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Mn-doped $NaFeO_2$ from a low purity-Fe precursor and its performance as cathode for Sodium-Ion Battery

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ABSTRACT

Research to produce Mn-doped $NaFeO_2$ was conducted from a low purity Fe-precursor aims to check the reliability for the inexpensive-mass production of the compound. The $NaFeO_2$ was prepared through the co-precipitation method from iron sand concentrate with Fe content of 86.72% consist of the hematite-ilmenite mixture. The reaction was conducted at 650 °C for 12 h under air argon atmosphere producing a mix of β-$NaFeO_2$ and α-$NaFeO_2$, which was then mixed with Mn_2O_3 to produce $Na_{1-x}[Fe_{1-x}Mn_x]O_{2-\delta}$ (NFMO) at various x of 0.02; 0.05; and 0.07. The result shows that Mn doping changed the crystal structure from orthorhombic into a hexagonal, *P63/mmc*. FTIR spectra provides peaks attributed to Na-O, Na-Fe, Mn-O, and Fe-O. Voltammetry analysis to NFMO-0.02 and NFMO-0.05 provide peaks attributed to Na^+/Na and Fe^{3+}/Fe^{4+} redox reaction. Meanwhile, the NFMO-0.07 provides Na^+/Na, Fe^{3+}/Fe^{4+}, and Mn^{3+}/Mn^{2+}. The NFMO-0.07 also shows the highest electrical conductivity of 1.372×10^{-4} Scm^{-1}. A split cell test developed with NFMO-0.07 as cathode produced an initial specific capacity of 50.57 $mAhg^{-1}$ and an initial discharge capacity of 36.29 $mAhg^{-1}$ correlate to 71.70% Columbic efficiency.

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Introduction

Nowadays, the battery is an important device to support life activities, in which Lithium-Ion Battery, LIB, is now dominating the world market. However, recently, lithium source limitation is being considered as an obstacle to the sustainability of future production. Some researchers start to calculate sodium to substitute lithium ions as charge carriers within a battery or named as Sodium-Ion Battery, SIB,[1,2] Sodium is cheaper than lithium and more abundantly available on earth,[3] has a competitive charge-discharge, good reversibility, and also provides a high Columbic efficiency.[4,5]

Some positive electrodes or cathodes have been studied for SIB such as sodium layer oxide, NaMO (M is metal), $NaFeO_2$ by Ni, delivering initial discharge capacity of 135 $mAhg^{-1}$ within $2.5-3.8$ V with an initial Columbic efficiency of 93%.[15]

A layered-sodium oxide is generally categorized within two kinds of O3 (octahedral) type, and P2 (prismatic) type.[12,16] The O3 α-$NaFeO_2$ type produces a capacity limit of 80 $mAhg^{-1}$ at 3.3 V. The capacity is less than half of its theoretical capacity, 242 $mAhg^{-1}$,[17,18] Meanwhile, the P2 α-$NaFeO_2$ can reach higher capacity. However, the P2 type is not stable due to structural degradation caused by Jahn-Teller distortion.[12] Therefore, doping might be a solution to stabilize the P2 structure. Some elements to dope into α-$NaFeO_2$ can be Ni,[15] Co,[19] and Mn.[12,20] The Mn-doped $NaFeO_2$ or $NaNiO_2$ has known to produce a high specific capacity SIB, such Mn-doped $NaFeO_2$ producing