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# Synthesis and characterization of $Na_xMnO_2$ as a cathode material for Sodium-ion rechargeable Batteries

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## ABSTRACT

Here we present the synthesis and characterization of $Na_xMnO_2$ as a cathode material for Sodium-ion batteries by changing the Sodium molar ratio in the material. The cathode material was synthesized by using solid state reaction of$MnO_2$ and $Na_2CO_3$ at higher temperature using different molar ratios. Then the Active material was mixed with 5% of carbon black and a paste of the compound was made by using a mixture of 01.00 mgdm$^{-3}$polyvinylidene fluoride (PvdF) dissolved in 1-methyl-2-pyrrolidinone solution. Films made using this paste was used to fabricate Na ion batteries which were then tested in anoxia conditions. Electrochemical properties such as cyclic voltammetry, capacity, charge-discharge performance and battery life cycle were analyzed. The X-ray diffraction data compared with the reference showed the formation of $NaMnO_2$ active material and the highest charging and discharging capacity was obtained for 1:0.8 molar ratio of $MnO_2$ and Na. The cyclic voltammetry further indicated that the highest capacity was given for 1:0.8 ratio with 5% of carbon black.

Key words: Sodium-ion, rechargeable batteries, Cathode, $NaMnO_2$, electrode.

## 1 INTRODUCTION

Currently among different rechargeable battery systems, nickel metal hydride and lithium-ion allow for reversibly storing and harnessing power on demand while providing high power and energy conversion efficiencies [1]. They have played a valuable role in driving the evolution of new technologies which are matching with the modern day uses such as electric vehicles, satellites, mobile phones, cameras, laptops etc [2]. Most of these storage devices are based on Lithium-ion rechargeable batteries. Lithium metal has a voltage of -3.04 V with respect to the standard hydrogen electrode and high volumetric capacity of 2.062 mAhcm$^{-3}$ [3]. However, it has problems such as passivation layer formation at the electrode-electrolyte interface, dendric growth of lithium in the electrolyte region coursing reduction in the life cycle and stability of the lithium-ion battery [3]. Due to demand of the Lithium-ion batteries for many applications, various modifications, developments and investigation for altenatives are done to enhance the performance to reduce the cost and also replace the litium-ion with low cost efficient material.

There are several reasons for investigating sodium-ion batteries. Sodium-ion batteries are a tempting low cost alternative to lithium-ion batteries because of vast resources of sodium and much lower materials costs. As the battery applications extend to large-scale storage such as electric vehicles or stationary storage connected to renewable energy production, high energy density becomes critical. Moreover, the abundance and low cost of sodium in the earth can become an advantage when a large amount of alkali is demanded for large scale applications. But most importantly, there may be significant unexplored opportunity in sodium based systems because sodium intercalation chemistry has been explored considerably less than lithium intercalation and early evidence seems to indicate that structures that do not function well as lithium intercalation compounds may work well with sodium [4]. The fundamental principles of the sodium-ion and lithium-ion batteries are identical, the chemical potential difference of the alkali-ion (Li or Na) between two electrodes (anode and cathode) creates a voltage on the cell. In charge and discharge the alkali ions shuttle back and forth between the two electrodes. Hence, there may be opportunity to find novel electrode materials for sodium-ion batteries [4].

Among the small number of oxide materials with potential interest identified, $NaMnO_2$ is a promising candidate as a positive electrode material for rechargeable Na batteries due to relatively high reversible capacity of more than 180 mAh/g, material abundance and low material cost [5]. $Na_xMnO_2$ was synthesized with different sodium compositions and synthesized material was characterized and used as cathode materials of sodium ion batteries to find the optimum composition in this study.

## 2 METHEDOLOGY

Single-phase $Na_xMnO_2$ powder was obtained through a classic solid-state reaction of $MnO_2$ (purity> 85%, HiMedia, India) and $Na_2CO_3$ (purity> 95.5%, Merck Specialities, India). Different molar ratios of $Na_2CO_3$ and $MnO_2$ were mixed by grinding. The mixture was sintered in 450 $^oC$ nearly 5 hours and grinned again and sintered at 850 $^oC$ for 10 hours. Then the compound was mixed with 10% (by weight) of polyvinylidene fluoride (PvdF) (purity > 99 %, Sigma Aldrich) dissolved in 1-methyl-2-pyrrolidinon(purity > 99.7 %, Sigma Aldrich) and plated in to stainless steel as a thin layer and dried it in an oven at 120 $^oC$ for few minutes. The prepared cathode material was characterized using X-ray diffraction spectroscopy in range of $0^0$-$70^0$ degrees under scanning rate of $5^0$ per minute. The electrochemical properties of the prepared cathode electrodes were tested by preparing a sodium-ion battery made by using sodium metal cathode and cellulose separator. A solution of 01.00 M $NaClO_4$ in propylene carbonate (PC) solution was used as the electrolyte. The electro chemical properties of the cathode material was measured using Potentiostat/Galvanostat ( HA-151A Hokuto Denko, Japan). Tests were carried out for Charge-discharge capacity and cyclic voltammetry.

## 3 RESULTS AND DISCUSSIONS

Figure 01 shows X-ray diffraction spectra of different compositions of NaxMnO2 samples. The peaks appeared in X-ray diffraction spectra are in consistent with the XRD data of previous studies [5].

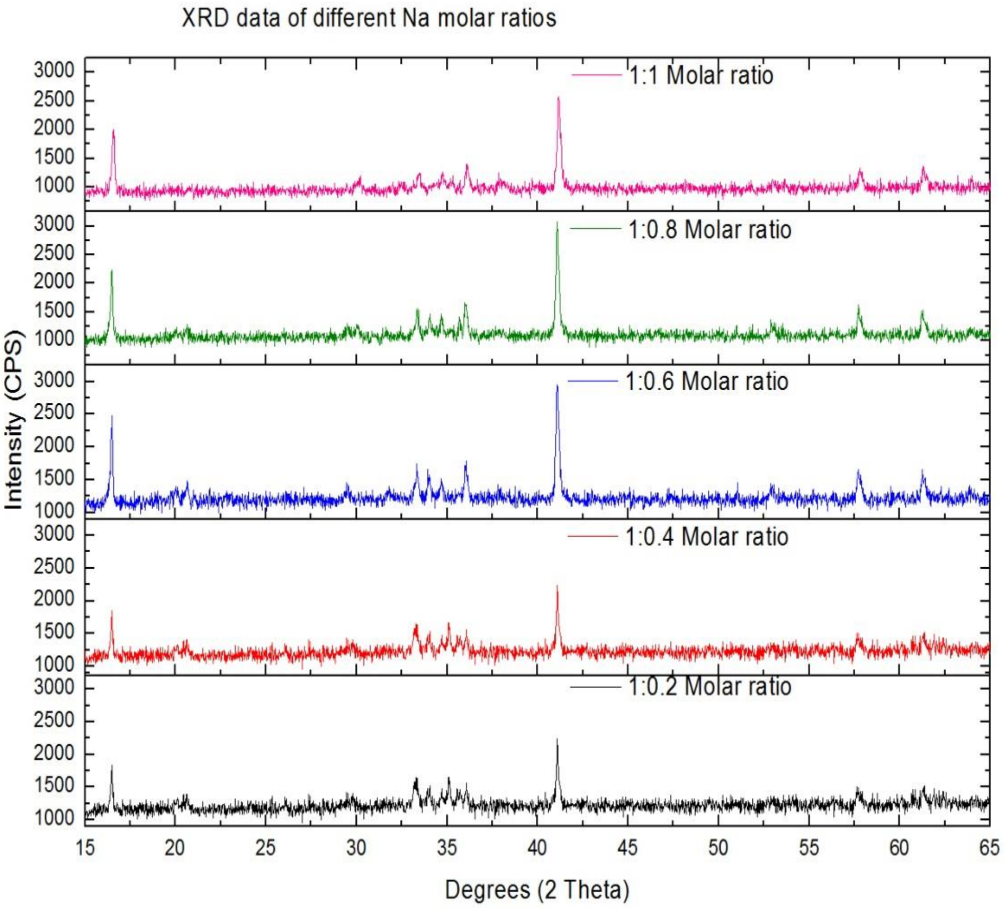

**Figure 01:** XRD data of each compound made in different Na molar ratios.

Increasing the Na content in the samples, height of the peaks appearing at 2θ values of $16.52^o$ and $41.2^o$ were gradually increased while increasing the sodium content upto 1:0.8 molar ratio and then decrease again in 1:1 ratio. This will indicate that the formation of crystal structure of the material was obtained at 1:0.8 composition.

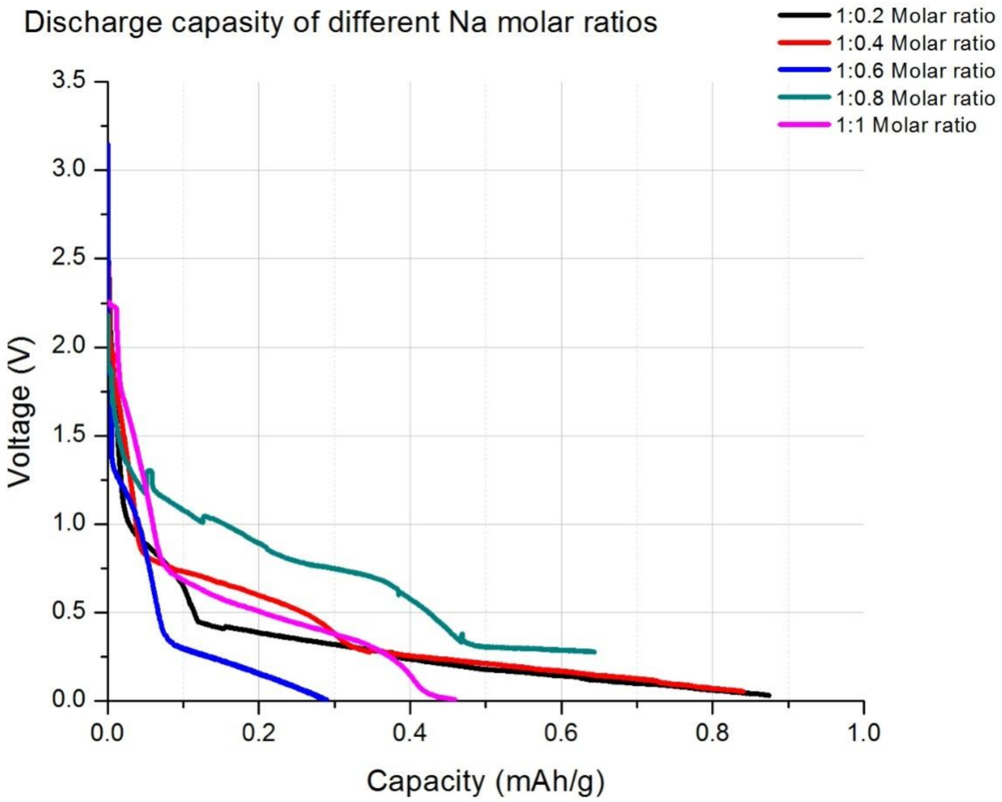

**Figure 02:** The Discharging capacity at 0.1 mA of cells in different Na molar ratios with one molar Mn.

After one hour of charging each cell galvano-statically discharge with 0.5 mA current, half cells made using active material with the sodium compositions, 1:02, 1:04, 1:06, 1:08 and 1:1 were reached to voltages of 1.60 V, 1.65 V, 2.35 V, 1.62 V, and 1.92 V respectively. Then discharge was done with 0.1 mA current for one hour. The voltage has dropped to 0.00 V in the cells made of active material having molar ratios of 1:0.6 and 1:1 very rapidly which had capacity of 0.3 mAh/g and 0.5 mAh/g respectively. But in molar ratios of 1:0.2 and 1:0.4 has capacity of 0.9 mAh/g when the voltage reached to zero. In 1:0.8 ratio showed a capacity of 0.65 mAh/g at a voltage of 0.25 V after one hour of discharge. This result further confirmed that the material is best synthesized at 1: 0.8 composition.

The capacity of an electrode can also be explained by using cyclic voltammetry considering the area of a cycle.

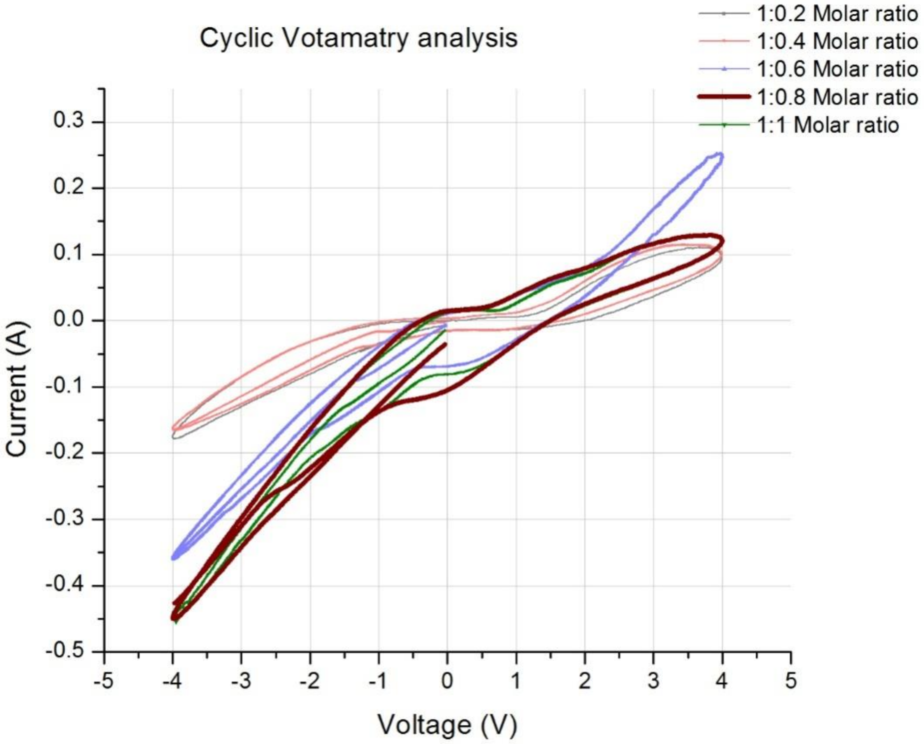

**Figure 03:** The Cyclic voltammetry curves of cells in different Na molar ratios with one mole of Mn in between ±4V.

The cyclic voltammetry curves were taken for cells made of electrodes of different molar ratio cycling between +4 V and -4 V. There were no any peaks appearing in the cyclic voltamonograms of the cells indicating that no any oxidation or reduction reactions take place. Thus the cycles were only related to intercalation and de-intercalation of sodium ions by the cathode material. Considering the capacities of each electrodes of different compositions , the largest area for a cycle was correspond to the material with the molar ratio 1:0.8 that shows the highest discharging capacity.

## 4 CONCLUSION

In this work, the focus was on analyzing the electrochemical properties and their changes with different Na molar ratios with the $MnO_2$. Comparing the X-ray diffraction data with literature values confirmed the synthesis of $Na_xMnO_2$ cathode material. The charging capacity and discharging capacity shows that maximum discharging capacity is with active material of 1:0.8 molar ratio of sodium. Area of cyclic voltammetry curve was also maximum for the cathode made of 1:0.8 molar ratio. Therefore it can be concluded that the sodium content for best performance of the sodium-ion battery made of $Na_xMnO_2$ as the active material is Na: $MnO_2$ at 1:0.8 molar ratio.

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