# Electrochemical Conversion Reaction of Copper(II) Chloride on Carbon

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Recently, anion transfer type batteries that use conduction of anions instead of lithium ions are one of candidates for new storage battery systems that replace lithium ion batteries. The transfer of electrons is carried out by the metal species, and the anions conduct in the electrolyte, so that many metal halides are candidates for the materials of cathode and anode. However, the reaction mechanism of the electrochemical redox reactions of the metal halide compounds has not been clarified. In this study, we analyzed the electrochemical reactions of $CuCl_2$ using the XAFS method.

Carbon supported copper(II) chloride was prepared by the impregnation method. An aqueous solution of copper(II) chloride was mixed with activated carbon, and the mixture was dried at 80 °C for 3 d. The obtained $CuCl_2$/C powder with the $CuCl_2$ loading of 20 wt% was mixed with polyvinylidene difluoride as the binder, and the mixed slurry diluted with 1-methyl-2-pyrrolidone was applied on an Al sheet as the current collector. The electrochemical cell was assembled using the $CuCl_2$/C electrode, a Li anode, two porous polypropylene films as the separator, and 1 mol $dm^{-3}$ $LiPF_6$ solution dissolved in a mixture of ethylene carbonate and ethyl methyl carbonate. After the charging and discharging treatments, the cell was disassembled in a glove box filled with Ar. The XAFS measurements at Cu L-edge were carried out at BL-11 of SR center (Ritsumeikan Univ.) by the total electron yield (TEY) and the fluorescence yield (PFY) mode.

The charge/discharge profile under the current rate of 0.01 C is shown in Fig. 1. The lower limit voltage of the discharge process was set to 1.0 V in order to avoid the $Li^+$ insertion reaction into carbon and the alloying reaction of Li and Al. The cell potential was gradually and continuously decreasing during the discharge process. The potential during the charge process was once kept constant at around 2.7 V and was increasing after the plateau. Figure 2 shows the XANES spectra at some potential values during the charge/discharge process as indicated in Fig.1 by circles. A characteristic peak at 931 eV was observed at the initial state, suggesting the existence of $Cu^{2+}$. The height of the peak was decreased during the discharge process, and a new peak was observed at 933 eV suggesting the generation of the reduced Cu species. After discharging to 1.0 V, the peak at 931 eV was disappeared in the TEY spectrum, although it was still existed in the PFY spectrum. It shows that the reduction reaction proceeded with consuming $Cu^{2+}$ completely on the particle surface, however $Cu^{2+}$ was remained in the inner part of the particle. During the charge process, the progress of the oxidation was apparently observed, however the initial spectrum was not completely recovered as shown in PFY spectrum at 3.5 V. The TEY spectrum was not obtained for the charged samples at 3.0 and 3.5 V, because the S/N ratio was quite poor. It suggests the formation of solid electrolyte interphase (SEI) on the electrode surface during the charging process above the plateau of 2.7 V.

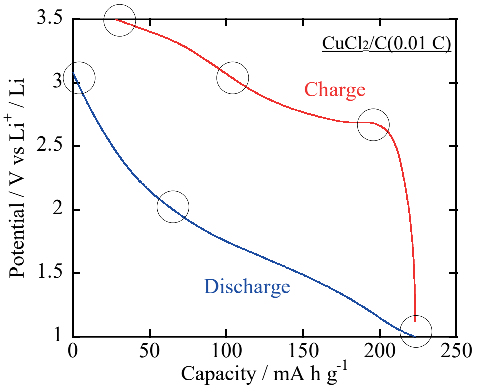

**Fig. 1** Charge/discharge profile (0.01 C) of the cell using $CuCl_2$/C for the positive electrode.

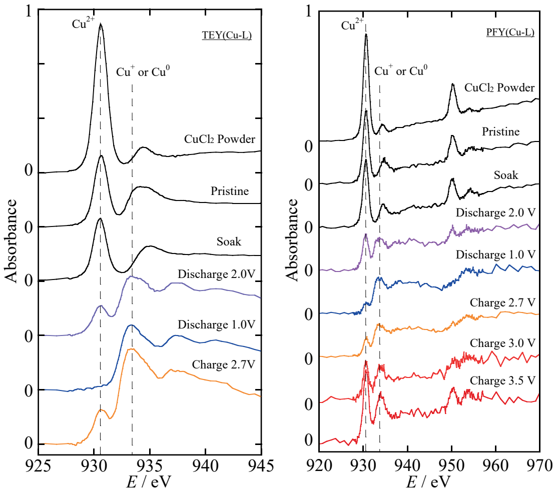

**Fig. 2** XANES spectra of $CuCl_2$/C electrodes measured in the TEY (left) and PFY (right) mode during the discharge and charge processes.