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INVESTIGATION OF SODIUM MANGANESE OXIDE NANOWIRES SYNTHESIZED BY HYDROTHERMAL METHOD FOR ALKALINE ION BATTERY

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Abstract. *Sodium manganese oxide (Na_xMnO_2) has attracted much attention as cathode materials for alkaline ion battery due to the ability of the fast charge and discharge of Na^+, in particular in nanoscale. We report on the synthesis of Na_xMnO_2 nanowires via hydrothermal synthesis route from Mn_2O_3 and NaOH solution. The morphological observation indicates that the obtained $Na_{0.44}MnO_2$nanowires with diameters of about 20 nm -30 nm, length up to several micrometers were formed by this process. The electrochemical properties of fabricated materials were investigated by means of cyclic voltammetry technique and show that sodium manganese oxide (Na_xMnO_2) is a promising material used for the alkaline ion battery.*

Keywords: alkali ion battery, cathode materials, $Na_{0.44}MnO_2$ nanowires.

I. INTRODUCTION

In recent years, electrode materials for ion batteries are of importance due to their basic ingredients for fabrication of ion rechargeable battery. The ion rechargeable batteries are used for portable electronics, electric vehicles and storage devices and are an important component of the green energy systems including wind, solar and hydrogen energy. It is well-known that lithium ion batteries can be used for electric vehicles owing to their advantages such as large energy density. Most popular electrode materials that are currently used are lithium ion storage materials as Li_xMO_2 where M is the transition metal. Among them, $LiMn_2O_4$ materials are considered to have many advantages such as cost-effective, eco-friendly and no gas releasing during operating in the electrolyte. However, the limitation of lithium as well as the difficulty in making large scale batteries makes it expensive for mass production. Aqueous rechargeable Na-ion batteries appear to be an attractive alternative to their lithium counterparts for electric energy storage, because of its abundant and low cost of sodium resources. High power rechargeable Na-ion batteries have attracted considerable interest recently, because the electric/hybrid vehicles require low cost and high power auxiliary power units. The use of abundant Na in the mobile charge could reduce the cost, while the Na-ion diffusion in the solid electrode, which is generally faster than the Li-ion diffusion, should enable higher power to output than that of the Li-ion rechargeable batteries [5]. There are three Na-ion transfer processes in the Na-ion battery: i) the Na-ion conduction in the liquid electrolyte, *ii*) the Na-ion transfer at the electrolyte electrode interface, and *iii*) the Na-ion diffusion in the solid electrode. In particular, the slow ionic diffusion in the solid electrode should be the rate limiting step when the Na-ion battery is charged/discharge at the high rate. Therefore, in order to achieve the high power Na-ion batteries, nanostructuring of the electrode materials is indispensable, which can reduce the Na-ion diffusion length and increase the surface area [9].

Similar to the case of lithium ion, metal oxides, metal fluoride and compounds of poly anion usually are capable of storing and exchanging Na-ion [2,3,6]. Among them, $Na_{0.44}MnO_2$ has been known as the cathode material for the Na-ion battery. A tunnel structure in $Na_{0.44}MnO_2$ exhibits the reversible Na-ion insertion/extraction reaction. For example, rod-like $Na_{0.44}MnO_2$ synthesized from the solid state reaction was reported to show the reversible capacity of 140 mAh/g at 3.5 V-2.0 V vs. Na/Na^+ [4]. It is higher than that of $LiMn_2O_4$ (120 mA/g) [5].

In this paper, we present the results on the synthesis and characterization of $Na_{0.44}MnO_2$ nanowires. The nanowires were fabricated by a hydrothermal method from Mn_2O_3 and NaOH solution. The crystal structure was investigated by using an X-ray diffractometer (D-5000 SIEMEN). The surface morphology of the samples was investigated by using a “Hitachi” field emission scanning electron microscope (HITACHI S-4800). In electrochemical studies, a three-electrode cell was used. The cell is composed of $Na_{0.44}MnO_2$ used as a cathode electrode and a platinum anode electrode separated by an electrolyte containing Na_2SO_4 1M. The electrochemical properties of fabricated materials were measured on an Auto-Lab Potentionstat PGS-30. In addition, the electrochemical properties were also investigated by cyclic voltammetry technique in the potential range of -1.0 V and 1.5 V. The results show that sodium manganese oxide (Na_xMnO_2) is promising material in the field of research and fabrication of alkaline ion battery.

II. EXPERIMENTAL SETUP

$Na_{0.44}MnO_2$ nanowires were fabricated by a hydrothermal method from Mn_2O_3 and NaOH solution. First, 0.2 g Mn_2O_3 was mixed in 80 ml solution of 5M NaOH, the mixture is then poured into a stainless steel autoclave (Teflon apparatus).The hydrothermal autoclave was placed in an oven, heated to 205˚C and maintained at that temperature for 46 hours and 96 hours. After hydrothermal process, $Na_{0.44}MnO_2$ was separated from the solution and washed several times with deionizer water and then dried at 120˚C in vacuum. For studying the influence of recrystallization on the electrochemical properties, the material is then annealed at 600˚C for 2 hours. Electrochemical properties of the material were examined by cyclic voltammetry using Auto Lab. PSG 30 system in a cell with 3 electrodes. The $Na_{0.44}MnO_2$ electrode was fabricated by spread method. $Na_{0.44}MnO_2$ powder was mixed with 15% CMC binder to form a paste. After that, the paste was spread onto copper foil and then dried in vacuum at 150˚C. The finished products were cut into equal parts with an area of approximately 1 cm^2 to make electrodes. The electrodes were used as cathodes in the electrochemical measurements. Electrolyte solution was 1M Na_2SO_4. Counter electrode was Pt grid and AgCl electrode was a reference electrode.

III. RESULTS AND DISCUSSION

Fig. 1 shows X-ray diffraction patterns of Na_xMnO_2 after hydrothermal synthesis at 205°C for two different growing times of 48 hours and 96 hours. A part of the sample after hydrothermal synthesis in 96 hours was annealed at 600° C for 2 hours. The results showed that for 48 hours hydrothermal samples, there is only received $Na_{0.55}MnO_2$; MnOH phase and Mn_2O_3 stay unreacted (Fig. 1.a). For hydrothermal samples in 96 hours, there is a phase of $Na_{0.44}MnO_2$, besides the very small portion of the oxide Mn_2O_3 (Fig. 1.b). Fig. 1.c shows the XRD pattern of the sample annealed at 600°C for two hours. The diffraction peaks at 2θ values of approximately 13.91°, 16.61°, 19.43°, 32.52°, 34.69°, 35.89°, 37.47°, 49.15° and 51.49° correspond to the (130), (140), (200), (340), (350), (360), (201), (2130), and (2101) planes of the orthorhombic structure of $Na_{0.44}MnO_2$. (JCPDS card No. 27-0750) [5]. The lattice parameters a= 0.910 nm, b = 2.632 nm and c= 0.282 nm were calculated from the peak positions (200), (350) and (201) by using the equation [7]: $\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$ where d is the measured space of (hkl) planes, which is determined by Bragg's law. *(hkl)* are the Miller's indexes of crystalline plane relevant to the measured d-spacing. $a, b$and c are the lattice parameters of a orthorhombic structure. The changes in structure of the materials obtained via hydrothermal process lasted for 48 hours and 96 hours indicate that the formation of $Na_{0.44}MnO_2$ consists of two stages, similar to the results presented in Ref. [1]. Firstly, the reaction of sodium hydroxide with Mn_2O_3 oxides occurred to create $Na_{0.55}MnO_2$ (birnessite) with lamellar structure. Prolonged hydrothermal time, the material layer continues to grow and divide into nanowires $Na_{0.44}MnO_2$. When the time of hydrothermal process increases to 96 hours, the materials completely transform to $Na_{0.44}MnO_2$ phase.

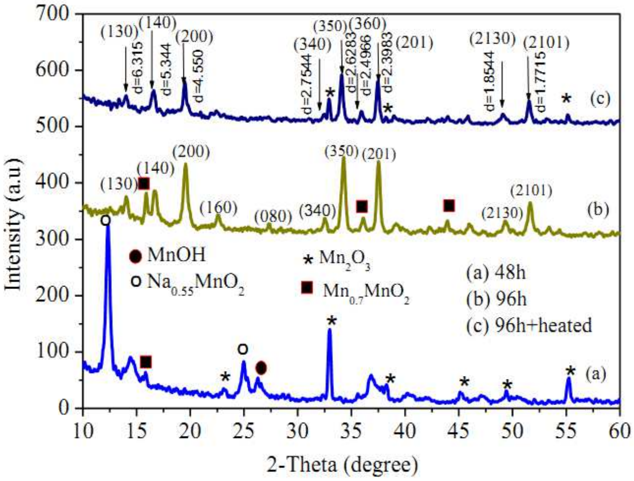

Fig. 1. XRD pattern of Na_xMnO_2 prepared via a thermal method at 200° C for 48 hours (a), for 96 hours (b), and for 96 hours then re-annealed at 600° C for 2 hours (c).

The phase changes in Na_xMnO_2 can be due to Na-vacancy ordering or transitions that involve the gliding of oxygen planes .[8]. The exact formation mechanism of $Na_{0.44}MnO_2$ is unknown but could be assigned to the high temperature diffusion of the sodium ions/atoms into a manganese oxide network followed by the recrystallization and grain growth step [1]. Morphology of the fabricated samples is presented in Fig. 2.

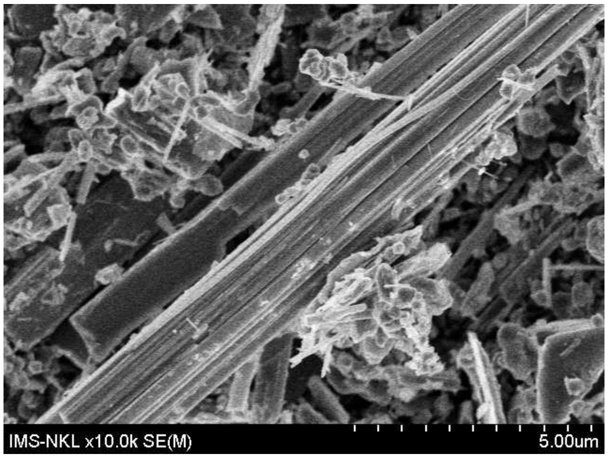

Fig. 2. SEM images of Na_xMnO_2 prepared via a hydrothermal method for 48 hours.

Fig. 2 shows a typical FE-SEM image of Na_xMnO_2 samples with a hydrothermal time of 48 hours. The sample is composed of various structures with different morphologies, including particles and bundles of wires with length up to 15 μm. The materials are considered as the residual Mn_2O_3 with a size of 100 nm - 200 nm and birnessite $Na_{0.55}MnO_2$ particles with a size of several micrometers. It can be inferred from XRD results presented in Fig.1, the multi-phase materials exist in which Mn_2O_3 and $Na_{0.55}MnO_2$ dominate. The morphology of 96 hours hydrothermal samples is presented in Fig.3 showing that the materials display a nanorod structure with the length of few hundred nanometers to several micrometers. At the better magnification (Fig. 3.b), the nanorods consist of numerous combined small bars with diameters of about 20 nm $\sim$ 30 nm. This again shows that $Na_{0.44}MnO_2$ nanorods formed in hydrothermal reaction are mainly separated from the intermediate birnessite $Na_{0.55}MnO_2$ materials [10]. After hydrothermal time was prolonged to 96 hours, $Na_{0.44}MnO_2$ was formed. The materials have nanorod structure with diameters in the range of 20 nm $\div$ 30 nm and lengths of up to several micrometers.

Electrochemical properties of $Na_{0.44}MnO_2$ materials were investigated by cyclic voltammetry technique (C-V) in an electrolyte solution with potential in range of -1.0 V$\div$1.5 V. Fig.4 shows the C-V curves of $Na_{0.44}MnO_2$ electrodes after a hydrothermal process and after re-annealing at 600° C for 2 hours. Both C-V curves in Fig. 4.a and Fig. 4.b clearly show separated sharp reduction-oxidation peaks corresponding to the insertion/extraction of Na^+ions. The process may be illustrated by the following reaction:

$$Na_{0.44}MnO_2 \quad \leftrightarrow Na_{0.44-x}MnO_2 + xNa^+ + xe^-$$

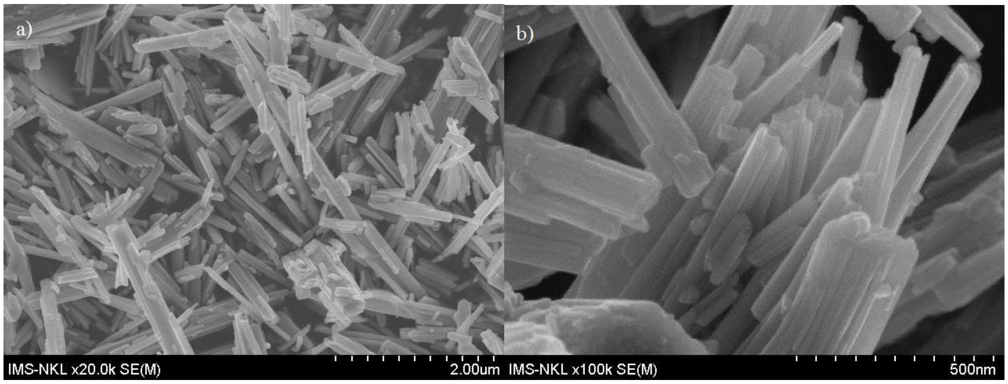

Fig. 3. SEM images of Na_xMnO_2 prepared via a hydrothermal method for 96 hours and re-annealed at 600° C for 2 hours at different magnification.

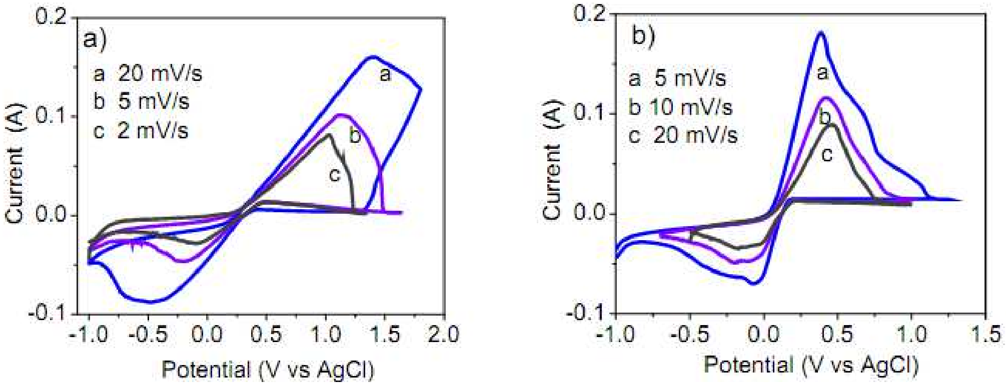

Fig. 4. C-V curves of $Na_{0.44}MnO_2$ electrodes after hydrothermal reaction (a), and after re-annealing at 600° C for 2 hours (b).

This result shows that the electrodes have a good Na-ion exchange capacity and the process is completely reversible. From Fig. 4.a, it is clear that C-V curves show one peak of oxidation corresponding to one peak of reduction in the samples without annealing. Voltage of oxidation peak and reduction peak change clearly when scan rate changes from 2 mV/s to 20 mV/s. The position of oxidation peak increases from 1 V to 1.4 V and the position of reduction peak decreases from -0.08 V to -0.4 V. Fig.4.b shows the C-V curves of the samples annealed at 600° C, the redox peaks are separated into different peaks. The position of the peaks hardly change when scan rate changes. The maximum position of oxidation and reduction peaks located at 0.38 V and -0.04 V, respectively. For the annealed sample, the distance between oxidation peak and reduction peak is about $\sim$0.42 V, whereas in the case of the samples without annealing, this value turns out to be $\sim$ 1.8 V, by far greater than that of annealed samples. It is clear evidence that the samples annealed at 600 ° C provide a significantly improved exchange rate of the Na-ion in the reduction-oxidation reactions.

IV. CONCLUSIONS

$Na_{0.44}MnO_2$ nanowires with diameters in the range of 20 nm $\sim$ 30 nm and lengths of up to several micrometers have been fabricated by the hydrothermal method from Mn_2O_3 and NaOH solutions. Hydrothermal synthesis to form $Na_{0.44}MnO_2$ consists of two stages. Initially, the reaction between sodium hydroxide with Mn_2O_3 oxide occurred to produce $Na_{0.55}MnO_2$(birnessite) with lamellar structure. Continue the hydrothermal process, the material layer grown and separated into $Na_{0.44}MnO_2$ nanowires. The electrodes made of $Na_{0.44}MnO_2$ nanowires display a good Na-ion exchange capacity and this process is completely reversible. This result suggests that the electrode made of $Na_{0.44}MnO_2$ nanowires is a potential candidate for the practical cathode material in the high power Na-ion battery.

ACKNOWLEGMENT

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