO/Zn system has once again attracted attention as a low-cost negative electrode system, and the research aimed at improving its performance is being actively conducted.2) Therefore, the purpose of this study was set to elucidate the reaction mechanism of the reduction process of ZnO nanoparticles supported on carbon, which is a model electrode material for the ZnO/Zn negative electrode. The ZnO nanoparticles supported on activated carbon have been prepared by the impregnation method, and the change in the chemical state of the Ni species during the electrochemical reduction/oxidation processes has been analyzed by the XAFS method.

2. Experimental

Zinc(II) nitrate hexahydrate was supported on activated carbon (AC) by the impregnation method under the incipient wetness condition. The obtained powder dried at 70 ˚C was subjected to the calcination at 300 ˚C under air. The formation of ZnO/AC was confirmed by the XRD and XAFS measurements.

ZnO/AC and a PVDF binder were mixed with the mass ratio of 7:3, and the mixture was applied on a Al foil to the thickness of 254 μm. An electrochemical cell was composed of a ZnO/AC electrode, a Li foil as the counter electrode, and a 1 mol dm^{-3} $LiPF_6$ solution as the electrolyte solution. The electrochemical cells were disassembled at some different reduction depth during the first reduction process, and the XAFS measurements at the Zn-K edge were carried out at BL-4 of the SR Center of Ritsumeikan University and BL-12C of Photon Factory (KEK) to determine the chemical state of the Zn species. After the complete reduction of ZnO to Zn, the XAFS measurements were similarly performed during the first re-oxidation process from Zn to ZnO.

3. Results and Discussion

The XANES spectral change during the first reduction process of ZnO/AC is shown in Fig. 1(A). The initial spectrum was consistent with that of ZnO, and the XANES spectrum changed to that of metallic Zn as the electrode voltage decreased. The Fourier transform of the EXAFS part for the final spectrum showed a reduced peak of the Zn–Zn interaction, and it was clarified that the particle size of Zn was reduced by the first electrochemical reduction on AC. The XANES change for the subsequent electrochemical oxidation process is shown in Fig. 1(B). The initial spectrum corresponding to the metallic Zn changed to a ZnO-like spectrum with a white line peak at 9.668 keV, accompanied by a higher energy shift in the absorption edge. Although this spectral change is apparently less than that of the previous reduction process given in Fig. 1(A), the Zn–Zn interaction peak of the Zn metal completely disappeared in the Fourier transform of the EXAFS part at the end of the oxidation process, suggesting the complete conversion from metallic Zn to ZnO. The nearest Zn-O interaction peak corresponding to ZnO existed in the Fourier transform, but the second-neighboring peak of the Zn–Zn interaction was very weak. These findings indicate that the metallic Zn particles that are refined by the first reduction process are oxidized to regenerate the minute ZnO particles at the subsequent oxidation process.

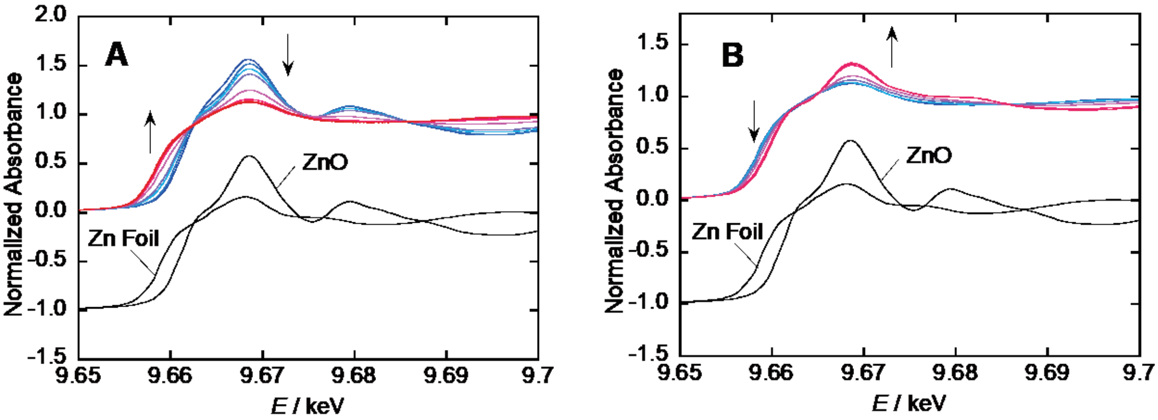

Fig.1 XANES spectral change of the Ni species supported on AC during the electrochemical reduction of ZnO (A) and oxidation of Zn(0) (B). The reference spectra of Zn foil and ZnO are given for comparison.

A linear combination fitting analysis of the XANES spectrum using the Zn foil and ZnO spectra as the standards was performed to obtain the composition change of the Zn species in the electrochemical reduction and oxidation processes. The obtained mole fraction of Zn(0) and ZnO was plotted in Fig. 2 as a function of the amount of specific electricity. It is

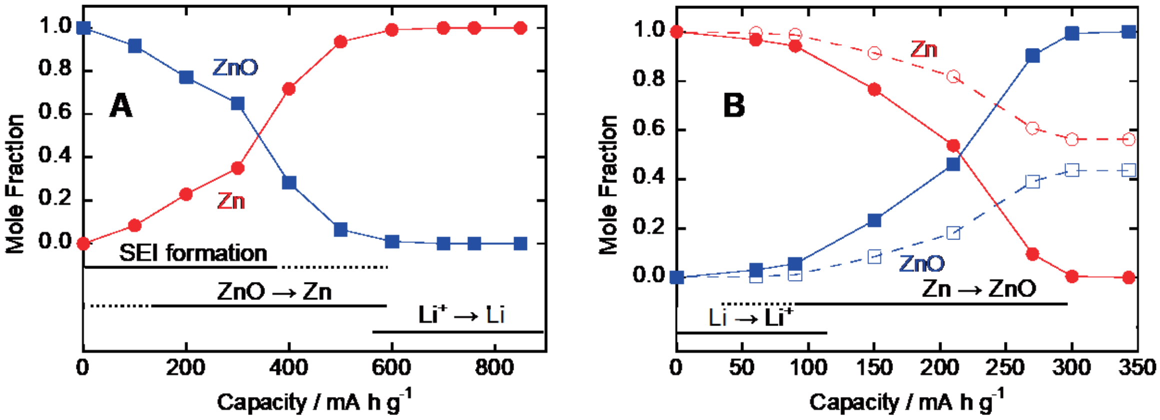

Fig.2 The mole fraction of Zn(0) and ZnO as a function of the amount of specific electricity during the electrochemical reduction (A) and oxidation (B) processes.

clarified that the reduction of ZnO proceeds slowly at the initial stage and then is reduced to Zn(0) at 0.5 V with respect to Li^+/Li in the range of 300 to 500 mA h g^{-1}. The voltage in the initial induction period is also 0.5 V vs. Li^+/Li, and it has been demonstrated that the carbonate compound deposits on the electrode at this stage from the XAFS analysis at the K edge of O in the electrochemical reduction process for NiO.3) The reduction current flowed at a voltage of less than 0.3 V vs. Li^+/Li after the reduction of NiO was completed, and it is considered that the reduction of Li^+ proceeded in the region of more than 600 mA h g^{-1}.

The composition analysis shown in Fig. 1(B) shows that the metallic Zn is maintained up to 100 mA h g^{-1}. The voltage at this state was less than 1 V, and it is considered that the metallic Li generated at the end of the preceding reduction process is being oxidized. The oxidation of metallic Zn proceeded from 100 to 300 mA h g^{-1}, and this amount of electricity was consistent with the complete oxidation of Zn to ZnO. The oxidation of Zn/AC proceeded in the voltage range of 1.0 to 1.5 V vs. Li^+/Li.

4. Conclusion

In this study, the chemical state change of ZnO/AC was clarified using the XAFS method during the electrochemical reduction/oxidation processes. It has been clarified that the induction stage is required for the reduction of ZnO and the particle size is reduced after the reduction.

References

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