

Redox Reaction of O3-Type Mg-Doped Fe-Mn Oxides as Positive Electrode Materials for Na-Ion Batteries

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Na-ion batteries have attracted much attention and have been extensively studied in the world because of abundant resources of sodium and electrodes with earth abundant elements such as iron, manganese, and carbon in the electrode materials and aluminium as a current collector. As the negative electrode material, hard carbon is known as one of the most promising candidates for practical use. On the other hand, no standard positive electrode materials are found so far. Layered transition-metal oxides, polyanion compounds, and Prussian blue analogues are mainly studied to enhance the electrode performances. Our group reported that P2-type $\text{Na}_{2/3}\text{Fe}_{1/2}\text{Mn}_{1/2}\text{O}_2$ (P2- $\text{Na}_{2/3}\text{FeMn}$) consisting of only Earth-abundant elements delivers large discharge capacity of ca. 200 mAh g⁻¹ [1]. However, P2-FeMn is Na-deficient and shows ca. 140 mAh g⁻¹ without Na compensation from the counter electrode of Na metal which is not used in the practical Na-ion full cells. In contrast, O3-type $\text{NaFe}_{1/2}\text{Mn}_{1/2}\text{O}_2$ (O3- NaFeMn) contains almost stoichiometric Na amount in the structure and shows large reversible capacity without Na compensation [2]. O3-FeMn, however, delivers smaller reversible capacity of ca. 150 mAh g⁻¹ than ca. 200 mAh g⁻¹ of P2-FeMn [1]. Recently, we synthesized an intermediate phase of O3-type $\text{Na}_{5/6}\text{Fe}_{1/2}\text{Mn}_{1/2}\text{O}_2$ (O3- $\text{Na}_{5/6}\text{FeMn}$) delivering ca. 160 mAh g⁻¹ on charge. Furthermore, Mg-doped O3- $\text{Na}_{5/6}\text{FeMn}$ (O3- FeMnMg) exhibited charge/discharge capacities of 190 mAh g⁻¹. In this study, charge compensation mechanism of O3- $\text{Na}_{5/6}\text{FeMn}$ and O3- FeMnMg is investigated by soft X-ray absorption spectroscopy.

Fe and Mn L_{2, 3}-edge and O K-edge XANES spectra of O3- $\text{Na}_{5/6}\text{FeMn}$ and O3- FeMnMg electrodes were collected in partial fluorescence yield (PFY) and total and partial electron yield (TEY, PEY) modes at BL-11, SR center. Mg K-edge XANES spectra of O3- FeMnMg electrodes were similarly collected at BL-10. The electrodes were prepared at pristine state, 4.0 and 4.3 V on charge, 2.2 and 1.5 V on discharge by constant-current/constant-voltage charging and discharging techniques.

Fe and Mn L_{2, 3}-edge XANES spectra of both O3- $\text{Na}_{5/6}\text{FeMn}$ and O3- FeMnMg electrodes before

and after charge/discharge mainly showed L₃ and L₂ peaks at 710 and 722 eV, respectively, attributed to trivalent iron ion. Although obvious difference is not observed during charge/discharge, the both samples show increase in intensity at 712 and 725 eV above 4.0 V, which indicates oxidation of iron by Na extraction on charge. The increase in the peak intensity of O3- FeMnMg is slightly higher than that of O3- $\text{Na}_{5/6}\text{FeMn}$. In contrast to Fe, Mn K-edge spectra of O3- $\text{Na}_{5/6}\text{FeMn}$ and O3- FeMnMg electrodes show continuous and reversible peak disappearance at 639.8, 641.5, 651.0 eV and appearance at 644 and 654.7 eV during charge. Indeed, both Fe and Mn contribute to the redox reaction of O3- $\text{Na}_{5/6}\text{FeMn}$ and O3- FeMnMg during charge/discharge. The corresponding charge capacities were ca. 50 mAh g⁻¹ higher than theoretical ones calculated on Fe^{3+/4+} and Mn^{3+/4+} redox couples in the both samples.

O K-edge spectra show obvious change in the intensity and peaks at 527.5 and 529.7 eV increase by charging O3- $\text{Na}_{5/6}\text{FeMn}$ and O3- FeMnMg . The peaks reversibly decrease by discharge. The change is more significant in O3- FeMnMg , which is consistent with higher charge capacity of O3- FeMnMg than O3- $\text{Na}_{5/6}\text{FeMn}$. Indeed, Mg K-edge spectra of O3- FeMnMg electrodes show reversible increase in the peak at 1316 eV without obvious energy shift, suggesting change in the local structure surrounding Mg.

The results clearly reveal contribution of oxide ion into the redox reaction of O3- $\text{Na}_{5/6}\text{FeMn}$ and O3- FeMnMg during charge/discharge. Furthermore, Mg influences local structure and enhances redox of the oxide ion in O3- FeMnMg . Enhancing the reversibility for the oxide-ion redox would further develop high-energy Na-ion batteries.

References

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