

IMPROVED ELECTROCHEMICAL PERFORMANCE OF Li-SUBSTITUTED $\text{NaNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ CATHODE MATERIAL FOR SODIUM-ION BATTERIES

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ABSTRACT

Low cost rechargeable batteries, made using abundant materials, operating in safe voltage window are much attractive for large scale energy applications involving solar energy integration and electric grids. In this regard, Sodium-Ion Battery (SIB) has become a promising solution for future issues related to the high demand for energy storage devices, mainly due to the high natural abundance and low cost of sodium resources. As a result, extensive research efforts have been directed to search for suitable functional materials, especially for the anode and the cathode of SIBs. Though few successful studies on this subject have been reported in recent years, many challenges are still remained in developing reliable electrodes for SIBs.

$\text{NaNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ adopts a layered structure, where the transition metal atoms are located in octahedral sites between oxygen layers. In attempting to improve the electrochemical performance of $\text{NaNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ substitution of Li for Ni was investigated under the parent study. Using X-ray diffraction (XRD) and scanning electron microscopy (SEM), the structure and morphology of the cathode material were characterized. The electrochemical performance of the Li doped cathode was investigated in terms of charge-discharge curves and cycleability at different C rates.

The XRD measurements demonstrated that these prepared materials have pure hexagonal P- type layered structure with R3m space group comparable with the parent structure. SEM images exhibited the existence of globular-shaped sub-micron primary particles that agglomerated to form into micron size, softly bounded secondary particles consists of different micron size cavities. The charge-discharge test exhibits that the Li-doped materials has an initial specific discharge capacity of 153 mA h g^{-1} at C/125 rate, which gradually decreased to 125 mA h g^{-1} after six cycles. However, further investigations have to be performed in order to study the cycling stability of the material for the cathode application in the sodium ion battery.

Keywords: Sodium-ion batteries (SIBs); Cathode; Transition metal oxides.

1. INTRODUCTION

Na-intercalation batteries are appearing as an important alternative to Li intercalation systems, hence extensive research efforts have been directed to develop high capacity cathode materials for Sodium Ion Batteries (SIB) [1-5]. Among them, layered transition metal oxides have become most reliable promising candidates for the positive electrodes of SIBs due to their high specific capacities [1-3]. Although promising, they exhibit capacity fading due to the structural instability during charging/discharging process. Therefore, most of recent research investigations have been focused to enhance the electrochemical performance by partially substituting different elements to the host structure, while keeping the structural stability of the material. In addition, some foreign ions can be used to improve the electrical conductivity and suppress phase transformation, which leads to the enhanced electrochemical performance of the materials. Recently, it was found that structural doping of lithium in manganese to be effective in enhancing the structural stabilization of the cathode upon cycling. Nevertheless, these transition metal oxide cathodes are still much inferior to that of Li-based cathode analogs, limiting their practical energy densities [4].

In this paper, we report for the first time the electrochemical performance of Li- substituted $\text{NaNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ synthesized by a wet chemical combustion method for the cathode of SIBs.

2. EXPERIMENTAL

2.1 Syntheses of cathode materials

The nominal composition of $\text{NaNi}_{(0.4-x)}\text{Mn}_{0.4}\text{Co}_{0.2}\text{Li}_x\text{O}_2$ ($x = 0.1, 0.2, 0.3$) samples were prepared by glycine nitrate combustion method. Analytical-grade chemicals, namely, NaNO_3 (Fisher Scientific), $\text{MnN}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$ (98%, Alfa Aesar), $\text{CoN}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ (BDH Lab.), $\text{NiN}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ (99.2%, VWR) and LiNO_3 (99.0%, VWR) were used as received. A stoichiometric ratio of each components were mixed with appropriate amount of distilled water and glycine, by keeping the Glycine:Nitrate ratio as 1:4. The resulted mixture was stirred well for 12 hours at room temperature. The resulting solution was heated at 110°C for several hours to form a gel. The temperature of resulting gel-form solution was stepwise increased from 110°C to 400°C to decompose the nitrate and organics. Finally, the resultant powder precursor was ground and then calcined at 900°C for 3 hours in air atmosphere.

2.2 Material characterization

Powder X-ray diffraction (XRD) studies were performed using a Raigaku Ultima IV instrument with $\text{Cu (K}_\alpha)$ radiation, at a rate of 1°min^{-1} between $2\theta = 10 - 80^\circ$. Elementary analysis of the synthesized material was carried out using an inductive coupled plasma mass spectrometer (ICP-MS). The morphology of the prepared sample was evaluated by scanning electron microscope (SEM, ZEISS sigma) instrument equipped with an energy dispersive X-ray spectroscopy (EDS).

2.2 Electrochemical characterization

The electrodes used for electrochemical testing were fabricated by mixing 80 wt% of the active material, 10 wt% of the super-P carbon and 10 wt% of PVdF binder. The component were thoroughly mixed in N-methyl-2-pyrrolidone (Sigma Aldrich, anhydrous 99.5%) to form uniform slurry and then cast on an aluminum foil current collector. The resulting electrode was dried at 120°C for 12 hours in vacuum oven and then punched into a disc of 1.0 cm in diameter. The electrochemical behavior of the fabricated electrode was evaluated by constructing 2032 coin cells containing pure sodium as the reference electrode and BMF (blown microfiber separator) as the separator, assembled in an argon filled glove box. The electrolyte was 1M NaPF_6 (sodium hexafluorophosphate) dissolved in a 1:1 volume ratio solution of ethylene carbonate (EC) and dimethyl carbonate (DMC). The Cyclic voltammetry and galvanostatic charge and discharge tests were performed in the voltage range of 1.5 - 4.6 V using an Auto lab instrument and a Neware battery cycling tester, respectively.

3. RESULTS AND DISCUSSION

The powder XRD diffraction pattern of $\text{NaNi}_{0.3}\text{Mn}_{0.4}\text{Co}_{0.2}\text{Li}_{0.1}\text{O}_2$ is shown in Fig.1. All the diffraction peaks can be assigned into the P2-phase structure within the $\text{P6}_3/\text{mmc}$ space group, except some extra peaks labeled by asterisks. The extra peak appearing around 19° can be due to the presence of a secondary phase of LiMnO_2 , as previously reported by Llave and Nayak [1]. Two other peaks, which could belong to extra secondary phases, can also be observed in between

50 - 60°. In addition, the proposed structure indicates of having a high degree of crystallinity evidenced by the high intensity of the main diffraction peaks.

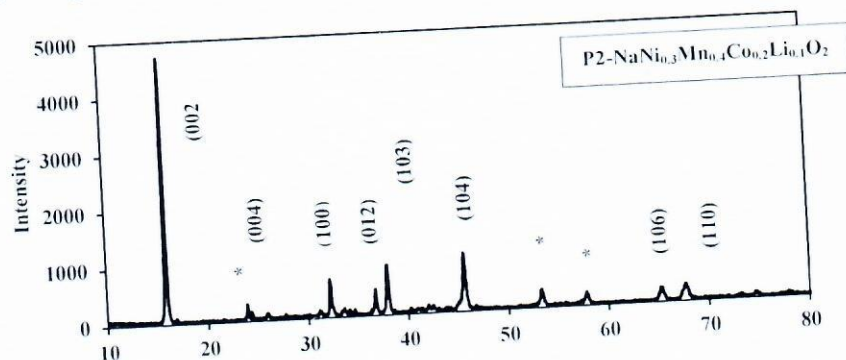


Fig.1. XRD patterns of $\text{NaNi}_{0.3}\text{Mn}_{0.4}\text{Co}_{0.2}\text{Li}_{0.1}\text{O}_2$ material prepared by glycine nitrate combustion method.

Fig.2 presents the SEM images of the as-prepared $\text{NaNi}_{0.3}\text{Mn}_{0.4}\text{Co}_{0.2}\text{Li}_{0.1}\text{O}_2$ material. These SEM images indicate the existence of spherical shaped sharply edged tiny globular practices of 200-500 nm in diameter. These primary particles are gathered and agglomerated together to form a porous micro structure. This porous microsphere structure could increase the specific surface area and hence the electrolyte-material interface that might be supportive to enhance its electrochemical performance. In addition, it could also support to maintain the stability of the structure during the discharge-charge cycling process, without any volume expansion. From ICP element analysis, the chemical composition of the sample prepared by this technique is estimated to be $\text{Na}_{0.86}\text{Ni}_{0.25}\text{Mn}_{0.3}\text{Co}_{0.2}\text{Li}_{0.1}\text{O}_2$, which is close to the targeted nominal material composition of $\text{NaNi}_{0.3}\text{Mn}_{0.4}\text{Co}_{0.2}\text{Li}_{0.1}\text{O}_2$.

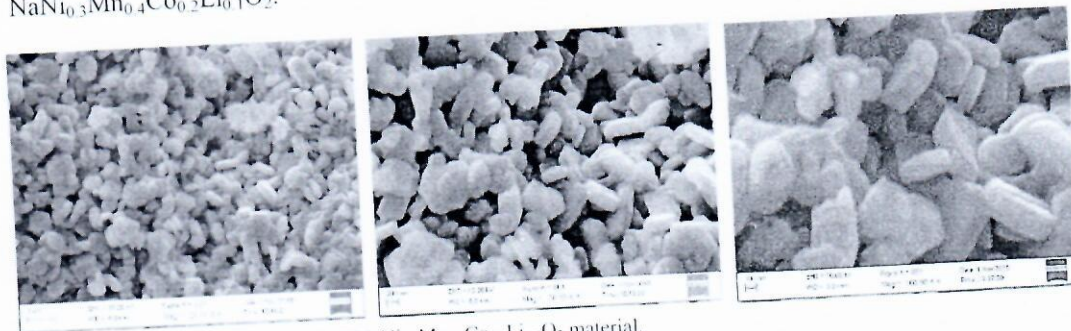


Fig.2. SEM images of the as-prepared $\text{NaNi}_{0.3}\text{Mn}_{0.4}\text{Co}_{0.2}\text{Li}_{0.1}\text{O}_2$ material.

The electrochemical behavior of the prepared $\text{NaNi}_{0.3}\text{Mn}_{0.4}\text{Co}_{0.2}\text{Li}_{0.1}\text{O}_2$ cathode material in a SIB half-cell is shown in Fig.03 as a typical galvanostatic charge-discharge behavior. The cells, assembled in argon atmosphere, were charged to 4.2 V (vs Na) and then discharged to 1.8 V (Vs Na) at constant rate (C/18) in standard coin-type cells. This cell delivered a 125 mAhg^{-1} of initial discharge capacity, which then gradually decreased to half of that value after 50 cycles. This declining of the discharge capacity may be due to the formation of SEI layer on the surface of cathode material upon cycling process [4]. The smooth voltage profile with broader sharp plateaus can be observed continuously during the charging/discharging process. Interestingly, it suggests

that a principal mechanism is involved in the sodium intercalation/deintercalation process without any distortions throughout the whole cycles. Also the electrochemical performance of the proposed cathode material at low current rate (C/125) is presented in Fig.04, in the same voltage window. It can clearly be seen that the initial specific capacity increases due to the slow mechanism of sodiation/desodiation process at low current density.

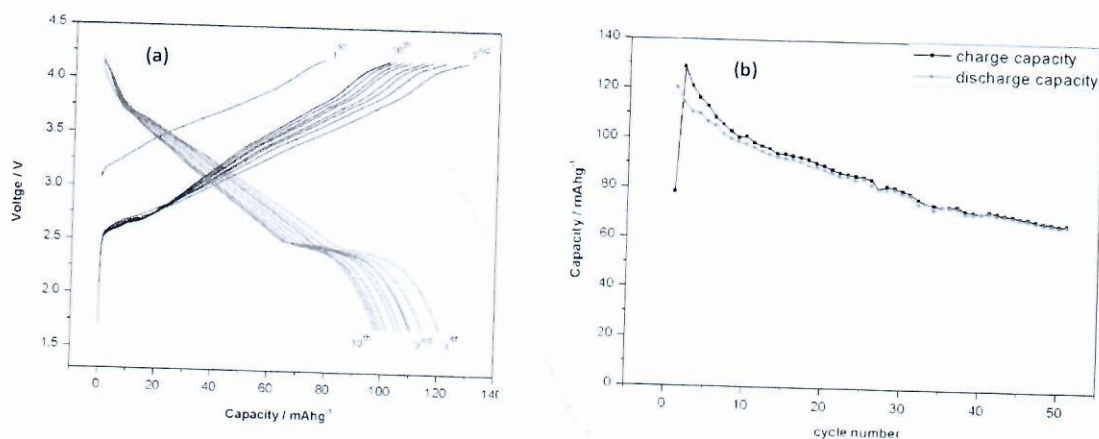


Fig.3. Electrochemical performance of $\text{NaNi}_{0.3}\text{Mn}_{0.4}\text{Co}_{0.2}\text{Li}_{0.1}\text{O}_2$ cathode, a) galvanostatic charge/discharge profile at C/18 rate. b) charge/discharge capacity plot vs. cycle number over the galvanostatic cycle between 4.2 and 1.8 V, at the same current rate.

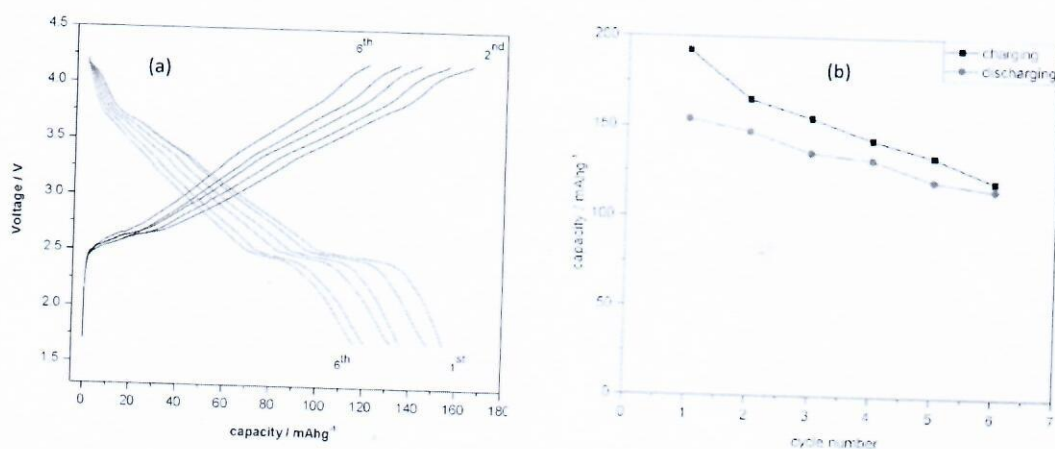


Fig.4. Electrochemical performance of $\text{NaNi}_{0.3}\text{Mn}_{0.4}\text{Co}_{0.2}\text{Li}_{0.1}\text{O}_2$ cathode at low current density, a) galvanostatic charge/discharge profile at C/125 rate. b) charge/discharge capacity plot vs. cycle number over the galvanostatic cycle between 4.2 and 1.8 V, at the same current rate.

Electrochemical properties of the prepared samples for the sodium ion insertion reaction were further characterized from both the differential capacity plot and cyclic voltammogram (CV). Fig.5 shows the differential dq/dv vs V profile and typical CV curve of the cathode material, at a scan rate of 0.1 mV s^{-1} . Oxidation and reduction of transition metal oxides at different voltage can be observed from the both differential plot and CV profile. This similar feature can be clearly

observed from the galvanostatic charge/discharge profile. Only significant peaks can be observed within 2 - 4.2 V and it can be clearly verified the upper voltage window of the material should be less than 4.5 V.

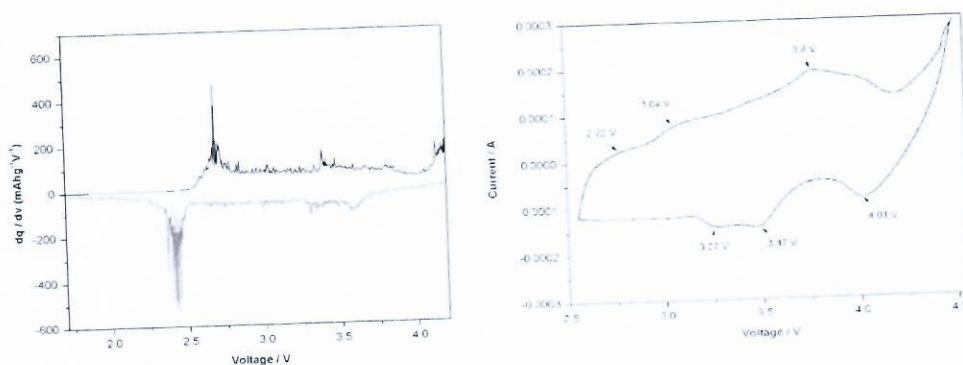


Fig.5. The differential capacity plot and (b) the cyclic voltammetry of the 1st cycle at a scan rate of 0.1 mV s⁻¹.

4. CONCLUSION

This study demonstrates the performance of partially lithium substituted sodium metal-transition metal oxide materials as the cathode material for sodium-ion rechargeable batteries, investigated using P2- $\text{NaNi}_{0.3}\text{Mn}_{0.4}\text{Co}_{0.2}\text{Li}_{0.1}\text{O}_2$ material synthesized by a wet chemical method. The incorporation with lithium enhances the structural stability of the material upon cycling and improves the cyclability of the cells. The discharge capacity of the material can be increased by operating at low current densities. The glycine nitrate combustion wet chemical synthesis technique is a cost effective and reliable method to obtain homogeneous nano structured particles having porous structure. Furthermore, high voltage window can be applied into this cathode material that is more supportive to influence its specific capacity. Therefore, this study reveals that the partially substituted Li transition metal oxides can perform as a promising cathode material for SIBs. However, further improvements are needed to enhance its columbic efficiencies, which are more important to boost practical application of sodium-ion batteries.

5. REFERENCES

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