^{99}Ru Mössbauer spectroscopy of Na-ion butteries of Na_2RuO_3 (I)

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Sodium-ion batteries have attracted considerable attention recently, because of their potential for large-scale applications: higher power and less expensive batteries compared to Li-ion batteries can be realized by utilizing abundant and polarizable sodium ion as a mobile charge carrier. One of the main obstacles to realizing high performance sodium-ion batteries is the low specific capacity of the electrode materials. Thus, it is particularly important to develop novel Na-ion cathode materials with a high capacity as well as a high operating potential.

Our group has recently reported the electrochemical properties of Na excess transition metal oxide $Na[Na_{1/3}Ru_{2/3}]O_2$, where the cation arrangement in the $[Na_{1/3}Ru_{2/3}]$ layer is controlled between the ordered and disordered states by synthetic conditions. Importantly, the ordered and disordered $Na[Na_{1/3}Ru_{2/3}]O_2$ exhibit significant differences in the electrochemical properties[1]. In this work, we conducted Ru Mössbauer spectroscopy for the ordered and disordered $Na[Na_{1/3}Ru_{2/3}]O_2$ to clarify the valence states of Ru ions during desodiation/sodiation.

The source nuclide, ^{99}Rh ($T_{1/2}$=15.0 d) for ^{99}Ru Mössbauer spectroscopy was produced via the ^{99}Ru (p,n) ^{99}Rh reaction. The 96%-enriched ^{99}Ru metal powder was irradiated by protons with E = 12 MeV and I = 10 μA at the AVF Cyclotron. The ^{99}Ru metal powder was packed into an Al holder, which was tightly fixed to the irradiation equipment for cooling by He gas flow and water flow during the irradiation. After irradiation for about 24 hours, the target was used as a ^{99}Rh Mössbauer source without being subjected to annealing or chemical treatment[2].

^{99}Ru absorption Mössbauer spectra of $Na[Na_{1/3}Ru_{2/3}]O_2$ samples were obtained using a conventional Mössbauer spectrometer. Owing to the relatively high energy of the Mössbauer γ-ray (89.8 keV), both the source and the absorbers were maintained at liquid-helium temperature in a cryostat.

The obtained spectra are shown in Fig. 1 and 2. The Mössbauer spectrum for the disordered $Na[Na_{1/3}Ru_{2/3}]O_2$ (Fig. 1 (a)) shows a broad singlet with isomer shift (δ) of −0.30 mm/s and linewidth (Γ) of 0.95 mm/s. The δ value is typical of Ru^{IV}, although the large linewidth suggests structural disorder around Ru. The Mössbauer spectrum for the ordered $Na[Na_{1/3}Ru_{2/3}]O_2$ (Fig. 1 (b)) shows a singlet with δ = −0.27 mm/s and Γ = 0.63 mm/s, indicating Ru^{IV}. Thus, regardless of the synthetic conditions, the valence states of Ru in both compounds are the same. However, the linewidth for the ordered compound is much smaller than that of the disordered one, most likely due to the ordered honeycomb arrangement of Na and Ru in the $[Na_{1/3}Ru_{2/3}]$ layer.

On charging the ordered compound, the Mössbauer spectrum, as shown in Fig.2, cannot determine the electronic structure accurately, in part due to the small amounts of the obtained sample. However, a preliminary result indicates oxidation of Ru from tetravalent to pentavalent, from the obtained δ value of +0.21 mm/s with a small quadrupole splitting of 0.60 mm/s. Further experiments with a larger amount of samples are now in progress to reveal the reaction mechanism of $Na[Na_{1/3}Ru_{2/3}]O_2$.

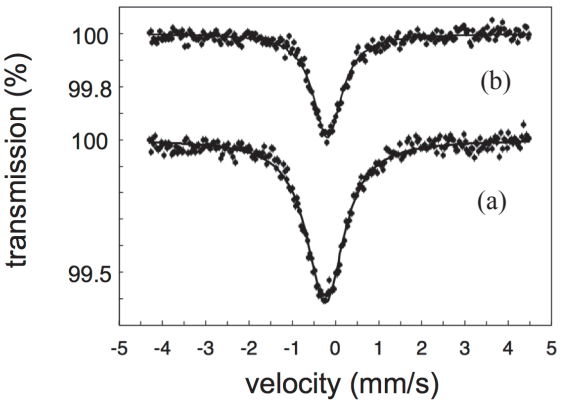

Fig. 1. ^{99}Ru Mössbauer spectra of (a) disordered and (b) ordered $Na[Na_{1/3}Ru_{2/3}]O_2$ at 4.2 K.

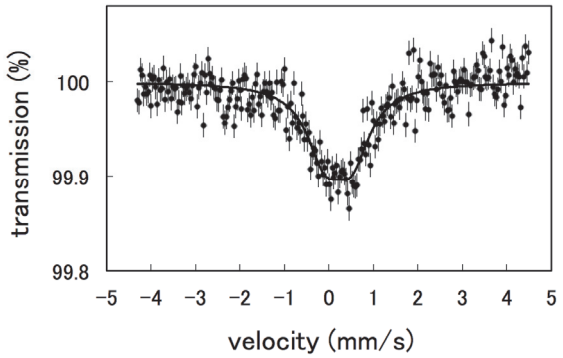

Fig. 2. ^{99}Ru Mössbauer spectra at 4.2 K of the ordered $Na[Na_{1/3}Ru_{2/3}]O_2$ after electric charge.

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References

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