



Effect of Na diffusion on the formation of fibrous microcrystals of manganese oxide

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Abstract

Diffusion of sodium through MnO_2 lattice in a high-temperature solid-state reaction can affect the original structure of manganese oxide. This effect is significantly concentration-dependent. For $x < 0.5$ in Na_xMnO_2 , the chemical structure of sodium manganese oxide is accompanied by the formation of manganese oxide nanowires. The amount of such nanowires increases by increasing the concentration. For $x > 0.5$, it tends to form conventional layered structure (with microscale particles). In the case of MnO_2 , this phenomenon is only for Na diffusion, when a chemical structure corresponding to $\text{Na}_{0.44}\text{MnO}_2$ (JCPDS: 27-0750) is formed.

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1. Introduction

Nanotechnology (and nanoscience) is indeed a scale gap between chemistry and physics [1]. Although a considerable attention has been paid to this issue in the realm of material science for applied purposes, a particular attention from physicochemical point of view is required to reveal mechanism of syntheses of nanostructured materials. Among available materials with nanostructures, metal oxides are of particular interest in this context, since physicochemical processes have significant effect on their formation. On the other hand, metal oxides have a vast variety of applications. For instance, manganese oxide is an interesting material for battery applications [2–5].

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To improve material properties of manganese oxide for practical performances, considerable efforts have been paid to fabricate manganese oxide nanowires via available template-based methods [6–8]. However, such methods are not always favorable due to the essential difficulties of working with nanostructured templates. Wang and Li have reported a hydrothermal synthesis for the preparation of MnO_2 nanowires/nanorods [9,10]. Coordination-polymer-precursor route has also been reported as an efficient method for the preparation of MnO_2 nanowires [11]. However, such methods are also accompanied by complicated process involving the preparation of polymer-based precursor. On the other hand, hydrothermal syntheses are not always favorable, and solid-state syntheses are still most advantageous method for the preparation of cathode materials for lithium battery applications [12]. We have found that it is possible to synthesize manganese oxide nanowires via a simple solid-state method [13,14]. In this case, individual nanowires tend to attach to each other to form large bunches of nanowires [14].

Contrary to template-based methods, formation of metal oxide nanowires via template-free methods are very complicated processes. Thus, as emphasized above, this issue should be clarified from physicochemical point of view to understand the mechanism of nanowire synthesis. This will also assist to enhance the synthesis procedure.

2. Experimental

Syntheses of alkali metal ions-intercalated manganese oxide samples were performed by a conventional solid-state route. Stoichiometric ratios of the reactants (alkali metal carbonate and MnO_2) were mechanically mixed. The heating process includes a 5-h heating at $600\text{ }^\circ\text{C}$ followed by 40-h heating at $800\text{ }^\circ\text{C}$. Then the samples were slowly cooled to the room temperature. Scanning electron microscopy (SEM) investigations were carried out using a Cambridge electron microscope, model Steroscan 360. Energy dispersive X-ray analysis (EDX) was performed using DDAX Leica-exL2. Powder X-ray diffraction (XRD) patterns were recorded using a Philips PW 1371 diffractometer with $\text{Co K}\alpha$ radiation. FULLPROF software was employed to analyze XRD measurements via Rietveld refinement.

3. Results and discussion

Insertion of sodium into MnO_2 structure leads to the formation of layered structure, but as it is well known that lithium insertion into MnO_2 structure tends to form stable spinel structure of LiMn_2O_4 . This significant difference is attributed to the size of inserting cation. On the other hand, the structure difference may also affect the material morphology due to the specified growth of individual particles in respect with the lattice structure. Synthesis of LiMn_2O_4 as a promising candidate of cathode material for lithium batteries has been extensively investigated. It is known that different methods (such as solid-state and sol-gel routes) lead to the formation of microparticles of LiMn_2O_4 spinel. Whereas, a conventional solid-state synthesis of $\text{Na}_{0.5}\text{MnO}_2$ is accompanied by the formation of nanowires, which is attributed to longitudinal diffusion of sodium across the layered structure of MnO_2 . However, this hypothesis needs further evidences and discussion to clarify this complicated physicochemical process.

Solid-state diffusion has a particular role in this context, as is able to persuade the nanowires to be formed in united directions (Fig. 1A). In other words, the Na ions diffused in one arbitrary direction will

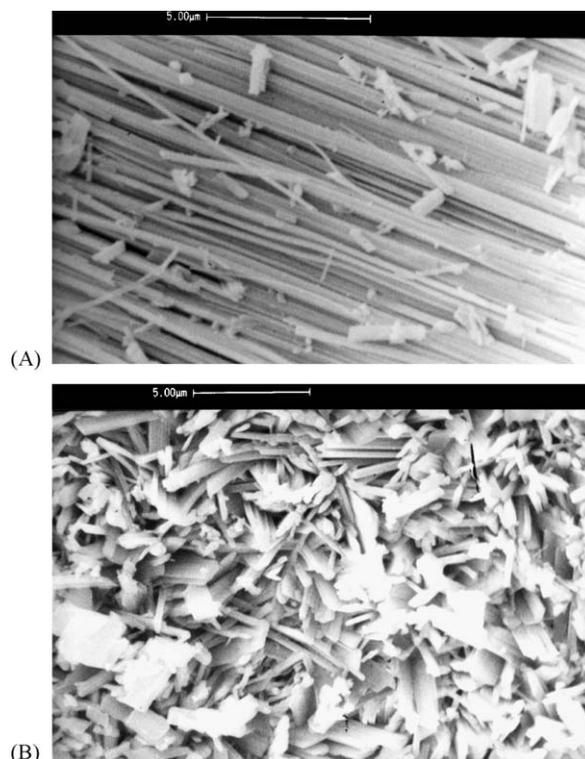


Fig. 1. SEM images of the $\text{Na}_{0.5}\text{MnO}_2$ samples prepared via (A) solid-state synthesis and (B) sol-gel route.

continue their diffusion in the same direction, as in the absence of hydrodynamical convection in solid-state, changing the diffusion direction is less probable. It should be emphasized that this type of efficient solid-state diffusion is only possible at high-temperature, which was applicable for our synthesis process. According to this hypothesis, solid-state synthesis at lower temperatures should not be accompanied by this phenomenon.

Since mixing of powders of raw materials is an important problem in solid-state synthesis, when the initial raw materials have been well mixed via a sol-gel route it is possible to perform synthesis process at low temperatures. Fig. 1B shows a typical SEM image of $\text{Na}_{0.5}\text{MnO}_2$ prepared by a solid-gel route. The detailed experimental procedure for this typical sol-gel route can be found in the literature [15]. It is obvious that no nanowire is formed at this low-temperature synthesis. However, the microparticles formed are highly uniform and similar. In other words, the diffusion process was not sufficient (like the case of high-temperature synthesis) to retain the nanostructure generated as a result of Na diffusion through the MnO_2 lattice.

The above-mentioned results just simply indicate the significant role of solid-state diffusion occurring at high temperatures to form manganese oxide nanowires. However, to inspect the role of diffusion process on the formation of such nanostructure, it is useful to investigate the effect of sodium concentration. In other words, if such nanowires have been formed as a result of Na diffusion through MnO_2 lattice, the concentration of the diffusing species should have a significant effect on the nanowire formation. The concentration of 0.5 in Na_xMnO_2 was chosen typically, as it is equal to that of lithium in conventional LiMn_2O_4 .

Fig. 2 presents the morphological structures of a series of Na_xMnO_2 samples as x varies from 0 to 1. The commercial sample of MnO_2 , which was used as a raw material in the solid-state synthesis, consists of common microparticles (Fig. 2A). As the Na diffusion through this raw material causes the formation

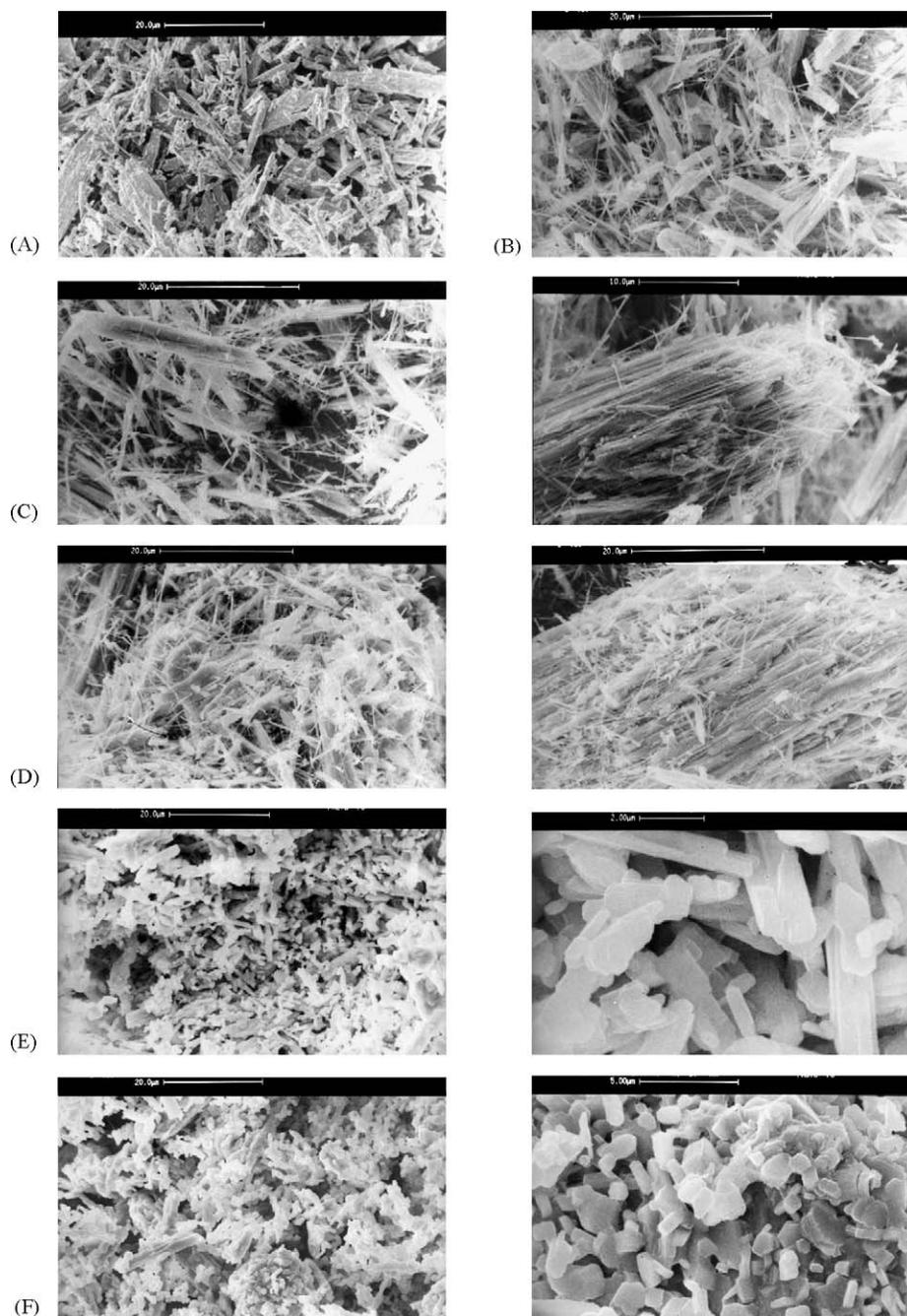


Fig. 2. SEM images of a series of the Na_xMnO_2 samples where x is (A) 0, (B) 0.1, (C) 0.25, (D) 0.5, (E) 0.75, and (F) 1.

of nanowires (comparison of Fig. 2A and B), the nanowire formation should be strengthened by increasing the Na concentration. It is exactly what observed for the concentration range of 0–0.5 (Fig. 2A–C). This indeed provides a strong evidence for the hypothesis proposed above for the role of Na diffusion on the nanowire formation. However, for the Na concentration above 0.5, the nanowire formation disappears and no nanowire is generated regardless of the Na concentration. This suggests that at high concentration, Na diffusion is not able to cause the nanowire formation. To inspect this phenomenon, it is useful to investigate crystallographic structure of different samples synthesized.

Powder X-ray diffraction (XRD) patterns of different Na_xMnO_2 samples are illustrated in Fig. 3. Several phases of sodium manganese oxide (Na_xMnO_2) with allotropic modifications can be formed depending on the values of x . For instance, known samples are $\text{Na}_{0.2}\text{MnO}_2$, $\text{Na}_{0.44}\text{MnO}_2$, $\text{Na}_{0.7}\text{MnO}_{2+\delta}$ ($0 \leq \delta \leq 0.25$), and NaMnO_2 [16,17]. According to the present results, three typical concentrations are of importance to discover the chemical structure of aforementioned nanowires: when $x < 0.5$, $x = 0.5$, and $x > 0.5$. In the case of $x < 0.5$, e.g., $\text{Na}_{0.25}\text{MnO}_2$, the XRD pattern can be well indexed to Bixbyte (Mn_2O_5) with JCPDS: 24-0508. Although, Na_2O does not exist, small amount of Na incorporated into the lattice can be found as $\text{Na}_{0.44}\text{MnO}_2$ with JCPDS: 27-0750. This means that for small amounts of Na, the chemical structure is mainly related to manganese oxide. In other words, Na intercalation is not as strong as needed for morphological transformation to nanowires.

When the amount of Na intercalated is sufficiently high, e.g., $\text{Na}_{0.5}\text{MnO}_2$, the XRD pattern can be completely indexed to $\text{Na}_{0.44}\text{MnO}_2$ with the standard pattern of JCPDS: 27-0750. No noticeable impurity is detected, and the XRD pattern of fibrous microcrystals of $\text{Na}_{0.5}\text{MnO}_2$ is in consistent with the theoretical lattice structure. This indicates that the synthesis procedure employed here is truly practical leading to an effective synthesis. In other words, the partial phase of $\text{Na}_{0.44}\text{MnO}_2$ (JCPDS: 27-0750) which appeared in $\text{Na}_{0.25}\text{MnO}_2$ sample is the main phase in $\text{Na}_{0.5}\text{MnO}_2$ sample. In fact, fibrous microcrystals of Na-intercalated manganese oxide correspond to the chemical structure of $\text{Na}_{0.44}\text{MnO}_2$,

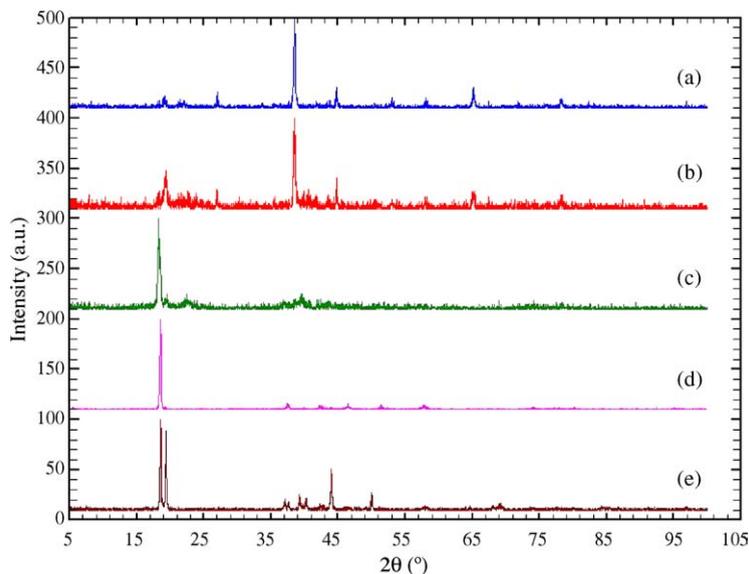


Fig. 3. XRD patterns of the samples illustrated in Fig. 2. (a) $\text{Na}_{0.1}\text{MnO}_2$, (b) $\text{Na}_{0.25}\text{MnO}_2$, (c) $\text{Na}_{0.5}\text{MnO}_2$, (d) $\text{Na}_{0.75}\text{MnO}_2$, and (e) $\text{Na}_{1.0}\text{MnO}_2$.

and partial formation of nanowires for smaller amounts of Na intercalated is due to partial existence of $\text{Na}_{0.44}\text{MnO}_2$.

This hypothesis can be proved by analyzing higher amounts of Na intercalated, as no nanowire is formed in this case. For instance, $\text{Na}_{0.75}\text{MnO}_2$ (Fig. 3d) is indexed to $\text{Na}_{0.7}\text{MnO}_{2.05}$ with the standard pattern of JCPDS: 27-0751. According to the literature [16,17], formation of this structure of sodium manganese oxide is common in the presence of appropriate amount of Na during solid-state reaction. In this case, $\text{Na}_{0.07}\text{MnO}_{2+\delta}$ (JCPDS: 27-0752) and tiny amount of MnO_2 (JCPDS: 24-0073) are found as impurities; however, $\text{Na}_{0.44}\text{MnO}_2$ (JCPDS: 27-0750), corresponding to the fibrous microcrystals is not detected. This indicates that high amounts of Na results in the formation of another Na-intercalated manganese oxide and disappearance of the chemical structure of aforementioned fibrous microcrystals.

In general, it can be expressed that known chemical structure of $\text{Na}_{0.44}\text{MnO}_2$ can have interesting structure of fibrous microcrystals, and we proposed a simple solid-state route for synthesis of this material. It has been reported that diffusion of counterion through nanostructured cathodes is accompanied by achievement of higher capacity [18]. This is also associated with a better thermodynamical behavior of the system [19,20].

4. Conclusion

Mechanism of nanowire formation via Na diffusion through MnO_2 lattice was described by appropriate experimental results and solid arguments. Two factors are responsible for the formation of manganese oxide nanowires: (i) sufficiently fast diffusion in solid-state at high temperature leading to the generation of permanent nanostructure and (ii) appropriate lattice structure of the manganese oxide in the presence of certain Na concentration which provides an opportunity for longitudinal diffusion of Na resulting in the nanowire formation. The present work as a typical physicochemical study with aim of inspecting the reason of nanowire formation indicated the required conditions and limitations for the nanowire formation.

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