Research Article

Synthesis and Surface Characterization of γ -MnO₂ Nanostructures

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A facile method was developed to synthesize γ -MnO₂ with different structures and surface properties in this paper. γ -MnO₂ was prepared by oxidation of MnSO₄ with Na₂S₂O₈ at 90°C for 2.0 h. γ -MnO₂ formed at initial pH 1.0 (M1) and 8.5 (M2) was composed of MnO_{1.93} · 0.23H₂O and MnO_{1.96} · 0.18H₂O, respectively. The higher ratio of pyrolusite in M2 (P_r = 43.90%) than that in M1 (P_r = 24.86%) indicated that compared with M1, M2 would absorb more protons since the planar oxygen atoms in pyrolusite were incompletely coordinated and liable to absorb the protons. Meanwhile, the higher oxidation valence of Mn in M2 than that in M1 revealed that the Mn atoms in M2 were more liable to draw the electron density from the surface oxygen atoms in hydroxyl groups. The structural and compositional differences between M1 and M2 were the major reasons why M2 possessed a higher surface potential and a weaker ability to absorb Zn²⁺ ions.

1. Introduction

Manganese dioxides are poor crystalline oxides exhibiting large ion adsorption capacities for the metal ions as Cu, Zn, Pb, and Cd [1], owing to their varying tunnel structures and large specific surface areas. The adsorption of Zn²⁺ by γ -MnO₂ in Zn/MnO₂ alkaline battery has been studied widely with the aim of improving the efficiency of Zn/MnO₂ batteries or enhancing the recovery of Zn from the spent batteries [2, 3]. The adsorption of the metal ions on the surfaces of manganese dioxides arises from the surface hydroxyl groups originated from dissociative chemisorption of water molecules [3–5].

γ -MnO₂ possesses a varying structure and composition, with the De Wolff disorder intergrowth of ramsdellite (1 × 2 tunnel) and pyrolusite (1 × 1 tunnel) [6]. As shown in Figure 1, there are two types of oxygen atom coordination in γ -MnO₂ [7]: the planar coordination occurred in pyrolusite (1 × 1 tunnel) and ramsdellite (1 × 2 tunnel), and the pyramidal coordination occurred only in ramsdellite (1 × 2 tunnel). The common formula for γ -MnO₂ is [6]

$$(\text{Mn}^{4+})_{1-x-y}(\square)_x(\text{Mn}^{3+})_y(\text{O}^{2-})_{2-4x-y}(\text{OH}^-)_{4x+y}, \quad (1)$$

where x and y represent the molar fraction of the cation vacancies ($\square$) and Mn³⁺ ions, respectively.

Many researchers have studied the control of the structures and the surface properties of MnO₂. The former work showed that the surface properties of MnO₂ were connected closely with the crystallographic structures as α -, β -, γ -, δ -, and amorphous MnO₂ [8–10]. In the case of γ -MnO₂, even though the electrochemical protonation and lithiation have been extensively studied [11], the knowledge about the control of the structure, and surface properties is still limited. For example, it was reported that the morphology, the inner structure and the surface properties of γ -MnO₂ were connected by the presence of the surfactants as hexadecyl trimethyl ammonium bromide (CTAB) sodium dodecyl benzene sulfonate (SDBS) [3], and so forth or by the heating treatment [7]. Up to now, little work was reported on the relationships between the structure and the surface properties of γ -MnO₂.

In this work, a facile method was developed to synthesize γ -MnO₂ with different structures and surface properties, using MnSO₄ as the raw material and Na₂S₂O₈ as the oxidant. The influence of the initial pH on the formation of γ -MnO₂ was investigated and the relationship between the structure and the surface properties was discussed.

FIGURE 1: Structure of γ -MnO₂.

2. Experimental

2.1. Experimental Procedure. In a typical experiment, certain amounts of NaOH (4.0 mol·L⁻¹) and H₂SO₄ (1.0 mol·L⁻¹) were used to adjust the initial pH of the MnSO₄ solution (0.17 mol·L⁻¹) to 1.0 and 8.5, respectively. Certain amount of Na₂S₂O₈ fine powder was then added to the MnSO₄ solution, keeping the molar ratio of Mn²⁺ to Na₂S₂O₈ at 1:1.2. After being stirred (400 min⁻¹) at 90°C for 2.0 h, the suspension was filtrated, washed with deionized water, and dried at 105°C for 12.0 h to get the γ -MnO₂ sample. Then the γ -MnO₂ was mixed with 0.025–1.5 mol·L⁻¹ ZnSO₄ at room temperature, keeping the initial molar ratio of Mn to Zn as 1.8–0.03. The slurry was stirred (400 min⁻¹) for 1.0 h and kept aging for 24.0 h and then centrifuged and the supernatant was collected for detection of Zn²⁺.

2.2. Analysis. The morphology of the samples was examined by the high resolution transmission electron microscopy (HRTEM, JEM-2010, JEOL, Japan). The structures and composition of the samples were identified by the X-ray powder diffractometer (D8 advance, Bruker, Germany) using CuK α radiation ($\lambda = 0.154178$ nm). The thermogravimetric (TG) analysis was carried out by the thermal analyzer (NETZSCH STA409, Germany). The solution pH was detected by pH meter (DELTA 320, METTLER-TOLEDO, China). The soluble Zn²⁺ was analyzed by the EDTA titration method.

3. Results and Discussions

3.1. Structure, Morphology, and Composition of γ -MnO₂. Figure 2 presents the XRD patterns of the γ -MnO₂ samples formed at varying initial pH. The samples formed at initial pH 1.0 and 8.5 were expressed as M1 and M2, respectively. Sole γ -MnO₂ phase was detected in both cases. The 2θ values of the diffraction peaks of 110, 221, and 240 planes were 22.16°, 56.00°, and 57.19° for M1 and 22.49°, 56.20°, and 57.09° for M2, respectively. The slight difference of the XRD peaks for M1 and M2 was connected with the change of the structures. The structure difference of the two γ -MnO₂ samples can be expressed by the P_r value which presents the molar fraction

of pyrolusite in γ -MnO₂. According to the models proposed by Chabre and Parmetier [12], the P_r values for M1 and M2 were calculated according to the following equations:

$$P_r = 0.602 \cdot \delta(DW) - 0.198 \cdot \delta^2(DW) + 0.026 \cdot \delta^3(DW),$$

$$\delta(DW) = 2\theta(110) - \delta(T_w) - 21.808 \quad (\text{in degrees}),$$

$$\delta(T_w) = -0.0054 \cdot T_w - 8.9 \times 10^{-5} \cdot T_w^2$$

$$(\text{in degrees, when } T_w < 55\%),$$

$$T_w = 100 - 68.17 \cdot \Delta 2\theta$$

$$(\Delta 2\theta : \text{peak splitting between } (221) \text{ and } (240)),$$

(2)

where T_w is the Twinning index of γ -MnO₂, varying from 0 for perfect ramsdellite (1 × 2 tunnel) structure to 100 for fully twinned structure; $\delta(T_w)$ is the Theoretical shift of line 110 in XRD analysis produced by microtwinning; DW is the Logogram for De Wolff; $\delta(DW)$ is the Shift of line 110 in XRD analysis corrected for microtwinning; and P_r values were 24.86% for M1 and 43.90% for M2. The lower P_r in M1 than that in M2 indicated that compared with M1, M2 would absorb more protons since the planar oxygen atoms in pyrolusite were incompletely coordinated and liable to absorb the protons.

Figure 3 shows the SEM image of the γ -MnO₂ samples. M1 appears to be the assembled nanorods with a diameter of 30–100 nm and a length of 1–2 μ m, while M2 is composed of the reunited spherical particles (D: 20–50 nm). Figure 4 shows the TEM image and the SAED patterns of the γ -MnO₂ samples. Both of M1 and M2 possessed the polycrystalline structures with defects due to the intrinsic De Wolff disorder intergrowth.

Figure 5 shows the TG curves of the γ -MnO₂. The weight loss (4.57% for M1 and 3.63% for M2) between 30–400°C should be connected with the release of the absorbed water from the samples. The molar ratio of MnO₂ to water was then estimated to be 1:0.23 for M1 and 1:0.18 for M2. The weight loss between 500 and 550°C (7.04% for M1 and 7.36% for M2) should be attributed to the decomposition of MnO₂ [13–15]:

Figure 6 shows the XPS spectra of the γ -MnO₂. The binding energy (BE) values of Mn 2p_{3/2} and 2p_{1/2} for M1 and M2 were 642.14/654.14 eV and 642.21/654.19 eV, respectively, quite similar with those of MnO₂, indicating that the major oxidation valence of Mn was +4 [16]. The peak splittings of Mn 3s, which can reveal the detail oxidation valence of Mn, for M1 and M2 were 89.77/85.25 eV and 89.73/85.26 eV, respectively. AOS (average oxidation state) was calculated using the following equation [17]:

$$\text{AOS} = 8.956 - 1.126\Delta E_s \quad (4)$$

$$(\Delta E_s : \text{peak splitting in Mn } 3s).$$

The ΔE_s was 4.52 eV for M1 and 4.47 eV for M2, then the oxidation valences of Mn in M1 and M2 were deduced as

FIGURE 2: XRD patterns of γ -MnO₂ formed at initial pH 1.0 (M1) and 8.5 (M2).

FIGURE 3: SEM ((a)-(b)) images of γ -MnO₂: (a) M1, (b) M2.

3.86 and 3.92, respectively. Considering together the analysis results of XPS and TG, the formulation for M1 was deduced as MnO_{1.93}·0.23H₂O and MnO_{1.96}·0.18H₂O for M2.

The different valences of Mn in M1 and M2 may be related to the different solution pH in the formation processes of γ -MnO₂. Mn²⁺ was oxidized to γ -MnO₂ by Na₂S₂O₈ via the following route:

Compared with the solution with an initial pH 1.0, the solution with an initial pH 8.5 favored the oxidation of Mn²⁺, producing γ -MnO₂ sample (M2) with higher oxidation valence.

3.2. Surface Property of γ -MnO₂. Figure 7 shows the zeta potential of the γ -MnO₂ samples formed at different initial pH. The negative zeta potentials of M1 and M2 in most of

the experimental conditions revealed that their surfaces were negative charged owing to the adsorption of hydroxyl groups in most cases. The higher zeta potentials for M2 than those for M1 indicated that compared with M1, M2 was more liable to absorb H⁺.

Figure 8 shows the adsorption of Zn²⁺ by the γ -MnO₂ samples normalized by surface area. The specific surface areas (BET) of M1 and M2 are 14.1 m²·g⁻¹ and 39.4 m²·g⁻¹, respectively. With the increase of the initial Zn²⁺ concentration from 0.025 mol·L⁻¹ to 1.0 mol·L⁻¹, the adsorption of Zn²⁺ increased from 0.021 to 8.63 mmol·m⁻² by M1 and 0.006 to 0.61 mmol·m⁻² by M2. Compared with M2, M1 showed a stronger ability to absorb Zn²⁺, which should be attributed to its lower zeta potential.

3.3. Relationship between Structure and Surface. Figure 9 shows the schematic drawing for Mn/O atoms on γ -MnO₂ surface. The surface properties of the γ -MnO₂ samples were closely connected with their structures. Containing more

FIGURE 4: TEM ((a)-(b), (e)-(f)) images and SAED ((c)-(d)) patterns of γ -MnO₂. (a), (c), (e) M1; (b), (d), (f) M2.

FIGURE 5: TG curves of γ -MnO₂.

pyrolusite units, M2 possessed more planar coordinated oxygen atoms O(planar) both in the bulk and on the surface. According to the Multisite Complex Model (MUSIC) developed by Hiemstra et al. [18, 19], the surface planar oxygen was coordinated incompletely with either one or two Mn atoms instead of three Mn atoms in the bulk, thus tending to absorb protons to become a neutralized state. The absorbed proton layer led to the increase of the surface potential of γ -MnO₂. Thus compared with M1, M2 possessed more planar

oxygen atoms O(planar) which would absorb more protons, thus showing a surface with higher potential. In addition, compared with Mn (+3.86) in M1, Mn (+3.92) in M2 was more liable to draw the electron density from the surface oxygen, thus decreased the basicity of the hydroxyl groups existed on the external surface and also increased the surface potential.

Based on the structure-surface analysis, the adsorption of Zn²⁺ is closely connected to the ratios of pyrolusite (1 × 1 tunnel) and ramsdellite (1 × 2 tunnel) in the structure of γ -MnO₂, which is affected by the initial pH in the synthesis process. It is speculated that the adsorption of Zn²⁺ and other divalent ions as Cu²⁺, Pb²⁺, Cd²⁺, and so forth on γ -MnO₂ should be quite similar.

4. Conclusions

A facile method was developed to synthesize γ -MnO₂ with different structures and surface properties. γ -MnO₂ was prepared by oxidation of MnSO₄ with Na₂S₂O₈ at 90°C for 2.0 h. γ -MnO₂ formed at initial pH 1.0 (M1) and 8.5 (M2) was composed of MnO_{1.93}·0.23H₂O and MnO_{1.96}·0.18H₂O, respectively. The ratio of pyrolusite in M2 (P_r = 43.90%) was higher than that in M1 (P_r = 24.86%). Compared with M1, M2 could absorb more protons since more planar oxygen atoms in pyrolusite were incompletely coordinated and liable to absorb the protons existed in M2. The higher oxidation valence of Mn in M2 than that in M1 revealed that the Mn

FIGURE 6: XPS spectra of γ -MnO₂. FIGURE 7: Variation of zeta potential of γ -MnO₂ with pH. FIGURE 8: Adsorption of Zn²⁺ by γ -MnO₂. FIGURE 9: Schematic drawing for adsorption model of Mn/O atoms on γ -MnO₂ surface.

atoms in M2 were more liable to draw the electron density from the surface oxygen atoms in hydroxyl groups. The structural and compositional differences between M1 and M2 were the major reasons why M2 possessed a higher surface potential and a weaker ability to absorb Zn²⁺ ions.

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