

A Study on Charge/Discharge Mechanism of Na in P2-Na_x[Mg_{0.28}Mn_{0.72}]O₂ as Positive Electrode Materials for Na-Ion Batteries

Kei Kubota^{a,b}, Naoaki Yabuuchi^{a,b,c}, Ryo Hara^a, Yoshiyuki Tahara^a, and Shinichi Komaba^{a,b}

^aDepartment of Applied Chemistry, Tokyo University of Science, Tokyo 162-8601, Japan

^bESICB, Kyoto University, Kyoto 615-8245, Japan

^cDepartment of Green and Sustainable Chemistry, Tokyo Denki University, Tokyo 120-8551, Japan

1 Introduction

Li-ion batteries have recently been used as energy sources not only for power sources of portable electric devices and (hybrid) electric vehicles but also for large-scale electricity storage from solar and wind farms serving as green energy resources. However, lithium is classified as a minor metal and its price is continuously increasing after the commercialization of lithium-ion batteries. In contrast to lithium, sodium is an attractive charge carrier on the basis of material abundance and its similarity as an alkali metal ion element. Rechargeable Na-ion batteries are, therefore, believed to be the ideal alternative to Li-ion batteries. We have demonstrated that P2-type Na_{5/6}[Li_{1/4}Mn_{3/4}]O₂ is the promising candidate as high-energy manganese-based positive electrode materials for Na-ion batteries.[1] However, lithium as a minor metal is still needed to activate a redox reaction of oxide ions. Very recently, we have succeeded in replacement of lithium by magnesium, which is the Earth-abundant element, and the magnesium-substituted manganese oxides show surprisingly large reversible capacity in Na cells.[2] In this study, we examined electric state surrounding manganese in P2-type Na_{2/3}[Mg_{0.28}Mn_{0.72}]O₂ to understand the reaction mechanism and the effect of magnesium substitution by X-ray absorption spectroscopy (XAS).

2 Experiment

Composite positive electrodes consisted of 80 wt% active materials, 10 wt% acetylene black, and 10 wt% polyvinylidene fluoride (PVdF), pasted on aluminum foil as a current collector. The electrolyte solution used was 1.0 mol dm⁻¹ NaPF₆ dissolved propylene carbonate : Ethylene carbonate : Diethyl carbonate = 1 : 1 : 3 vol.%. Electrochemical testing was conducted using R2032-type coin cells with Na metals as negative electrodes. The coin cells were assembled in an Ar-filled glovebox and cycled at 10 mA g⁻¹. After the electrochemical tests, composite electrodes were taken out from the cell, and the electrodes were rinsed with DMC and sealed in a water-resistant polymer film in the Ar-filled glovebox.

3 Results and Discussion

X-ray absorption near edge structure (XANES) spectra of P2-Na_{2/3}[Mg_{0.28}Mn_{0.72}]O₂ at Mn K-edge are shown in Figure 1. The spectrum slightly shifted toward higher energy after charge to 3.8 V, suggesting the oxidation of

small amount of trivalent into tetravalent manganese. After fully charge to 4.4 V, a shape of the spectrum slightly changed without a significant energy shift. Furthermore, higher intensity of two pre-edge peaks without peak shift was observed in comparison to that of the electrode charged to 3.8 V, indicating that a stronger contribution of electric dipole transition presumably due to hybridized orbital with electrons of oxygen induced by Na extraction. After 1 cycle, the spectrum shifted to lower energy region of pristine, suggesting that higher amount of Na ions are inserted after discharge to 1.5 V compared to that of pristine. From these results, it is concluded that manganese ions are mainly tetravalent in pristine sample and the remained trivalent manganese ions are oxidized during charge and then reduced during discharge. Further study using soft X-ray absorption spectroscopy at Mg and O K-edge is under progress to confirm the contribution of magnesium and oxide ions in charge and discharge reaction in Na cells.

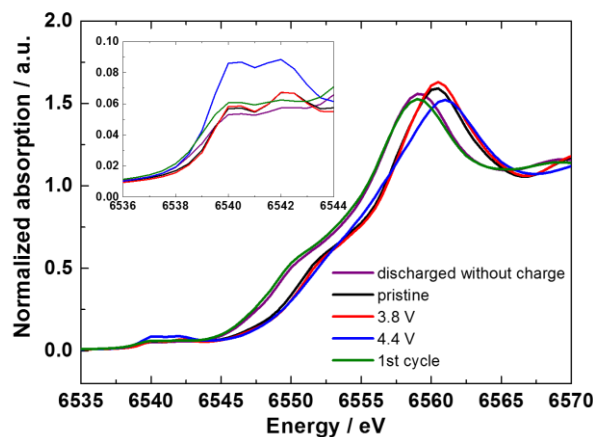


Fig. 1 Mn K-edge XANES spectra of P2-Na_{2/3}[Mg_{0.28}Mn_{0.72}]O₂ electrodes before and after charge/discharge in Na cells.

References

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* komaba@rs.kagu.tus.ac.jp