# Synthesis and Characterization of P2-Na<sub>2/3</sub>Fe<sub>x</sub>Mn<sub>1-x</sub>O<sub>2</sub> for Na-Ion Batteries

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### Introduction

The layered oxides  $Na_xMO_2$  (M = transition metal) electrode materials can be categorized into three main groups using the classification proposed by Delmas et al.; O3, P2, and P3 types where the alkali atoms occupy either octahedral or prismatic sites, respectively [1]. Recently, P2-Na<sub>2/3</sub>Fe<sub>1/2</sub>Mn<sub>1/2</sub>O<sub>2</sub> has attracted attentions because the rechargeable capacity exceeded 190 mAh/g against Na after 2<sup>nd</sup> cycle [2]. The aforementioned phase can be obtained by various precursors under different synthesis conditions. The most important factor is the firing temperature and the Na:Fe:Mn ratio [2-4]. In order to investigate the phase stability, we tried to synthesize  $Na_{2/3}Fe_xMn_{1-x}O_2$  series. In this work, we report the synthesis and characterization of P2-Na<sub>2/3</sub>Fe<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub> phase as our best the cathode material among them in Naion batteries.

## **Experimental**

Solid-state reaction was utilized to synthesize the compounds. (Wako Pure Chemical Industries, Ltd. 97% purity)  $Na_2O_2$  (Sigma-Aldrich Co. LLC),  $Fe_2O_3$  (99.7%) and  $Mn_2O_3$  (98%) were used respectively as precursors.  $Na_2O_2$  serves not only as a source of Na, but also as an oxidizer that helps to get a single-phase pure material.

Stoichiometric amounts of Na-Fe-Mn precursors were mixed in an Ar-filled glove box and pelletized. The pellets were calcined at 900 °C for 12h in the air and quenched to room temperature by taking the samples out of the furnace. The samples were stored into an Ar-filled glove box. Cathodes were prepared by ball-milling of 80 wt% active material with 10 wt% acetylene black, and then the powders were mixed with an appropriate amount of 5 wt% PVDF solution in NMP. The slurry was pasted on Al current collector and dried under vacuum at 80°C. Battery test was performed using 2032 coin-type cells. The separator was a porous polypropylene film (Celgard 3501) and sodium metal foil was used as a counter electrode. 1 M NaPF<sub>6</sub> in ethylene carbonate (EC) : diethyl carbonate (DEC) (1:1 v/v) solutions were used as the electrolyte. The coin-cells were assembled in an Ar-filled glove box with a dew point below -80 °C. The cycling tests were conducted between 1.5 V and 4.3 V at a rate of 12 mA g<sup>-1</sup>.

### **Results and Discussion**

Figure 1 shows the Rietveld refinement of the XRD pattern of as-synthesized P2-Na<sub>2/3</sub>Fe<sub>1/2</sub>Mn<sub>1/2</sub>O<sub>2</sub> with the following lattice parameters: a = 2.913 Å, c = 11.269 Å (P 63/m m c). All the peaks are sharp and well defined indicating that the crystallinity of the compound is high. The refinement is in a good agreement with P2-single

phase without any impurities. We believe that these are the main reasons for the superior performances of our material in comparison with the same type of materials prepared by the other synthesis routes [3].

Figure 2 shows the voltage profiles and the cyclability of  $Na_{2/3}Fe_{1/3}Mn_{2/3}O_2$  in 1 M NaPF<sub>6</sub> EC:DEC(1:1 v/v) electrolyte. The second charge/discharge capacities are around 210 mAh/g and 200 mAh/g, respectively. After 20 cycles, the discharge capacity is still 160 mAh/g. The redox couple at the first sloppy region are  $Mn^{3+/4+}$ , and the second region in the high voltage are  $Fe^{3+/4+}$ , which were confirmed by X-ray absorption spectroscopy (XAS). The reversibility and thermal stability is being investigated and mapped among  $Na_{2/3}Fe_xMn_{1-x}O_2$  series.



Fig. 1. XRD pattern of P2-type  $Na_{2/3}Fe_{1/3}Mn_{2/3}O_2$ . The refinement was carried out by Rietveld method using the FullProf software package. The refinement was performed in the P 63/m m c space group and the R-factors are  $R_{wp}$ =2.00,  $R_B$ =10.20.



Fig. 2. The voltage profiles and the cyclability of  $Na_{2/3}Fe_{1/3}Mn_{2/3}O_2$  at a rate of 12 mA/g in the voltage range of 1.5 V and 4.3 V.

# **References:**

[1] C. Delmas, C.Fouassier, P. Hagenmuller, *Physica B+C* **99**, 81-85 (1980).

[2] N. Yabuuchi, M. Kajiyama, J. Iwatate, H. Nishikawa, S. Hitomi, R. Okuyama, R. Usui, Y. Yamada, S. Komaba, *Nat. Mater.*, **11**, 512-517 (2012).

[3] B.Mortemard de Boisse, D. Carlier, M. Guignard, C. Delmas, *J. Electrochem. Soc.*, **160** (4) A569-A574(2013).

[4] M. Yoncheva, R. Stoyanova, E. Zhecheva, E. Kuzmanova, M. Sendova-Vassileva, D. Nihtianova, D. Carlier, M. Guignard, C. Delmas, *J. Mater. Chem.*, **22**, 23418 (2012).