

Preparation Conditions of Nickel Particle Supported on Lithium Iron Phosphate for Its Carbon Modification Treatment

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The preparation process of metallic Ni(0) particles supported on LiFePO₄ was analyzed using the *in-situ* XAFS technique in order to produce the carbon nanotube on LiFePO₄ by methane decomposition reaction catalyzed by metallic Ni(0) for its utilization as an active material of a lithium ion battery. The Ni species was supported on LiFePO₄ by the impregnation method. The LiFePO₄ was oxidized to FePO₄ during the calcination process. The *in-situ* XAFS analysis for the reduction process revealed that LiFePO₄ was regenerated at the temperature range between 380 °C and 490 °C. In this reduction process, the supported Ni species was changed from NiO to metallic Ni(0). This study achieved to find out the appropriate preparation conditions of the metallic Ni(0) particle on LiFePO₄.

1. Introduction

A performance improvement of compact secondary batteries, which can operate with the ability of the reversible charge and discharge, has been extensively conducted to achieve the advancement of portable electronic devices. The lithium ion secondary batteries (LIBs) have attracted much attention because of their energy density and cycle life. The material development for LIBs is an important issue to develop the new technologies for high performance secondary batteries. The active material and the electrolytes have been widely investigated to find out the potential compound with the improved performance, and it has been first reported in 1997 that LiFePO₄ has a potential to be used as the active material of the positive electrode with the thermal stability, the good cycle characteristics, and the high capacity of 169 mA h g⁻¹ [1]. However, it has a weak point for the operation with a large current, and the discharge potential is dropped when it is discharged at the high rate. The enlarged polarization for the high-rate operation is related to its low electrical conductivity (10⁻⁹–10⁻¹ S cm⁻¹). The refinement of the LiFePO₄ particle [2] and the surface coating of the LiFePO₄ particle with the conducting carbon [3] have been attempted to improve the electric performance.

An addition of the conducting material, such as carbon powder, into the active material is the conventional method to compensate the low electrical conductivity, because it can reduce the internal resistance of the electrode and suppress the potential difference between the charge and discharge processes. However, it is required that the amount of carbon in the electrode is minimized, because the addition of carbon causes a decrease in the energy density per weight. It is also reported

that the shape of the carbon particle used as a conductive additive and its particle size influence the charge and discharge characteristics [4,5]. The control of the condition of carbon is therefore important to achieve the high performance for LIBs. The carbon nanotube (CNT) is one of the effective candidates of that purpose, because it has larger surface area and higher conductivity rather than those of carbon black and acetylene black. However, there has been little study done concerning the accurate evaluation on the effect of CNTs as a conductive additive in the LIBs.

It has been reported that the supported Ni catalyst has an activity for the methane decomposition reaction shown in eq (1), and the CNT is formed as the reaction product [6].



There are various preparation methods for the supported Ni catalyst, and the impregnation method is the simplest preparation method. A Ni precursor salt such as Ni(NO₃)₂ is deposited on a supporting material from the aqueous solution, and the precursor is decomposed to NiO by the calcination treatment. After that, the metallic Ni particles with the catalytic activity for the methane decomposition are formed by the reduction treatment with a reducing gas such as H₂.

In this research, the optimal conditions for the preparation of metallic Ni particle supported on LiFePO₄ will be discussed in order to generate the CNTs on the surface of the LiFePO₄ particle as the active material of LIBs with excellent performance. The knowledge of the catalyst preparation will be applied to form the Ni precursor on the LiFePO₄ particle, and then it is necessary to reduce the NiO particle, which is obtained by the calcination treatment, without any modification to the structure of LiFePO₄. Therefore, in this study, the

preparation of the Ni catalyst supported on LiFePO_4 ($\text{Ni}/\text{LiFePO}_4$) has been tested using the above mentioned method, and the chemical state change of the Fe and Ni species has been analyzed during the temperature-programmed reduction (TPR) process after the calcination treatment in order to establish the preparation conditions of $\text{Ni}/\text{LiFePO}_4$.

2. Experimental

The powder of LiFePO_4 was added in an aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and the mixture was stirred for 1 h. After drying at 60°C for 72 h to prepare the Ni(II) nitrate salt supported on LiFePO_4 , and the calcination was carried out at 300°C for 3 h in air. The obtained powder was used as the starting sample for the *in-situ* XAFS experiments described below. The amount of supported Ni species was set to be 20 wt%.

The XAFS measurements were carried out at BL-9C of the Photon Factory (High Energy Accelerator Research Organization) on the basis of the preliminary experiments performed at BL-3 of the SR Center (Ritsumeikan), which were necessary to decide the experimental conditions. The *in-situ* XAFS measurements were performed at the Ni K and Fe K edges during the TPR process of the sample after the calcination. The XAFS spectra were recorded in the X-ray energy range from 6606 to 9432 eV including two absorption edges. The amount of measurement sample was calculated based on the absorption coefficient estimated by the composition of all constituent elements. The starting sample was diluted by boron nitride, and the mixed powder was packed in a sample holder made of glass. The glass reaction cell was used and heated to 600°C at $4^\circ\text{C}/\text{min}$ under a flow of 10 vol% H_2 balanced by He. The heating treatment was temporarily stopped at 350°C and 370°C , and several XAFS measurements were carried out to monitor the spectral change.

3. Results and Discussion

Figure 1 shows the XANES change observed at the Ni K edge during the TPR process. The initial spectrum was identical to that of the reference NiO, and it was found that the calcination treatment in air at 300°C converted the deposited Ni(II) nitrate to NiO. The X-ray absorbance at the white line peak was decreased with the increasing temperature, and the absorption edge was shifted to the lower energy side during the TPR process. The NiO species was reduced by H_2 , and the absorption edge at 450°C was in agreement with that of Ni metal. After that, a slight spectral change was observed in the temperature range from 480 to 600°C as shown in Fig. 1(b). The final XANES

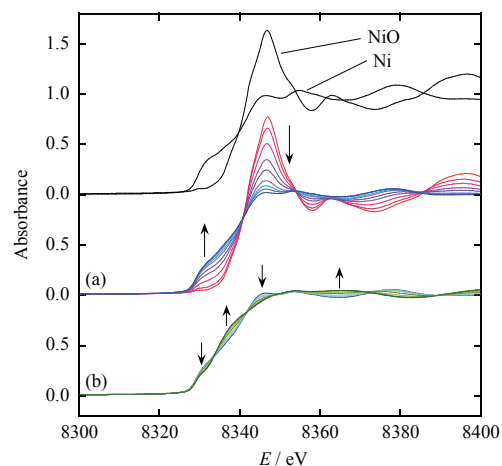


Fig. 1 XANES change at the Ni K edge during the TPR process of the sample after the calcination. The spectra were separately shown in the temperature range from 27°C to 480°C (a) and from 480°C to 600°C (b).

spectrum was clearly different from that of Ni metal, although the absorption edge energy indicated that the valence of the Ni species was zero. It was suggested that the Ni metal converted to the alloy with the reduced Fe species as discussed later.

The absorbance change at 8347 eV is shown in Fig. 2 as a function of temperature. A drastic change started at 350°C , and it continued until *ca.* 500°C . The absorbance at 8332 eV changed similar to that at 8347 eV with the opposite direction, whereas it was turned off at *ca.* 500°C .

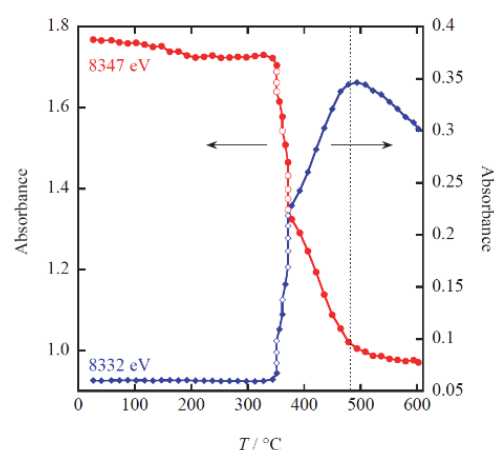


Fig. 2 Absorbance change at 8332 eV (blue) and 8347 eV (red) during the TPR process of the sample after the calcination. The results measured without the temperature change are plotted using the open marks.

This two-step change indicated that the initial NiO species was first converted to Ni metal and it was further changed to the FeNi alloy at above 500 °C, because the final XANES spectrum was approached to that of the FeNi alloy prepared independently. Because the change at 8332 eV was not completed at 600 °C, the alloy was not formed quantitatively.

The Fourier transform functions observed at three characteristic temperatures, *i.e.*, 27 °C, 480 °C, and 600 °C, are shown in Fig. 3. The shape of the initial sample before TPR was the same as that of NiO. The all peaks of NiO were completely replaced with those of Ni metal at 480 °C. Furthermore, the shape at 600 °C was clearly different from that of Ni metal to indicate the partial formation of the FeNi alloy phase.

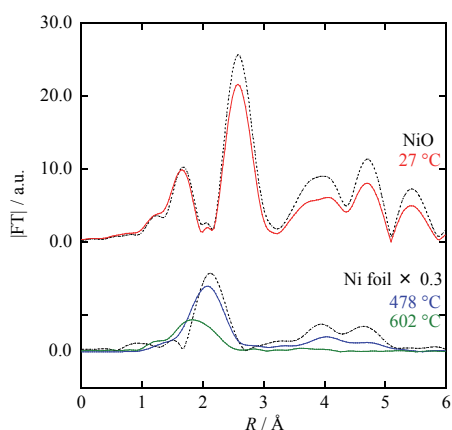


Fig. 3 Fourier transform functions at three temperatures during the TPR process compared with those of reference samples.

Figure 4 shows the XANES change observed at the Fe K edge during the TPR process. The comparison with the reference samples revealed that the initial state after the calcination was reasonably assigned to FePO₄. Therefore, LiFePO₄ was converted to FePO₄ at the calcination process, and it was thus speculated that Li⁺ existed as Li₂O or Li₂CO₃ in the sample (*vide infra*). The absorption edge was shifted to lower energy side, and it was found that the XANES spectrum at 380 °C was perfectly in agreement with that of LiFePO₄. It was revealed that FePO₄ was reduced to LiFePO₄ with the incorporation of Li⁺ during the TPR treatment. It was concluded that the electrochemically active material, LiFePO₄, was regenerated by the reduction treatment of the sample after the calcination, in which LiFePO₄ was decomposed to the mixture of FePO₄ and the Li compound. However, the further increase of temperature lead the regenerated LiFePO₄ species to be reduced. The absorbance at the white line peak of LiFePO₄ (7124 eV) was decreased at above

480 °C, and the absorption edge further shifted to the lower energy side. The final energy of the absorption edge was consistent with the metallic Fe species, but the shape of the XANES spectrum at 600 °C was different from that of Fe metal. In considering the results observed at the Ni K edge, a part of the regenerated LiFePO₄ species was converted to the FeNi alloy phase at above 480 °C.

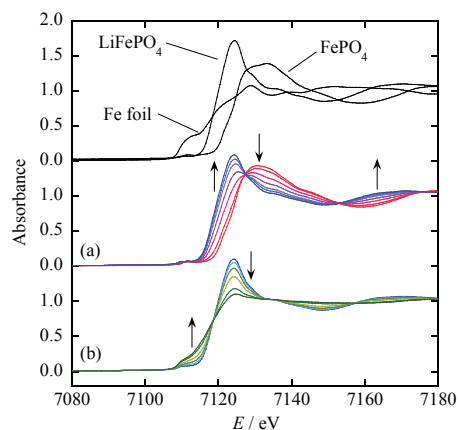


Fig. 4 XANES change at the Fe K edge during the TPR process of the sample after the calcination. The spectra were separately shown in the temperature range from 27 °C to 380 °C (a) and from 450 °C to 600 °C (b).

The X-ray absorbance change at 7125 eV and 7133 eV is plotted in Fig. 5 as a function of temperature during the TPR process. It was revealed that the regeneration of LiFePO₄ was started at *ca.* 240 °C and was completed at 380 °C. The absorbance at the white line peak of LiFePO₄ (7124 eV) was decreased at above 480 °C. The present *in-situ* XAFS analysis clarified that the LiFePO₄ species could exist at the temperature

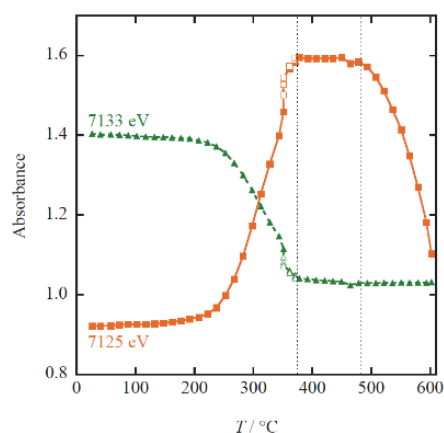


Fig. 5 Absorbance change at 7125 eV (orange) and 7133 eV (green) during the TPR process. The results measured without the temperature change are plotted using the open marks.

between 380 °C and 480 °C during the TPR process.

As seen in Fig. 6, the Fourier transform function of the initial sample was consistent with that of FePO_4 , and the TPR treatment at 380 °C converted it to LiFePO_4 . These results strongly supported that LiFePO_4 was decomposed to FePO_4 by the calcination process and the LiFePO_4 was regenerated by the TPR treatment. The final Fourier transform function implied the formation of the FeNi alloy due to the excess reduction of LiFePO_4 .

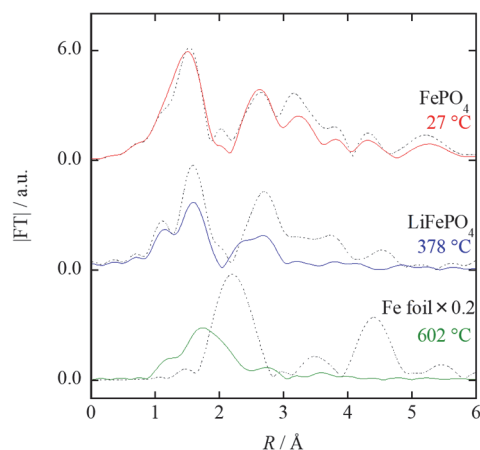


Fig. 6 Fourier transform functions at three temperatures during the TPR process compared with those of reference samples.

A schematic diagram of the reactions during the TPR process is illustrated in Fig. 7. The Fe(II) center in LiFePO_4 is oxidized to Fe(III) by the calcination in air accompanied by the delithiation to form FePO_4 , and the NiO species supported on FePO_4 is formed before the TPR process. Because LiFePO_4 is regenerated during the TPR process at

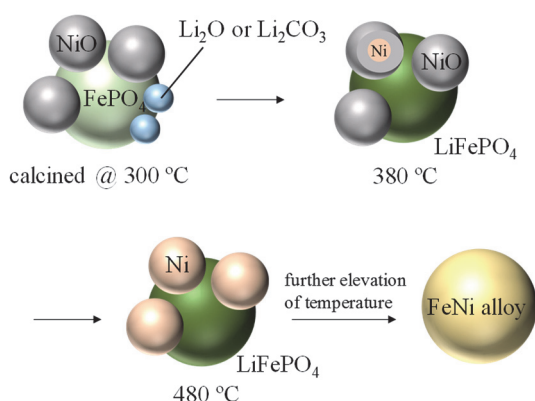


Fig. 7 Schematic diagram of the reactions during the TPR process of the sample after the calcination.

the temperature range between 380 °C and 480 °C, the released Li^+ exists as Li_2O or Li_2CO_3 in the sample after the calcination. The reduction of the supported NiO species on LiFePO_4 is successfully driven by the TPR process at the temperature range between 380 °C and 480 °C. The further elevation of temperature is not permitted because of the excess reduction of the electrochemically active LiFePO_4 .

4. Conclusions

The present *in-situ* XAFS analysis has achieved to find out the preparation conditions of the metallic Ni particle supported on LiFePO_4 . It has been clarified the precise temperature control between 380 °C and 480 °C is necessary to form the target Ni/ LiFePO_4 species, because both of the insufficient and excess temperatures lead to the oxidized and reduced state of LiFePO_4 , respectively, which is the active material for LIB. The further elevation of temperature causes the reduction of both Ni and Fe, and the FeNi alloy species is finally generated. This study has presented the certification to execute the methane decomposition reaction, which is driven by the Ni catalyst supported on LiFePO_4 . The available LiFePO_4 particle modified by CNT will possess the good electrical conductivity, and it will contribute to improve the LIB performance.

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