

^{99}Ru and ^{57}Fe Mössbauer spectroscopic studies of $\text{Na}_2\text{Ru}_{1-x}\text{Fe}_x\text{O}_3$ of sodium-ion battery electrode

K. Hamano,^{*1,*2} Y. Kobayashi,^{*1,*2} H. Haba,^{*2} and H. Ueno^{*2}

Sodium-ion batteries have attracted attention as the next generation of batteries after Li-ion batteries for large-scale applications owing to the abundance and low cost of sodium.^{1–3} The use of Na-excess metal oxides, Na_2MO_3 (M: transition metals), as cathode materials may realize large capacities through an additional oxygen redox reaction. Among Na-excess metal oxides, Na_2RuO_3 is expected to be the leading cathode material. In this study, we demonstrate the oxidation states and coordination environments of Ru ions in Na_2RuO_3 and $\text{Na}_2\text{Ru}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0.01$ and 0.05) after repeating the charge/discharge processes by means of ^{99}Ru and ^{57}Fe Mössbauer spectroscopy, XRD, and electrochemical measurements. Mössbauer spectroscopy is a powerful tool to understand the oxidation states of Ru ions. However, the measurements of ^{99}Ru Mössbauer spectra can only be performed at low temperatures because the Mössbauer transition energy is relatively high ($E_\gamma = 89.8$ keV).^{4,5} A ^{57}Fe -doped sample of $\text{Na}_2\text{Ru}_{1-x}\text{Fe}_x\text{O}_3$ was prepared to estimate the temperature dependence of the oxidation states of Ru sites by ^{57}Fe Mössbauer spectroscopy.

Na_2RuO_3 has a layered structure in which the first layer is composed of Na^+ and the second layer contains Na^+ and Ru^{4+} in the ratios 1:3 and 2:3, respectively. It is known that Na_2RuO_3 has two phases, namely, *ordered* and *disordered* arrangements, which correspond to sintering times of 48 h and 12 h, respectively. Ordered Na_2RuO_3 has honeycomb-type cation ordering in the $[\text{Na}_{1/3}\text{Ru}_{2/3}]\text{O}_2$ layers, whereas *disordered* Na_2RuO_3 has a random distribution of Na^+ and Ru^{4+} in the $[\text{Na}_{1/3}\text{Ru}_{2/3}]\text{O}_2$ layers. The two polymorphs exhibit significant differences in electrochemical properties.³

A sample of *disordered* $\text{Na}_2\text{Ru}_{0.99}\text{Fe}_{0.01}\text{O}_3$ was prepared through a solid-state reaction. A stoichiometric mixture of RuO_2 , NaHCO_3 , and Fe_2O_3 was pressed and sintered at 850°C for 12 h in an Ar atmosphere. The $\text{Na}_2\text{Ru}_{0.99}\text{Fe}_{0.01}\text{O}_3$ sample was confirmed to be in a single phase by XRD. For ^{99}Ru Mössbauer spectroscopy, the source nuclide ^{99}Rh ($T_{1/2} = 15.0$ d) was produced through the $^{99}\text{Ru}(p,n)^{99}\text{Rh}$ reaction at the AVF Cyclotron. ^{99}Ru Mössbauer spectra were obtained by a conventional arrangement, but both the source and absorbers were maintained at 4.2 K in a liquid He cryostat during the measurements.

The ^{57}Fe Mössbauer spectrum of *disordered* $\text{Na}_2\text{Ru}_{0.99}\text{Fe}_{0.01}\text{O}_3$ shows a doublet peak, as shown in Fig. 1. The doublet was analyzed with the distribu-

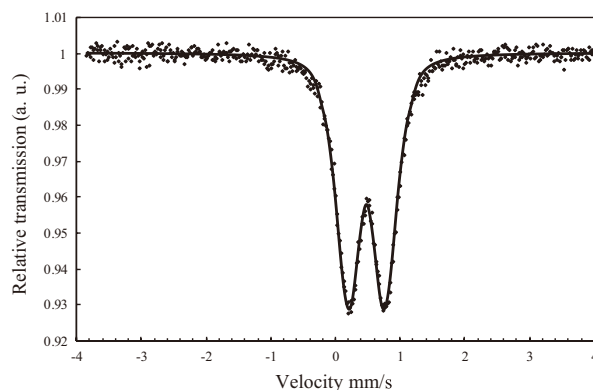


Fig. 1. ^{57}Fe Mössbauer spectrum of *disordered* $\text{Na}_2\text{Ru}_{0.99}\text{Fe}_{0.01}\text{O}_3$ measured at 15.0 K.

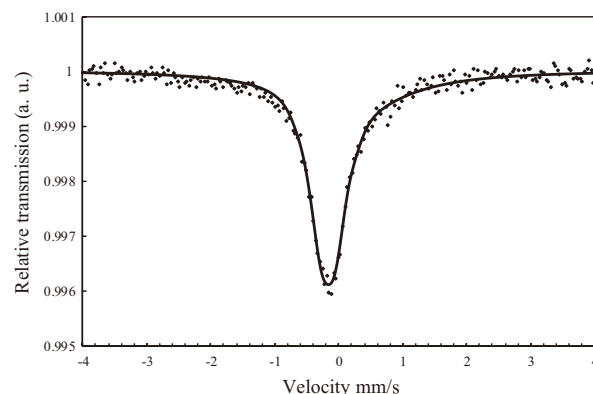


Fig. 2. ^{99}Ru Mössbauer spectrum of *disordered* $\text{Na}_2\text{Ru}_{0.99}\text{Fe}_{0.01}\text{O}_3$ measured at 5.0 K.

tion of quadrupole splitting (ΔE_Q) because Fe ions were randomly present at on Na and Ru sites. The mean values of the obtained distributions of the isomer shift (δ) and ΔE_Q were $0.48(1)$ mm/s and 0.64 mm/s, respectively. Fe ions were in a trivalent state in the $[\text{Na}_{1/3}\text{Ru}_{2/3}]\text{O}_2$ layers. The ^{99}Ru Mössbauer spectrum shows a broadened and asymmetric single line, as shown in Fig. 2. The isomer shift was $-0.30(1)$ mm/s, and the Ru ion was in a typical Ru^{4+} state. It is speculated that the line broadening is caused by an increase in the oxidation state of a part of the Ru ions from Ru^{4+} to Ru^{5+} and a significant distortion of the octahedron of RuO_6 with the introduction of a Fe^{3+} ion.

References

- 1) K. M. Mogare *et al.*, *Z. Anorg. Allg. Chem.* **630**, 547 (2004).
- 2) M. Tamaru *et al.*, *Electrochem. Commun.* **33**, 23 (2013).
- 3) B. M. de Boisse *et al.*, *Nature Commun.* **7**, 11397 (2016).
- 4) K. Takahashi *et al.*, *RIKEN Accel. Prog. Rep.* **48**, 242 (2015).
- 5) Y. Kobayashi *et al.*, *J. Phys.* **217**, 012023 (2010).

*1 Dep. of Eng. Sci., University of Electro-Commun.

*2 RIKEN Nishina Center