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ELECTROCHEMICAL PERFORMANCE OF $Na_{0.44}MnO_2$ SYNTHESIZED BY HYDROTHERMAL METHOD USING AS A CATHODE MATERIAL FOR SODIUM ION BATTERIES

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Abstract. *Orthorhombic* $Na_{0.44}MnO_2$ *with an S-shape tunnel structure was successfully synthesized by a hydrothermal method. The* $Na_{0.44}MnO_2$ *material has lattice parameters of a = 9.0842 Å, b = 26.2889 Å, and c = 2.8245 Å. Scanning electron microscope analysis reveals that the morphologies of* $Na_{0.44}MnO_2$ *consist of* $Na_{0.44}MnO_2$ *nanowires with diameters of about 30-50 nm and* $Na_{0.44}MnO_2$ *particles with the size in the range of 200 to 500 nm. The first charge and discharge capacities of* $Na_{0.44}MnO_2$ *cathode, at 0.1 C between 2.0-4.0 V, are 66.2 mAh* g^{-1} *and 62.7 mAh* g^{-1}*, respectively. The* $Na_{0.44}MnO_2$ *has excellent cycle stability with 85.3% of capacity retention over 50 cycles. The coulombic efficiency of* $Na_{0.44}MnO_2$ *material is approximately 90% after 70 cycles. It is suggested that the structure of* $Na_{0.44}MnO_2$ *is stable during cycling and* $Na_{0.44}MnO_2$ *can be a promising cathode material for sodium ion batteries.*

Keywords: cathode materials, hydrothermal method, $Na_{0.44}MnO_2$, sodium ion battery.

Classification numbers: 82.45.Aa, 82.45.Fk.

I. INTRODUCTION

Lithium ion batteries (LIBs) have been widely used in many fields such as electronic vehicles, portable electronic devices, robots, computer, etc. The usages of LIBs lead to a high demand of lithium metal. However, the lithium resources are limited, therefore the price of LIBs have risen rapidly in recent years. Finding other elements that can substitute for lithium becomes an essential issue. Recently, sodium ion batteries (NIBs) were emerged as a potential candidate that can replace LIBs in many applications, particular in large scale energy storage field. NIBs have advantages of inexpensive sodium resources, simple fabrication and environmental safety. The insertion/extraction chemistry mechanisms of NIBs and LIBs are similar. However, the ionic size of sodium ion is larger than lithium ion that causes the movement of sodium ions in cathode material structure more difficult than lithium ions. Thus, developing electrode material structure and morphology to make these materials suitable for sodium ions diffusion is necessary.

Various cathode materials for NIBs were reported in literature such as Na_xMO_2(M = transition metals) layered structure [1–4], $Na_{0.44}MnO_2$ tunnel structure [5,6], Na^+ superionic conductors [7, 8], metal oxides [9, 10], etc. Among them, Na_xMO_2 materials with layered structure have been extensively investigated due to its high capacity and long cycling ability. Layered structure $Na_{0.6}MnO_2$ shows a capacity approximately 155 mAh g^{-1} and the capacity loss about 55% after 10 cycles [11]. Substituting manganese by other transition metals improves the electrochemical performance of $Na_{0.6}MnO_2$ material. Zhao et al. reported that layered structure $Na_{2/3}Ni_{1/3}Mn_{2/3}$ prepared by a combustion method shows a discharge capacity $\sim$ 150 mAh g^{-1} and capacity retention is about73% after 30 cycles [12].The combination of more transition metals in the Na_xMO_2 materials enhances discharge capacity and cycling stability. The capacity of $Na_{0.67}Mn_{0.65}Fe_{0.35-x}Ni_xO_2$ is 208 mAh g^{-1} and capacity retention is about 71% over 50 cycles [2]. However, layered structure Na_xMO_2 materials are sensitive against air that causes some difficulties during synthesizing and conserving. Furthermore, the low cycling ability of Na_xMnO_2 materials remains a problem need to improve. In this research, we are interested in synthesis and electrochemical investigation of $Na_{0.44}MnO_2$ orthorhombic structure, in which sodium ions can easily diffuse in S-shape tunnel that could lead to high electrochemical properties.

Rod-shaped $Na_{0.44}MnO_2$ particles synthesized by modified Pechini method shown a modest specific capacity of 40 mAh g^{-1} at 0.1 C between 2.0-3.8 V [13] and the cycling ability of the material was not revealed in their report. Rod-liked $Na_{0.44}MnO_2$ particles synthesized by solid-state reaction method have a discharge capacity approximately 80 mAh g^{-1} and capacity retention is about 50% after 45 cycles [14]. $Na_{0.44}MnO_2$ nanowires prepared by hydrothermal method exhibit a high discharge capacity of 115 mAh g^{-1}, at a low current density of 0.042 C, and the capacity retains about 83% after 20 cycles [15]. Cao *et al.* reported that single crystalline $Na_4Mn_9O_{18}$ material fabricated by a polymer-pyrolysis method reveals remarkable electrochemical properties with a high capacity of 110 mAh g^{-1} at 0.5 C, high rate capability and an excellent cycling ability [16]. The material retains about 77% initial capacity after 1000 cycles. It is clearly indicated that the morphology of materials has a crucial role on electrochemical performance of cathode materials for NIBs. Using hydrothermal method, which commonly used to get nanorod or nanowire morphologies, to synthesize $Na_{0.44}MnO_2$, we expect that possibly enhances the cycling ability of $Na_{0.44}MnO_2$ material. As the expectation, the achieved material shows an extraordinary cycling ability with the capacity retention is about 85.3% after 50 cycles, which was higher than the cycling ability of $Na_{0.44}MnO_2$ synthesized by the same method [15] or different methods such as solid-state reaction [14], and modified Pechini method [13].

II. EXPERIMENTAL

$Na_{0.44}MnO_2$ material was synthesized by a hydrothermal method using Mn_2O_3 powder (Sigma-Aldrich, $\geq$99%) and NaOH powder (Xilong Scientific, $\geq$96%). A stoichiometric amount of NaOH was dispersed in distilled water to form 5M NaOH aqueous solution, 2 g of Mn_2O_3 oxide was then added in 160 ml of 5M NaOH and stirred for 30min to achieve a homogeneous suspension. The mixed solution was placed in a stainless steel Teflon autoclave (200 ml). The autoclave was heated at 205°C for 48 hours. After cooling to room temperature, the precipitated material was filtered and washed several times with distilled water. The hydrothermal process was repeated one more time, the precipitated material added in 160 ml of 5M NaOH solution and again heated at 205 ° C for 48 hours. After filtering and washing, the obtained powder was dried at 120 ° C in vacuum and then annealed at 600° C for 6 hours to get $Na_{0.44}MnO_2$ material.

The structure of $Na_{0.44}MnO_2$ material was analyzed on an X-ray diffractometer (D-5000 SIEMEN) using CuKα radiation with scanning angles (2θ) of 5° to 70°. The morphology of $Na_{0.44}MnO_2$ material was examined using scanning electron microscopy (SEM) (HITACHIS-4800).The $Na_{0.44}MnO_2$ material was mixed with carbon black (super P and KS4) and polyvinylidene fluoride (PVDF) in N-methyl-pyrrolidone (NMP) solvent at a ratio weight of 70:20:10, which were then ball milling to form cathode slurry. The slurry was coated on an aluminum foil and subsequently dried at 100°C in a vacuum oven for 12 hours to make cathode tape. The cathode tape was pressed and punched into circular shape, which was used as positive electrode. A circular sodium foil was used as negative electrode. The separator was polyethylene/polypropylene/polyethylene. The electrolyte was 1 M $NaClO_4$ in EC/DEC (1:1 volume ratio). A two electrode CR2032 coin cell type was assembled to examine the electrochemical performance of $Na_{0.44}MnO_2$ material using a battery testing system (AcuTech Systems, BAT-750B).

III. RESULTS AND DISCUSSION

X-ray diffraction pattern of an as-prepared $Na_{0.44}MnO_2$sample is shown in Fig. 1. The sharp peaks can be indexed to the orthorhombic $Na_{0.44}MnO_2$ phase, *Pbam*space group, (JCPDS # 27-0750) with lattice parameters a, b, c and unit cell volume are 9.0842 Å, 26.2889 Å, 2.8245 Å and 674.5355 $Å^3$, respectively. The peak located at 2θ angle of 55.2° could be attributed to the minor impurity of the Mn_2O_3 phase, which corresponds to the raw Mn_2O_3oxide non-reacted. The results shown that,in the orthorhombic $Na_{0.44}MnO_2$ structure, manganese ions occupy two different sites, which are octahedral sites (MnO_6) and square-pyramidal sites (MnO_5). These sites linked together to create two types of tunnels. One type is a large S-shape tunnel and another type is smaller pentagonal tunnel [14]. In the S-shape tunnel, there are two sites in which sodium ions can located (Na1 and Na2 sites) and only one sodium ion located in the smaller tunnel (Na3 site). During discharging and charging processes sodium ions diffuse along c axis. The sodium ions are reversibly insert/extract into/from the Na1 and Na2 sites, while the sodium ion located in the smaller tunnel is trapped in the Na3 site.

Figure 2 shows the SEM images of as-prepared $Na_{0.44}MnO_2$ powder at different magnifications. The morphologies of obtained product consist of $Na_{0.44}MnO_2$ particles and $Na_{0.44}MnO_2$

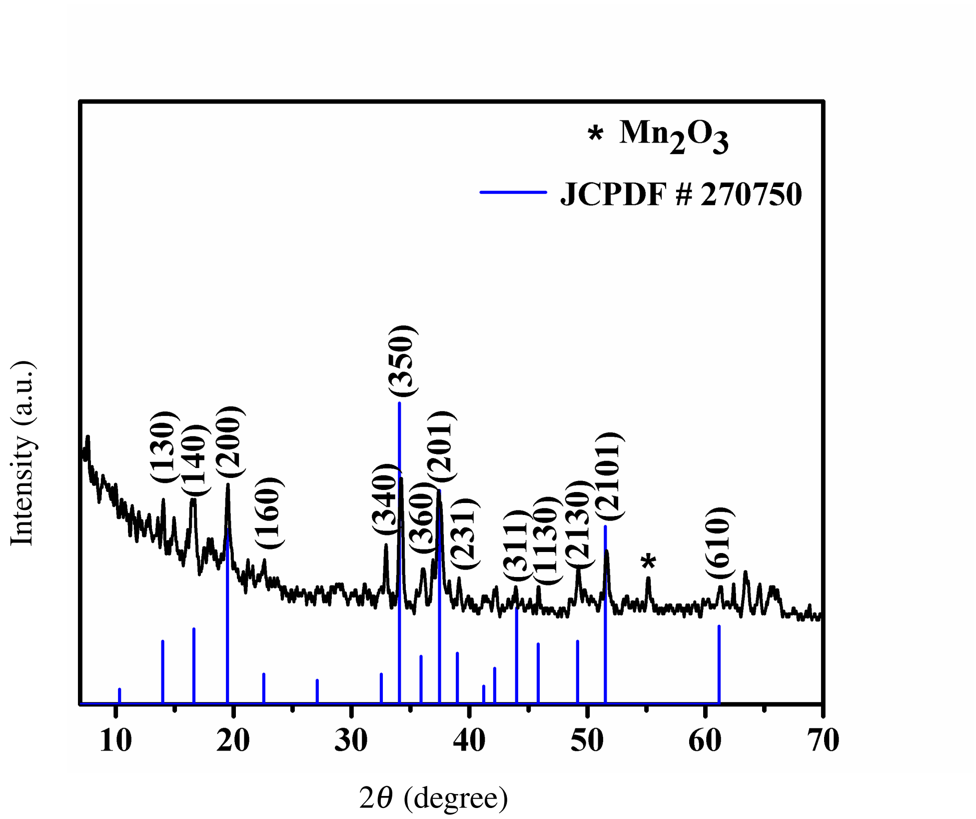

Fig. 1. XRD pattern of $Na_{0.44}MnO_2$ powder synthesized by ahydrothermal method at 205°C for 96 hours then annealed at 600° C for 6hoursin air. The pattern of the JCPDF # 27-0750 file is shown for comparison.

nanowires (Fig. 2a and b). The major portion of $Na_{0.44}MnO_2$ material has particle morphology. The size of a single particleis in the range of 300 nm to 1 μm (Fig. 2c) and these particles are agglomerated to form the secondary particles in the size range of 3 μm to 5 μm (Fig. 2b). The minor portion of $Na_{0.44}MnO_2$ material has nanowire morphology. The $Na_{0.44}MnO_2$ nanowires have average diameters in the range of 30 nm to 100 nm and approximately 1 μm lengths (Fig. 2d). Sauvage *et al.* reported that the capacity of rod-shape $Na_{0.44}MnO_2$ particles synthesized by solid state reaction method is approximately 80 mAh g^{-1} and after 40 cycles the capacity retention is about 40 mAh g^{-1} [14]. The $Na_{0.44}MnO_2$ particles with similar rod-like morphology have a modest discharge capacity of 40 mAh g-1and the cycling ability of the material is not revealed [13]. Bearing in mind that the morphology can affects on the electrochemical performance of materials. We expect that the combination of particle morphology and nanowire morphology possibly improves the electrochemical properties of fabricated $Na_{0.44}MnO_2$ material.

Figure 3a shows the 1^{st}, 10^{th}, and 20^{th} charge/discharge curves at current density of 0.1 C between 2.0-4.0 V. The discharge capacities of the 1^{st}, 10^{th}, and 20^{th} are 62.7 mAh g^{-1}, 64.0 mAh g^{-1}, and 65.8 mAh g^{-1}, respectively. These values are comparable with the capacity of carbon

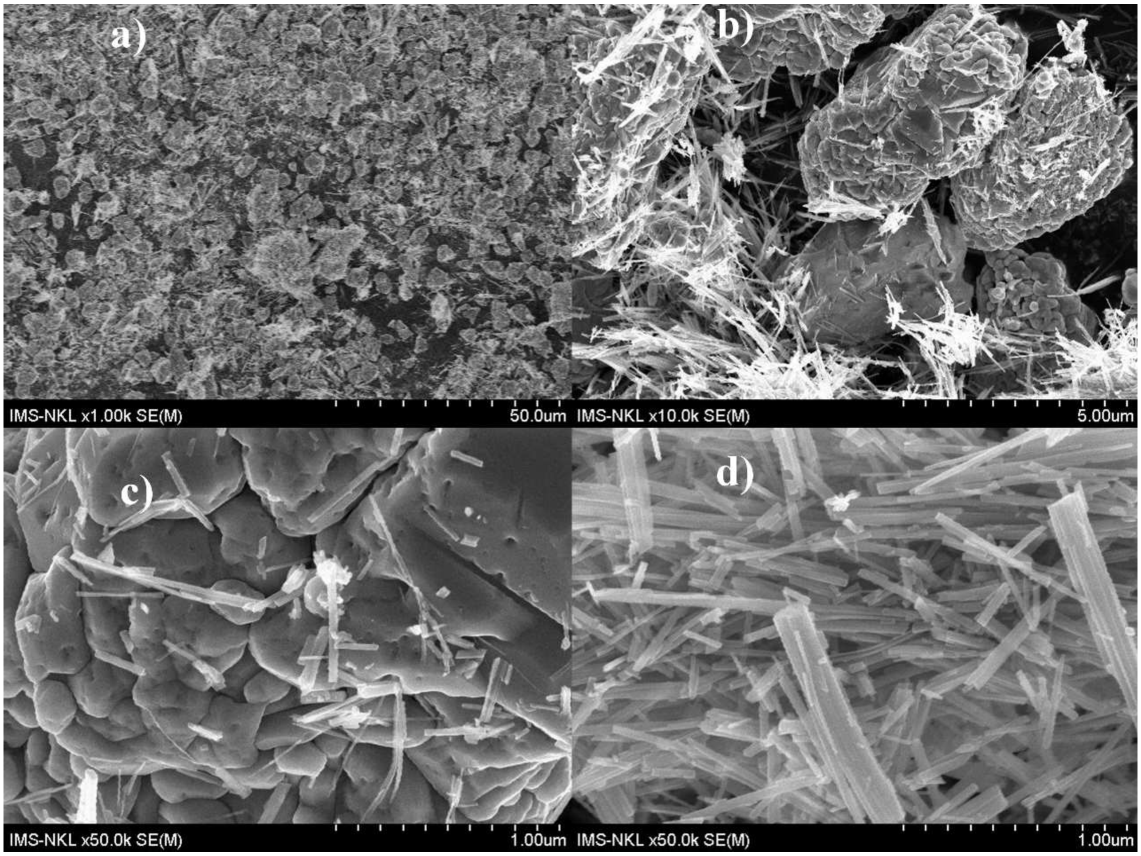

Fig. 2. SEM images of as-prepared $Na_{0.44}MnO_2$ powder.

coated $Na_{0.44}MnO_2$ [14]. The first discharge capacity of the $Na_{0.44}MnO_2$/C composite is approximately 80 mAh g^{-1}. The higher discharge capacity of $Na_{0.44}MnO_2$/C material can be attributed to the carbon layer on the surface of $Na_{0.44}MnO_2$ particles which lead to a higher electronic conductivity compare to bare $Na_{0.44}MnO_2$ particles. Both charge and discharge curves have several voltage plateaus indicating that the $Na_{0.44}MnO_2$ material has suffered multiple biphasic transitions during cycling. The similar charge/discharge curves of $Na_{0.44}MnO_2$ cathode were also reported in literatures [15, 17]. The discharge curves clearly show five voltage plateaus located at 3.4, 3.2, 2.9, 2.6, and 2.4 V, which present the different sodiation steps into $Na_{0.44}MnO_2$ structure. The charge curves display corresponding five voltage plateaus situated at 3.5, 3.25, 3.0, 2.7, and 2.5 V, which illustrate the corresponding desodiation steps from $Na_{0.44}MnO_2$ structure. Reported cyclic voltammorgram data exhibit six pairs of redox peaks, which correspond to six different intercalation/deintercalation steps [14, 17, 18]. In this study, only five voltage plateaus in the charge and discharge curves were observed due to the weak and broadened redox peaks located at 2.1 V contribute a small capacity therefore possibly cannot form a voltage plateau in the charge/discharge curves.The situation of charge voltage plateaus and corresponding discharge voltage plateaus are closed indicating a very low voltage polarization, which lead to a reversible sodium ion intercalation/deintercalation into/from $Na_{0.44}MnO_2$ structure. In addition, the charge and discharge curves are similar and well overlap suggesting that the $Na_{0.44}MnO_2$ material has a high cycling ability.

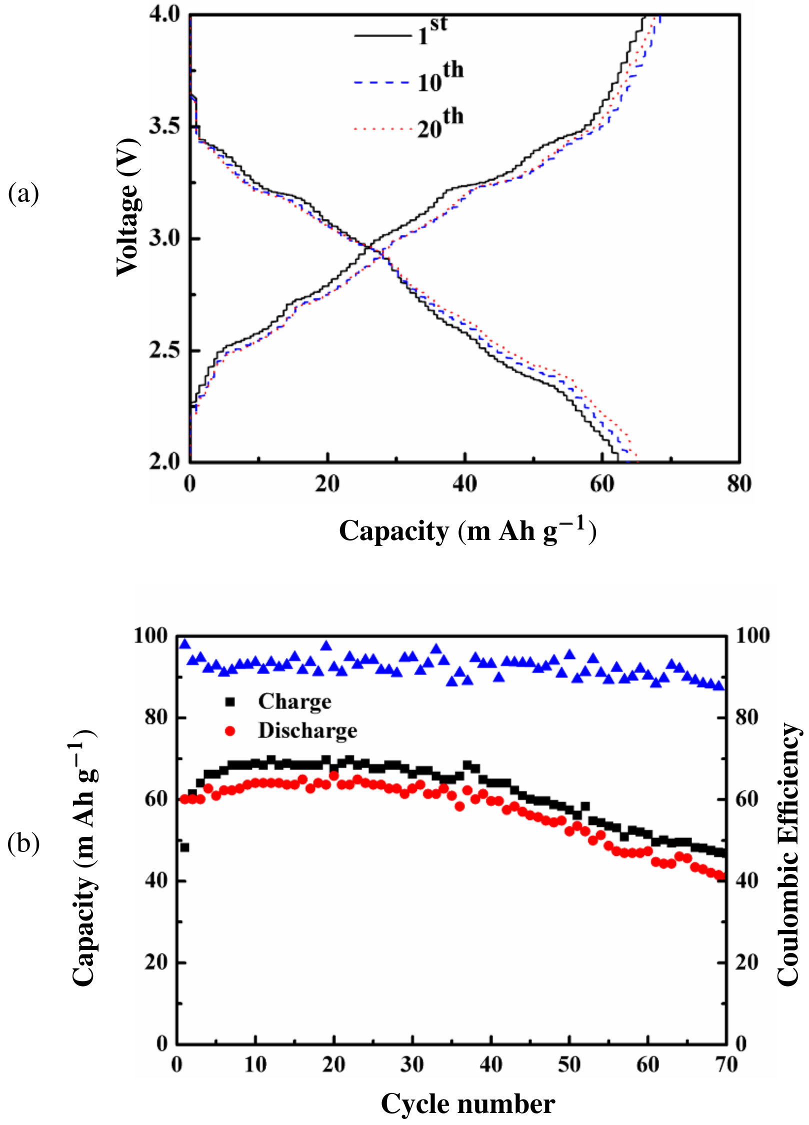

Fig. 3. The 1^{st}, 10^{th}, and 20^{th} charge/discharge curves of $Na_{0.44}MnO_2$ cathode material (a), and cycling ability at current density of 0.1 C between 2.0-4.0 V(b).

The cycling behavior and coulombic efficiency of $Na_{0.44}MnO_2$ cathode material cycled at 0.1 C between 2.0-4.0 V are shown in Fig. 3b. The charge/discharge capacities are gradually increase from 66.2/62.7 mAh g^{-1} to 68.4/64.0 mAh g^{-1} at the first 10 cycles. The capacities remain stable for the next 30 cycles and then slowly decrease to 46.9/41.1 mAh g^{-1} after 70 cycles. The capacity increase in the initial 10 cycles represents the activation process of $Na_{0.44}MnO_2$ material. The activation process of positive electrode also observed for $NaLi_{0.2}Ni_{0.2}Mn_{0.6}O_2$cathode material [4]. After 50 cycles, the capacity retention is approximately 85.3%, which is higher than that of $Na_{0.44}MnO_2$/C composite (about 50% after 50 cycles) [14] and $Na_{0.44}MnO_2$ nanowire [15]. The coulombic efficiency is about 90%, which is stable over 70 cycles. The high coulombic efficiency confirms that sodium ions are reversibly intercalated/deintercalated into/from $Na_{0.44}MnO_2$ orthorhombic structure for a long period of time.

IV. CONCLUSIONS

$Na_{0.44}MnO_2$ material with the orthohombic structure was successfully synthesized by the hydrothermal method. The major portion of $Na_{0.44}MnO_2$ material has particle morphology and a minor portion of the material has nanowire morphology. During cycling, the highest charge/discharge capacities of $Na_{0.44}MnO_2$ cathode are 67.5/65.8 mAh g^{-1}. The capacity retention is approximately 85.3% after 50 cycles. The coulombic efficiency is about 90% over 70 cycles. The electrochemical performance of $Na_{0.44}MnO_2$ material suggests that the $Na_{0.44}MnO_2$ can be a potential cathode material for sodium ion batteries.

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