Precise-Control Synthesis of α-/β-MnO_2 Materials by Adding $Zn(acac)_2$ as a Phase Transformation-Inducing Agent and Their ORR Performance

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Abstract: In this paper, we present an approach for the precise-control phase transformation of MnO_2 to synthesis of different compositions of α-/β-MnO_2 materials by adding a trace $Zn(acac)_2$ as the phase transformation-inducing agent in a hydrothermal reaction. The single-atomic dispersion of Zn might reduce the barrier of phase transformation of δ-MnO_2 to β-MnO_2. The ratio of Zn species present in single-atomic dispersion and nanoclusters might dominated the generations of α-MnO_2 and β-MnO_2. The oxygen reduction reaction results indicated the MnO_2 materials have potential applications values as promising catalysts in electrochemical catalysis.

Keywords: α-/β-MnO_2, phase transformation-inducing agent, oxygen reduction reaction.

1. Introduction (11-point boldface)

Many types of synthetic techniques have been developed in the last decade to obtain MnO_2 with precise phase and tunnels to control the material properties.[1] However, because of different types of MnO_2, phase transformation of MnO_2 usually occurs in the process of hydrothermal synthesis of MnO_2 polymorphs when chalcogen elements or metal ions are introduced to reduce $KMnO_4$ to MnO_2 nanostructures. However, it is very difficult to obtain the precise phase content of MnO_2 materials because of the complexity of phase transformation process. Moreover, the synthesised products often contain significant amounts of cations, chalcogenide, and protons. Hence, the additive in hydrothermal synthesis is the key factor to control the phase transformation process, precisely controlling the phase content of MnO_2.[2] Although a polymorph of MnO_2 with the same phase could be obtained, when the doping ions were introduced into the lattice or tunnel of MnO_2, the properties of MnO_2 changed. Therefore, it is important to control the amount of doping ions because the intrinsic property of MnO_2 can be affected by adding a large amount of ions.

2. Experimental (or Theoretical)

In a typical procedure for the synthesis of mixed-MnO_2, an aqueous solution (75 mL) containing $MnSO_4 \cdot H_2O$ (2.4840 g), $KMnO_4$ (1.6590 g), and desired amounts of $Zn(acac)_2$ (The $Zn(acac)_2$ was weighed using a thermogravmetric microbalance with a precision of 0.0001 mg) were put into a 100 mL Teflon-lined stainless steel autoclave, and then it was sealed, and maintained at 160 °C for 24 h. The resulting black slurries were filtered, washed with deionized water for four times, and then dried at 110 °C for 24 h. All the samples were calcined at 500 °C in air for 6 h before use.

3. Results and discussion

The Rietveld refined XRD patterns of the five MnO_2 samples are shown in Fig. S1 (for details, see ESI). The XRD patterns and phase composition of β–MnO_2 are shown in Fig. 1. Without $Zn(acac)_2$, the sample (Fig. 1B-a) can be indexed to a pure tetragonal phase [space group: I4/m (87)] of α-MnO_2 with lattice constants a = 9.7847 Å and c = 2.8630 Å (JCPDS 44-0141). Fig. 1B shows the XRD pattern of the mixed-MnO_2: α-MnO_2 was transformed to β-MnO_2, and also the β-MnO_2 returned the original phase (α-MnO_2) with the increase in the amount of $Zn(acac)_2$ in the hydrothermal reaction. When the molar ratio of Zn and Mn was in the range of 0 to 1.75×10^{-3}, α-MnO_2 gradually transformed to β-MnO_2 with an increase in the amount of $Zn(acac)_2$. For example,

two phases (34.9% of α-MnO_2 and 65.1% of β-MnO_2; Fig. 1B-b) were observed when 3.32 mg of $Zn(acac)_2$ (Zn/Mn = 5.0×10^{-4}) was added to the solution. This mixed-phase was assigned α-MnO_2 and the other tetragonal phase [space group: P42/ mnm (136)] of β-MnO_2 with lattice constants a = 4.4071 Å and c = 2.8740 Å (ICSD 98-002-0229). As the amount of $Zn(acac)_2$ increased to 11.62 mg (Zn/Mn = 1.75×10^{-3}), only β-MnO_2 was obtained. When the amount of $Zn(acac)_2$ was increased further, β-MnO_2 disappeared and the original phase (α-MnO_2) gradually reappeared. For example, at the Zn/Mn molar ratio of 2.00×10^{-3} (13.28 mg), two phases (14.7 % of α-MnO_2 and 85.3 % of β-MnO_2; Fig. 1d) reappeared. Although, when the quantity of $Zn(acac)_2$ was high up to 255.64 mg (Zn/Mn = 3.85×10^{-2}), the phase of the sample returned to α-MnO_2 with the incipient phase, but the crystal was not as perfect as the original α-MnO_2 due to the presence of Zn species.

The ORR experimental results are shown in the Fig. 2 and Table 1. All the CVs conducted in N_2 did not show any obvious peaks, indicating that no reaction occurred in the N_2-saturated solution. In contrast, CVs in the O_2-saturated PBS solution showed distinct oxygen reduction peaks for all the MnO_2 samples. The reduction peaks appeared at more positive potentials (ca. >0.2 V) for all the MnO_2 samples containing β-MnO_2, while they appeared at a much less positive potential for singe-phase α-MnO_2 samples. Moreover, the results indicate that β-MnO_2 (Zn/Mn = 1.75×10^{-3}) catalysed ORR at lower overpotentials than the other MnO_2 samples; combined with the observed high peak currents, this shows the superior ORR activities of β-MnO_2 (Zn/Mn = 1.75×10^{-3}). The preliminary results obtained from this ORR activity study indicate that the ORR activities of MnO_2 samples strongly depend on their crystallographic structures and follow the order: β-MnO_2 (Zn/Mn = 1.75×10^{-3}) > α-/β-MnO_2 (Zn/Mn = 5.0×10^{-4}) > α-/β-MnO_2 (Zn/Mn = 2.00×10^{-3}) > β-MnO_2 (commercial) > α-MnO_2 (Zn/Mn = 0) > α-MnO_2 (Zn/Mn = 3.85×10^{-2}).

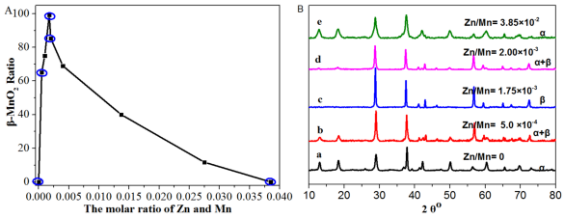

Figure 1. Contents of β-MnO_2 in the mixed-MnO_2 obtained by Rietveld refinement (A), XRD patterns of different compositions of mixed-MnO_2 (B).

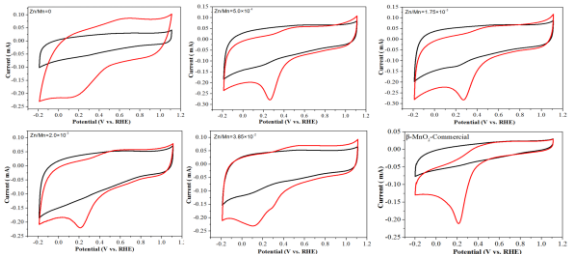

Figure 2. CV curves of different MnO_2 under N_2-saturated (black line) and O_2-saturated (red line). 0.1 M PBS aqueous solutions at a scan rate of 100 mVS^{-1} between -0.2 and 1.1 V.

Table 1. Summary of the ORR Catalytic Performance Revealed from CV curves

Mix-MnO_2 sample (Zn/Mn atom ratio)	Oxygen reduction potential (V)	Oxygen reduction currents (mA)
0	0.16	-0.21
5.0×10^{-4}	0.26	-0.21
1.75×10^{-3}	0.27	-0.28
2.00×10^{-3}	0.22	-0.22
3.85×10^{-2}	0.12	-0.23
β-MnO_2-Commercial	0.21	-0.21

4. Conclusions

In summary, a novel route for the precise-control phase transformation of MnO_2 to synthesise novel α-/β-MnO_2 materials with different phase compositions by adding a trace amount of $Zn(acac)_2$ as a PTIA in hydrothermal reactions. The results indicate that the ORR activities of the MnO_2 samples strongly depend on the crystallographic structures and follow the order: β-MnO_2 (Zn/Mn = 1.75×10^{-3}) > α-/β-MnO_2 (Zn/Mn = 5.0×10^{-4}) > α-/β-MnO_2 (Zn/Mn = 2.00×10^{-3}) > β-MnO_2 (commercial) > α-MnO_2 (Zn/Mn = 0) > α-MnO_2 (Zn/Mn = 3.85×10^{-2}).

References

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