^{99}Ru and ^{57}Fe Mössbauer spectroscopic studies of $Na_2Ru_{1-x}FexO_3$ of sodium-ion battery electrode (2)

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Sodium-ion batteries have the potential to be the next-generation batteries to replace lithium-ion batteries owing to the abundance of its raw materials. Na_2RuO_3 is a kind of Na-excess layered oxide and is promising as a cathode material for Na-ion batteries.[1)] In this study, we demonstrate the oxidation states and the coordination environments of Ru ions in Na_2RuO_3 after charging and discharging processes via Mössbauer spectroscopy, X-ray diffraction (XRD), and electrochemical analysis.[2)]

A sample of $Na_2Ru_{0.99}Fe_{0.01}O_3$ was prepared *via* a solid-state reaction. Stoichiometric mixtures of RuO_2, $NaHCO_3$, and Fe_2O_3 were pressed and sintered at 850°C for 48 h in an Ar atmosphere. The sample was confirmed to possess a single phase by XRD.[2)] In the electrochemical treatment, a mixture of $Na_2Ru_{0.99}Fe_{0.01}O_3$, acetylene black, and polyvinylidene difluoride as a binder was applied on an Al foil. The Al foil with $Na_2Ru_{0.99}Fe_{0.01}O_3$ and a carbon sheet were used as the cathode and the anode, respectively. As the electrolyte, 1 M $NaBF_4$ solution was used.[1)] These materials were packed in a battery cell and subsequently charged by applying with a DC current of 4 V for 0.5 h. In the XRD pattern after charging, the characteristic peaks of triclinic ilmenite-type $NaRuO_3$ were assigned, in addition to those of honeycomb-type Na_2RuO_3.

For performing ^{99}Ru Mössbauer spectroscopy, the source nuclide ^{99}Rh ($T_{1/2}$ = 16.1 d) was produced by the nuclear reaction of ^{99}Ru$(p,n)^{99}$Rh at the AVF Cyclotron. ^{99}Ru Mössbauer spectra were measured at 5 K in a conventional liquid He cryostat.[3)] The ^{99}Ru Mössbauer spectra of $Na_2Ru_{0.99}Fe_{0.01}O_3$ obtained at 5 K before and after charging are shown in Figs. 1(a) and (b), respectively. The spectrum before charging was fitted by a broadened single line, indicating Ru^{4+} with the isomer shift $\delta = -0.27(1)$ mm/s.[2,3)] The spread of the linewidth was considered to be caused by the doping of Fe atoms. Concurrently, the spectrum measured after charging had a poor quality owing to the small amount of sample packed into the battery cell. However, this spectrum was analyzed to consist of two components having hyperfine magnetic fields (H_{hf}) with quadrupole splitting (ΔE_Q). The red component ($\delta = -0.27(4)$ mm/s, $\Delta E_Q = 0.51(9)$ mm/s, $H_{hf} = 4.7(2)$ T) was consistent with the oxidation state of Ru^{4+} before charging. The blue component ($\delta = -0.01(4)$ mm/s, $\Delta E_Q = 0.07(7)$ mm/s, $H_{hf} = 17.9(9)$ T) presented a larger isomer shift and a larger internal magnetic field. The value of δ indicated that the oxidation state of Ru after charging changed from 4+ to 5+. It is probable that the oxidation number of Ru ions increased as Na^+ ions were removed by charging, and that H_{hf} was generated as the structure changed to a three-dimensional ilmenite structure from a two-dimensional layer structure with a Na^+ deficiency. This speculation is supported by the observation of magnetic splitting in the ^{57}Fe Mössbauer spectrum at low temperatures. The ratio of the area intensity of the blue component was approximately 66%, which is almost consistent with the Coulomb number of the one-electron oxidation reaction under the electrochemical conditions of 4 V for 0.5 h.

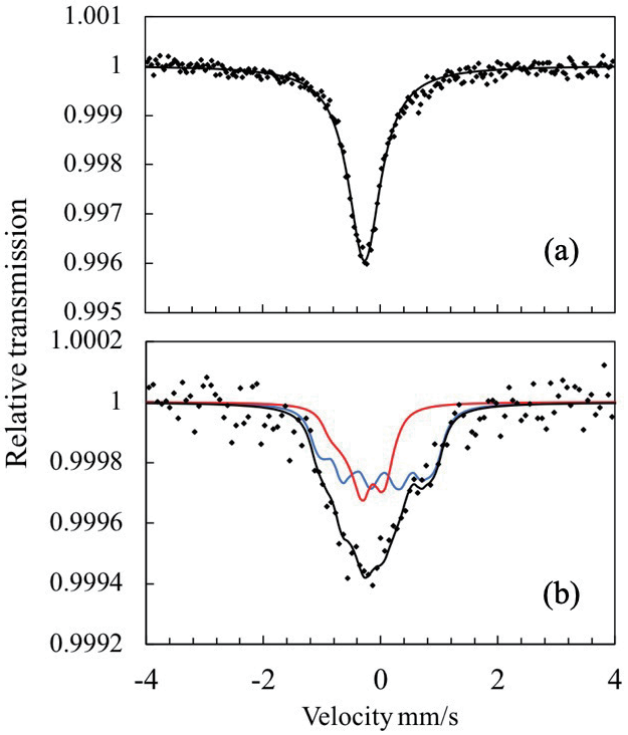

Fig. 1. ^{99}Ru Mössbauer spectra of $Na_2Ru_{0.99}Fe_{0.01}O_3$ (a) before charging and (b) after charging.

References
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