99Ru and 57Fe Mössbauer spectroscopic studies of Na2Ru1−xFexO3 of sodium-ion battery electrode (2)

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

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. Na2RuO3 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 Na2RuO3 after charging and discharging processes via Mössbauer spectroscopy, X-ray diffraction (XRD), and electrochemical analysis.2) A sample of Na2Ru0.99Fe0.01O3 was prepared via a solid-state reaction. Stoichiometric mixtures of Ru2O3, NaHCO3, and Fe2O3 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 Na2Ru0.99Fe0.01O3, acetylene black, and polyvinylidene difluoride as a binder was applied on an Al foil. The Al foil with Na2Ru0.99Fe0.01O3 and a carbon sheet were used as the cathode and the anode, respectively. As the electrolyte, 1 M NaBF4 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 NaRuO3 were assigned, in addition to those of honeycomb-type Na2RuO3.

For performing 99Ru Mössbauer spectroscopy, the source nuclide 99Rh (T1/2 = 16.1 d) was produced by the nuclear reaction of 99Rh(p, n)99Rh at the AVF Cyclotron. 99Ru Mössbauer spectra were measured at 5 K in a conventional liquid He cryostat.3) The 99Ru Mössbauer spectra of Na2Ru0.99Fe0.01O3 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 Ru4+ with the isomer shift δ = −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 (Hhf) with quadrupole splitting (∆EQ). The red component (δ = −0.27(4) mm/s, ∆EQ = 0.51(9) mm/s, Hhf = 4.7(2) T) was consistent with the oxidation state of Ru4+ before charging. The blue component (δ = −0.01(4) mm/s, ∆EQ = 0.07(7) mm/s, Hhf = 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 Hhf 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 57Fe 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.

References

*1 Dep. of Eng. Sci., University of Electro-Commun
*2 RIKEN Nishina Center