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Study of Synthesis and characterization of P2 type layered $Na_{2/3}[Ni_{1/3}Mn_{2/3}]\ O_2$ cathode material for sodium ion secondary batteries

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Abstract:- *Sodium ion batteries are an attractive alternative to lithium ion batteries thatalleviate problems with lithium availability and cost. Sodium is a cheap, non-toxic and abundant element that is uniformly distributed around the world and therefore would be ideal as a transporting ion for alternative rechargeable batteries. Despite several studies of cathode materials for sodium ion batteries involving layered oxide materials, there are few low-voltage metal oxide cathode capableof operating sodium ion reversibly at room temperature. The P2type*$Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ *is a high-voltage cathode material for Na-ion batteries with a theoretical capacity of173mAh/gandalong operation voltage plateau of 4.2V. In this study, Sodium deficient nickel–manganese oxides* $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$*were prepared from acetate precursors. We first synthesize and characterize some properties of the P2 type* $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ *cathode material by conventional solid state method by different calcination temperature. Hereby, theX-ray diffractionanalysis exhibits the purity of the crystalline structure and the infrared spectra were recorded on Fourier Transform Spectrometer in the mid–infrared region (MIR) within the range (400-4500 cm-1).IR absorption of the functional groups may vary over a wide range.*

Key words: *Sodium Ion battery, P2 type layered structure, solid state method.*

Introduction

Lithium (Li)-ion batteries (LIB) have overseen the current worldwide rechargeable battery market due to their outstanding energy and power capability. In particular, the LIB's role in endowing electric vehicles (EVs) has been highlighted to replace the current oil-driven vehicles in order to reduce the usage of oil resources and generation of CO_2 gases. Unlike Li, sodium is one of the most abundant elements on Earth and exhibits similar chemical properties as Li, indicating that Na chemistry could be applied to a similar battery system [1].Exceptional to the plenty and stumpy cost of sodium resources, many researchers have given their curiosity to the field of the sodium ion batteries (SIBs) [2-5].Conversely, numerous electrochemicallyactive systems for sodium-ion batteries (SIBs) have been thoroughly explored during and afterthe year 2010, addressing several apprehensions including poor capacity retention, low reversible capacity, etc. [6-13]. One of the most conceivable cathode candidates for sodium-ion batteries is layered rock salt Na_xMO_2(M ¼ transition metal). Na_xMO_2 can be characterized into three maingroups using the arrangement proposed by Delmas et al.; that is O3,P2, and P3 types [14]. Here P2 type Layered sodium transition metal oxides are regarded as promising candidates for stationary and mobile energy storage. Thechallenge is to develop low cost batteries operating in a similarfashion as their lithium counterparts at room temperature In the 1980s, surveys, done mainly by Delmas and group [15-17], the Jahn-Teller distortion of Mn (III)is a most significant factor on the structural stability for Mn-based oxides during ion insertion. A general approach to improve this problem is to introduce foreign metallic ions to diminutionthe Mn (III) content and stabilize the crystal structure [18]. Recently,Manikandan et.al. synthesized using sol-gel technique, the compound $Na_{0.5}[Ni0_{.25}Mn_{0.75}]O_2$ with a layered P2-type structure that exhibits excellent electrochemical performance by delivering a high discharge capacity [19]. In this work we have synthesized P2 type layered $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$cathode material for sodium ion secondary battery by conventional solid state method and found thevirtuous manifestation of the layered$Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ material which can revealtremendouselectrochemical performance with decent charge-discharge capacities.The prepared aggregates are characterized for their physical properties using XRD, FTIR and Raman analysis methods.

EXPERIMENTAL

Synthesis of $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$

The cathode material P2- $Na_{2/3}[Ni_{1/3}Mn_{2/3}]\ O_2$ was prepared through conventional solid state method. Stoichiometric amounts of the precursor was prepared by mixing desirable amount of $Ni(CH_3COO)_2.4H_2O$, Mn $(CH_3COO)_2\ .4H_2O$ and CH_3COONa with high purity of 99.9% from sigma Aldrich chemicals ,then the precursor materials was well ball milled by using RETSCH planetary ball miller model PM 100 at 300rpm with BPRs(Ball to Powder Ratio) of 5:1 for 6 h followed by calcination at various temperature such as 700,800 and 900°C for 12 h in Argon atmosphere. The final product was well ground by hand and the $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$prepared cathodematerialwas methodically characterized for its physical properties.

Material characterization

The crystallinity and phase formation of the prepared samples were characterized by powder X-ray diffraction (XRD) using Cu Kα radiation on the PANalytical X'pert diffractometer in the 2Θ=10–70°. 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-redregion (MIR) within the range (400-4500 cm-1). Due to the complex interaction of atoms within the molecule, IR absorption of the functional groups varies over a wide range. However, ithas been found that many functional groups give characteristic IR absorption at specific narrowfrequency range. Stretching & bendingvibrations are varied after formulation can be observed.

RESULTS AND DISCUSSION

Fig. 2 shows the XRD sketches of P2-$Na_{2/3}[Ni1_{/3}Mn_{2/3}]O_2$ samples with different calcination temperatures. All peaks in the XRD patterns of $Na_{2/3}[Ni_{1/\ 3}Mn_{2/}3]O_2$ can be indexed to P2 layer structure with space group $P6_3/mmc$. All the products were found to be single phase with some impurities of $NiMn_2O_4$(JCPDS:54-0894), but, the presence of more impurities of other oxides was reduced when calcined at 900°C and below that more impurities are presented; so high pure crystalline structure with lower impurities can be obtained only at higher temperature range. This can be perceived from the XRD analysis of prepared materials of P2-$Na_{2/3}[Ni1_{/3}Mn_{2/3}]O_2$.

Fourier Transform Infrared Spectroscopy &Raman analysis

Fig. 3displays the FTIR spectra of $Na_{2/3}[Ni1_{/3}Mn_{2/3}]O_2$samples. The FTIR spectra of P2- $Na_{2/3}[Ni1_{/3}Mn_{2/3}]O_2$display two intensive adsorption bonds at approximately 619 and 866 cm $^{-1}$, which could be attributed to the asymmetric stretching modes of MO_6 groups and bending mode of O-M-O bonds.Further, weak shoulder at approximately 620 cm^{-1}is also observed in respect of other metal oxide group. The existence of bond at 1441 cm $^{-1}$ would indicate the presence of sodium content on the surface of the composite. Fig.4displays the spectra of P2-$Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$; the broadening of the Raman spectra, could be explained either by lattice disorder in the polycrystalline sample or possible sub-lattice formation in the matrix.The strong peak appears at high frequency (188 cm^{-1}) indicates the presence of sodium contentin Raman spectra.

CONCLUSION

The P2 type layered $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ cathode materials was prepared successfully by conventional solid state method. XRD analysis reveals that the structure of prepared materials was confirmed asJCPDS:54-0894 XRD patterns of $Na_{2/3}[Ni_{1/\ 3}Mn_{2/}3]O_2$and can be indexed to P2 type layer structure with space group $P6_3/mmc$. The high purity of sample hasobtained only at higher temperature by dropping the moistness of output materials.The FTIR spectra of P2-$Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$display two intensive adsorption bonds at approximately 619 and 866 cm^{-1}. The existence of bond at 1441 cm^{-1} would indicate the presence of sodium content on the surface of the compositeRaman spectra could be explained either by lattice disorder in the polycrystalline sample or by possible sub-lattice formation in the matrix.The durable peak appears at high frequency is (188 cm^{-1}) specifies the presence of sodium content. Finally, from the study of synthesis and characterization of theP2 type layered $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$,it is strongly confirmed that this material could be suitable for being a cathode material in sodium ion secondary battery fabrication.

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FIGURE CAPTIONS

Figure 1.P2 Type layered structure

Figure 2.XRD patterns of P2 type layered Na$_{2/3}$[Ni$_{1/3}$Mn$_{2/3}$]O$_2$ (JCPDS card no: 54-0894)

Figure 3.FTIR spectra of as-synthesized P2 type layered Na$_{2/3}$[Ni$_{1/3}$Mn$_{2/3}$]O$_2$ composites.

Figure 4. Raman spectra of the P2 type layered Na$_{2/3}$[Ni$_{1/3}$Mn$_{2/3}$]O$_2$ cathode materials

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Figure: 1

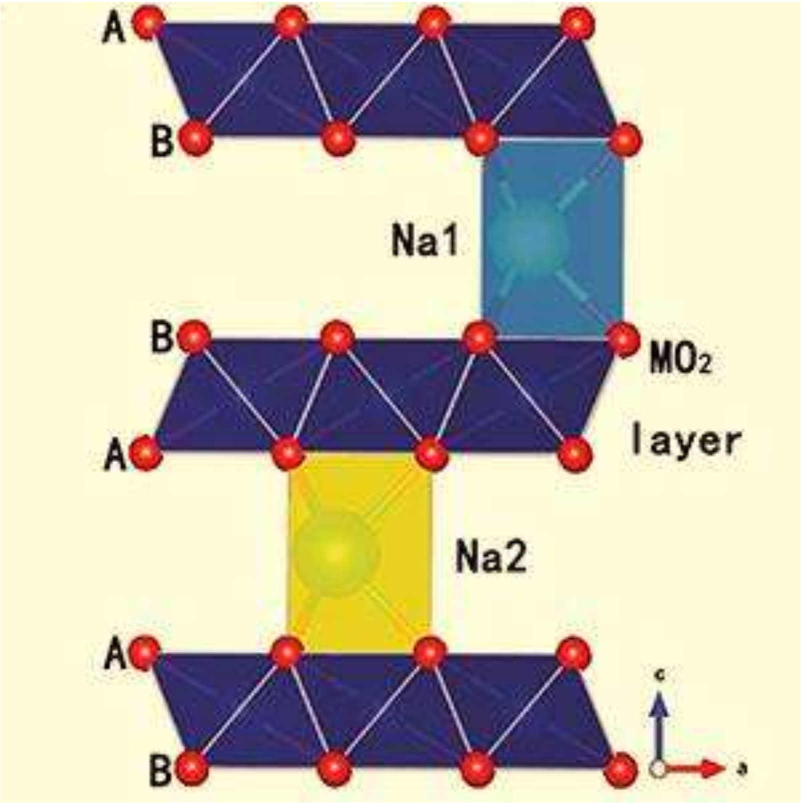

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Figure: 2

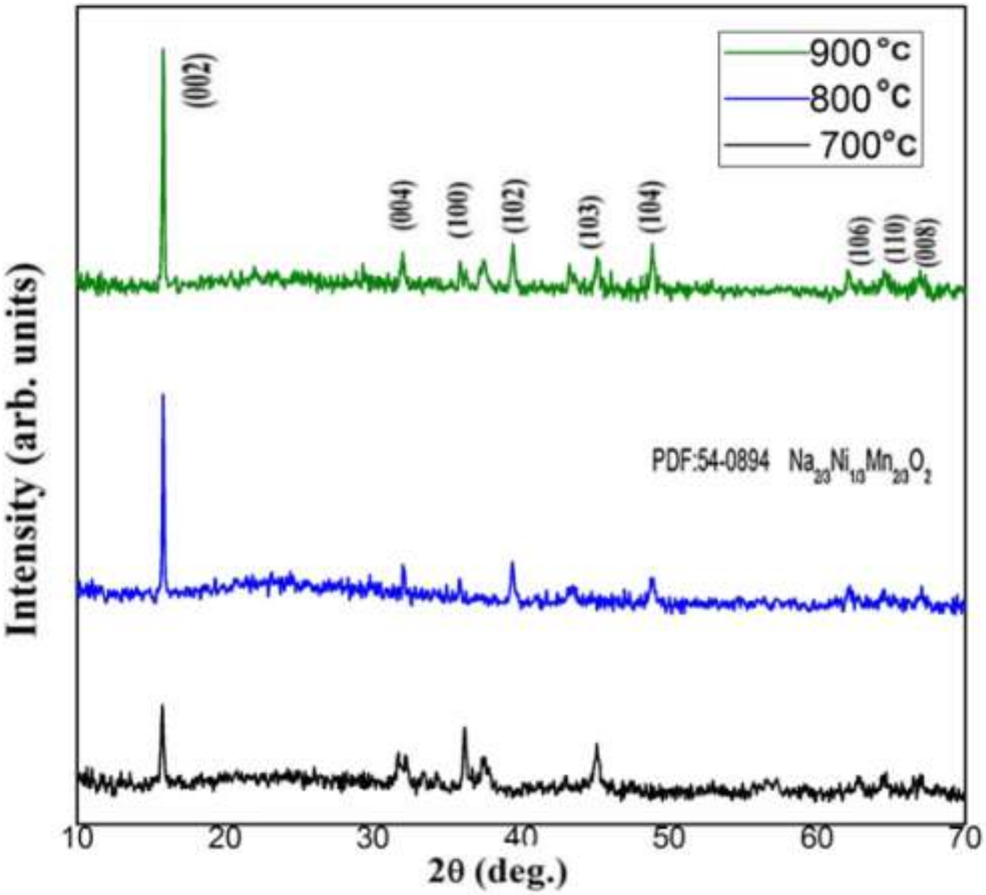

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Figure:3

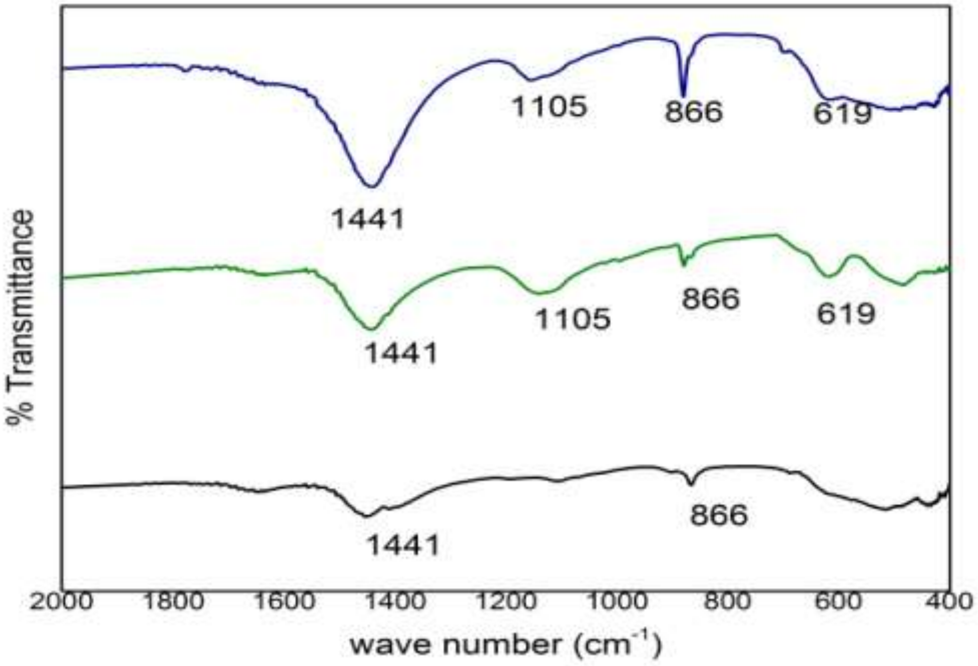

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Figure: 4