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Structural and Valence Changes in Na_2RuO_3 Upon Charging probed by XAFS

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1 Introduction

Li-ion-based batteries power a wide range of portable electronic devices, and their energy storage capability is becoming increasingly important for large-scale applications such as electric vehicles and power grids. However, lithium resources are limited and unevenly distributed across the globe; hence, it is essential to explore alternative battery technologies that can support future energy demands. Among these, Na-ion-based batteries are considered promising options for large-scale energy storage systems, because of the high natural abundance and low cost of sodium. As a result, Na-ion (de)intercalation compounds have been explored thoroughly [1, 2]. In this study, we employed Na_2RuO_3 as a positive electrode material for sodium-ion batteries.

Na_2RuO_3 exhibits a layered structure, comprising $[Na_{1/3}Ru_{2/3}]O_2$ slabs and interlayer Na^+ ions [3]. During charging and discharging, these Na^+ ions migrate in and out of the interlayers through a one-electron redox reaction. The aim of this study is to clarify changes in the oxidation state and local coordination environment of Ru during the charging process. The oxidation state and local structure of Ru in Na_2RuO_3 before and after charging were evaluated using X-ray absorption fine structure (XAFS) measurements.

2 Experiment

Na_2RuO_3 was synthesized via a solid-state reaction following a reported method, in which the precursor was annealed at 850 °C for 48 h under an Ar atmosphere [4]. Before XAFS measurements, XRD was performed in our laboratory on samples before and after charging to confirm their crystal structures.

The oxidation state and local structure of Ru were then investigated using XAFS spectroscopy at the Ru K-edge in transmission mode on the NW10A beamline at the Photon Factory Advanced Ring (PF-AR), KEK.

3 Results and Discussion

Laboratory X-ray diffraction (XRD) measurements showed that the interlayer distance of Na_2RuO_3 decreased from 5.40 Å before charging to 5.19 Å after charging, indicating that Na^+ ions were extracted from the interlayer region.

Figure 1 shows the XAFS of Ru K-edge before and after charging for Na_2RuO_3. A shift of the Ru K-edge to higher energy was observed in the XAFS measurements upon charging, indicating an increase in the oxidation state of Ru.

Furthermore, changes in the spectral characteristics within the EXAFS region were observed, suggesting modifications in the local bonding environment related to Na^+ deintercalation.

In summary, these results indicate that Na^+ extraction upon charging leads to Ru oxidation and induces changes in its local structural environment. In the XAFS measurements, a shift of the Ru K-edge to higher energy was observed upon charging, indicating an increase in the oxidation state of Ru.

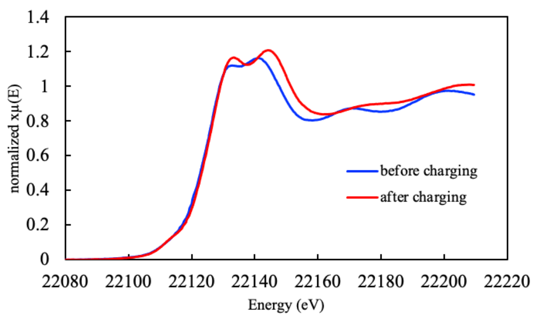

Fig. 1: Ru K-edge X-ray absorption spectra before and after charging for Na_2RuO_3.

References
[1] N. Yabuuchi *et al*., Chem. Rev. **114**, 11636 (2014).
[2] M. Tamaru *et al*., Electrochem. Commun. **33,** 23(2013).
[3] B. M. de Boisse *et al*., Nature Commun. **7**, 11397 (2016).
[4] K. M. Mogare *et al*., Z. Anorg. Allg. Chem. **630**, 547 (2004).

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