

Preparation and characterization of pure P2 and O3-phase $\text{Na}_x\text{Mn}_x\text{Fe}_{2/3-x}\text{O}_2$ compounds.

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Although the search to find new and high performance cathodes for electrochemical applications in lithium batteries is still ongoing [1], cathode materials for Na-ion batteries are getting more attention recently ever since they were firstly investigated in 1980's. [2,3]

Among the possible Na-ion cathodes, layered oxides including NaMnO_2 [4], NaNiO_2 [5], and $\text{Na}_x\text{Mn}_{1-y}\text{Fe}_y\text{O}_2$ [6-8] are extensively studied because of their relatively simple structure, formation of excellent layered oxide crystalline structure, and high theoretical capacity.

We have focused our research on Na-Mn-Fe-O systems and we succeeded to synthesize pure P2 and O3 phases with the same stoichiometry at $\text{Na}_x\text{Mn}_x\text{Fe}_{2/3-x}\text{O}_2$.

Pure P2 and O3-phases have been obtained by a solid state reaction under oxygen atmosphere. Structural and morphological studies are performed with various analytical techniques including XRD, SEM, and TEM. In addition, ICP was used for determining the stoichiometric composition of Na, Mn, Fe.

The electrochemical behaviour of P2 and O3-phase electrodes were analysed in nonaqueous coin cells (CR2032-type) and Swagelok cells, which were assembled in an Ar-filled glove box. Sodium was used as the negative electrode, while for the positive electrode a mixture of as-synthesized P2 or O3-phase powder, carbon Super C65 and a binder (EPDM 5% in cyclohexane) in an 80:10:10 mass-ratio was laminated onto an aluminium sheet. A solution of NaPF_6 0.5M in EC: DMC 1:1 was used as the electrolyte. Electrochemical data were collected using the Maccor battery testing system and Biologic VMP3 potentiostat in galvanostatic mode at different C/rates between 2-4V.

Fig. 1 shows the XRD pattern of P2 and O3-phase $\text{Na}_x\text{Mn}_x\text{Fe}_{2/3-x}\text{O}_2$. X-ray diffraction pattern of P2 can be fully indexed with the P63/mmc space group and hexagonal lattice whereas O3 is fitted with the R-3m space group and a rhombohedral cell.

Capacity values for the synthesized P2 and O3 are in good agreement with the published literature by Yabuuchi [6] and Thorne [8] for similar Na-layer materials. Due to the different electrochemical processes of $\text{Mn}^{3+}/\text{Mn}^{4+}$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$, two slight plateaus were observed. The experimental capacity of P2 and O3 phases for the first five cycles is comparable and around 130 mAh/g within the voltage range of 2-4V. A more detailed comparison between both systems will be presented in this work.

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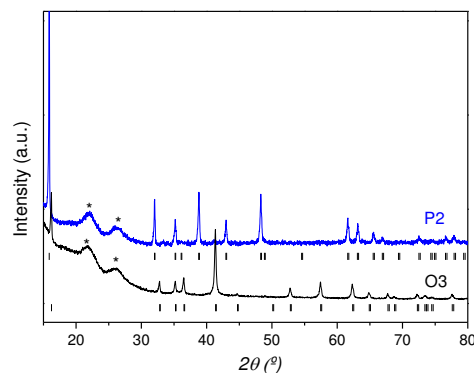


Fig. 1. X-ray diffraction patterns of P2 (blue line) and O3 (black line) $\text{Na}_x\text{Mn}_x\text{Fe}_{2/3-x}\text{O}_2$. The broad signals labelled with asterisks belong to the Kapton foil used to make the air sensitive measurements. Vertical bars indicate the positions of the Bragg peaks of the P2 and O3 phases.

References

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