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

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Na_2RuO_3 with a two-dimensional layered structure of $[RuO_3]2^-$ is expected as an electrode material for next-generation Na-ion batteries.[1–3] Until now, we have studied the crystal structures and oxidation states of Ru ions in Na_2RuO_3 and Na-Ru oxides with different ratios of Na/Ru using X-ray diffraction patterns and ^{99}Ru Mössbauer spectroscopy. It was revealed that the structures changed from two-dimensional to three-dimensional properties with Na deficiencies. In this paper, we report the result of the chemical states of Ru ion in Na_2RuO_3 observed before and after a charging experiment. A sample of Na_2RuO_3 was prepared through a solid-state reaction. A mixture of RuO_2 and $NaHCO_3$ was pressed and sintered at 850 °C for 12 h in Ar atmosphere. 95 wt% of Na_2RuO_3 was mixed with 5 wt% of amorphous carbon powder, and pressed to create a pellet for electrochemical measurements. The pellet sample and carbon rod were used as a cathode and an anode, respectively. 1 mol/L $NaPF_6$ in ethylene carbonate and diethyl carbonate (1:1 by volume) was used as an electrolyte. The charging experiment, which was an anodic process (Na^+ de-intercalation), was conducted at 20 mA/g and 4.0 V for 0.5 h and 2.0 h in an Ar-filled glove box. After the charging experiment, the Na_2RuO_3 electrode was washed with anhydrous dimethyl carbonates and then dried in a vacuum desiccator. For ^{99}Ru Mössbauer spectroscopy, the ^{99}Rh ($T_{1/2}$ = 15.0 d) of the source nuclide was produced by the ^{99}Ru(p, n)^{99}Rh reaction in an AVF cyclotron. ^{99}Ru Mössbauer spectra were obtained by employing a conventional arrangement with the source and absorber maintained at 4.2 K in a liquid He cryostat.[4,5] The XRD pattern of Na_2RuO_3 after the charging experiment showed that interlayer distance was significantly decreased from 5.45(1) Å to 5.18(3) Å. It was indicated that Na^+ ions were extracted from the $[Na_{1/3}Ru_{2/3}]O_2$ layers. The ^{99}Ru Mössbauer spectrum of Na_2RuO_3 after charging for 0.5 h showed two doublet peaks, as shown in Fig. 1. The spectrum was analyzed by D1 with an isomer shift (δ) of −0.32(1) mm/s and a quadrupole splitting (ΔE_Q) of 0.28(2) mm/s and D2 with δ = +0.20(5) mm/s and ΔE_Q = 1.52(8) mm/s. The ratio of absorption intensities was D1:D2 = 85:15. The isomer shift of D2 is a typical value of Ru^{5+}, for example, +0.19 mm/s for Ca_2EuRuO_6 and +0.11 mm/s for Na_3RuO_4. It was found that the de-intercalation of Na^+ ions increased the oxidation state of the Ru ion from Ru^{4+} to Ru^{5+} and significantly distorted the octahedron of RuO_6. Further details of the electronic structure of Ru ions in Na_2RuO_3 for the electrochemical procedure will be discussed with density functional calculations.

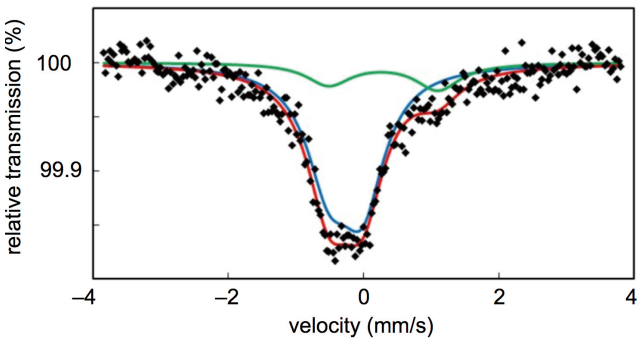

Fig. 1. ^{99}Ru Mössbauer spectrum of Na_2RuO_3 used as a cathode after charging (20 mA/g, 4.0 V) for 0.5 h. The blue and green lines correspond to components of D1 and D2, respectively. The spectrum was measured at 5.0 K.

References

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