

^{99}Ru Mössbauer spectroscopy of Na-ion batteries of Na_2RuO_3 (II)K. Takahashi,^{*1} Y. Kobayashi,^{*1,*2} H. Haba,^{*2} and M. Okubo^{*3}

Sodium-ion batteries are candidates for next-generation rechargeable batteries that use Na^+ ions as charge carriers. High-power and low-cost batteries incorporating Na^+ ions are strongly expected to be energy storage devices, because sodium is much more abundant and easier to isolate compared to lithium. There have been many investigations targeting the development and production of novel Na^+ -containing electrodes as suitable cathodes. It is particularly important to develop novel cathode materials with high capacity as well as high operating potential. Yamada et al. recently reported the electrochemical properties of a new Na–Ru–O system, incorporating $\text{Na}[\text{Na}_{1/3}\text{Ru}_{2/3}]\text{O}_2$, as the cathode material. Na_2RuO_3 has a layered structure in which the first layer is composed of Na while the second layer contains Na and Ru in the ratios 1:3 and 2:3, respectively, and provides the redox reaction associated with Na^+ ion extraction and insertion, leading to the possibility of high energy density of 140 mAh/g¹.

The crystal structure of $\text{Na}[\text{Na}_{1/3}\text{Ru}_{2/3}]\text{O}_2$ has two possible phases, *ordered* and *disordered*, depending on the synthetic conditions^{1,2}. The two phases exhibit significant differences in their electrochemical properties. In this study, the *ordered* Na_2RuO_3 as the starting composition and Na-deficient $\text{Na}_{2-x}\text{RuO}_3$ were characterized by means of XRD and ^{99}Ru Mössbauer spectroscopy in order to clarify the change of oxidation state and coordination environment of the Ru atoms caused by the deficiency of Na^+ ions.

$\text{Na}_{2-x}\text{RuO}_3$ ($x=0, 0.5, 1.0, 1.5$) samples in the *ordered* phase were prepared by a solid-state reaction. A mixture of RuO_2 and NaHCO_3 were pressed and sintered at 850°C for 48 h in an Ar atmosphere. Powdered samples were used for XRD and ^{99}Ru Mössbauer spectroscopy.

The source nuclide, ^{99}Rh ($T_{1/2}=15.0$ d) of ^{99}Ru Mössbauer spectroscopy was produced by the $^{99}\text{Ru}(p,n)^{99}\text{Rh}$ reaction at the AVF Cyclotron (K70-MeV). For the (p,n) reactions, the p -beam was used to bombard the 96 %-enriched ^{99}Ru metallic powder target. The energy and intensity of the p -beam were 12 MeV and 10 μA , respectively. After p -irradiation for about 24 h, the Mössbauer source was estimated to have an activity of 500 MBq³. ^{99}Ru Mössbauer spectra were obtained using a Mössbauer spectrometer (Wissel, MVT-1000) and a multichannel analyzer (FAST, MCS3). Due to the relatively high energy of the Mössbauer γ -ray (89.8 keV), both the source and the absorbers were maintained at low

temperature in a liquid-helium cryostat during the measurements. The Mössbauer γ -rays were detected by a 2-mm-thick $\text{NaI}(\text{Tl})$ scintillator. Velocity was calibrated by measuring the Mössbauer absorption lines of ^{57}Fe in an iron foil sample against a $^{57}\text{Co}/\text{Rh}$ source.

The XRD pattern of *ordered* Na_2RuO_3 indicated that this compound crystallized in a monoclinic unit cell with $a = 0.541$ nm, $b = 0.937$ nm, $c = 1.085$ nm, $\beta = 99.64^\circ$ ³. The ^{99}Ru Mössbauer spectrum of Na_2RuO_3 obtained is shown in Fig. 1(a). The spectrum shows a doublet with isomer shift (δ) of $-0.30(5)$ mm/s, quadrupole splitting (ΔE_Q) of $0.29(5)$ mm/s, and linewidth (Γ) of 0.33 mm/s. The δ value is typical of Ru^{IV} . The linewidth observed in *ordered* Na_2RuO_3 is much smaller than that of $\text{Na}[\text{Na}_{1/3}\text{Ru}_{2/3}]\text{O}_2$ ⁴, due to the calcination temperature and period for sample preparation. The Mössbauer spectrum of Na-deficient $\text{Na}_{0.5}\text{RuO}_3$ (Fig. 1 (b)) shows a doublet with $\delta = -0.41(1)$ mm/s and $\Delta E_Q = 0.46(1)$ mm/s, also indicating Ru^{IV} . It means that the Ru ions are located in an equivalent coordination environment, despite the considerable sodium-ion deficiency. The XRD pattern of $\text{Na}_{0.5}\text{RuO}_3$ indicated a modification of the crystal structure from monoclinic in the starting material to tetragonal in the product due to the reduction of Na between RuO_6 layers. Detailed discussion about the oxidation states and coordination environment of the Ru atoms as a function of the deficiency of Na in $\text{Na}_{2-x}\text{RuO}_3$ is under consideration.

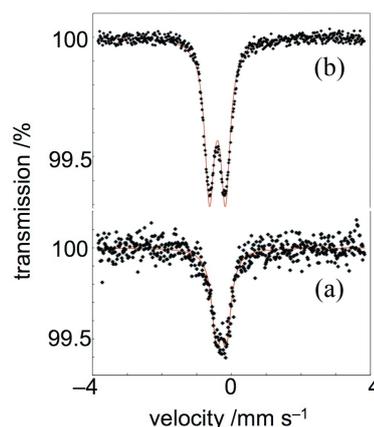


Fig. 1. ^{99}Ru Mössbauer spectra of (a) *ordered* Na_2RuO_3 and (b) Na-deficient $\text{Na}_{0.5}\text{RuO}_3$ at 4.2 K.

References

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