

Electrochemical Properties of Hexagonal P2-Structure $\text{NaLi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ as a Cathode Material for Na-ion Batteries

Nguyen Van Nghia, Ripon Bhattacharjee, and I-Ming Hung

Abstract—Hexagonal P2-structure $\text{NaLi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ oxide was synthesized by solid-state reaction method. The $\text{NaLi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ material has layered structure, space group $P6_3/mmc$, and its lattice parameters are $a = 2.854$ (Å) and $c = 11.0405$ (Å). The electrochemical result show that the $\text{NaLi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ material has the first, second discharge capacity of 140 and 112 mAh g^{-1} between 1.5-4.5 V at current density of 26.6 mA g^{-1} , respectively and high coulombic efficiency of 83% for second cycle. The second discharge capacity of the $\text{NaLi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ material remains 77% after 20 cycles.

Keywords—Hexagonal P2-structure, Layered structure, Na-ion batteries, Sodium Mn-based oxides, Solid-state reaction.

I. INTRODUCTION

RECENTLY, Na-ion batteries have attracted wide attention because of low cost, more environmentally benign and simple to synthesize. Various Sodium Mn-based oxides with different structure have been reported as cathode materials for Sodium-ion batteries such as: tunnel-structure $\text{Na}_{0.44}\text{MnO}_2$ [1]-[3], P2-structure Na_xMnMO_2 (M=transition metals) [4]-[9] and O3-structure NaMn_xMO_2 [10]-[12].

Among these materials, P2-structure Sodium Manganese-based Na_xMnO_2 oxides are promising cathode materials for Sodium-ion batteries, because of its high capacity, low cost, abundance and non-toxicity of both sodium and manganese [4], [5], [13]. However, those materials were synthesized by complicated methods such as hydrothermal method, sol-gel method or solid-state reaction routine combined with sol-gel method. A single phase of $\alpha\text{-Na}_{0.7x}\text{Mn}_x\text{O}_2$ prepare by conventional solid-state reaction is difficult [14]. Using a small amount of lithium substituted for manganese can help to synthesize the single phase of $\alpha\text{-Na}_{0.6}\text{Li}_{0.2}\text{Mn}_{0.8}\text{O}_2$ by conventional solid-state reaction [15], [16], due to Li^+ can stabilize P2-structure at low temperatures. These materials were used as cathode for Lithium-ion batteries after using an ion-exchange method to substitute sodium ions by lithium ions.

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In this work, we select alkali Lithium substitution for partial Manganese to improve the electrochemical properties of NaMnO_2 . The electrochemical performances of new layered P2-structure of Sodium Mn-based oxide $\text{NaLi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ is investigated as a cathode material in Na-ion batteries for the first time as we know.

II. EXPERIMENTAL SECTION

The $\text{NaLi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ powder was prepared by conventional solid-state reaction method. A stoichiometric amounts of Na_2CO_3 (Sigma-Aldrich, 99.8%), 5wt% excess of Na was added because of sodium evaporation during calcination process, Li_2CO_3 (J.T Baker, 100.0%) and MnCO_3 (Aldrich, $\geq 99.9\%$) were ground carefully using mortar and pestle. The mixed powders were heat-treated at 500°C for 10 hours in air to eliminate carbonate. As the temperature cool down to room temperature, the powders were ground again and then finally calcined at 730°C for 20 hours in air, and quenched to obtain the final product.

The crystalline structure of material was characterized by X-ray powder diffraction (XRD) on a Shimadzu Lax XRD-6000 diffractometer with Cu $K\alpha$ radiation. The XRD spectra were collected in scanning range (2θ) of 10° to 80°. The morphology, crystallinity and grain size of powder were examined by TEM, HRTEM and SAED analyses.

The cathode was prepared by mixing the active material (70 wt%), super P and KS4 (carbon black) (20wt%) as the conducting additives, and polyvinylidene difluoride (PVDF, 10 wt%) as binder in n-methyl-2-pyrrolidone (NMP) solvent to form a slurry. The negative electrode was sodium foil. The electrolyte solution was 1M NaClO_4 in ethylene carbonate/diethylene carbonate (EC/DEC) with a volume ratio of 1:1. The R2032 coin-type cells were assembled in argon-filled glove box.

III. RESULTS AND DISCUSSION

Fig. 1 shows X-ray diffraction pattern of as-prepared $\text{NaLi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ material. In comparison with JCPDS No 27-0751, the main peaks can be indexed as a hexagonal structure, space group $P6_3/mmc$. A few weak peaks between ~20-30° could be due to a superstructure [15], [16]. The XRD pattern is similar to the results published for $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ [15], $\text{Na}_{2/3}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ [16] that reaffirm the layered P2-structure was obtained. Using Unit Cell software to calculate

the lattice parameters of structure, the parameters of $\text{NaLi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ are $a = 2.854$ (Å) and $c = 11.0405$ (Å), cell volume = 77.8806 (Å³). These values are consisted well with the previous reported materials which had the layered structure [4], [5], [16].

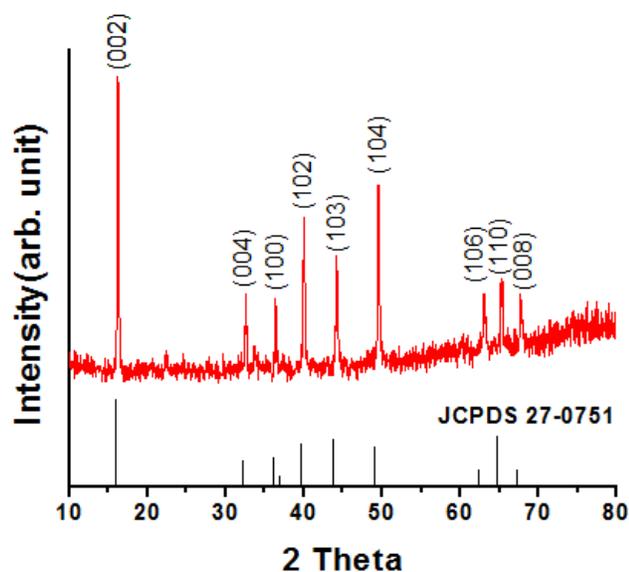


Fig. 1 XRD pattern of as-prepared $\text{NaLi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ powders

The Transmission Electron Microscopy (TEM) was conducted to study morphology of as-prepared $\text{NaLi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ powder. As displayed in Figs. 2a and b, $\text{NaLi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ powders look like sphere-shape with the grain size in range of 30-50 nm and the particles are agglomerated. One single grain can be clearly observed in Fig. 2b.

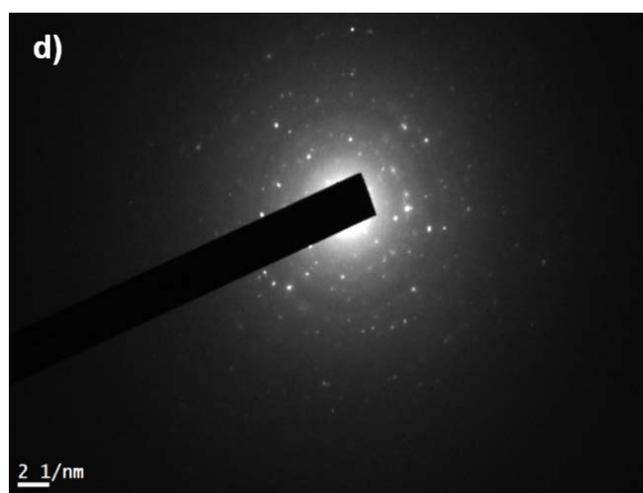
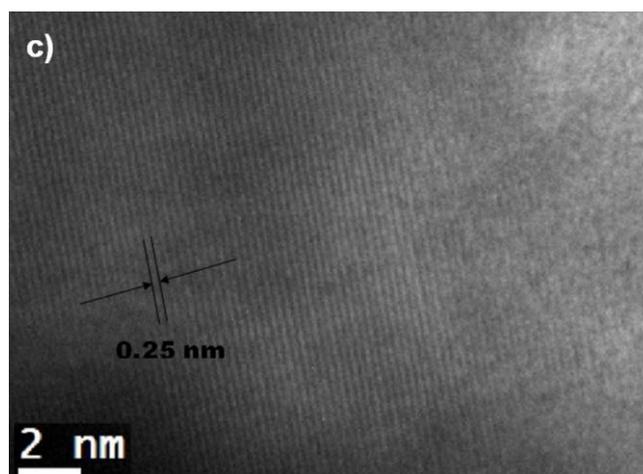
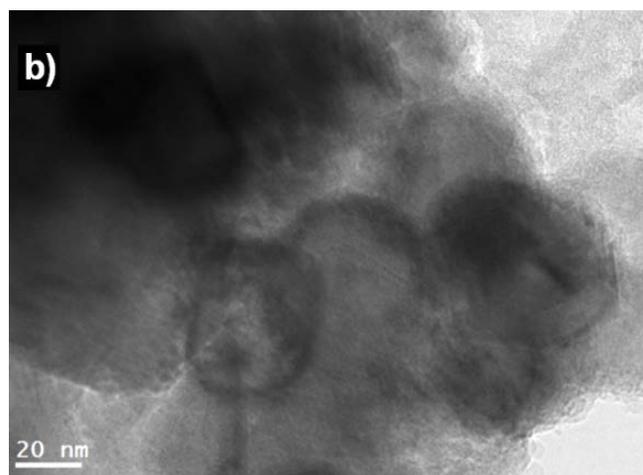
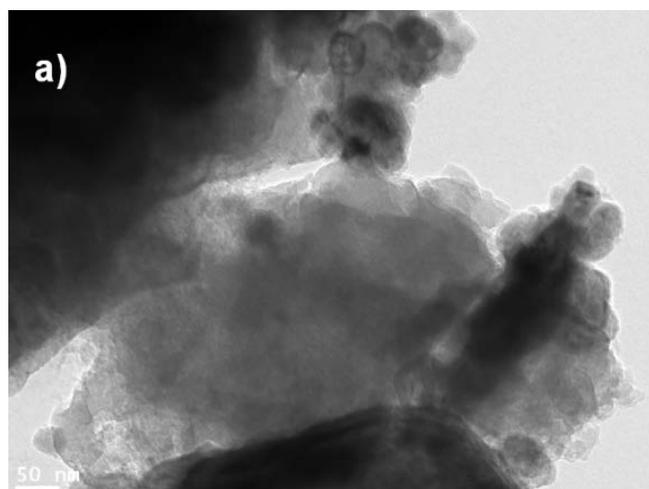


Fig. 2 The TEM images of as-prepared $\text{NaLi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ powder

The high resolution transmission electron microscopy (HRTEM) of the sample (Fig. 2c) clearly depicts lattices fringes. Which mean that the $\text{NaLi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ material is high crystallization. The d spacing is 0.25 nm, corresponding to the distance between two (100) adjacent planes in the XRD pattern. The selected area electron diffraction (SAED) ring pattern of sample (Fig. 2d) is consisted with the results of XRD analysis.

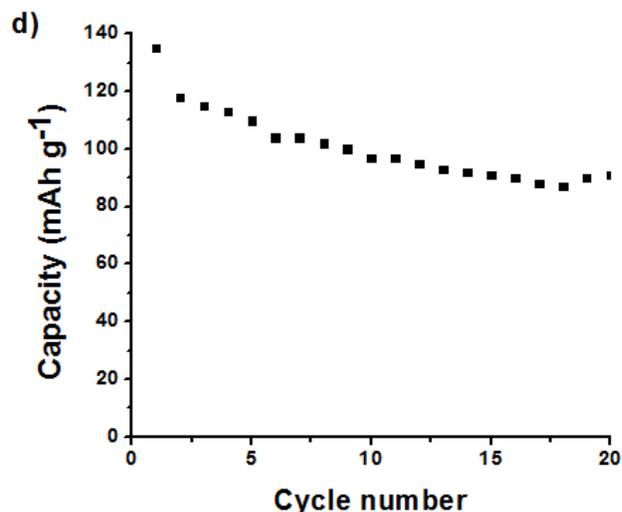
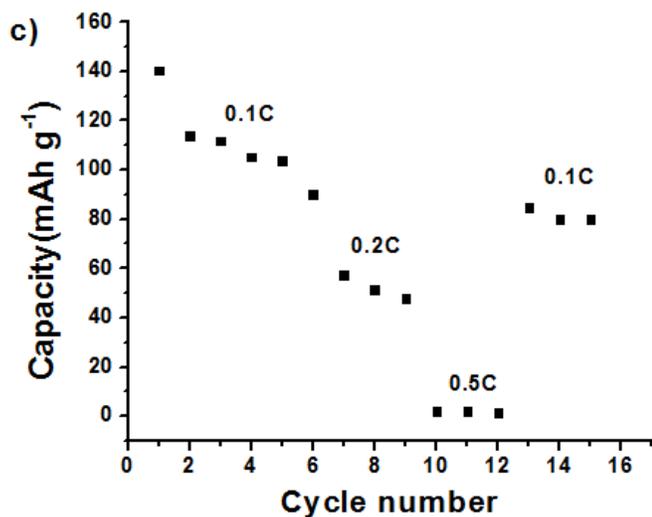
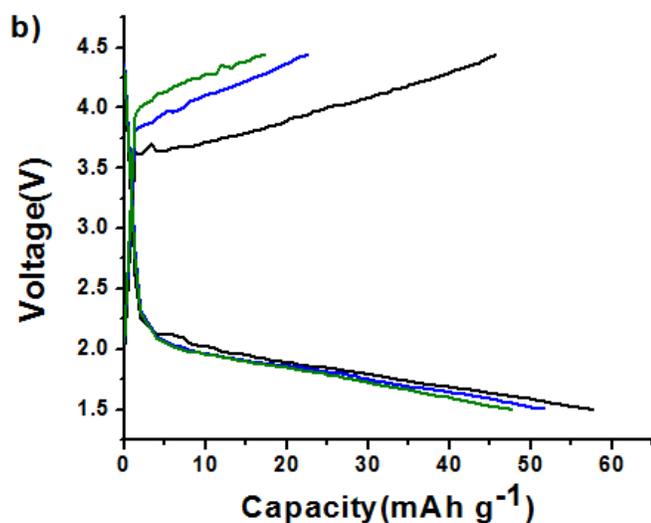
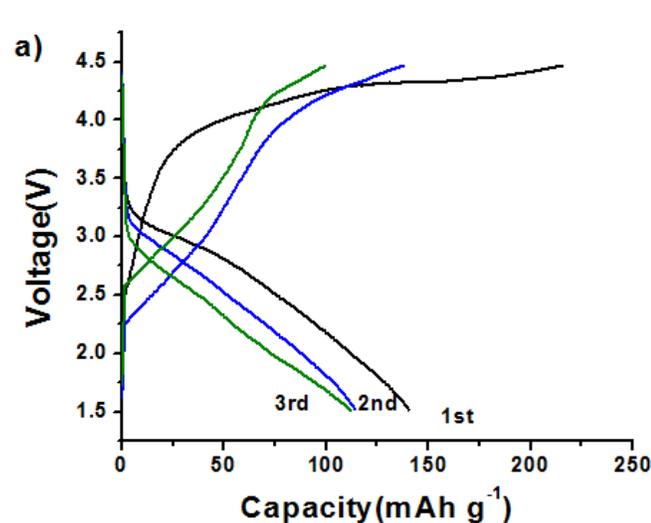


Fig. 3 $\text{NaLi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ charge-discharge curves at a) 0.1C, b) 0.2C current density; c) the cycling performance of the $\text{NaLi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ at different C-rates and d) at 0.1C for 20 cycles

Fig. 3a shows the first to third charge-discharge curves of $\text{NaLi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ between 1.5 and 4.5V versus Na^+/Na at a current density of 26.6 mA g^{-1} at room temperature. The $\text{NaLi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ material delivers the first, second and third charge/discharge capacity of $215/140 \text{ mAh g}^{-1}$, and $138/114 \text{ mAh g}^{-1}$ and $99/112 \text{ mAh g}^{-1}$, respectively. It shows that the charge capacity of the first cycle is much higher than discharge capacity. This can be attributed to the existence of lithium ions in $\text{NaLi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ material. Due to the existence of lithium, the low coulombic efficiency at the first cycle is only 65%. After lithium extraction, the coulombic efficiency increases to 83% for the second cycle.

The discharge capacity of the first cycles is much higher than that of $\text{NaLi}_{0.2}\text{Ni}_{0.25}\text{Mn}_{0.75}\text{O}_2$ (105 mAh g^{-1} at 15 mA g^{-1}) [6] and $\text{Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ material (87.8 mAh g^{-1} at C/20) [7] which were synthesized by the same method (solid state-reaction method). The capacity of $\text{NaLi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ material is comparable with that of P2-structure Sodium Manganese-based cathode materials which have been reported recently [4]-[9]. However, the structure of $\text{NaLi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ material, Sodium manganese-based oxide, is not suitable for charging/discharging at high current density. The capacity of cells reduced seriously as the cells are charged and discharged at 0.2C and 0.5C, as shown in Figs. 3 b and c. The discharge capacity remains only 50% of the second one when $\text{NaLi}_{0.2}\text{Ni}_{0.25}\text{Mn}_{0.75}\text{O}_2$ cycled at 0.2C and down to nearly zero when the cells cycled at 0.5C. Fig. 3d shows the cycling performance of $\text{NaLi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ between 1.5-4.5V at 0.1C. The discharge capacity slowly decreases and remains 77% of the second one after 20 cycles.

Figs. 4a and b show XRD patterns of as-prepared $\text{NaLi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ and the sample charged to 4.2V, respectively. It is obviously observed that the main peaks of hexagonal P2-structure of $\text{NaLi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ powders are remained after charging. The peaks with asterisk mark indicate reflection peaks of Aluminum substrate (JCPDS No 030932).

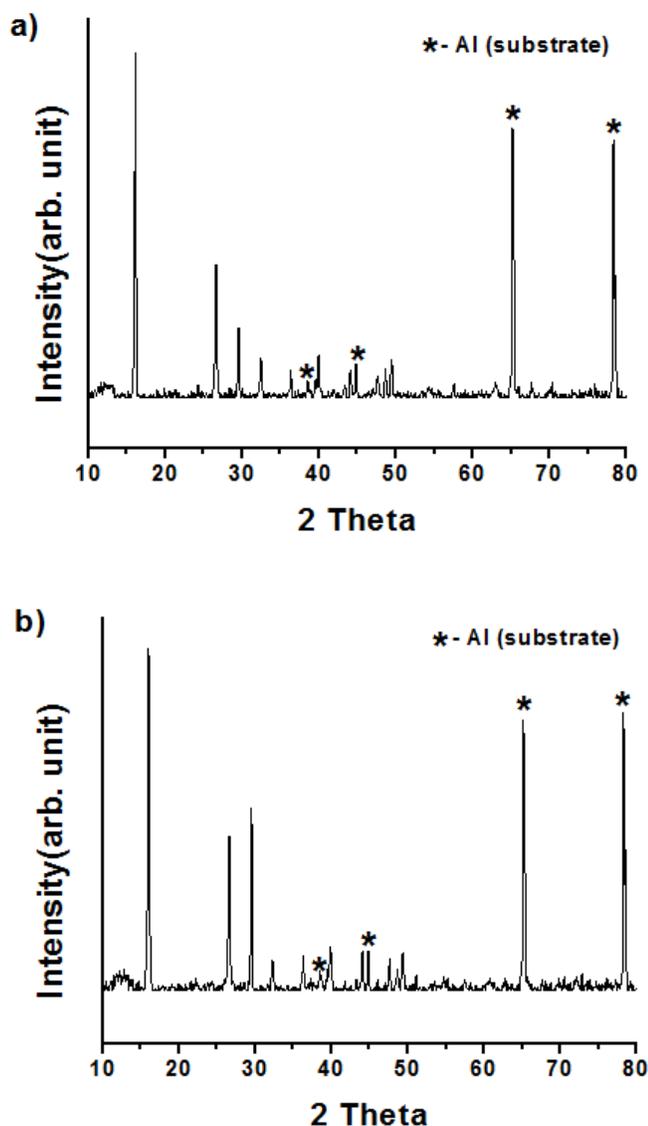


Fig. 4 XRD pattern of a) as-prepared cathode disc and b) cathode disc charged to 4.2V. The asterisk mark in a indicate reflection peaks of aluminium substrate (JCPDS No 030932)

This result indicates that the crystal structure of the $\text{NaLi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ cathode was not change during the intercalation and de-intercalation of sodium ions. It means that the P2-structure $\text{NaLi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ material is a potential new cathode material for Na-ion batteries.

IV. CONCLUSION

The $\text{NaLi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ material with layered structure was successfully synthesized by conventional solid-state reaction method. X-ray diffraction analysis reveals that the as-prepared material is relative to the hexagonal P2-structure of $\text{Na}_{0.7}\text{MnO}_2$ (JCPDS-270751) phase, space group $\text{P6}_3/\text{mmc}$. The lattice parameters of $\text{NaLi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ are $a = 2.854$ (Å) and $c = 11.0405$ (Å). TEM image shows that single grain size is in range of 30-50 nm. HRTEM and SAED characterization confirm the high crystallinity of $\text{NaLi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ grains. Lithium doping can stabilize P2-structure of Sodium Manganese-based oxide even

though the mole ratio of sodium is up to one. The $\text{NaLi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ material delivers a charge capacity of 215 mAh g^{-1} and discharge capacity of 140.4 mAh g^{-1} for the first cycle.

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