^{99}Ru Mössbauer spectroscopy of Na-ion batteries of Na_2RuO_3 (III)

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Sodium-ion batteries are attractive energy storage media owing to its abundance of sodium, compared with lithium-ion batteries. There have been many investigations of the development of Na^+-containing electrodes as new cathodes.[1,2] We recently reported the electrochemical properties of Na_2RuO_3 as the cathode material.[3] 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. It was known that layered Na_2RuO_3 has two phases in the $[Na_{1/3}Ru_{2/3}]O_2$ layers, namely *ordered* and *disordered* arrangements, depending on the sintering time. The *ordered* Na_2RuO_3 phase has honeycomb-type cation ordering in the $[Na_{1/3}Ru_{2/3}]O_2$ layers. On the other hand, the *disordered* Na_2RuO_3 phase has a random distribution of Na and Ru in $[Na_{1/3}Ru_{2/3}]O_2$ layers. The two polymorphs exhibit significant differences in electrochemical properties.

In this study, the *disordered* Na_2RuO_3 phase and the Na-deficient oxides that imitate discharged samples of Na_2RuO_3, which were obtained after a short sintering time of 12 h were characterized by XRD and ^{99}Ru Mössbauer spectroscopy to understand the change of oxidation state and coordination environment of the Ru atoms caused by the deficiency of Na^+ ions.

Disordered Na_2RuO_3 and non-stoichiometric Na-Ru oxides (atomic ratios of Na/Ru = 1.5, 1.0, 0.5, and 0.2) were synthesized by conventional solid-state reaction.[2] RuO_2 and $NaHCO_3$ were mixed with different atomic ratios of Na/Ru thoroughly and sintered at 850ºC for 12 h in an Ar atmosphere. The source nuclide, ^{99}Rh ($T_{1/2}$=15.0 d) of ^{99}Ru Mössbauer spectroscopy was produced by the ^{99}Ru(p,n)^{99}Rh reaction at the AVF Cyclotron. After p-irradiation for 24 h, the target was used as the Mössbauer source with no chemical treatment. ^{99}Ru Mössbauer spectra were obtained by a conventional arrangement, but both the source and the absorbers were maintained at 4.2 K in a liquid He cryostat during the measurements.[4,5]

The XRD pattern of *disordered* Na_2RuO_3 showed a trigonal structure with a = 0.313 nm and c = 1.605 nm. The parameters were consistent with those reported in Ref. 3. The ^{99}Ru Mössbauer spectrum of *disordered* Na_2RuO_3 obtained at 5.0 K is shown in Fig. 1 (a). The spectrum is similar to that of *ordered* Na_2RuO_3, reported in Ref. 4, and is reasonably fitted by a doublet with an isomer shift (δ) of –0.34(1) mm/s and a quadrupole splitting (ΔE_Q) of 0.30(5) mm/s. The linewidth of 0.44(5) mm/s was slightly broadened compared to that *ordered* Na_2RuO_3 owing to the shorter sintering time.

The XRD of non-stoichiometric Na-Ru oxides sintered with Na/Ru = 1.5 indicated that the sample crystallized in two phases of Na_2RuO_3 (85%) and $NaRu_2O_4$ (15%). $NaRu_2O_4$ is in the orthorhombic space group *Pnm* and consists of double chains of edge sharing RuO_6 octahedra.[6] The Mössbauer spectrum of Na-Ru oxides with Na/Ru = 1.5 is shown in Fig. 1 (b). It was difficult to analyze the two separated components, Na_2RuO_3 and $NaRu_2O_4$. However, assuming that the spectrum consists of one component, the Mössbauer spectrum could have δ = −0.42(1) mm/s and ΔE_Q = 0.49(1) mm/s. The value of δ indicated that the oxidation state of Ru ions was reduced from Ru^{4+} to $Ru^{3.5+}$ on average. The detailed discussion between the oxidation states of the Ru atoms and the Na/Ru ratios of non-stoichiometric Na-Ru oxides is under consideration.

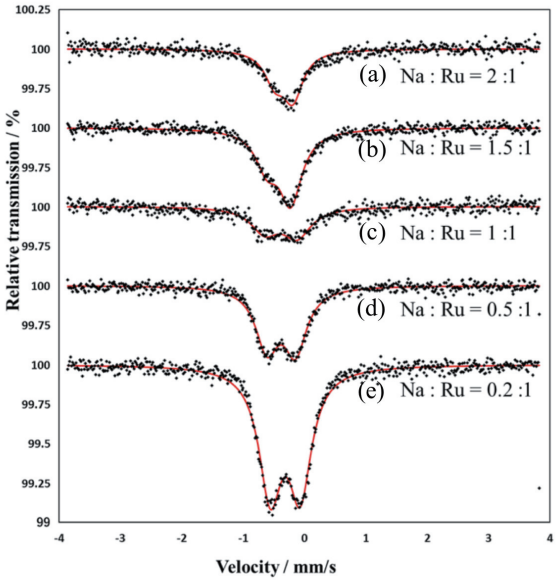

Fig. 1. ^{99}Ru Mössbauer spectra of (a) *disordered* Na_2RuO_3 and non-stoichiometric Na-Ru oxides (Na/Ru = (b) 1.5, (c) 1.0, (d) 0.5, and (e) 0.2) obtained by sintering at 850 ºC for 12 h in an Ar atmosphere.

References

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