

Short communication

# The dissolution mechanism of cathodic active materials of spent Zn–Mn batteries in HCl

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## Abstract

The cathodic active materials of spent Zn–Mn batteries are complicated. The majority materials that they contain are  $\text{Mn}(\text{OH})_2$ ,  $\text{Mn}_2\text{O}_4$ ,  $\lambda\text{-Mn}_2\text{O}_2$ ,  $\text{ZnMn}_2\text{O}_4$ ,  $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$ ,  $[\text{Zn}(\text{OH})_2]_4\cdot\text{ZnCl}_2$ , etc. Dissolving these kinds of materials is important to the environmental pollution control and materials recycle. In present paper we investigated the dissolution mechanism of the cathodic active materials in HCl by testing the factors that can influence the dissolution procedure, including temperature, time, and the concentration of HCl and  $\text{H}_2\text{O}_2$ . Our results showed that both neutralization and oxidation–reduction reactions occurred in the dissolution process, and that  $\text{H}_2\text{O}_2$  had a great effect on the dissolution efficiency.

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*Keywords:* Spent Zn–Mn batteries; Cathodic active materials; Dissolution mechanism

## 1. Introduction

Due to the convenience and lower price, batteries, especially Zn–Mn batteries, have been being used widely for various purposes. This popular usage results in a quick increase of accumulation of waste batteries. Although the so-called “mercury-free batteries” has been used for decades [1,2], the waste batteries still caused a serious concern due to their toxicity, abundance and permanence in the environment. Study on recycling spent batteries is necessary and imperative.

Numerous studies on recycling spent batteries have been done in the past years, which can be summarized as pyrometallurgy and hydrometallurgy. Pyrometallurgy means that the spent batteries should just be recycled in high temperature furnaces. Pace et al. [3] recycled spent dry batteries by heating them to the temperature over  $800^\circ\text{C}$ . The residue content of the most toxic metals in the treated waste is lowered below 100 mg/kg. Toita et al. [4] and Krebs [5] tried in different ways. They heated spent Zn–Mn batteries in an oxidation

furnace or a melting furnace, and obtained high purity metals after a series of treatment. Other pyrometallurgical methods used to treat spent batteries were hammer mill grinding, magnetic separation, size separation, specific gravity separation, etc. [6]. The disadvantages of pyrometallurgy are high cost, spending more energy and complicated operations. The hydrometallurgy means that a solvent must be used in the recycling process. One of the methods used is to obtain manganese zinc ferrite by treating waste Zn–Mn dry cell though dissolving, co-precipitating and oxidizing procedures [7]. Another method [8] is to obtain pure  $\text{ZnCl}_2$  and  $\text{MnO}_2$  by water washing, HCl dissolving and heating. Waste dry cells were dissolved in basic ammonium carbonate solution to recover Zinc [9].

Various industrial recycling processes have been proposed, and some of them are being operated, for example, Batrex AG (in Switzerland) operates an industrial plant for recycling used dry batteries with a production capacity of 3200 tonnes per year [5]. Batens process operates a plant in Germany with a capacity of 7500 tonnes per year [10]. But usually they recycle any type of spent dry batteries just in almost the same way, thus they are not specific or efficient.

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There is only one specific recovery process operated in USA. They recover metals from the exhausted nickel–cadmium, –iron and –metal hydride batteries. The capacity of this plant is about 2300 tonnes per year [11]. Due to the limitation of the industrial recycling plant, the spent dry batteries are mainly disposed as domestic refuse in most countries, especially in developing countries. Exploring economic recycling process will be significant for the environmental pollution control. Because Zn–Mn batteries are widely used, we try to find a better way to recover used Zn–Mn batteries by combining the advantages of both pyrometallurgy and hydrometallurgy. The key steps of hydrometallurgy are to dissolve, extract, and recover the useful components. Therefore, we intend to study the dissolution mechanism of the cathodic active materials of Zn–Mn batteries in HCl.

The anode of Zn–Mn battery is mainly Zn, which can be easily dissolved in HCl. Its cathodic active materials mainly contain  $\text{Mn}(\text{OH})_2$ ,  $\text{Mn}_2\text{O}_4$ ,  $\gamma\text{-Mn}_2\text{O}_2$ ,  $\text{ZnMn}_2\text{O}_4$ ,  $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$ ,  $[\text{Zn}(\text{OH})_2]_4 \cdot \text{ZnCl}_2$  and a little natural mineral materials [12,13]. The specific composition depends on some characteristics of the batteries such as discharge state, stocking conditions, etc. Our previous work studied the dissolving conditions in HCl, but the dissolution mechanism has not been illustrated. In present paper, we investigated the dissolution mechanism of cathodic active materials in HCl. We found that both neutralization and oxidation–reduction reactions occurred in the dissolution process and  $\text{H}_2\text{O}_2$  could have a great effect on the dissolution efficiency. These results provided some useful basic data for practical study in the future.

## 2. Experimental

### 2.1. Materials and methods

Analytical grade HCl and  $\text{H}_2\text{O}_2$  were purchased from Beijing Chemical Plant (China). Zn–Mn batteries used in this experiment were size R20 Zhonghua brand battery made in Xinxiang Battery Plant (Henan, China).

The cathodic active materials were taken out of the splitting spent Zn–Mn batteries, roasted at  $300^\circ\text{C}$  for 2 h in a furnace of the muffle type (Tianjin Dongya Electric Oven Plant, China), milled in a mortar, and sieved with a 315-micron-mesh sieve. The final products, samples, were put into an exsiccator.

The schematic of experimental apparatus was shown in Fig. 1. Certain amount of HCl was weighed in a beaker and heated to a certain temperature in a super constant temperature tank (Shanghai Instrument Co., China), and then the sample and  $\text{H}_2\text{O}_2$  were added with stirring.

After cooling down to room temperature, the solution was filtered decompressively with  $G_3$  core glass crucible. The filter residue then was dried to a constant weight at  $100 \pm 2^\circ\text{C}$ . The filtrate was analyzed to measure Zn and Mn by Z-5000 atomic absorption spectrophotometer (HITACHI,

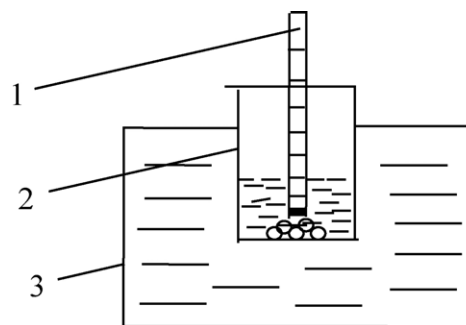


Fig. 1. Schematic of experimental apparatus: 1, thermometer; 2, beaker; 3, super constant temperature oven.

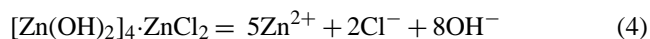
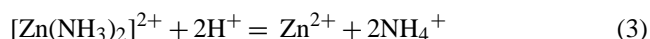
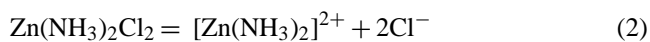
Japan). The dissolution ratio was calculated according to the following form:

$$\phi = \frac{G - m}{G} \times 100 \quad (1)$$

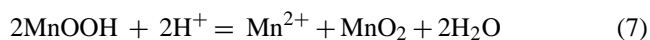
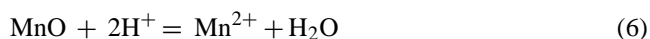
where  $\phi$  stands for the dissolution ratio of sample (%),  $G$  and  $m$  represent the mass of sample (g) and the filter residue after being dried (g), respectively.

### 2.2. Theory analysis

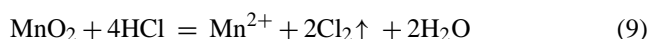
The cathodic active materials of the size R20 Zhonghua brand battery mainly contains  $\text{Mn}(\text{OH})_2$ ,  $\text{MnO}_2$ ,  $\gamma\text{-Mn}_2\text{O}_2$ ,  $\text{ZnMn}_2\text{O}_4$ ,  $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$ ,  $[\text{Zn}(\text{OH})_2]_4 \cdot \text{ZnCl}_2$ , and a few natural mineral materials. When put into HCl,  $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$ , and  $[\text{Zn}(\text{OH})_2]_4 \cdot \text{ZnCl}_2$  in the active materials should react with HCl as follows:



Then  $\text{MnO}(\text{OH})$ ,  $\text{MnO}$ , and  $\text{ZnMn}_2\text{O}_4$ , which are more difficult to dissolve in water, would react with HCl as follows:



Under appropriate conditions,  $\text{Mn}_2\text{O}_4$  could react with HCl according to the following equation:



From analysis above, we can conclude that both neutralization reactions and oxidation–reduction reactions occurred in the dissolution process. Many reactions are heterogeneous phase, therefore, the process must be very complicated and the reaction time would be very long.

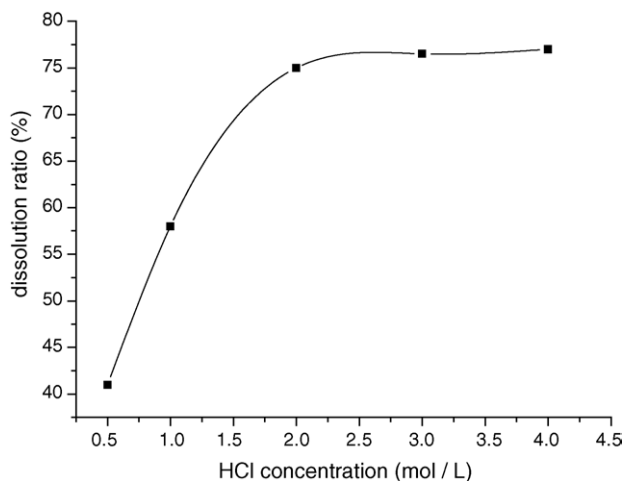


Fig. 2. The effect of HCl concentration on dissolution ratio (time: 50 min;  $\text{H}_2\text{O}_2$  concentration: 3%; temperature:  $50^\circ\text{C}$ ).

### 3. Results and discussion

#### 3.1. The effect of acid concentration

As shown in Fig. 2, the effect of HCl concentration on the dissolution ratio is quite obvious. When the concentration of HCl was increased from 1 to 2 mol/L, the dissolution ratio increased dramatically. After that, the dissolution ratio reached a plateau stage. There was no further significant increase while increasing the concentration of HCl. At the same time, the smell of chlorine became stronger while increasing HCl concentration. This suggested that there was chlorine released from the reaction. It indicated that oxidation–reduction reactions occurred in the reaction process.

There are many kinds of multivalent compounds of Mn existing in the cathodic active materials. The reactions of these different components with HCl would be different. For example, the reaction of MnO with HCl is neutralization (as Eq. (6)), but reactions of  $\text{ZnMn}_2\text{O}_4$  and  $\text{Mn}_2\text{O}_4$  with HCl are oxidation–reduction reactions (Eqs. (8) and (9)). The release of chlorine during the dissolution process confirmed that the reaction in the form of Eq. (9) really existed. However, this reaction only occurred when HCl was in high concentration. Because the dissolution ratio would not increase when the concentration of HCl exceed 3 mol/L, we conclude that increasing the concentration of HCl is not essential to the increase of the dissolution ratio.

#### 3.2. The effect of reaction time

Reaction time is another factor that can influence the dissolution process. The effect of reaction time on the dissolution ratio is shown in Fig. 3.

Generally, the neutralization reactions are very fast, but the oxidation–reduction reaction is slow. If there were only neutralization reaction in the dissolution process, it would

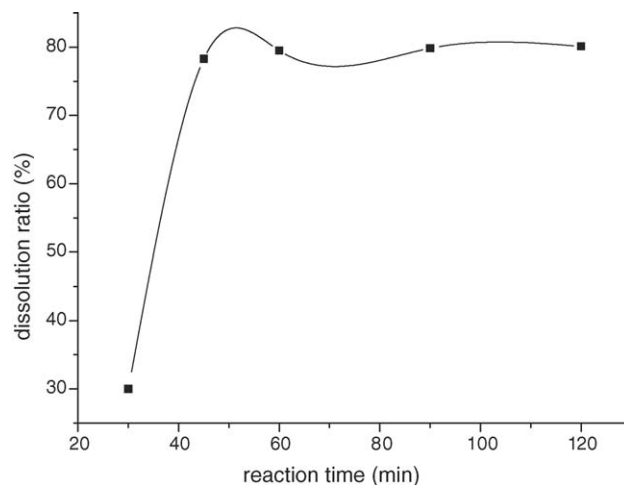


Fig. 3. The effect of reaction time on dissolution ratio (HCl concentration: 2 mol/L;  $\text{H}_2\text{O}_2$  concentration: 3%; temperature:  $50^\circ\text{C}$ ).

not need so much time to get the maximum dissolution ratio. As shown in Fig. 3, the suitable dissolution time was about 60 min. This implied that both neutralization and oxidation–reduction reactions occurred in the dissolution process.

#### 3.3. The effect of $\text{H}_2\text{O}_2$ concentration

$\text{H}_2\text{O}_2$  is the third factor we investigated that has effects on the dissolution process. Using different concentration  $\text{H}_2\text{O}_2$  will have different effect on the dissolution process. As shown in Fig. 4, the dissolution ratio increased dramatically when increasing the concentration of  $\text{H}_2\text{O}_2$ . The dissolution ratio reached its peak value when the concentration of  $\text{H}_2\text{O}_2$  reached 3% (wt.%). And then the dissolution ratios decreased slowly while the concentration of  $\text{H}_2\text{O}_2$  increased further. Hence, we can infer the reaction mechanism as follows.

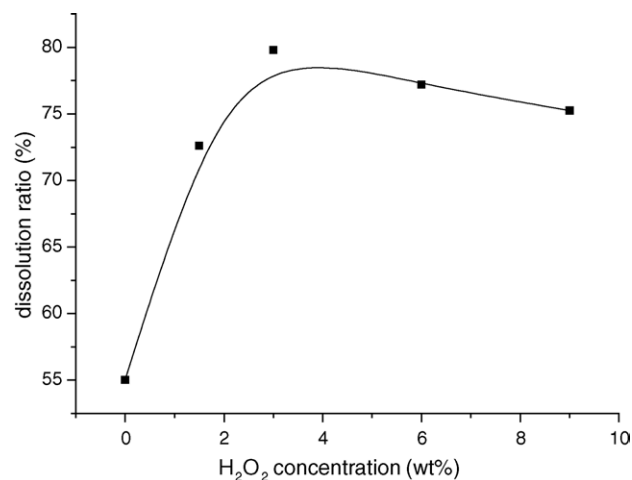
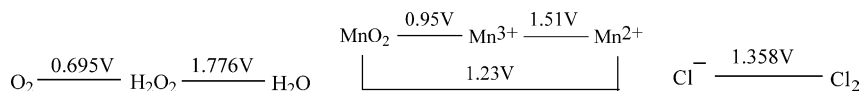


Fig. 4. The effect of  $\text{H}_2\text{O}_2$  concentration on dissolution ratio (HCl concentration: 2 mol/L; time: 60 min; temperature:  $50^\circ\text{C}$ ).

Table 1  
The data of Gibbs free energy [14]

Elements	$\Delta_f G_m^\ominus$ (kJ mol <sup>-1</sup> )
MnO <sub>2</sub> (s)	-466.1
H <sub>2</sub> O <sub>2</sub> (l)	-113.97
H <sub>2</sub> O (l)	-228.59
HCl (aq)	-131.17
Mn <sup>2+</sup> (aq)	-223.4
Cl <sup>-</sup> (aq)	-131.17
O <sub>2</sub> (g)	29.36
Cl <sub>2</sub> (g)	33.93

Some  $E_0$  values of relevant electric pairs are [14]:



Therefore, the following reaction will occur when H<sub>2</sub>O<sub>2</sub> concentration is lower and there is plenty of MnO<sub>2</sub>:



As we know, MnO can be easily dissolved in HCl and the solubility of MnO<sub>2</sub> in diluted HCl without H<sub>2</sub>O<sub>2</sub> is very low. Thus the dissolution ratio of the cathodic active materials increases when H<sub>2</sub>O<sub>2</sub> concentration is lower and MnO<sub>2</sub> is more.

As shown in Table 1, the Gibbs free energy ( $\Delta G$ ) of Eq. (10) is -71.15 kJ/mol. This suggests that Eq. (10) could occur spontaneously. This may be the main reason why the dissolution ratio of spent cathodic active materials increased greatly when H<sub>2</sub>O<sub>2</sub> existed. Eq. (10) was also demonstrated by the experimental phenomenon that the released gas could make a little wooden sparked-rod burn again, which showed that the gas is oxygen.

When H<sub>2</sub>O<sub>2</sub> concentration is higher, however, the Mn<sup>2+</sup> in the solution will react with H<sub>2</sub>O<sub>2</sub> as the following equation:

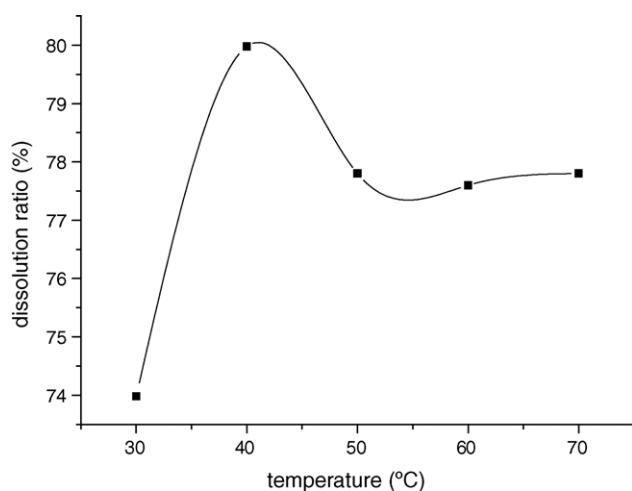
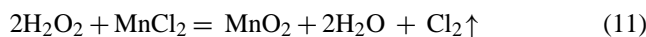


Fig. 5. The effect of reaction temperature on dissolution ratio (HCl concentration: 2 mol/L; time: 60 min; H<sub>2</sub>O<sub>2</sub> concentration: 3%).

The strong chlorine smell released in the experimental process showed that Eq. (10) really occurred. Because MnO<sub>2</sub> is hard to dissolve in HCl, the dissolution ratio decreased when the concentration of H<sub>2</sub>O<sub>2</sub> was higher than 3% (wt.%).

As mentioned above, we can learn that H<sub>2</sub>O<sub>2</sub> has a great effect on the dissolution ratio of active materials, and that the dissolution mechanism is much more complicated.

### 3.4. The effect of reaction temperature

Fig. 5 shows the curves of dissolution ratio versus leaching temperature. The dissolution ratio increased dramatically

with the increase of temperature before it reached 40 °C. However, the dissolution ratio decreased slightly with a further increase of leaching temperature over 40 °C. This can be explained as follows: in the dissolution reaction mixture, there are three main activities, dissolution of the sample, decomposition of H<sub>2</sub>O<sub>2</sub>, and volatilization of HCl. When the temperature is below 40 °C, the speed of decomposition of H<sub>2</sub>O<sub>2</sub> and volatilization of HCl is very low. The dissolution ratio will increase when increasing the temperature. However, when the temperature is above 40 °C, the speeds of decomposition of H<sub>2</sub>O<sub>2</sub> and volatilization of HCl are much higher. This will result in the decrease of concentration of H<sub>2</sub>O<sub>2</sub> and HCl, and then the dissolution ratio.

The relationship of the decomposition speed of H<sub>2</sub>O<sub>2</sub> with temperature is [15]:

$$(T_2 - T_1) \lg a = 10 \lg(k_2/k_1) \quad (12)$$

where  $k_1$  and  $k_2$  stand for the reaction speed when temperatures are  $T_1$  and  $T_2$ , respectively;  $a$  stands for the coefficient of temperature. When the temperature increases 10 K, the speed of decomposition of H<sub>2</sub>O<sub>2</sub> will increase by 2.2-fold correspondingly [15]. This is probably the main reason that causes the decrease of the dissolution ratio when the temperature is over 40 °C.

## 4. Conclusions

One of the keys to recycling spent Zn–Mn batteries hydrometallurgically is to extract the useful materials. The anodic material of spent Zn–Mn batteries, zinc, is comparatively easy to dissolve in HCl. The cathodic active materials, however, are difficult to dissolve in HCl. The dissolution ratio of cathodic active materials in HCl changes largely with the dissolution conditions. We study the dissolution mechanism of the cathodic active materials in HCl in order to recycle the Zn–Mn batteries to the full extent.

The experimental results showed that the dissolution ratio was affected by the leaching temperature, time, the concen-

tration of HCl and H<sub>2</sub>O<sub>2</sub>, and so on. There was much oxygen and chlorine released in the experimental process. Both neutralization and oxidation–reduction reactions occurred in the dissolution process. H<sub>2</sub>O<sub>2</sub> could have a great effect on the dissolution process. A deeper knowledge of the dissolution mechanism appears to be very prompting for recycling spent Zn–Mn batteries.

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