Cu K- and L-edge XAFS Analysis on Conversion Process between Copper Chloride(II) and Metallic Copper

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The electrochemical process of $CuCl_2$ supported on active carbon (AC) was analyzed by the XAFS measurements at the Cu K- and L-edge. It was clarified that a part of $CuCl_2$ was reduced to metallic Cu by the galvanic corrosion before the first discharge process. The XAFS analyses clarified that the remaining $CuCl_2$ was reduced during the discharge process up to 1.0 V vs. Li^+/Li and that $CuCl_2$ was recovered by the charge process up to 4.5 V vs. Li^+/Li. This study demonstrates the reversible redox reaction of $CuCl_2/Cu$ pair on AC and its reasonable applicability to an active material of the chloride shuttle battery system.

1. Introduction

Lithium-ion batteries (LIBs) are commonly used as a power source for small electronic devices such as mobile phones and laptop computers, and recently, many studies have been carried out to develop next-generation batteries for electric vehicles [1]. The current LIBs using the lithium-ion extraction/insertion reaction show the satisfactory and safety charge/discharge cycles, however, the achievable energy density is limited due to the weight and volume of the carbon material added to achieve the electronic conductivity.
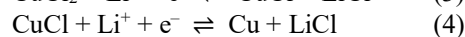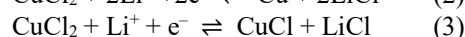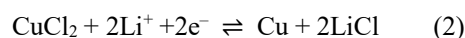
One of the solutions for the energy problem is to use a halide ion (X^-) transfer reaction which can provide a high capacity at the high electric potential and may be anticipated to become an excellent active material of rechargeable batteries. A general formula of the X^--ion transfer reaction between MX_n and Li to form M and LiX is given by equation (1).
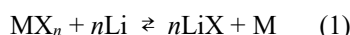
$$MX_n + nLi \rightleftharpoons nLiX + M \quad (1)$$
M = Transition metal (Cu, Ni, Co, Fe, Mn, etc.)
n = Oxidation state of M

It is known that the rechargeable battery system is achieved by using some combinations of M and X. The battery system based on the conversion reaction between MX_n and M is expected to realize much higher energy density required for electric vehicles as well as small electronic devices. Such battery system is accepted as the anion shuttle battery that utilizes the conduction process of an anion instead of lithium ion. The metal species is responsible for the transfer of electrons for the anion shuttle battery, and the anions are conducted in an electrolyte solution. Many metal halides are candidates for cathode and anode materials. For example, for an anion shuttle battery using $CuCl_2$ as an active material of the cathode and the electrolyte containing Li^+, the charge/discharge reaction is expressed by equation (2), and it is divided into two elementary steps of equations (3) and (4).

$$CuCl_2 + 2Li^+ + 2e^- \rightleftharpoons Cu + 2LiCl \quad (2)$$
$$CuCl_2 + Li^+ + e^- \rightleftharpoons CuCl + LiCl \quad (3)$$
$$CuCl + Li^+ + e^- \rightleftharpoons Cu + LiCl \quad (4)$$

The theoretical capacity of equation (2) is 399 mA h g^{-1}, which is larger than those of typical LIB cathode materials of transition metal oxides containing lithium [2-5]. However, it is suggested that transition metal chloride may dissolve in nonaqueous electrolyte solution and a side reaction may proceed during the operation of the chloride shuttle battery [6-8]. It is also reported that the reversible conversion reactions proceed by suppressing the dissolution of metal halides in electrolyte solutions [2-4], and thus the evaluation of chemical state change of the metal species during the electrochemical redox processes is an important finding for establishment and practical application of the anion shuttle battery. The knowledge about the particle size in addition to the chemical state
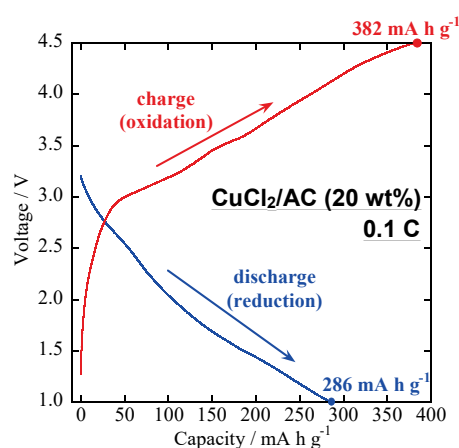

Fig. 1 Charge/discharge profile (0.1 C) of the electrochemical cell with the $CuCl_2/AC$ electrode.

is also useful to achieve the safe and long-life operation.

Therefore, in this study, we have analyzed the electrochemical reactions of $CuCl_2$ supported on active carbon (AC) by means of the XAFS method and aimed to understand the chemical state conversion of the Cu species in the $CuCl_2$/AC electrode. The Cu K-edge measurements provide the bulk information, and the surface species is analyzed by the L-edge measurements.

2. Experimental

The electrode material, $CuCl_2$/AC (20 wt%), was prepared by the impregnation method. The powder of AC was added in an aqueous solution of $CuCl_2\cdot2H_2O$, and the mixture was stirred for 1 h at 60 ºC and dried at 80 ºC for 3 d. The obtained $CuCl_2$/AC powder was mixed with polyvinylidene difluoride (PVDF) as the binder and 1-methyl-2-pyrrolidone (NMP) as the diluent, and the mixed slurry was applied on an Al sheet as a current collector to prepare a $CuCl_2$/AC electrode sheet. The mass ratio of the composed $CuCl_2$/AC and PVDF was 8:2. In a glove box filled with Ar, an electrochemical cell was assembled with the $CuCl_2$/AC electrode, a Li foil as a counter electrode, the porous polypropylene films as separators, and a 1 mol dm^{-3} $LiPF_6$ solution dissolved in a mixture of ethylene carbonate and diethyl carbonate.

After the charge and discharge treatments at the current rates of 0.1 C and 0.01 C, the electrochemical cell was disassembled in the glove box. The XAFS measurements at the Cu K-edge were carried out at BL-4 of the SR Center (Ritsumeikan University) and BL-9C of Photon Factory (High Energy Accelerator Research Organization) by the transmission mode. The XAFS measurements at Cu L-edge were carried out at BL-11 of the SR Center by measuring the total electron yield (TEY) and the partial fluorescence yield (PFY). The X-ray energy was calibrated using the XANES spectrum of a standard sample.

3. Results and Discussion

The charge/discharge profile at the current rate of 0.1 C is shown in Fig. 1. The potential limit was set to 1.0 V and 4.5 V vs. Li^+/Li for the discharge and charge process, respectively. The initial electric potential was about 3.1 V vs. Li^+/Li and was gradually decreased through the discharge process. The first discharge capacity was 286 mA h g^{-1}, which corresponded to 72 % of the theoretical capacity. The electric potential was quickly increased to about 3.0 V vs. Li^+/Li at the subsequent charge process and was then gradually increased up to the maximum limit. The charge capacity was 382 mA h g^{-1} and was almost comparable to the theoretical value. The charge capacity was larger than the discharge capacity, but it was identical to the theoretical one to oxidize the Cu species in the
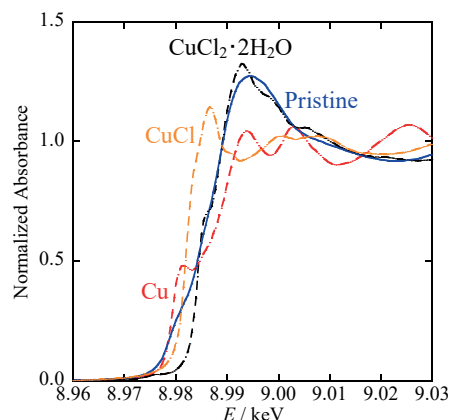

Fig. 2 Cu K-edge XANES spectra of pristine $CuCl_2$/AC electrode and reference samples.
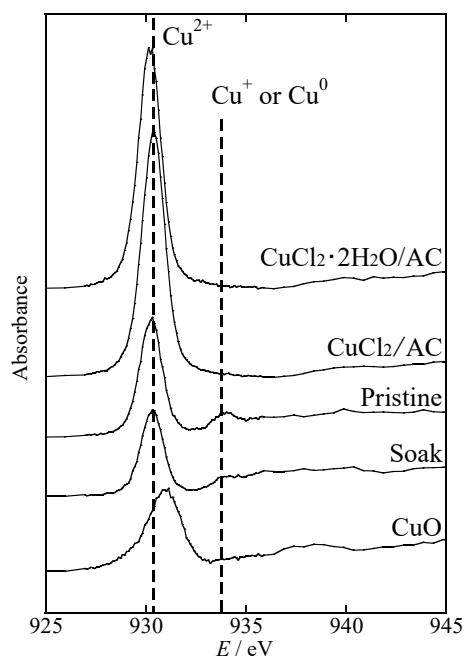

Fig. 3 Cu L-edge XANES spectra of the pristine and soaked cathode and reference samples measured by the PFY mode.

electrode. It is suggested that a part of $CuCl_2$ has already been reduced at the initial state. It is considered that this reduction is due to the Al sheet used as the current collector by the galvanic corrosion to generate both $AlCl_3$ and the reduced Cu species.

The Cu K-edge XANES spectra of a pristine cathode is compared in Fig. 2 with the reference samples. The X-ray energy of the white line peak for the pristine cathode was in agreement with that of $CuCl_2\cdot2H_2O$, whereas the threshold energy at the absorption edge coincided with that of metallic Cu.
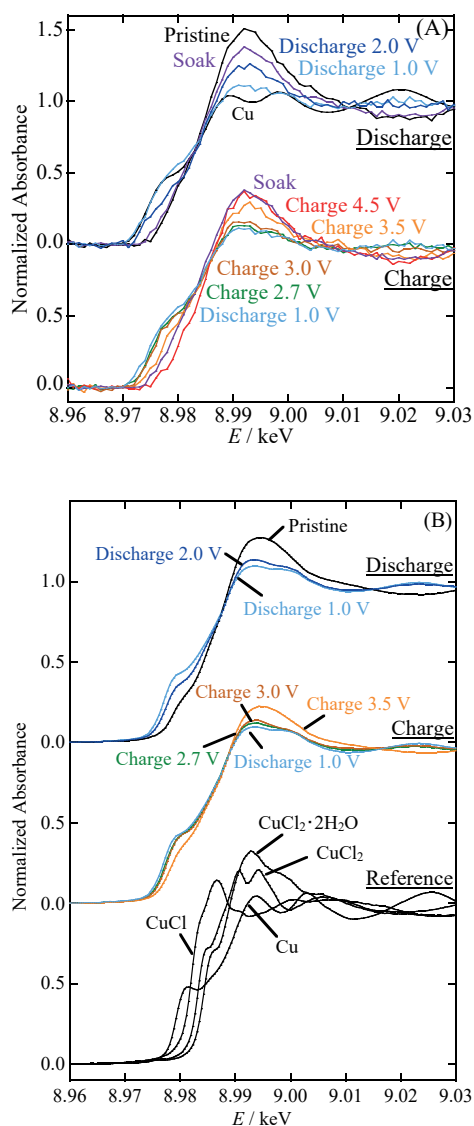
Fig. 4 Cu K-edge XANES spectra of the disassembled cathode at various electric potentials during the discharge/charge process under the current rates of 0.1 C (A) and 0.01 C (B).

Therefore, it is estimated that about 30 % of the Cu species was reduced to Cu(0) at the initial state before the first discharge process. The excess capacity of *ca.* 100 mA h g^{-1} at the first charge process is quantitatively explained by the previous reduction of $CuCl_2$ before the initial discharge process.

The XANES spectra measured at the Cu L-edge by the PFY mode are depicted in Fig. 3 for the pristine and soaked cathode. An absorption peak observed around 930 eV indicates the presence of Cu^{2+} [9]. The peak energy of $CuCl_2$/AC was slightly higher than that of $CuCl_2 \cdot 2H_2O$/AC, and the corresponding peak of the pristine cathode is consistent with that of $CuCl_2$/AC, indicating the desorption of hydrated water in the
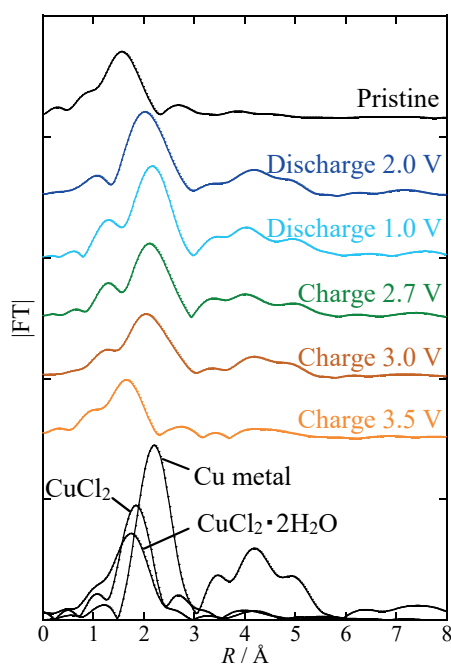

Fig. 5 Fourier transform functions of the disassembled cathode at various electric potentials during the discharge/charge process under the current rate of 0.01 C.

preparation procedures of the electrode. However, the peak intensity is obviously lowered for the pristine and soaked cathode compared to $CuCl_2$/AC, and an additional peak appears around 934 eV, corresponding to the presence of Cu^+ or Cu^0 [9]. The partial reduction of $CuCl_2$ at the initial stage (pristine and soaked electrode) was in accordance with the result of the Cu K-edge measurement. In addition, because the peak position of CuO is by *ca.* 0.5 eV different from that of $CuCl_2$ (see Fig. 3), it is clarified that the Cu species supported on AC is not CuO but $CuCl_2$.

The discharge/charge process was stopped at various capacities (electric potentials) and the electrochemical cell was disassembled to obtain the cathode sheet during the electrochemical process for the XAFS measurements. The Cu K-edge XANES spectra are shown in Fig. 4 under the current rates of 0.1 C (A) and 0.01 C (B). It is observed at both current rates that the X-ray absorbance at the white line peak top was decreased with decreasing the electric potential during the discharge process and the absorption edge shifted to the low energy. The threshold energy at the absorption edge for the discharged cathode up to 1.0 V vs. Li$^+$/Li was almost consistent with that of Cu metal, whereas the double peak structure was not seen just above the absorption edge. This difference can be explained by the refinement of the Cu(0) particle. The opposite change

was observed for the XANES spectra during the charge process. The shoulder structure at the absorption edge suggesting the existence of metallic Cu disappeared completely in the final spectrum charged up to 4.5 V vs. Li$^+$/Li, the spectrum of which is in agreement with that of CuCl$_2$. The XANES spectral change clarifies that remaining CuCl$_2$ at the initial stage is converted to metallic Cu by the discharge process up to 1.0 V vs. Li$^+$/Li and CuCl$_2$ is recovered by the charge process up to 4.5 V vs. Li$^+$/Li.

The redox cycle between CuCl$_2$ and Cu is also observed in the Fourier transform functions of the disassembled cathodes during the discharge/charge process at the current rate of 0.01 C, as shown in Fig. 5. The main peak at *ca.* 2.2 Å of the discharged electrode at 1.0 V vs. Li$^+$/Li clearly indicated the nearest-neighboring Cu–Cu interaction of metallic Cu. The low peak height suggested the existence of small Cu particles. The main peak position was drastically shifted to *ca.* 1.8 Å in the potential range above 3.0 V vs. Li$^+$/Li during the charge process. It is revealed that the gain of the charge capacity in the potential range above 3.0 V vs. Li$^+$/Li (see Fig. 1) corresponds to the oxidation of the Cu species. The final pattern after the charge process was almost in agreement with that of CuCl$_2$, indicating the drive of redox cycle of the CuCl$_2$/Cu pair.

It should be noted that the existence of stable monovalent Cu species, such as CuCl, is not supported by the present XAFS analyses during the discharge/charge process. The standard redox potentials of the Cu^{2+}/Cu$^+$ and Cu$^+$/Cu pairs are +0.154 V and +0.520 V vs. NHE, respectively, in aqueous solutions. It means that the Cu$^+$ species spontaneously converts to the Cu^{2+} and Cu species by the disproportionation. It is considered that the Cu species in the CuCl$_2$/AC electrode also have the standard redox potentials similar to those in aqueous solution.

The Cu L-edge XANES spectra are shown in Fig. 6 for the disassembled cathode after the discharge/charge process at various electric potentials. The peak intensity at *ca.* 930 eV corresponding to CuCl$_2$ is decreased during the discharge process, and a new peak appears around 934 eV, indicating the conversion from CuCl$_2$ to Cu(0). When the cell was discharged to 1.0 V vs. Li$^+$/Li, the peak at 930 eV almost disappeared in the TEY and PFY spectra, indicating the quantitative reduction of remaining CuCl$_2$ after the discharge process. The absorption peak around 934 eV was diminished for the charged electrode up to 3.5 V vs. Li$^+$/Li. As suggested in the discussion on the K-edge analysis, it is necessary to be charged up to 4.5 V vs. Li$^+$/Li in order to reproduce CuCl$_2$. The observed charging capacity, which is comparable to the theoretical value, is thus supported by the L-edge XANES observations in addition to the K-edge XAFS analyses. Furthermore, it is
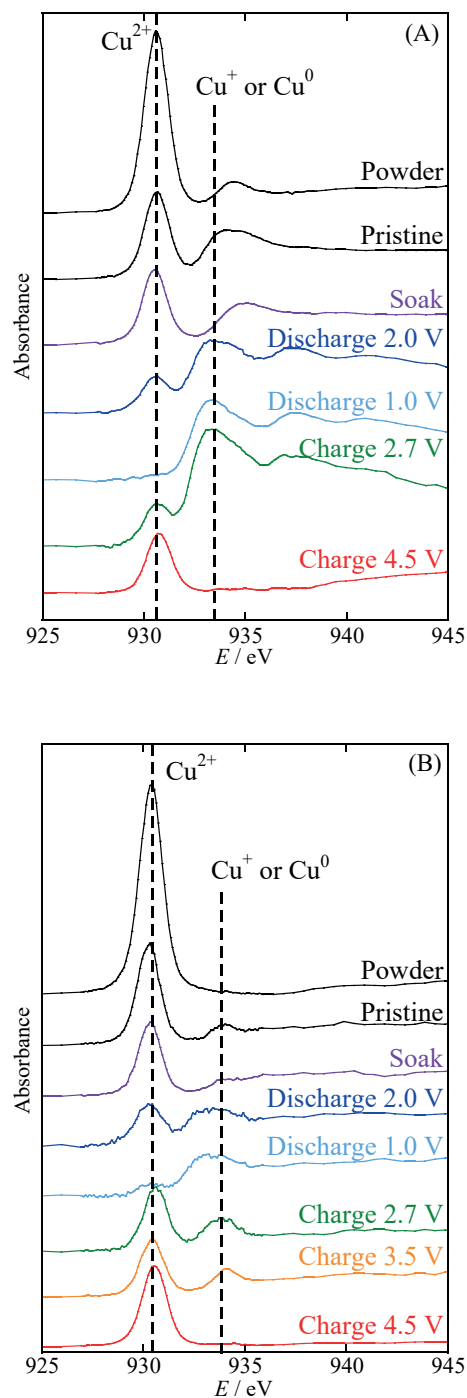

Fig. 6 Cu L-edge XANES spectra of the disassembled cathode at various electric potentials during the discharge/charge process measured by the TEY (A) and PFY (B) mode.

demonstrated that the reproduced divalent Cu species is CuCl$_2$, which is clearly distinguished from CuO according to the Cu L-edge XANES spectrum (see Fig. 3). The peak energy of the charged electrode at 4.5 V vs. Li$^+$/Li is consistent with that of CuCl$_2$ for both

detection modes. It means that the Cl⁻ ion should be stored in the electrode when it is discharged to form the Cu(0) species.

4. Conclusion

In this study, the CuCl$_2$/AC powder was prepared as the active material for the chloride shuttle battery using the impregnation method, and the electrochemical reaction was analyzed using the XAFS method. The discharge/charge reaction worked properly for the electrochemical cell using the CuCl$_2$/AC cathode and the Li counter electrode. The Cu K- and L-edge XANES spectra of the pristine cathode showed the existence of CuCl$_2$, but it was clarified that *ca.* 30 % of the Cu species was reduced to Cu(0), suggesting the galvanic corrosion to form Cu(0) and AlCl$_3$ from CuCl$_2$ and Al. The chemical state of the Cu species was clarified by measuring the XAFS spectrum for the disassembled cathodes, that were stopped at various electric potentials during the discharge/charge process. The reduction of CuCl$_2$ proceeds in the discharge process, and the reduction to Cu(0) is achieved at 1.0 V vs. Li$^+$/Li. Furthermore, the oxidation of Cu(0) is started above the electric potential of *ca.* 3.0 V vs. Li$^+$/Li during the charge process, and the recovery of CuCl$_2$ is achieved at 4.5 V vs. Li$^+$/Li. This study demonstrates the chemical state conversion for the redox process of the CuCl$_2$/Cu pair and its reasonable applicability to an active material of the chloride shuttle battery system.

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