

A simple synthesis of manganese oxide nanowires

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Manganese oxide nanowires were prepared from MnO_2 with Na ions inserted within the raw MnO_2 by a simple solid-state process.

The preparation of nanowires and nanorods of metal oxides is of considerable interest. The common method consists in the use of templates with well-defined nanostructures.^{1–3} However, complicated processes are required for fabricating base templates with desirable structures. The fabrication of a required template and the separation of the nanowires from the base template are time-consuming and expensive processes. Although template-free methods do not lead to the formation of highly ordered nanowires, they are of great interest due to their simplicity.

Manganese dioxide is a promising cathode material for lithium batteries.^{4–7} It is of importance to prepare nanostructured MnO_2 since the diffusion of Li ions is easier in this case (and can be considered as 3D diffusion) leading to a better battery performance.⁸ The common technique to fabricate MnO_2 nanowires is template-based,³ and the preparation of MnO_2 nanowires/nanorods by template-free methods is restricted to a few recent reports.^{9–11} Wang and Li^{9,10} have reported a hydrothermal synthesis of MnO_2 nanowires/nanorods.

A coordination–polymer–precursor route is also an efficient method for the preparation of MnO_2 nanowires.¹¹ However, it is accompanied by complicated processes involving the preparation of a polymer-based precursor. On the other hand, hydrothermal syntheses are not always favourable, and solid-state syntheses are the most advantageous methods for the preparation of cathode materials for lithium batteries. Another disadvantage of such methods is the cost of raw materials. Thus, it is of great interest to design a new synthetic route to produce MnO_2 nanowires using inexpensive MnO_2 as an excellent raw material.

Here, we report an efficient procedure for the preparation of MnO_2 nanowires based on a simple solid-state reaction using MnO_2 . In this process, Na ions insert into the MnO_2 structure to form nanowires. This is of particular interest to lithium battery

applications since an almost ideal layered arrangement of the lithium and manganese ions occurs in LiMnO_2 cathode materials obtained from $\alpha\text{-NaMnO}_2$ by Li ion exchange.^{5,12,13} However, Na ions can be simply extracted from the NaMnO_2 nanowires to form pure MnO_2 nanowires.

The stoichiometric mixtures of the reactants (lithium or sodium carbonate and MnO_2) were heated for 5 h at 600 °C followed by heating at 800 °C for 40 h. The samples were slowly cooled to room temperature. Scanning electron microscopy (SEM) investigations were carried out using a Stereoscan 360

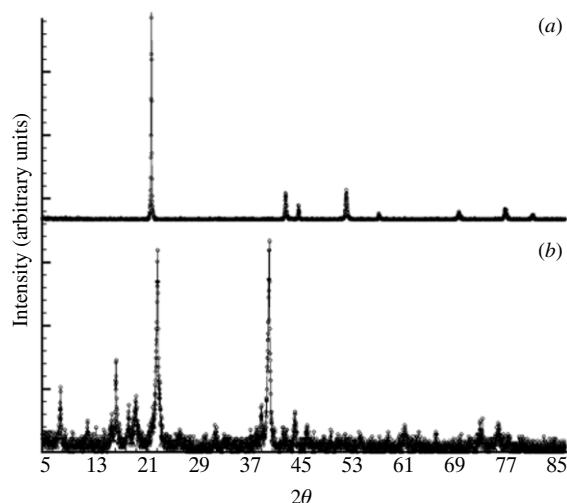


Figure 1 XRD patterns of (a) the LiMn_2O_4 spinel and (b) $\text{Na}_{0.5}\text{MnO}_2$ layered oxide prepared using a solid-state reaction.

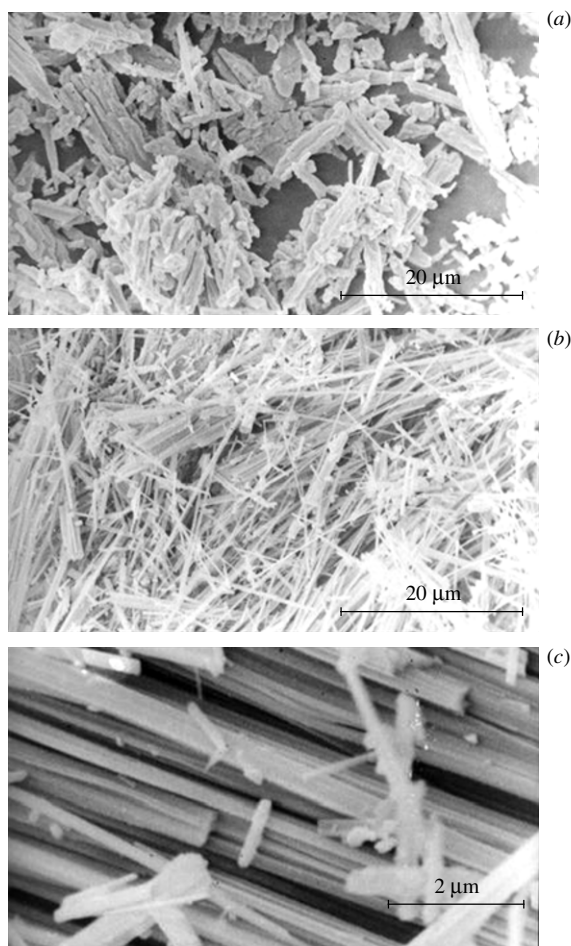


Figure 2 SEM images of (a) the LiMn_2O_4 spinel, (b) the $\text{Na}_{0.5}\text{MnO}_2$ sample, and (c) highly ordered (Na-intercalated) manganese oxide nanowires aligned in one direction.

Cambridge electron microscope. Energy dispersive X-ray analysis (EDX) was performed using a DDAX Leica-exL2. Powder X-ray diffraction (XRD) patterns were recorded using a Philips PW 1371 diffractometer with $\text{CoK}\alpha$ radiation. The FULLPROF software was employed to analyse XRD measurements *via* the Rietveld refinement.

Figure 1 presents the XRD patterns for samples prepared by the solid-state intercalation of Li or Na into manganese dioxide. The intercalation of Li results in the formation of LiMn_2O_4 with a well-defined spinel structure [Figure 1(a)]. When Na is used as an intercalating alkali metal, the intercalated manganese oxide has a well-defined layered structure rather than a spinel structure [Figure 1(b)]. This is due to a larger size of Na, which cannot fill the 8a sites of the spinel structure.

It is well known that the intercalation of Li into MnO_2 leads to the formation of a highly crystalline spinel structure. The LiMn_2O_4 spinel has a cubic structure with the space group $Fd\bar{3}m$. However, the intercalation of Na into MnO_2 is different as can be judged by a comparison of XRD patterns (Figure 1). The compound tends to form a structure with the space group $Cmcm$. It is an analogue to $\beta\text{-Na}_{0.52}\text{MnO}_2$.¹⁴ In this case, a high crystallinity corresponding to the specified structure is not observed. Due to the poor fit obtained without structural constraints, the exact Rietveld refinement is impossible. Of course, this is common for this class of materials;¹⁵ it can be attributed to the random stacking of O(2) and O(4).

The SEM images of LiMn_2O_4 spinel and $\text{Na}_{0.5}\text{MnO}_2$ layered oxides prepared under the same experimental conditions are illustrated in Figure 2. Although the particles of LiMn_2O_4 have a conventional morphology with sizes of 1–10 μm , the intercalation of Na into MnO_2 tends to form $\text{Na}_{0.5}\text{MnO}_2$ nanowires. In the latter case, manganese oxide nanowires with diameters of 50–200 nm are produced. Relatively long nanowires (even

longer than $\sim 50 \mu\text{m}$) form during the solid-state synthesis. An extensive study by EDX revealed that Na intercalation into raw MnO_2 is uniform.

We found that the proposed method leads to the formation of highly ordered nanowires, which are aligned in specified directions, as illustrated in Figure 2(c). Although the results are strongly reproducible and different runs of this solid-state synthesis lead to the formation of similar nanowires, experimental conditions have significant effects on the structure of the nanowires.

We found that the amount and structure of these nanowires strongly depend on the Na concentration employed for the solid-state synthesis. Although an increase in the Na concentration (up to $x = 0.5$ in Na_xMnO_2) was favourable for the formation of nanowires, no nanowires were formed upon a further increase ($x > 0.5$ in Na_xMnO_2). This is expected in accordance with the structural change of Na_xMnO_2 due to the concentration of intercalated sodium.¹⁴

When x was close to 0.44, a double-tunnel compound containing both MnO_6 octahedra and MnO_5 square pyramids was formed.^{16,17} This is an excellent case for lithium battery applications since this double-tunnel compound is stable and does not rearrange to spinel, which is a common problem for layered manganese oxides.¹⁸ At this specified Na concentration, it is possible to control the size of nanowires, which has a significant effect on battery performance characteristics.¹⁹ The proposed method for the preparation of cathode materials for lithium batteries does not need filtration and drying processes, which are essential for hydrothermal methods.^{9,10}

Note that the results reported here are related to the Na-intercalated form of manganese oxide nanowires. However, Na can be completely extracted from the manganese oxide structure or replaced by Li *via* ion exchange. In the former case, chemical extraction²⁰ is efficient. The latter case is simpler (*cf.* refs. 5, 12 and 13).

Thus, we developed a simple procedure for the preparation of manganese oxide nanowires, which are of great interest for lithium battery applications.

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