

Electrode Performance of Lithium Containing Layered Sodium Iron Manganese Oxides for Rechargeable Na-Ion Batteries

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Introduction

Rechargeable sodium batteries are the promising candidate for large-scale applications because the sodium resources are unlimited everywhere. Recently, our group reported that P2-type $\text{Na}_{2/3}[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ consisting of abundant elements in natural resources provides 190 mAh g^{-1} of reversible capacity in the sodium cell[1]. This reversible capacity is higher than those of O3- NaFeO_2 and O'3- NaMnO_2 electrodes. However, the P2-type phase is generally known to be a sodium deficient phase, which leads to an excess discharge capacity at the initial cycle. Our group also reported that P2-type $\text{Na}_{5/6}[\text{Li}_{1/4}\text{Mn}_{3/4}]\text{O}_2$, containing a higher amount of sodium as P2-phase, delivers a larger initial charge capacity compared to P2- $\text{Na}_{2/3}[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ phase[2]. In this study, to increase the initial charge capacity and further increase a reversible capacity, the solid solution of $\text{Na}_{2/3}[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2 - \text{Na}_{5/6}[\text{Li}_{1/4}\text{Mn}_{3/4}]\text{O}_2$ is synthesized, and its structural and electrochemical properties are studied.

Experimental

Solid solution between $\text{Na}_{2/3}[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ and $\text{Na}_{5/6}[\text{Li}_{1/4}\text{Mn}_{3/4}]\text{O}_2$ was synthesized by a solid-state reaction. Na_2CO_3 , Li_2CO_3 , $\text{MnCO}_3 \cdot \text{H}_2\text{O}$ and $\alpha\text{-Fe}_2\text{O}_3$ were mixed by mechanical milling, pelletized and then heated at $700 - 900^\circ\text{C}$ for 12 hours in air. Crystal structure and morphology of the samples were examined by using powder synchrotron X-ray diffraction measurements and scanning electron microscopy. Electrochemical properties were tested using coin-type cell. Positive electrodes consisted of the active material, acetylene black and polyvinylidene fluoride (PVDF) with a gravimetric ratio of 80:10:10. Metallic sodium was used as a negative electrode. The electrolyte used was $1.0 \text{ mol dm}^{-3} \text{ NaClO}_4 / \text{PC} : \text{FEC} (98 : 2)$ [3].

Results and Discussion

Figure 1 shows the synchrotron X-ray diffraction (XRD) patterns of $x\text{Na}_{2/3}[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2 - (1-x)\text{Na}_{5/6}[\text{Li}_{1/4}\text{Mn}_{3/4}]\text{O}_2$ ($x = 0, 1/3, 1/2, 2/3$ and 1.0). All Bragg diffraction lines, except a superlattice line at ca. 7 degrees, are indexed based on the P2-type layered structure with a space group $P6_3/mmc$, indicating the formation of the solid solution between $\text{Na}_{2/3}[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ and $\text{Na}_{5/6}[\text{Li}_{1/4}\text{Mn}_{3/4}]\text{O}_2$. As increasing a portion of $\text{Na}_{2/3}[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$, a peak profile of $10l$ lines broadens. Therefore, the existence of stacking faults is expected to be significant, especially for the sample of $x = 2/3$. Initial charge and discharge curves for two end-members of P2-type $\text{Na}_{2/3}[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ and $\text{Na}_{5/6}[\text{Li}_{1/4}\text{Mn}_{3/4}]\text{O}_2$, and the one-to-one solid solution ($x = 0.5$), are shown in Fig. 2. For the sample of $x = 0.5$, the excess discharge capacity is effectively decreased compared with that of $\text{Na}_{2/3}[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$, and higher reversible capacity of approximately 200 mAh g^{-1} than

those of two end-members is achieved. A characteristic initial charge plateau, similar to Li_2MnO_3 -based high capacity electrode materials, is observed as increase in the lithium contents. The partial oxygen loss is, therefore, expected similar to the observation for Li_2MnO_3 -based materials[4]. From these results, the relationship between the crystal structures and electrochemical properties will be further discussed.

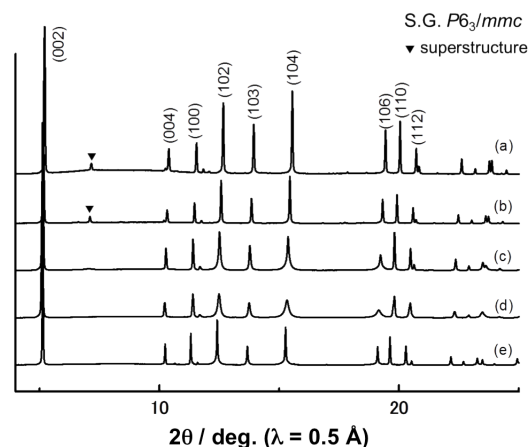


Fig. 1 Synchrotron XRD patterns of the solid solution samples of $x\text{Na}_{2/3}[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2 - (1-x)\text{Na}_{5/6}[\text{Li}_{1/4}\text{Mn}_{3/4}]\text{O}_2$ for $x =$ (a) 0, (b) 1/3, (c) 1/2, (d) 2/3, and (e) 1.0. The end-members of P2- $\text{Na}_{5/6}[\text{Li}_{1/4}\text{Mn}_{3/4}]\text{O}_2$ ($x = 0$) and $\text{Na}_{2/3}[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ ($x = 1$) were synthesized at 700 and 900°C , respectively. The samples of $x = 1/3, 1/2$ and $2/3$ were synthesized at 800°C .

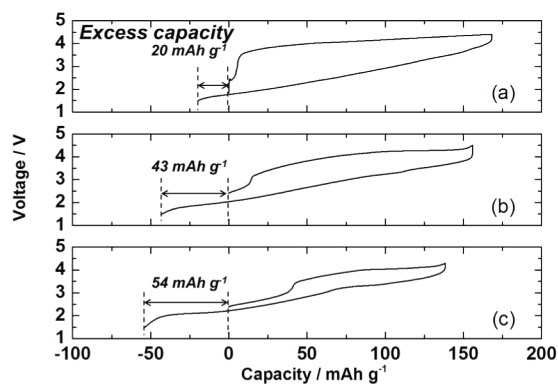


Fig. 2 Initial charge and discharge curves of Na cells using the solid solution samples of $x\text{Na}_{2/3}[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2 - (1-x)\text{Na}_{5/6}[\text{Li}_{1/4}\text{Mn}_{3/4}]\text{O}_2$ for $x =$ (a) 0, (b) 1/2 and (c) 1.0 at C/20 rate.

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