

Thermochemical Reduction Process of Metal Chlorides Supported on Silica as a Reference for Electrochemical Reduction in Battery Electrodes

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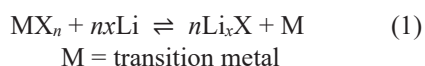
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We have studied the thermochemical reduction processes in which NiO, NiCl₂, CuO, and CuCl₂ supported on silica are reduced to metal particles by hydrogen gas analyzed by means of *in-situ* XAFS method. The reduction temperatures for oxides and chlorides are nearly identical for both metal elements, and the Ni compounds require higher temperature conditions to be reduced. These data on reduction temperature indicate the difference in thermal stability between the metal(II) compound and metal(0) states, and are a good reference when proceeding the reduction reaction electrochemically in the battery electrode. In fact, it has been clarified that the redox potential between NiO and metallic Ni is almost the same as that of the NiCl₂/Ni pair, and that the redox reaction of CuCl₂ proceeds at a positive potential of about 2 V compared to NiCl₂.

1. Introduction

Improving the performance of secondary batteries is important as one of the approaches to the energy and environmental issues in modern society. As one of the possibilities for solving those problems, extensive research has been conducted on an electrode reaction system that allows multi-electron transfer which exceeds the capacity performance of lithium-ion batteries. That is a conversion battery system that uses metal halides or metal oxides as electrode active materials and utilizes the process of converting them into metals. A number of transition metal oxides [1-10] and halides [11-23] have been extensively characterized as the conversion battery electrodes. Most of these studies focus on the evaluation of battery characteristics, and the clarification of the chemical state of the metal species in electrodes is essential for understanding the charge/discharge characteristics.

For electrodes using oxides or halides (MX_n) as the active material, it is considered that the migration of anions (X^{x-}) ensures the charge of the metal species. In the case of a battery system using Li metal as the counter electrode, the charge/discharge reaction is generally represented by eq. (1).



Such battery system is accepted as the anion shuttle battery that utilizes the conduction process of an anion instead of lithium cation for the conventional lithium-ion batteries. In this battery system, the electrode is also expected to be a mixture of an active material, a conductive additive, and a binding material. In addition to the movement of anions, the conduction of electrons is also required in the electrode composite, and it is thus necessary to ensure electron conduction pathways within the electrode mixture. Because these factors affect the charge/discharge characteristics of a

battery, the evaluation of the charge/discharge characteristics is insufficient as information for improving the battery performance. Many studies have been conducted on the electrode reactions using *operando* XAFS technique, but in order to understand the factors that govern the chemical state change of active materials, it is necessary to study the migration behavior of anions under conditions in which the electron conduction does not affect the chemical conversion. It is possible to understand the state change of metal species without being restricted by electronic conduction by investigating redox reactions of metal species with gas molecules.

To understand the chemical state changes of catalytically active species during the synthesis and reaction processes of heterogeneous catalysts, we have conducted *in-situ* XAFS analyses for the processes in which transition metal species change their oxidation states in the solid state by the redox reactions with gaseous reagents [24-27]. By measuring XAFS with increasing temperature, it is possible to know the temperature at which the metal species change their chemical states. Although the temperature is slightly affected by the particle size, it is possible to find the characteristics of the chemical state change for each metal species. In this study, we used silica as a stable oxide support over a wide temperature range and analyzed the temperature of the reduction process of oxides and chlorides of Ni and Cu supported on silica. Comparison of their reduction temperatures reveals relative differences in the conversion behavior from oxides or chlorides to metals. By comparing the results of the thermochemical conversion with the potential in the electrode reaction of the conversion battery, we will clarify the relationship between the conversion temperature observed in the thermochemical process and the electrochemical behavior.

2. Experimental

The powder samples of CuO, CuCl₂, NiO and NiCl₂ supported on SiO₂ (JRC-SIO-10) were prepared by the impregnation method for the *in-situ* XAFS measurements of the thermochemical reduction process. For the chlorides, an aqueous solution of each chloride hexahydrate was used for the impregnation under the incipient wetness conditions, followed by drying at 60 °C (Cu) or 80 °C (Ni). The powder of metal oxides was obtained by the incipient wetness impregnation using each metal nitrate as a precursor followed by the calcination at 600 °C in air.

The *in-situ* XAFS experiments in the transmission mode were carried out at BL-3 of the SR center (Ritsumeikan Univ.) and at BL-9C of the Photon Factory (KEK). The XAFS measurements were carried out at the Ni and Cu K edge during the temperature-programmed reduction (TPR) process under the 10 vol% H₂ gas flow diluted by He with the total flow rate of 100 cm³/min. The sample powder was mounted in a quartz ring and was set in the flow-type observation cell, and was heated with the rate of 10 °C/min.

The powder of NiO supported on acetylene black (NiO/AB) was prepared by the conventional impregnation method as the electrode active material. An aqueous solution of nickel(II) nitrate was added in the AB powder and dried at 70 °C, which was calcined in air for 1 h at 300 °C to convert to NiO. The powders of NiCl₂ and CuCl₂ supported on active carbon (NiCl₂/AC and CuCl₂/AC) were prepared by the similar impregnation method using an aqueous solution of each chloride salt. A mixture slurry of the synthesized powder and a binder polymer (polyvinylidene difluoride) was applied on a current collector foil to prepare the electrode sheet. The electrochemical cell was assembled using the prepared electrode sheet, a Li foil as the counter electrode, a porous polypropylene film as the separator, and 1 mol dm⁻³ LiPF₆ solution dissolved in a mixture of ethylene carbonate and diethyl carbonate. The electrochemical cell was used to evaluate the charge-discharge properties of the prepared active materials. Because the prepared electrode was operated with respect to the Li counter electrode, the discharge operation corresponds to the reduction process of the active material.

3. Results and Discussion

3.1. Thermochemical Reduction Process

Figure 1(A) shows the XANES spectral change during the temperature-programmed reduction process of the CuCl₂ species on SiO₂ by gaseous H₂. Because the impregnation was performed using an aqueous solution of CuCl₂, the initial spectrum was consistent with that of the dihydrate. The spectrum changed to that of anhydrous CuCl₂ by 75 °C, and the hydrate

water molecules were desorbed at elevated temperature in dry H₂. The anhydride species was maintained with the subsequent temperature rise, and the absorption edge then shifted to lower energies above 220 °C, and a white line peak appeared at 8.982 keV. The XANES spectrum with a peak at 8.982 keV observed around 300 °C was in good agreement with that of the reference sample CuCl, suggesting the progression of eq. (2). When the temperature was further increased, the peak at 8.982 keV disappeared and changed to the XANES spectrum of metallic Cu with a shoulder structure around 8.978 keV. The reduction of CuCl to metallic Cu represented by eq. (3) proceeded at around 330 °C.

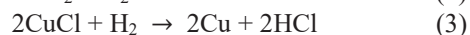


Figure 1(B) plots the X-ray absorbance as a function of temperature at 8.992 keV and 8.982 keV, which are the white line peak energy of CuCl₂ and CuCl, respectively. As can be clearly seen, the intermediate state of the reduction process, CuCl, is formed at 285 °C, and the Cu species are converted to CuCl quantitatively.

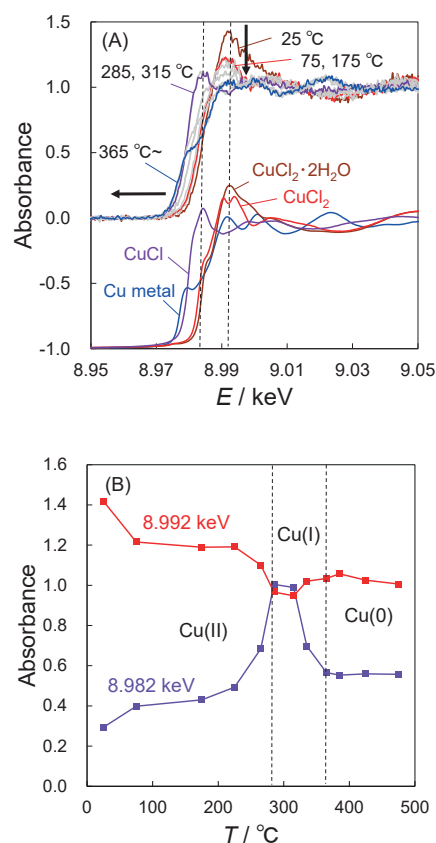


Fig. 1 XANES spectra (A) and X-ray absorbance change (B) measured at Cu K edge during the temperature-programmed reduction process of CuCl₂ on SiO₂.

The results of *in-situ* XAFS analysis of the temperature-programmed reduction process of CuO/SiO₂ have been previously reported [28]. As in the case of CuCl₂, the reduction process from CuO to metallic Cu goes through Cu₂O or Cu(I) as a transient state. However, there is a difference in the stability of the Cu(I) state, and the reduction of Cu₂O to metallic Cu proceeds without producing Cu₂O quantitatively. In CuCl₂, two-step one-electron reduction proceeds sequentially, while in CuO, two-electron reduction to metallic Cu tends to proceed easily. The thermochemical reduction of CuO to metallic Cu by H₂ gas proceeds in the temperature range of 270 to 340 °C, and Cu₂O is most abundant (about 30 %) at 300 to 320 °C [28]. The temperature at which the reduction proceeds is almost the same for CuCl₂ and CuO, and thus it can be interpreted that the reduction characteristics of both are equivalent. This fact predicts that those chemical species will be reduced at essentially the same potential when CuCl₂ and CuO are electrochemically reduced.

The XANES spectral change during the temperature-programmed reduction process of a sample in which NiCl₂ is supported on SiO₂ by H₂ gas is given in Fig. 2(A). The initial state was the nitrate salt of hexahydrated Ni(II) ion, and its characteristic intense white line decreased the absorbance up to 150 °C. The XANES spectrum at that temperature was in good agreement with anhydrous NiCl₂, and the hydrated water molecules were desorbed by increasing the temperature in a dry gas atmosphere. With subsequent temperature rise, the white line of NiCl₂ disappeared and the absorption edge shifted to lower energy, finally matching the spectrum of metallic Ni. The two-electron reduction from NiCl₂ represented by eq. (4) proceeded in one step.

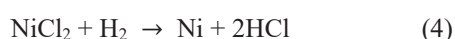


Figure 2(B) shows the change in X-ray absorbance as a function of temperature at 8.342 keV, which is the white line peak of NiCl₂, and at 8.332 keV, where only metallic Ni has the absorbance. Anhydrous NiCl₂ formed above 150 °C was found to convert to metallic Ni at 350–400 °C.

The reduction process of NiO on SiO₂ was previously discussed in terms of the effects of the NiO loading and the particle size [24,26]. The reduction of NiO, which is strongly stabilized at the SiO₂ interface, requires a high temperature of 550 to 650 °C, whereas the reduction temperature of NiO without such stabilization is 300 to 400 °C. As the reduction temperatures of CuCl₂ and CuO were similar, it can be pointed out that the reduction temperatures of NiCl₂ and NiO are equivalent, suggesting the similarity of their electrochemical properties.

The Ni(II) salts were completely converted to Ni(0)

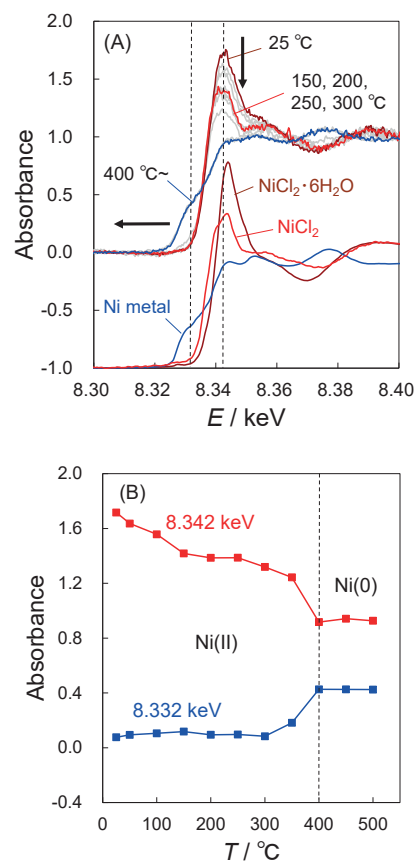


Fig. 2 XANES spectra (A) and X-ray absorbance change (B) measured at Ni K edge during the temperature-programmed reduction process of NiCl₂ on SiO₂.

above 400 °C. On the other hand, the Cu(I) salts were reduced to Cu(0) above 370 °C, and the reduction of the Cu(II) salts to Cu(I) were completed at 280 °C. The comparison between the Ni and Cu species reveals that the Ni compounds require higher temperature conditions to be reduced both for chlorides and oxides. It is a reaction between the solid-phase particles of metal compounds and the gaseous molecules, and it is considered that the diffusion process of gas-phase molecules does not affect the dynamics of the entire reaction. Therefore, the thermochemical reaction temperature with H₂ gas presented in this study is a good reference for understanding the driving force of chemical state conversion in those metal species.

3.2. Electrochemical Redox Process

Figure 3 shows the charge-discharge curves of electrodes with CuCl₂/AC, NiCl₂/AC, and NiO/AB as the active material for an electrochemical cell with a Li metal counter electrode and a 1.0 M LiPF₆ solution as an electrolyte. Since all +2 species are the starting state, the cell was initially operated in the direction of reduction. In all batteries, a capacity exceeding the theoretical capacity was observed during the initial

reduction (discharge) process. This was due to the generation of the solid electrolyte interphase (SEI) required for advancing oxidation-reduction of the active material particles [29-33]. The initial discharge process is an aging process of the battery and is not included in Fig. 3. After the metal(II) species were completely reduced in the first discharge process, reversible charge-discharge proceeded with almost constant capacity. A set of charge-discharge curves during the reversible cycles was given in Fig. 3. The metal species were oxidized and reduced at the charge and discharge processes, respectively.

As is clear from Fig. 3, the charge-discharge curves of the NiCl_2/AC and NiO/AB electrodes have very similar potentials for their electrochemical redox processes, indicating that the redox potentials of both NiCl_2/Ni and NiO/Ni pairs are equivalent. For these electrodes, the reduction of NiCl_2 or NiO to Ni proceeded at voltages of 1.7 to 0.8 V vs. Li^+/Li , and the reverse reaction proceeded at 1.2 to 2.2 V vs. Li^+/Li . regarding the oxidation reaction from metallic Ni , it is surprising that they proceed at the same voltage although the generated species are different between NiCl_2 and NiO . Oxide ions released from NiO at the discharge process are unstable as the single ion and are expected to remain in the electrode together with counter ions such as Li^+ supplied from the electrolyte solution. Chloride ions generated at the discharge process of NiCl_2 may be eluted into the electrolyte, but because they are reversibly cycled after the succeeding charge process, it is possible that they remain in the electrode in the same way as oxide ions. The analysis of the thermochemical reduction process showed that the reduction properties of NiCl_2 and NiO are essentially similar. The reduction potentials of NiCl_2 and NiO were similar in the electrochemical reduction process. The electrochemical oxidation process also proceeded at the same potential when counter ions (oxide ions or chloride ions) were present in the

electrode that were taken up when the Ni metal was oxidized.

The redox process of the NiCl_2/Ni pair proceeded around 1.5 ± 0.5 V vs. Li^+/Li , whereas the CuCl_2/Cu pair proceeded in the more positive potential region by about 2 V. As shown in the analysis of the thermochemical reduction process, the reduction of NiCl_2 requires higher temperature conditions than CuCl_2 , and it is thus difficult to be reduced. This trend was also observed when NiCl_2 and CuCl_2 were electrochemically reduced. The more positive potential of the CuCl_2/Cu pair than the NiCl_2/Ni pair was consistent with the difference in the easiness of the chloride-to-metal reduction process. Based on the results above mentioned, it is expected that the redox process of the CuO/Cu pair will proceed in the corresponding potential range to that of NiO/Ni when the charge-discharge characteristics are evaluated for an electrode using CuO as an active material.

4. Conclusion

In this study, the thermochemical reduction processes for NiO , NiCl_2 , CuO , and CuCl_2 supported on silica by gaseous H_2 were analyzed by means of *in-situ* XAFS method. It was found that the reduction temperatures for oxides and chlorides were nearly identical for both metal elements, and the Ni compounds require higher temperature conditions to be reduced. The obtained thermochemical reduction temperature by H_2 gas is a good reference for understanding the driving force of chemical state conversion. The electrochemical measurements for the CuCl_2/AC , NiCl_2/AC , and NiO/AB electrodes clarified that the redox potential of the NiO/Ni pair was almost the same as that of NiCl_2/Ni , and that the redox reaction of CuCl_2 proceeded at a positive potential compared to NiCl_2 . This study found a good correlation between the reaction temperature in the thermochemical reduction process and the potential in the electrochemical redox process. This study revealed that the reaction temperature of the thermochemical process is a good reference for clarifying the effects of complex factors on the redox potential for the battery electrode.

Acknowledgements

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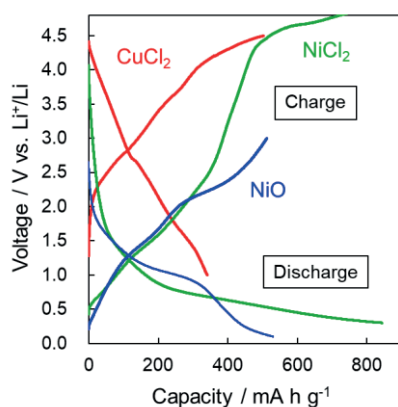


Fig. 3 Charge-discharge curves of the CuCl_2/AC (red), NiCl_2/AC (green), and NiO/AB (blue) electrode.

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