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Influence of cation (NH_4^+) on electrochemical characteristics of MnO_2 nanowire synthesized by hydrothermal method

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Abstract Nanowires of MnO_2 were prepared by a simple method in which the commercial granular $\gamma\text{-MnO}_2$ powders were hydrothermally treated in water or ammonia solution at 150 °C. These 1D nanostructured manganese oxides were characterized physically by X-ray diffraction, scanning electron microscopy and transmission electron microscopy tests. Cyclic voltammetry and constant current discharge experiments were employed to explore the diversity of electrochemical performances; and the reasons for the difference are discussed. The experimental results indicate that the existence of NH_4^+ in the preparation solution has depressed the electrochemical performances of the final product; This is further confirmed by the electrochemical impedance spectra of the electrodes.

Keywords Manganese dioxide · Hydrothermal synthesis · Electrochemical performance · Electrochemical impedance spectra

Introduction

Manganese dioxide can form many kinds of polymorphs, such as the α -, β -, γ -, and δ -type, offering distinctive properties and wide applications as catalysts, ion-sieves, and especially as electrode materials in Li/MnO_2 batteries [1, 2]. Of all the MnO_2 structures, $\gamma\text{-MnO}_2$ is well known as an electrode material for the battery industry. The structure of $\gamma\text{-MnO}_2$ is considered to be a random intergrowth of 1×1 tunnels of pyrolusite and 2×1 tunnels

of ramsdellite, which are constructed of MnO_6 octahedral units with edge or corner sharing [3, 4]. $\gamma\text{-MnO}_2$ materials can usually be prepared by electrochemical oxidation of acidic MnSO_4 solutions, as well as by chemical methods; however, these powdered particles prepared in the usual methods are irregularly shaped [5].

Much effort has been made to prepare low dimensional nanostructured crystalline MnO_2 , because dimensionality is a crucial factor in determining the properties of nanomaterials [6]. Bach et al. [7] have especially pointed out that the electrochemical properties of MnO_2 strongly depend on parameters such as powder morphology, crystalline structure, and bulk density. Nanorod-shaped and nanofibrous $\alpha\text{-MnO}_2$ [8–11], $\beta\text{-MnO}_2$ [11], $\gamma\text{-MnO}_2$ [12], and $\delta\text{-MnO}_2$ [13] have been prepared by several research groups. Kozauia et al. [14] have found that in the synthesis process of MnO_2 , exotic ionics, such as Na^+ , Mg^{2+} , Al^{3+} , have almost no effect on the performances of the product, but K^+ and NH_4^+ obviously influence the performance of the product. As of now, how and what effect these ions have is unknown. Qi et al. [15] also reported that in the synthesis process of MnO_2 , interminging some ionics could obtain different crystalline products. In this paper, we have explained the preparation of MnO_2 nanowires using a simple method of facile hydrothermal treatment of commercial battery grade granular $\gamma\text{-MnO}_2$ crystals in water or ammonia solution at low temperature, examined the electrochemical difference of the as-prepared MnO_2 nanowires in alkaline condition, and discussed the influence of cation ionic (NH_4^+) that existed in the preparation solution on the electrochemical performance of MnO_2 nanowire.

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Experimental

Synthesis of $\gamma\text{-MnO}_2$ nanowire

Commercial battery grade $\gamma\text{-MnO}_2$ powder (I.C.No.1, Japan) was used as the raw material. In a typical syn-

thesis, 1 g of commercial battery grade γ - MnO_2 powder was added to 50 ml of distilled water or 5% NH_4OH solution in a Teflon-lined 80-ml-capacity autoclave. After stirring for 1 min with a stainless-steel muddler, the autoclave was sealed, and heated at 150 °C for 24 h. The system was then allowed to cool to room temperature. The resulting product was collected by filtration and washed with distilled water, and then dried at 40 °C.

Physical measurements

X-ray diffraction (XRD) patterns were recorded on a diffractometer (MAC M18XCE) with $\text{Cu-K}\alpha$ radiation. Scanning electron microscopy (SEM) was carried out with a microscope (Leo1430VP) operated at 20 keV. Transmission electron microscopy (TEM) investigations were carried out using a microscope (Hitachi-600, Japan). TEM specimens were prepared by dispersing the powder in alcohol by ultrasonic treatment, dropping onto a glass plane, and then dried in air.

Electrochemical measurements

Electrochemical measurements were made using the traditional three-electrode system. In the fabrication of the electrodes, a mixture containing the as-prepared γ - MnO_2 , graphite and acetylene black with weight ratios of 5:2:1 was first mixed and grounded in an agate mortar. Then the mixture was placed into a typical battery molder, followed by pressing it at $3 \times 10^7 \text{ kg/cm}^2$ for 5 min to prepare the working electrode; the diameter of the electrode was about 1 cm^2 . When the above procedure was performed completely, two drops of 40% KOH solution was added into the battery molder and it was maintained at room temperature for 8 h. Hg/HgO electrode was used as the reference electrode and a platinum foil as the counter electrode. Forty percent KOH solution was used as the electrolyte. Cycle voltammetry measurement was carried out on the CHI 660A electrochemical workstation system (CH Instrument, Cordova TN). Discharge performance was characterized with galvanostatic charge-discharge unit (Arbins AT2042, US).

Results and discussion

XRD analysis

The XRD patterns of the synthesized materials are shown in Fig. 1. As can be seen from the patterns, the positions of the main diffraction peaks of the as-prepared materials, which synthesized in water or 5% ammonia solution at 150 °C, are almost similar, except for a small amount of α - MnO_2 which is present in the

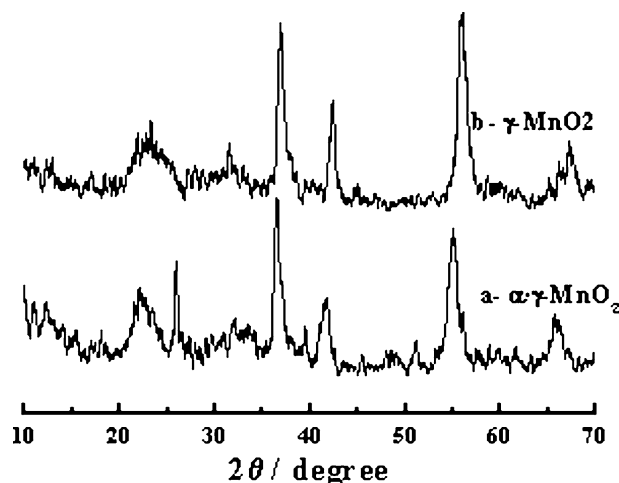


Fig. 1 X-ray diffraction (XRD) patterns: a materials obtained by hydrothermal treatment at 150 °C in 5% ammonia solution and b in water

XRD pattern in the Fig. 1a. These results indicate that the crystalline phase of both the resulting products is different. The product synthesized in water is composed of the single phase of γ - MnO_2 , whereas that synthesized in 5% ammonia solution consists of α - MnO_2 and γ - MnO_2 phase. The pattern displayed suggests a more intimate mixture (smaller domains) of the two phases and possibly some intergrowth. Hill et al.'s [16] work displayed a structural interconnectivity between the two phases, similar to that reported by Johnson et al. [17]. They noted the product as α - γ - MnO_2 . It is apparent that the ion (NH_4^+) has played an important role in determining the crystal structure of the final product in 5% ammonia solution. α - MnO_2 and γ - MnO_2 are all constructed from chains of MnO_6 octahedral, which are linked in different ways so that they have 2×2 and 1×2 tunnels in their structures, respectively. Under the hydrothermal conditions in 5% ammonia solution, γ - MnO_2 transformed partly into α - MnO_2 , and the specific amounts of NH_4^+ play an important role in stabilizing the 2×2 tunnel structure of α - MnO_2 [18]. From the above results, we can point out that the electrochemical performances of both materials are probably different.

Morphology analysis

In order to examine the morphology of the synthesized materials, SEM images are presented in Fig. 2. From these images, there are no evident differences in the morphology of the products. Both have a large quantity of fibrous nanowires and agglomerates. TEM experiments further confirmed the existence of nanowires and disclosed a well-organized nanostructure of these wires. Figure 2a is a low-magnification TEM image of the obtained γ - MnO_2 nanowires synthesized in water. The filament-like nanowires are distributed uniformly, and have different length average from several tens of nanometers to several hundred nanometers. One single rod-like

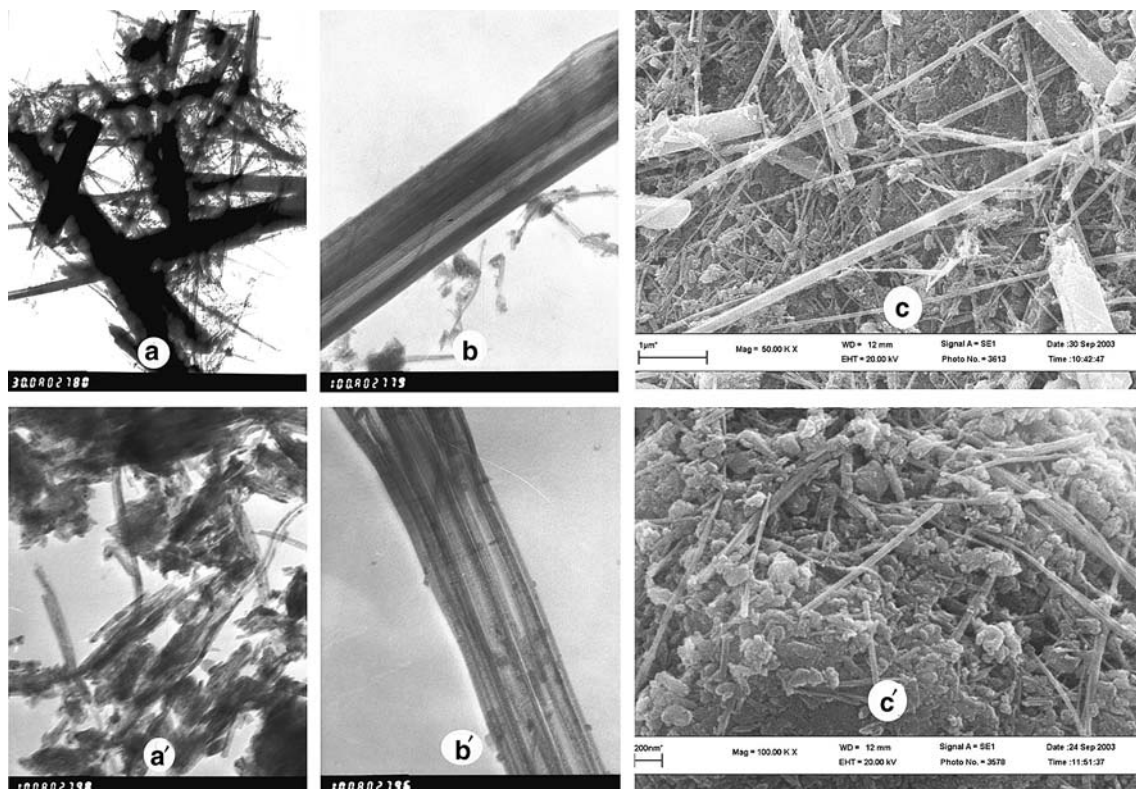


Fig. 2 a, b, c Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images of MnO₂ prepared in water; a', b', c' as-prepared in 5% ammonia solution

nanowire was selected in Fig. 2b, and was found to have many multi-line nanowires.

It is worth noticing that nanowires synthesized in water or 5% ammonia solution have similar nanofibrous morphologies, as revealed by the SEM and TEM images disclosed in Fig. 2. These results indicated that the existence of NH₄⁺ in the preparation solution does not affect the morphologies of the final products.

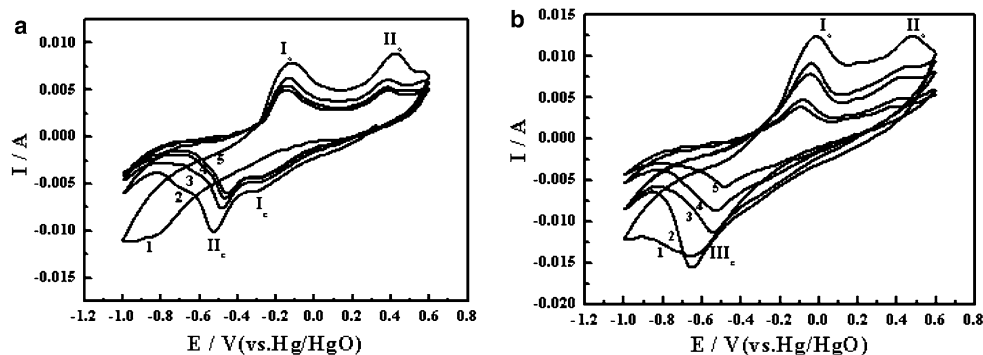
Cyclic voltammetry experiments

There is general agreement that the two-electron reduction of manganese dioxide in alkaline medium

takes place in two steps as proposed by Kozawa et al. [19–21]. The first electron reduction called the “electron-proton insertion process” involves the insertion of protons (H⁺) from the electrolyte into the γ -MnO₂ structure and the reaction can be represented as Mn(IV) → Mn(III). The second step can be described as Mn(III) → Mn(II).

Using as-prepared materials to make MnO₂ electrodes, cyclic voltammetry experiments have been carried out to explore the electrochemical performances of MnO₂ electrodes in alkaline solution. The voltammograms (Fig. 3a) between −1.0 V and +0.6 V show two cathodic and anodic peaks which respond to continuous reduction reactions of Mn(IV) → Mn(III) → Mn(II) (corresponding to peaks I_c and II_c) and back-sweep continuous oxidation reactions of Mn(II) → Mn(III) → Mn(IV) (corresponding to peaks I_a and II_a). At the same time, the peak currents have been gradually

Fig. 3 Cyclic voltammograms of the prepared MnO₂ a in water b in 5% ammonia solution. Scan rate: 0.5 mV/s



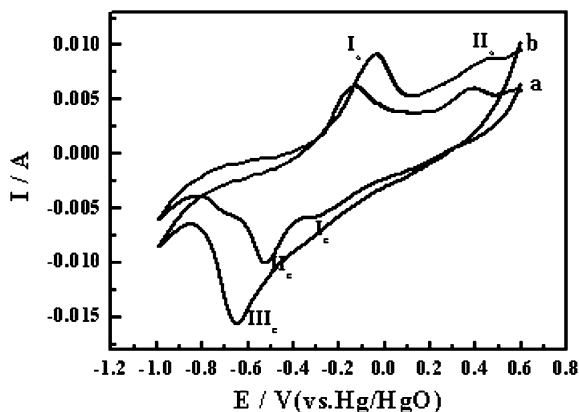


Fig. 4 The second cyclic voltammograms of the prepared MnO_2 a in water b in 5% ammonia solution. Scan rate: 0.5 mV/s

decreased with the increase of cyclic number. However, Fig. 3b shows obviously different characteristics. Between voltage range from -1.0 V to $+0.6$ V, there is only one reduction peak corresponding to $\text{Mn(IV)} \rightarrow \text{Mn(II)}$ (peak III_c) reaction, no reduction peak respond to $\text{Mn(IV)} \rightarrow \text{Mn(III)}$ reaction. This is probably due to the fact that as-prepared MnO_2 , which is constituted with $\alpha\text{-MnO}_2$ and $\gamma\text{-MnO}_2$, fabricates the electrode. And the fact that during the preparation of MnO_2 in 5% ammonia solution, NH_4^+ may intercalate into the tunnels of $\alpha\text{-MnO}_2$ and $\gamma\text{-MnO}_2$, and further inhibit the intercalation of H^+ into the material during the redox process.

In order to further confirm the existence of ammonium cation in the structure of manganese dioxide, it is necessary to draw the representative voltammogram from above-mentioned two cases. Here, the second cycle voltammograms for manganese dioxide prepared in water and in 5% ammonia solution were picked out, as is shown in Fig. 4. It is very obvious that during the anodic procedure, there are two-oxidation processes, i.e. $\text{Mn(II)} \rightarrow \text{Mn(III)} \rightarrow \text{Mn(IV)}$ (corresponding to peak I_a and II_a), occurred for two cases, but not at the same potentials. The potentials of anodic oxidation for manganese dioxide prepared in 5% ammonia solution were more positive than that of manganese dioxide prepared

in water. As ammonium cation is positively charged, the existence of ammonium cation in the structure of manganese dioxide leads to the deviation of the positive voltage direction during the anodic polarization. That is, to make out that the ammonium cation existed in the structure of manganese caused more polarization in the process of anodic reduction.

Discharge results

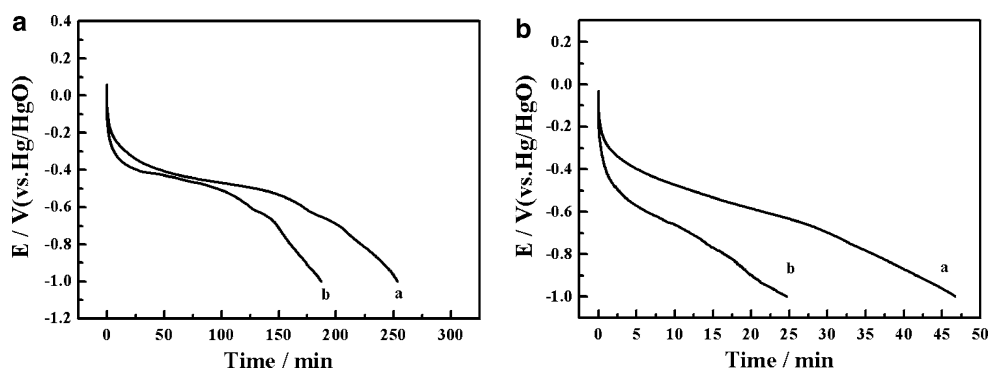
Discharge experiments further confirmed the difference of as-prepared MnO_2 in water and in 5% ammonia solution. From Fig. 5, it is clear that the discharge performances of as-prepared materials are vastly different. The discharge time and working voltage of both materials of the MnO_2 prepared in water are evidently longer and higher, respectively, than that of the MnO_2 prepared in 5% ammonia solution. The discharge parameters are shown in Table 1.

At the middle load 62.5 mA/g, the special discharge capacity of MnO_2 prepared in water is 35% higher than that of MnO_2 prepared in 5% ammonia solution, and at heavy load the special discharge capacity of the former is 90% higher than that of the latter. Based on these figures, we have found that the discharge performance of the MnO_2 prepared in 5% ammonia solution is much poorer than that of MnO_2 prepared in water, especially; at the heavy load this difference is more evident. The reason for this difference is that the existence of NH_4^+ in the preparation solution intercalates into the tunnel of the material to inhibit the intercalation of H^+ , and does not lead to the reduction reaction of $\text{Mn(IV)} \rightarrow \text{Mn(III)}$ when discharge occurs, which has been evidenced by the

Table 1 Discharge parameters of prepared MnO_2 in alkaline solution

Discharge current (mA/g)	Discharge capacity (mAh/g) MnO_2 prepared in water	Discharge capacity (mAh/g) MnO_2 prepared in 5% ammonia
62.5	264.23	194.97
250	194.72	102.14

Fig. 5 Discharge curves of the prepared MnO_2 a in water b in 5% ammonia solution (A) middle load 62.5 mA/g and (B) heavy load 250 mA/g



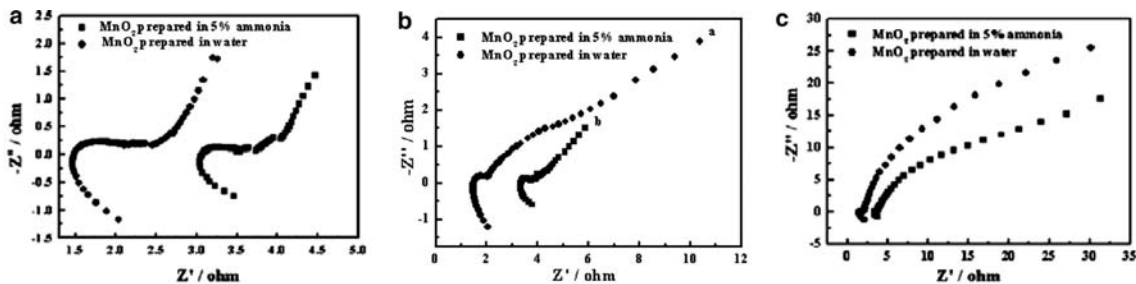


Fig. 6 The EIS spectra for electrodes using MnO_2 prepared in 5% ammonia and water a open circuit b -0.2 V and c -0.4 V

cyclic voltammetry described above. As for the difference of working voltage at different discharge currents, much more polarization occurred at heavy load than that at middle load, consequently leading to a more quick drop in the working voltage.

EIS analysis

Typical AC impedance spectra for electrodes using MnO_2 prepared in 5% ammonia and water are shown in Fig. 6, which were carried out in an open-circuit voltage (OCV), -0.2 V and -0.4 V. The Nequist impedance spectra appear gradually as two different sizes of semicircles with the voltage moving in the negative direction between the measuring frequencies. At a high frequency, besides the existence of some induction, the Nequist plot is composed of a small-depressed semicircle, which is attributed to the ohm polarization and the interface capacity of the electrodes. At the more negative voltage, the low frequency semicircle is caused by the electrochemical polarization of the air electrode. The electrolyte resistance between electrode surface and bulk electrolyte is determined by the point of intersection of the high-frequency semicircle with the real axis. From the changes of AC impedance spectra for the two MnO_2 electrodes, we can clearly see that the difference of electrolyte resistance and ohm polarization for the two electrodes is decreases gradually with the voltage changing negative, whereas the difference of electrochemical polarization resistance for the two electrodes clearly increases between the test voltage ranges. Specially, electrochemical polarization resistance for MnO_2 prepared in 5% ammonia solution is much clearer. These results indicate that the as-prepared MnO_2 in 5% ammonia solution has relatively poor conductivity and electrochemical reaction activity, which is mainly due to the NH_4^+ playing an important role. NH_4^+ inserts into the crystal lattice and restrains the $\text{Mn(IV)} \rightarrow \text{Mn(III)}$ reduction reaction, thereby resulting in the increase of electrochemical polarization of the electrode during the test process. The results discussed here are also in good agreement with that of the cyclic voltammetry measurements.

Conclusion

In summary, manganese oxide nanowires can be prepared by a simple hydrothermal method. Using different preparation solutions can result in different crystalline products. Commercial $\gamma\text{-MnO}_2$ treated in water by hydrothermal method at 150°C produced single-crystalline $\gamma\text{-MnO}_2$, whereas the one treated in 5% ammonia solution at the same temperature produced a crystalline mixture of $\alpha\text{-MnO}_2$ and $\gamma\text{-MnO}_2$. The electrochemical performances of these two products are obviously different, which are greatly affected by the existence of NH_4^+ . Electrochemical examinations have illustrated that the NH_4^+ ion has depressed the electrochemical performances of the as-prepared manganese dioxide nanowires.

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