

Synthesis and characterization of P2- $\text{Na}_x[\text{Fe}_{1/2} \text{Mn}_{1/2}]\text{O}_2$ iron and manganese based electrode material for sodium ion rechargeable batteries

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Abstract - Large-scale high-energy density batteries with electrode materials made from the earth-abundant elements are needed to achieve sustainable energy development. On the basis of material abundance, rechargeable sodium batteries with iron- and manganese based electrode materials are the ideal candidates for large-scale batteries. Layered sodium oxides with the formula Na_xMO_2 (where x is comprised between 0 and 1, M is a transition metal) have been intensively studied there last thirty years either for their unique physical properties or with a view for their use in sodium-ion batteries. More recently, advanced electrochemical properties of some Na_xMO_2 systems containing only one transition metal have been re-investigated and new complex materials with several transition metals in the MO_2 layers have been synthesized and studied. In particular, systems containing non-toxic and abundant elements such as manganese and iron appear very attractive and first results in the P2- $\text{Na}_x[\text{Fe}_{1/2} \text{Mn}_{1/2}]\text{O}_2$ system have showed a capacity as high as 190 mAh/g. The promising results were obtained in other compositions in manganese and iron based systems. Sodium deficient iron-manganese oxides $\text{P2-Na}_x\text{Fe}_{1/2} \text{Mn}_{1/2}\text{O}_2$ are prepared from acetate precursors. We first synthesis and characterize some properties of the P2- $\text{Na}_x[\text{Fe}_{1/2} \text{Mn}_{1/2}]\text{O}_2$ cathode material by conventional solid state method with higher calcination temperature. Hereby the X-ray diffraction analysis the purity of the crystalline structure is observed in good manner and the infrared spectra are recorded on Fourier Transform Spectrometer in the mid-infrared region (MIR) within the range (400-4500 cm^{-1}). IR absorption of the functional groups varies over a wide range. The prepared sample is also studied by Raman spectroscopy.

Key words: Sodium Ion battery, iron-manganese, P2 Type layer, solid state method, cathode material

1. INTRODUCTION

Sodium-ion batteries (SIBs) have attracted much attention as a promising alternative to Lithium ion batteries for large-scale energy storage, due to the natural abundance and low cost of sodium resources[1-3]. One of the most

conceivable cathode candidates for sodium-ion batteries is layered rock salt Na_xMO_2 (M transition metal). Na_xMO_2 can be categorized into three main groups using the classification proposed by Delmas et al.; the O3, P2, and P3 types[4]. Fe and Mn are the most attractive elements for cathodes of large batteries, because of the low environmental impact and cost. O3-type $\alpha\text{-NaFeO}_2$ and $\alpha\text{-NaMnO}_2$ also show electrochemical activity. However, only about 0.4 Na in $\alpha\text{-NaFeO}_2$ and less than 0.8 Na in $\alpha\text{-NaMnO}_2$ could be reversibly extracted, respectively [5-7]. P2 type Layered sodium transition metal oxides are regarded as promising candidates for stationary and mobile energy storage. The challenge is to develop low cost batteries operating in a similar fashion as their lithium counterparts at room temperature. In the 1980s, surveys, done mainly by Delmas's group[7-10], the general approach to improve crystal structure stability is to introduce foreign metallic ions to diminution the Mn (III) content and stabilize the crystal structure[11] recently N.Yabuuchi et.al. Synthesized electrode material P2- $\text{Na}_{2/3}[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$, that delivers 190mAhg⁻¹ of reversible capacity in the sodium cells with the electrochemically active $\text{Fe}^{3+}/\text{Fe}^{4+}$ redox. These results will contribute to the development of rechargeable batteries from the earth-abundant elements operable at room temperature [12]. In this proposed work we have Synthesized P2 type layered $\text{Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ cathode material for sodium ion secondary battery by conventional solid state method and the prepared materials are characterized for their physical properties using XRD, FTIR and Raman analysis.

1.1 EXPERIMENTAL

Preparation of $\text{Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$

The cathode material P2- $\text{Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ was prepared through conventional solid state method. Stoichiometric amounts of the precursor was prepared by mixing desirable amount of $\text{Fe}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and CH_3COONa with high purity of 99.9%

from sigma Aldrich chemicals, then the precursor materials well ball milled by using RETSCH planetary ball miller model PM 100 at 250 rpm for 6 h, the well ground materials followed by calcination at temperature 850°C for 12 h in argon atmosphere. The final product was well ground by hand, the $\text{Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ cathode material was methodically characterized for its physical properties.

1.2 Material characterization

The crystallinity and phase materialization of the prepared samples were described by powder X-ray diffraction (XRD) using $\text{Cu K}\alpha$ radiation on the PANalytical X'pert diffractometer in the 2θ range 10 – 80°. The functional group vibrations were analyzed through Fourier Transform Infrared Spectroscopy (Thermo Nicolet – 380 FTIR spectrophotometer using KBr pellets) the infrared spectra are recorded on Fourier Transform Spectrometer in the mid-infra-red region (MIR) within the range (400-4500 cm^{-1}). Due to the complex interaction of atoms with in the molecule, IR absorption of the functional groups varies over a wide range. However, it has been found that many functional groups give characteristic IR absorption at specific narrow frequency range. Stretching & bending vibrations are varied after formulation can be observed.

2. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of P2- $\text{Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ prepared sample. All peaks in the XRD patterns of $\text{Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ can be indexed rhombohedral lattice with space group R3m, that is, the same as for O3-type NaFeO_2 space group $\text{P6}_3/\text{mmc}$. All the products were found to be single phase with some impurities of Mn_2O_4 (JCPDS: 53-0349) and the presence of more impurities of other oxides may reduced with calcination temperature at 850°C and above. In this work some impurities are observed, so highly purity crystalline structure with lower impurities can obtained may at higher temperature range its can alleged from the XRD analysis of prepared materials of P2- $\text{Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$.

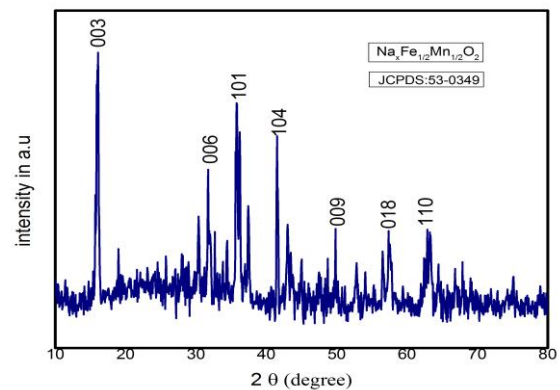


Fig-1: XRD patterns of P2 type layered - $\text{Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$

Raman analysis & Fourier Transform Infrared Spectroscopy studies

Fig. 2 displays the FTIR spectra of P2- $\text{Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ samples. The FTIR spectra of P2- $\text{Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ display two intensive adsorption bonds at approximately 866 cm^{-1} and 1105 cm^{-1} , which could be attributed to the inconsistent stretching modes of MO_6 groups and bending mode of O-M-O bonds. Further, weak shoulder at approximately 620 cm^{-1} also observed. The presence of bond at 1441 cm^{-1} would indicate the being of sodium content of the prepared composite. Fig. 3 displays spectra of P2- $\text{Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ the broadening of the Raman spectra, the peak appears at frequency range (188 cm^{-1}) is indicates the presence of sodium content then there is no more peaks observed in Raman spectra.

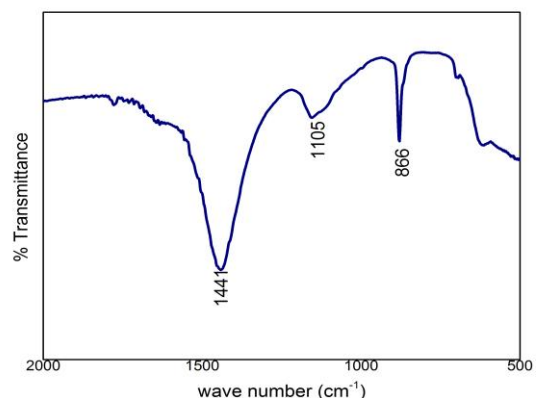


Fig-3: FTIR spectra of as-synthesized P2 type layered - $\text{Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ composites

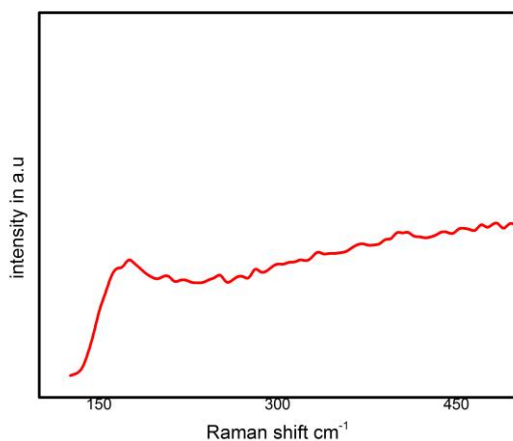


Fig-3: Raman spectra of the P2 type layered - $\text{Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ cathode materials

3. CONCLUSION

The P2 type layered $\text{Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ cathode materials prepared successfully by conventional solid state method by the XRD analysis, the structure of materials is compared with standard XRD patterns of P2- $\text{Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ can be indexed to P2 layered structure with space group P3/m. The purity of the sample obtained only at higher calcination temperature by dropping the moistness of output materials. The FTIR spectra of P2- $\text{Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ display two intensive adsorption bonds at approximately 866 cm^{-1} and 1105 cm^{-1} . The presence of bond at 1441 cm^{-1} would strongly confirms the presence of sodium content on the material. The sturdy peak appears at 188 cm^{-1} frequency is specifies the manifestation of sodium content from the observed revision of synthesis and characterization of the P2 type layered P2- $\text{Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ strongly imitates it had better for cathode material for sodium ion rechargeable batteries.

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BIOGRAPHIES



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