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Development of High Capacity $Na_{0.7}(Ni_{0.4}Mn_{0.4}Co_{0.1}Fe_{0.1})O_2$ Cathode Material for Sodium Ion Batteries

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Abstract. Sodium ion battery (SIB) has great potential as sustainable large scale energy storage application compared to lithium-ion battery due to abundance and cost effectiveness of sodium. $Na_{0.7}(Ni_{0.4}Mn_{0.4}Co_{0.1}Fe_{0.1})O_2$ as new cathode material for SIB is prepared by solid state reaction synthesis method. The structure of the new cathode material was characterized by X-ray diffraction using Co-Kα radiation. Morphologies and particle size range (0.37-1.9 microns) of the $Na_{0.7}(Ni_{0.4}Mn_{0.4}Co_{0.1}Fe_{0.1})O_2$ cathode material have been identified by scanning electron microscope. Electrochemical performance of the cathode material for coin cell battery using sodium as anode and $NaClO_4$ as electrolyte was examined in constant current mode. The material cycling performance showed very good reversibility between 2.0 - 4.3 V with reversible capacity of 202 mAh g^{-1} at 0.11 mA current. At C/10 reversible capacity of 191 mAh g^{-1} have been found. The prepared material shows considerable (40%) retention capacity after 45 cycle of charging and discharging with retention capacity of 79 mAh g^{-1}. Electrochemical impedance spectroscopy analysis has been performed between 100 kHz to 10 mHz frequency range and after 10 cycles the resistance for grain and grain boundaries are found to be 26.20 Ω and 354.7 Ω respectively. $Na_{0.7}(Ni_{0.4}Mn_{0.4}Co_{0.1}Fe_{0.1})O_2$ can be a promising cathode material for SIB as it shows very good charging and discharging characteristics with high reversible capacity.

1. Introduction

World-wide sodium ion battery is considered a better promising alternative to present Li-ion battery as it has great potential due to high abundance and cheap availability of sodium compound [1]. Efforts are being made to develop sodium batteries for electric vehicles and grid energy storage applications. Last few years most interest in Na-ion batteries have been in development of high capacity reversible cathode materials. Layered transition-metal oxides ($NaMO_2$, M = Co, Cr etc.) were proposed to be the cathode materials for Na-ion batteries. Cobalt and chromium are costly and toxic component. Moreover these materials usually show poor life cycle and low thermal stability [2]. Many alternatives cathode material for sodium ion batteries replacing (partly/completely) Co and Cr by other cheap and benign transition metals (Fe, Mn, Ni etc) have been searched like $Na(Ni_{1/3}Co_{1/3}Fe_{1/3})O_2$ [3], $Na_{0.45}Ni_{0.22}Co_{0.11}Mn_{0.11}O_2$ [4], $Na_{2/3}Ni_{1/3}Mn_{2/3-x}Ti_xO_2$ [5], $Na_3V_2(PO_4)_3$ [6], $Na_4Co_{2.4}Mn_{0.3}Ni_{0.3}(PO_4)_2P_2O_7$ [7], $Na[Ni_{1/3}Fe_{1/3}Mn_{1/3}]O_2$ [8], $Na[Li_xNi_{0.34-x}Mn_{0.47}Co_{0.19}]O_2$ where (x = 0.10,0.20.0.30) [9]. Sodium ion battery cathode materials are generally of P2 and O3 types. In P2 type structure Na as prismatic coordination with oxygen with 2 transition metal layer in repeat unit perpendicular to the layering. In O3, Na is as octahedral coordination with oxygen with 3 transition metal layer in repeat unit perpendicular to the layering. The P2 crystal structure of $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ [10] could be well maintained for long term cycling in 2.0–4.0 V. When the $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ cell was cycled between 1.6 V and 3.8 V, the first discharge capacity increased to the 135 mA g^{-1} at C/10. To make the material cheaper and environmentally, manganese has been found as an alternative source. Mn-based materials, such as P2-$Na_{0.67}[Fe_{0.5}Mn_{0.5}]O_2$ [12], $NaNi_{1/3}Mn_{1/3}Co_{1/3}O_2$[13] etc. possess some advantages. Addition of transition metals such as Ni and Co shows that the synthesized material possess better reversible capacity of 165 mA g^{-1} at C/20. In this paper we show that, addition of another transition metal Fe in the base material (Mn, Ni) improves the reversible capacity of the cathode material to 191 mA g^{-1} at C/10.

2. Experimental method

2.1 Synthesis method

$Na_{0.7}(Ni_{0.4}Mn_{0.4}Co_{0.1}Fe_{0.1})O_2$ was prepared by a solid-state synthesis method from Na_2CO_3 (99.5% pure form Merck), $Ni(OH)_2$ (98% pure form Aldrich), Mn_2O_3 (99% pure form Aldrich), $CoCO_3$ (95% pure form Aldrich), Fe_2O_3 (90% pure form Merck) mixed in mass ratio of 0.30:0.27:0.25:0.09:0.06. The mixture were thoroughly ball milled using Retsch 67 (PM100) for 30 hours at 415 rpm using acetone as the liquid medium. The slurry sample obtained was dried in the open air muffle oven for evaporation of acetone. The dried ground material then pressed into pellets using 5 ton hydraulic press. The pellets were heated at 860°C for 24 hours for calcination in air. Then the calcine was cooled to room temperature and stored in an argon-filled glove box until use.

2.2 Characterization (XRD)

The structure of the prepared materials has been evaluated with X-ray diffractometer (XRD BRUKER, D8 Advance) using Co-Kα radiation. The XRD spectra were collected with diffraction angle (2θ) value ranging from 10° to 120° with 0.02° step size. The morphologies of the cathode material were studied by a scanning electron microscope (ZEISS, EVO 60).

2.3. Methods of Electrochemical Measurements

Sodium chlorate and glass fibre have been used as electrolyte and separator respectively to prepare the Na-ion battery. The synthesised cathode material is mixed with polyvinylidene fluoride (PVDF) binding agent and Acetylene Black (to increase the conductivity) in the ratio of 8:1:1. This mixture is then coated on an aluminium foil. The coated aluminium foil is dried in vacuum oven at 80◦C for 24 hours. The foil is punched into circular cross sections of diameter 15 mm to act as cathode. This cathode is then assembled inside a glove box with spacer, separator, spring, Na anode of same circular cross section, spring, top case and bottom case to form the CR2032 coin cell. The weight of the active material in the prepared battery is found to be 0.0032 grams.

A potentiostat-galvanostat system (Gamery instrument, G-750) using (PITE 200) software and electrochemical analysis using (EIS 300) software for cyclic voltammetry and impedance spectroscopy measurements respectively. Electrochemical impedance spectroscopy was performed range 100 KHz to 10 MHz with 5mV. Electrochemical cyclic voltammetry was carried out one cycle charging and discharging at a scan rate of 0.1 mV s^{-1} for 2 to 4.3 volt potential range. Charging and discharging performance of the cell was evaluated at different current rates between 2 to 4.3 V.

3. Results and discussion

The powder X-ray pattern is shown in Fig 1. From X pert High Score analysis it has been revealed that the main phase of the material can be indexed as R-3m(166) space-group with the rhombohedral structure. Lattice parameters are found to be a = 2.95510 Å, c = 16.56300 Å. Some minute quantities of NiO are found in the synthesized cathode material. The scanning electron microscopy (SEM) image of the synthesized $Na_{0.7}(Ni_{0.4}Mn_{0.4}Co_{0.1}Fe_{0.1})O_2$ are shown in Fig (2-5). Irregular agglomerated particles are seen and particle size ranges between 0.37 - 1.9 μm are observed of the cathode material. As the particles are agglomerated to each other, they form several micro-sized secondary particles. According to the X-ray energy dispersive spectra (EDS), as shown in Fig (6-7), the estimated Na : Ni :

Mn : Co : Fe : O atomic ratios are found to be 18.9 : 10.4 : 10.3 : 2.7 : 2.8 : 54.9 respectively in the cathode material as given in Table 1.

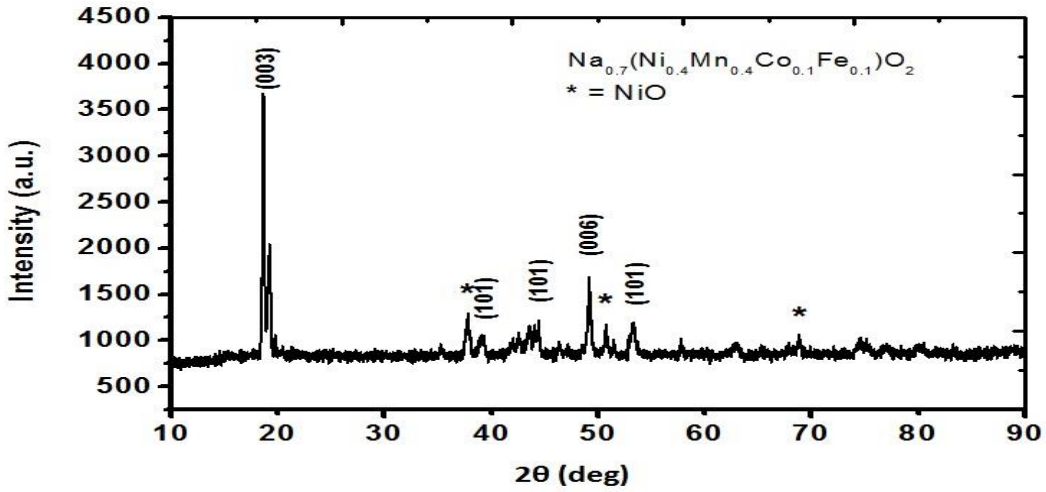

Figure 1. XRD pattern of $Na_{0.7}(Ni_{0.4}Mn_{0.4}Co_{0.1}Fe_{0.1})O_2$ material

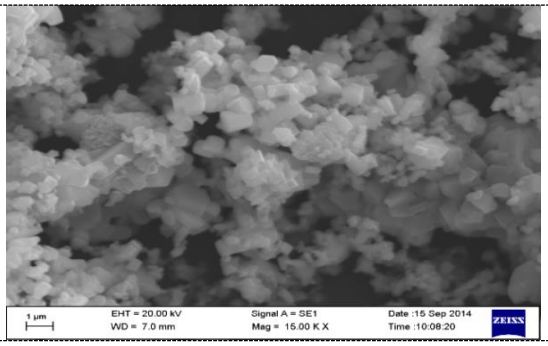

Figure 2. SEM image at 15.00 KX magnification.

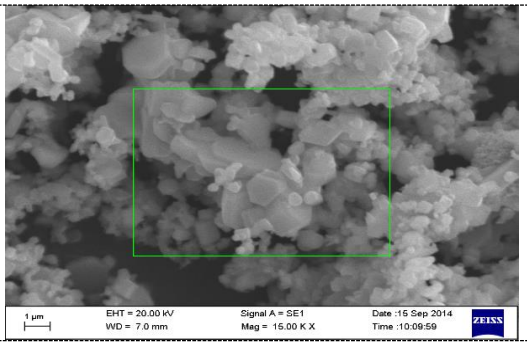

Figure 3. SEM image at 15.00 KX magnification.

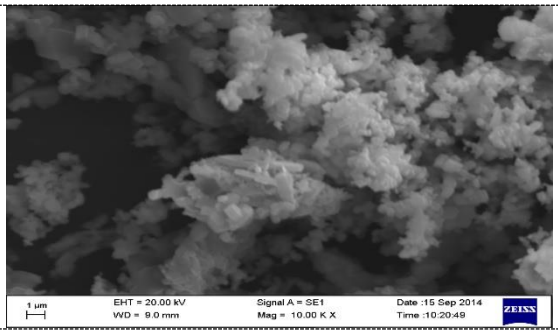

Figure 4. SEM image at 10.00KX magnification.

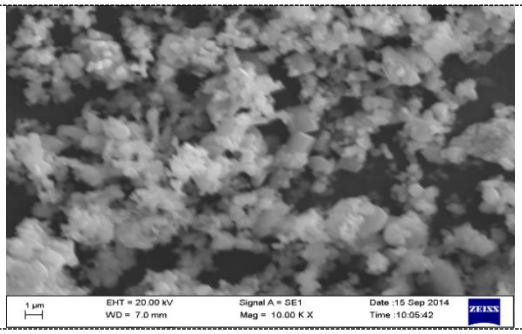

Figure 5. SEM image at 10.00KX magnification.

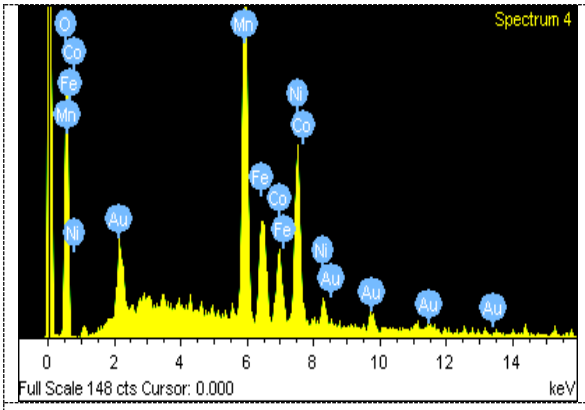

Figure 6. X-ray energy dispersive spectra of $Na_{0.7}(Ni_{0.4}Mn_{0.4}Co_{0.1}Fe_{0.1})O_2$.

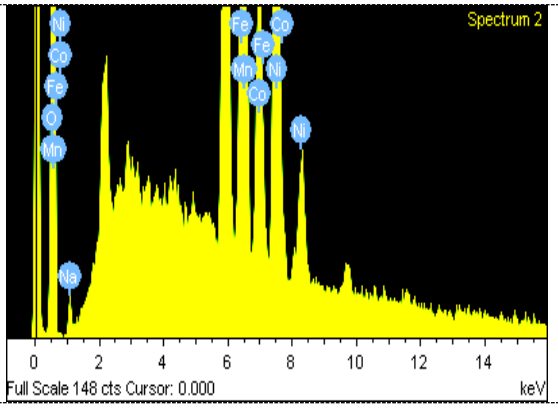

Figure 7.X-ray energy dispersive spectra of $Na_{0.7}(Ni_{0.4}Mn_{0.4}Co_{0.1}Fe_{0.1})O_2$.

Table 1. EDS analysis of the synthesized material

Element	Weight %	At %
Na	15.82	18.9
Ni	21.43	10.4
Mn	20.45	10.3
Co	5.80	2.7
Fe	5.50	2.8
O	31	54.9

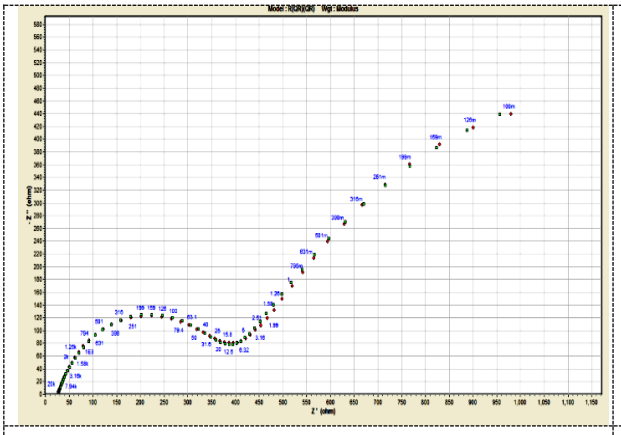

Figure 8. Nquist plot before 10 cycles of charging and discharging.

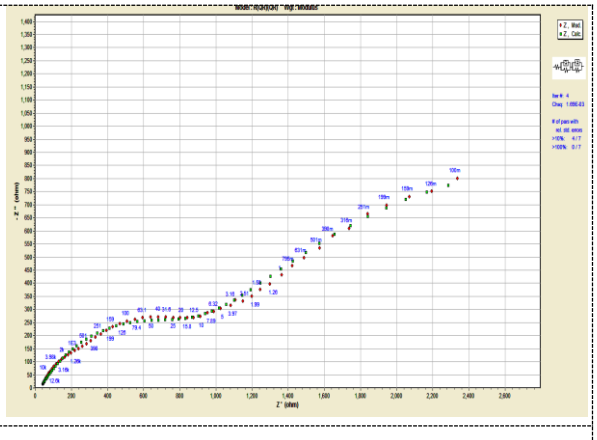

Figure 9. Nquist plot after the 40 cycles of charging and discharging

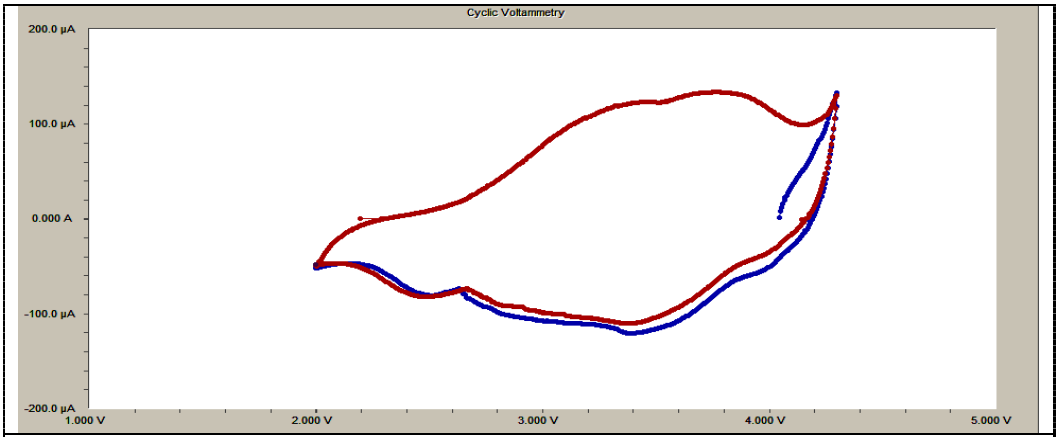

Figure 10. Cyclic voltammogram profiles of the $Na_{0.7}(Ni_{0.4}Mn_{0.4}Co_{0.1}Fe_{0.1})O_2$ cathode material at scan rate of 0.1 mV/s.

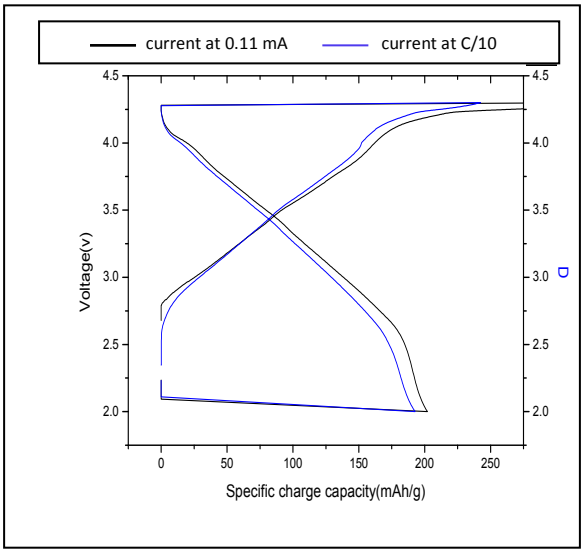

Figure 11. Full specific discharge capacity

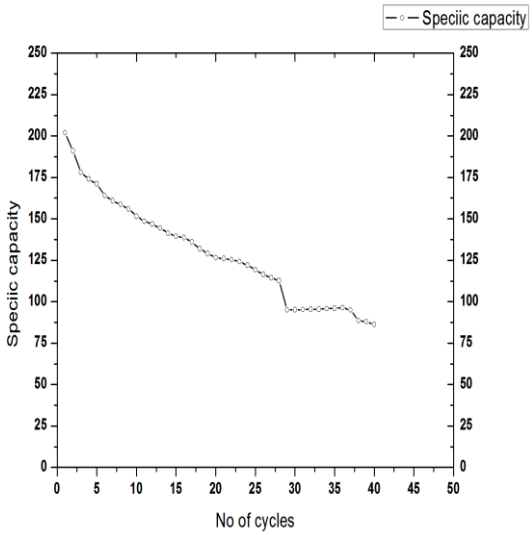

Figure 12. Specific charge capacity vs. Number of cycles

Electrochemical performance of the synthesized $Na_{0.7}(Ni_{0.4}Mn_{0.4}Co_{0.1}Fe_{0.1})O_2$ cathode material was evaluated by making a CR2032 type coin cell and then galvanostatic cyclic discharge-charge characteristics was performed in the 2.0 to 4.3 V voltage range at 0.11 mA current. Electrochemical impedance spectroscopy analysis has been performed and the corresponding Nquist plot has been shown in Fig 8. It is found that after 10 cycles the resistance for grain and grain boundaries were 26.20Ω and 354.7Ω respectively. After continuous charging and discharging for 40 cycles it was noticed that the resistance values for grains and grain boundaries were 26.18Ω and 836.7Ω respectively as shown in Fig 9. This drastic increase in grain boundary resistance at higher discharge cycle can be attributed to the degradation of the cathode material. Electrochemical cyclic voltammetry were performed for one cycle charging and discharging at a scan rate of 0.1 mV s^{-1} between 2 to 4.3 Volt potential range is shown in Fig 10. CV was performed to determine the extent of oxidation and reduction of the transition metals in the cell, and after CV test we observed that broad peaks, due to

presence of a number of transition metals. Similar peaks position both during charging and discharging and complete reversibility indicate good stability and minimal polarization of the cathode material during charging and discharging. The material cycling performance was carried out between cyclic 2.0 - 4.3 V and reversible capacity of 202 mAh g^{-1} at 0.11 mA current was observed as shown in Fig. 11. At C/10, reversible capacity of 191 mAh g^{-1} have been found and shown in Fig 11. The prepared material shows considerable retention capacity (40%) after 45 cycle of charging and discharging with retention capacity of 79 mAh g^{-1}.

4. Conclusion

$Na_{0.7}(Ni_{0.4}Mn_{0.4}Co_{0.1}Fe_{0.1})O_2$ cathode material for sodium ion battery has been prepared by solid state synthesis with uniform size range with desired structure. Electrochemical charging-discharging characteristic using the synthesized material as cathode in a coin cell battery indicate it to be a promising material for sodium ion battery. The material cycling performance showed very good reversibility between cyclic ranges 2.0 - 4.3 V with reversible capacity of 202 mAh g^{-1} and 191 mAh g^{-1} at 0.11 mA and C/10 current respectively. The prepared material shows considering retention capacity (40%) after 45 cycle of charging and discharging with retention capacity of 79 mAh g^{-1}. $Na_{0.7}(Ni_{0.4}Mn_{0.4}Co_{0.1}Fe_{0.1})O_2$ can be a promising cathode material for SIB as it shows very good charging and discharging characteristics with high reversible capacity.

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