Short Communication

Effect of H_2SO_4 concentration on preparation and activity of activated manganese dioxide

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Abstract

In the preparation of activated manganese dioxide (AMD), H_2SO_4 solution is a better medium for dissolution of Mn_2O_3 and disproportionation of Mn^{3+} ions. The preparation and activity of AMD is affected greatly by the H_2SO_4 concentration in the solution. Mn_2O_3 cannot dissolve completely if the H_2SO_4 concentration is too low. By contrast, less porous AMD is formed if the H_2SO_4 concentration is too high.

Keywords: Manganese dioxide; Sulfuric acid

1. Introduction

Many kinds of manganese dioxide have been prepared for use in Zn/MnO_2 batteries, e.g., activated manganese dioxide (AMD), chemical manganese dioxide (CMD), electrolytic manganese dioxide (EMD), electrocatalytic manganese dioxide (ECMD) [1–3]. AMD is prepared from Mn_2O_3 in acidic solution, based on the following reactions:

$$Mn_2O_3 + 6H^+ \rightarrow 2Mn^{3+} + 3H_2O \quad (1)$$

$$2Mn^{3+} + 2H_2O \rightarrow MnO_2 + Mn^{2+} + 4H^+ \quad (2)$$
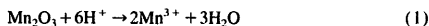
Mn_2O_3 is made from roasted MnO_2 or roasted $MnSO_4$. Compared with other methods, AMD preparation is simple and economic, especially when Mn_2O_3 is derived from roasted natural manganese dioxide (NMD). The preparation and characteristics of AMD have been investigated widely [4–9]. The preparation conditions used by researchers are very different.

Acidic solution must be used for the dissolution of Mn_2O_3, i.e. reaction (1) above. H_2SO_4, HCl and HNO_3 solutions have been used for this purpose. It is widely accepted that the temperature for reactions (1) and (2) must be over 80 °C to obtain a product with high activity. HCl and HNO_3 solutions are unsuitable because at this temperature:

(i) the Cl^- ion behaves as a reductant and reacts with Mn_2O_3 according to:

$$Mn_2O_3 + 6HCl \rightarrow 2MnCl_2 + Cl_2 + 3H_2O \quad (3)$$
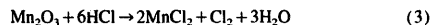
(ii) the NO_3^- ion behaves as an oxidant and reacts with Mn^{2+} ions formed from reaction (2) according to:

$$Mn^{2+} + 2NO_3^- \rightarrow MnO_2 + N_2O_4 \quad (4)$$

The latter product, MnO_2, has low activity and the N_2O_4 is toxic [10]. Accordingly, it is considered that H_2SO_4 solution is a better medium for the preparation of AMD.

This paper studies the effect of H_2SO_4 concentration in the solution on the preparation and the activity of AMD (reactions (1) and (2)).

2. Experimental

Mn_2O_3 was obtained by roasting a Ghana NMD at 700 °C for 6 h. A sample of 100 g roasted NMD was treated in 300 ml solution with different H_2SO_4 concentrations. It was stirred continuously at 90 °C for 1 h. AMD was obtained by washing the deposit until the pH of the washing water was greater than 5, then drying at 90 °C for 24 h. The yield is the mass of the product AMD. The MnO_2 content of AMD and other samples was determined by the reduction of oxalate [11]. The conversion of Mn_2O_3 was calculated as follows:

$$\text{conversion} = \frac{\text{mass of } MnO_2 \text{ determined in product}}{\text{mass of } MnO_2 \text{ calculated from reaction (2)}}$$

$$\times 100\% \quad (5)$$

The discharge performance was determined by discharging the model battery shown in Fig. 1. The positive mixture con-
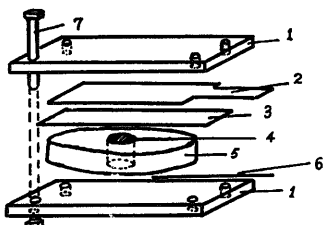
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Fig. 1. Model battery for determination of discharge performance: (i)poly-vynil chloride; (2) zinc; (3) membrane; (4) positive mixture; (5) carbon; (6) platinum wire, and (7) screw.

tained 0.1 g MnO_2 sample, 0.1 g aldehydene black and 0.5 g graphite. This was mixed with electrolyte (5 M $NH_4Cl + 2$ M $ZnCl_2$) and a small amount of polytetrafluoroethylene (PTFE). Discharging was performed at a constant current of 10 mA by means of a potentiostat (Model 553, USA). The voltage–discharge time behaviour was recorded with an x–y recorder (Model 862A, USA). The discharge capacity is the number of mAh and the usable energy is obtained from integration of the battery voltage versus discharge capacity curve.

The apparent area was determined by the zinc ion adsorption (ZIA) method [12,13]. X-ray diffraction analysis was performed with an X-ray diffractometer (Model D/MAXA, Japan) using Cu Kα radiation, 40 kV, 40 mA.

EMD used for comparison was made in Japan. Other reagents used were of analytical grade. The test solutions were prepared with deionized water.

3. Results and discussion

The characteristics of EMD and NMD are given in Table 1.
It is well known that EMD is one of the best MnO_2 materials for Zn/MnO_2 batteries. Although the MnO_2 content of

NMD is very high, (less than 10% lower than that of EMD), the activity of NMD is very poor, namely, the discharge capacity is only about half, and the usable energy only about one-third, that of EMD. The apparent area shows that NMD is less porous, and this is the cause of the low activity. Preparing AMD from NMD with high MnO_2 content but low activity is the best way to obtain battery-grade material [9].

Solutions with different H_2SO_4 concentrations (from 0.6 to 6.1 M) were used to prepare AMDs. Some of the physical and chemical properties of these AMDs are given in Table 2.

The lower the H_2SO_4 concentration, the higher the yield of AMD and the conversion calculated from formula (3), but the lower the MnO_2 content of the AMD. When the H_2SO_4 concentration is lower than 3 M, the conversion is over 100%. This shows that Mn_2O_3 cannot dissolve completely in the solution at such concentrations and some of the Mn_2O_3 exists in the product. When the H_2SO_4 concentration is higher than 3 M, the conversion is below 100%. Thus, some of the Mn^{3+} ions do not disproportionate and exist in solution. This can be explained by the stable existence of Mn^{3+} ions in solutions with high H_2SO_4 concentrations [14].

As the H_2SO_4 concentration increases, the MnO_2 content of AMD increases, but the activity of AMD (as represented by the discharge capacity) changes as shown in Fig. 2.

There is a concentration (viz., 3 M) at which AMD has the best activity. AMD behaves as Mn_2O_3 to some extent when the H_2SO_4 concentration is below 3 M. Thus, the activity of AMD is lower. When the H_2SO_4 concentration is above 3 M, the Mn^{3+} ion is more stable in the solution so that reaction (2) is slower. AMD formed under this condition is less porous as the apparent area in Table 2 shows; accordingly, the activity of AMD is lower.

The relationship between the activity (represented by the discharge capacity) and the apparent area of AMD is shown in Fig. 3. The activity of AMD is directly proportional to its apparent area. The principle for the determination of the

Table 1
Characteristics of EMD and NMD

Sample	MnO_2 (%)	Apparent area ($m^2 g^{-1}$)	Discharge capacity (0.9 V) ($mAh g^{-1}$)	Usable energy (0.9 V) (relative to EMD)
EMD	90.1	41.8	232.0	1
NMD	80.8	8.9	140.0	0.35

Table 2
Effect of H_2SO_4 concentration on the preparation and activity of AMD

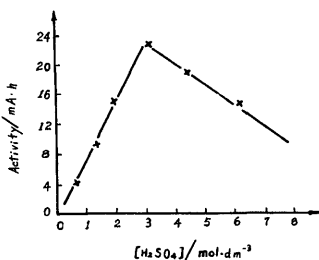| H_2SO_4 concentration (M)	Yield (%)	MnO_2 (%)	Conversion (%)	Apparent area ($m^2 g^{-1}$)	Discharge capacity (0.9 V) ($mAh g^{-1}$)	Usable energy (0.9 V) relative to EMD))
0.6	88.3	58.2	111.9	15.6	39.0	0.10
1.2	76.0	61.1	111.5	22.0	96.0	0.49
1.8	64.7	71.6	110.9	36.5	152.0	0.66
3.0	58.5	75.8	100.3	60.1	232.0	0.97
4.3	52.5	78.1	98.4	57.7	192.0	0.68
6.1	51.3	78.3	96.5	47.6	154.0	0.59

Fig. 2. Activity of AMD vs. H_2SO_4 concentration in the solution for the preparation of AMD.
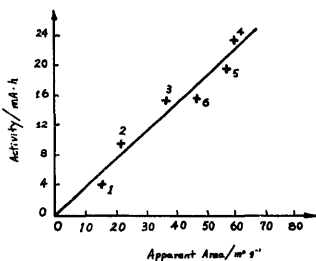

Fig. 3. Activity vs. apparent area of AMD. H_2SO_4 concentration: (1) 0.6 M; (2) 1.2 M; (3) 1.8 M; (4) 3.0 M; (5) 4.3 M, and (6) 6.1 M.
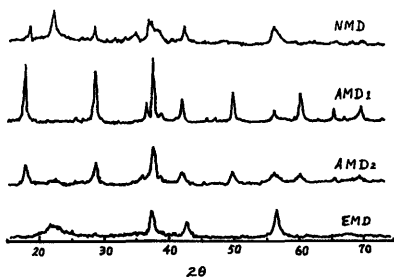

Fig. 4. X-ray diffraction patterns of NMD, EMD, AMD1 and AMD2.

apparent area is based on the exchanging of zinc ions in the solution used to determine the apparent area with H^+ ions in the OH^- group combined with Mn^{4+} on the surface of the sample. The decreased activity of AMD is caused by the smaller amount of MnO_2 when the H_2SO_4 concentration is lower, or by less porous MnO_2 when the H_2SO_4 concentration is higher.

The X-ray diffraction patterns of NMD, EMD and two AMD samples are presented in Fig. 4. AMD1 is prepared in a solution with 3 M H_2SO_4, while AMD2 is prepared in a

solution with 6.1 M H_2SO_4. Based on the diffraction peaks, it is concluded that EMD is characteristic of α-MnO_2 and NMD is characteristic of β-MnO_2. AMD1 and AMD2 have diffraction peaks at the same diffraction angles. This is different from NMD and is characteristic of α-MnO_2. There are, however, differences in the density and the shape of the diffraction peaks for AMD1 and AMD2. The diffraction peaks of AMD2 are higher and more narrow than those of AMD1. Thus, the structure of AMD2 has better crystallinity than that of AMD1. This proves that reaction (2) for the preparation of AMD is slower when the H_2SO_4 concentration is higher.

The X-ray diffraction pattern of AMD prepared in a solution with less than 3 M H_2SO_4 was also obtained. It contains the diffraction peaks of Mn_2O_3 and α-MnO_2. Moreover, the diffraction peak of Mn_2O_3 is stronger as the H_2SO_4 concentration is lowered. This is identical with the results obtained from the conversion and the apparent area.

The above experimental data show that an AMD with high activity can be prepared in 3 M H_2SO_4 solution. This AMD has nearly the same discharge capacity and usable energy as EMD, though the MnO_2 content is over 10% lower.

4. Conclusions

The preparation and the activity of AMD is affected by the H_2SO_4 concentration in the solution for the dissolution of Mn_2O_3 and the disproportionation of Mn^{3+} ions. Mn_2O_3 cannot dissolve completely and exists in the product when using solutions with low H_2SO_4 concentrations. The disproportionation of Mn^{3+} ion is slower and a less porous product is formed in solutions with higher H_2SO_4 concentrations. AMD obtained under these latter conditions has poor battery activity.

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