The HCl additional effect in the electrolyte of manganese dry battery

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Abstract

In this paper, cells with added HCl in the electrolytes were prepared respectively. The result of HCl added sample shows a higher open circuit voltage (OCV) than a commercial one and even higher than that of a theoretical one. Its current density also shows 0.02 A/cm^2 higher than that of commercial one. It will be an advantage in redox reaction through removal of reaction product and decreasing of pH by HCl. From the XRD result of anode Zn plate, $ZnCl_2 \cdot 4Zn(OH)_2 \cdot H_2O$ was mainly found on the plate. On the other hand, the HCl added sample shows only one species of ZnO and $Zn(OH)_2$. This result can explain that $ZnCl_2 \cdot 4Zn(OH)_2 \cdot H_2O$ is easily disrobed in HCl solution. These results suggest that another reaction occurred at the same time with the normal redox reaction by HCl addition. In addition, standard electrode potential will change with pH of electrolyte. It is easy to realize from Nernst equation and a decrease of pH will raise OCV and current density. In this paper, the possibility of high performance manganese dry battery is shown.

Key words

manganese dry battery, $ZnCl_2 \cdot 4Zn(OH)_2 \cdot H_2O$, HCl addition, anode reaction, $ZnCl_2$ aqueous electrolyte

1. Introduction

The manganese dry battery is well known as a practical primary cell. Many efforts have been carried out for its practical use, and succeeded, but most attentions were paid for the cathode material (Tanase, 2010). Tanase and Yuguchi showed better cell performance by adding carbon black in the cathode fixed-dose (Tanase, 2011). They also examined a separator of the cell and concluded that coffee dripping paper is suitable (Tanase and Yuguchi, 2014). On the other hand, there is less attention to the electrolyte. Tanase prepared the electrolyte with a concentration of $ZnCl_2$ as 20 wt% (Tanase, 2010). There is a necessity for an estimate concentration of $ZnCl_2$.

In this paper, 0.03 mL and 0.06 mL of HCl were added to electrolyte of manganese dry battery, instead of investigating $ZnCl_2$ concentration. A manganese dry battery was used as an educational tool, which is the same as Tanase and Yuguchi (Tanase, 2010; 2011; Tanase and Yuguchi, 2013; 2014). White ash in the 20 wt% $ZnCl_2$ aqueous solution was found and disappeared with HCl addition. Before an estimate $ZnCl_2$ concentration, it was necessary to understand this phenomenon and figure out the effect on the manganese dry battery. In this paper, the alteration of open circuit voltage, current density, and anode surface reaction product with HCl addition in the manganese dry battery was reported.

2. Experiment

The manganese dry battery test cells for experiment were fabricated with Zn plate (Kenis co.) and carbon powder (Kishida Chemical co.), filter paper, carbon rod, PP (polypropylene) case, MnO_2 (Kishida Chemical co.), and $ZnCl_2$ (Kanto Chemical co.). 10 mL of 20 wt%, and 60 wt% $ZnCl_2$ aqueous solution were prepared. The electrolyte concentration of standard battery was 20 wt% $ZnCl_2$ aqueous solution, and 2 mL of 60 wt% $ZnCl_2$ aqueous solution was added to carbon-MnO_2 fixed-dose. The HCl was added only to 20 wt% $ZnCl_2$ electrolyte for 0.03 mL and 0.06 mL, respectively. The appearance and assemble of the cell was the same as the recent paper of Tanase and Yuguchi (Tanase and Yuguchi, 2013, 2014). For comparison, operation with the same measurement as a commercial battery and R6PNB type (IEC 60086 / JIS C 8500) manganese dry battery was used, made by Panasonic®.

The 1.8 Ω of resistance was connected to the cell, and the Keithley 2000 digital multimeter was connected as parallel to the resistance for voltage measurement. The voltage data was taken a every 3 minutes during an hour. The relation between the voltage and discharge time was exchanged to the current and discharge time by the equation of $E = IR$ (1). The obtained current is proportional to the anode area. The area of the Zn plate in a commercial battery and the test cell is not the same, so current density (A/cm^2) was calculated to compare each cell.

The XRD (Rigaku Ultima IV/SN) was used for the phase determination of white ash in $ZnCl_2$ aqueous solution and Zn plate. The Cu$K\alpha$ radiation was used for measurement, and its range was 10 ° through 80 ° for 2θ display.

3. Results and discussions

3.1 Impurity in the electrolyte

There is white ash in 20 wt% $ZnCl_2$ aqueous solution and it becomes turbid. On the other hand, no turbidity was found in the 60 wt% aqueous solution. The resulting white ash was removed by filtration and dried in an oven at 100 °C for 24 hrs. White powder was observed and phase by XRD was estimated. The result of XRD is shown in Figure 1.
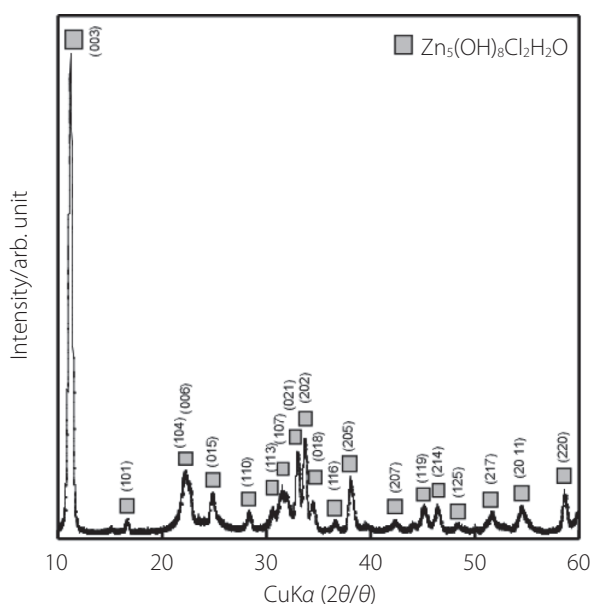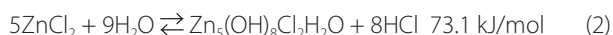

Figure 1: The XRD pattern of dried white ash in the 20 wt% $ZnCl_2$ aqueous solution

White ash, obtained in 20 wt% $ZnCl_2$ aqueous solution, was identified as $Zn_5(OH)_8Cl_2H_2O$. These results indicate that $Zn_5(OH)_8Cl_2H_2O$ is not only a reaction product, but also produced by dissolving $ZnCl_2$ in water.

$$5ZnCl_2 + 9H_2O \rightleftarrows Zn_5(OH)_8Cl_2H_2O + 8HCl \quad 73.1 \text{ kJ/mol} \quad (2)$$

At a high concentration, 60 wt% $ZnCl_2$ aqueous solution for example, above equilibrium lies so far to the left. The $ZnCl_2$ in aqueous solution will ionize and seems to be clear.

3.2 XRD analysis of anode Zn plate

Figure 2 shows the XRD result of the anode Zn plate. There are three figures in Figure 2. The top and middle show the anode of HCl added sample and standard $ZnCl_2$ electrolyte sample after measurement, respectively. The bottom one is pure Zn plate which is before measurement.

From the figure, the standard electrolyte sample shows the existence of $Zn_5(OH)_8Cl_2H_2O$. This result was already noted by Tanase and Yuguchi (Tanase, 2010; Tanase and Yuguchi, 2013). On the other hand, in the HCl added sample, no peaks of $Zn_5(OH)_8Cl_2H_2O$ colud be found at all. This result indicates that
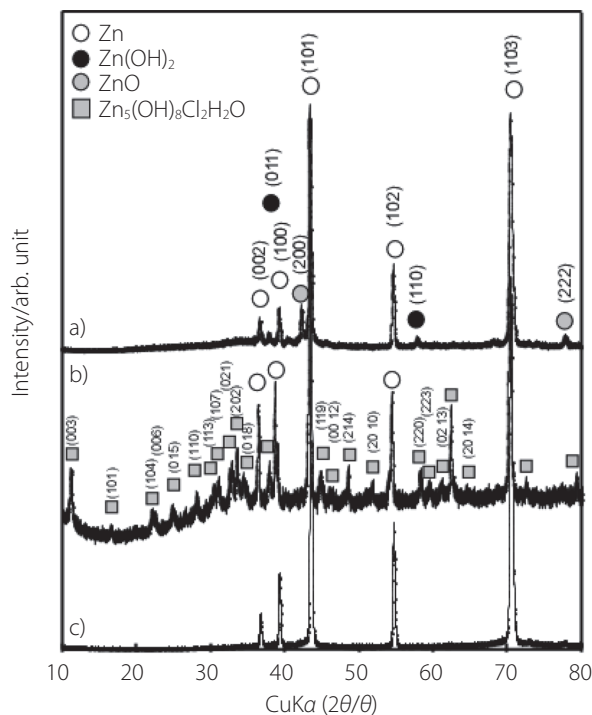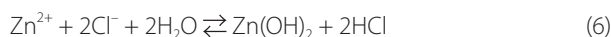

Figure 2: Phase analysis of anode Zn plate
Note: These phases are estimated by X-ray diffraction. The Zn metal is anode plate measured before experiment. Other results were obtained after measurement.

the addition of HCl may remove reaction product. To make it simple, $Zn_5(OH)_8Cl_2H_2O$ will show as $ZnCl_2 \cdot 4Zn(OH)_2 \cdot H_2O$. The reaction at the anode of HCl added sample will be as shown below.

$$ZnCl_2 \cdot 4Zn(OH)_2 \cdot H_2O + 8HCl \rightarrow 5ZnCl_2 + 9H_2O \quad (3)$$
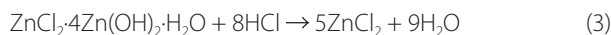
The reaction product $ZnCl_2 \cdot 4Zn(OH)_2 \cdot H_2O$ is solid and it covers the surface of the anode. In the situation of HCl aqueous solution, the above reaction and following reaction may occur at the same time.
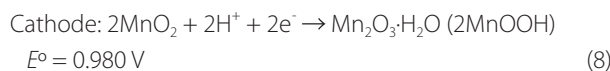
$$ZnCl_2 \rightleftarrows Zn^{2+} + 2Cl^- \quad (4)$$

$$Zn^{2+} + 2Cl^- + H_2O \rightleftarrows ZnO + 2HCl \quad (5)$$

$$Zn^{2+} + 2Cl^- + 2H_2O \rightleftarrows Zn(OH)_2 + 2HCl \quad (6)$$

The XRD result of HCl electrolyte sample shows few peaks of ZnO and $Zn(OH)_2$ and the above reaction will explain this result. Another reason is attributed to the solubility product of Zn ion. The Zn^{2+} ion will change into $Zn(OH)_2$ at around pH 7 (Einaga, 2000). Adding HCl will decrease pH in the electrolyte, and this result is not independent of XRD result. Reaction in the electrolyte is complicated and difficult to estimate individual reaction. Further investigation and experiments are necessary for future work to discuss the relation between pH,

XRD result, and $ZnCl_2$ concentration.

3.3 Open Circuit Voltage (OCV) of manganese dry cell

Table 1 shows the open circuit voltage (OCV) of each cell. The theoretical voltage of the manganese battery is 1.743 V, which is shown as below (Tanase, 2010; Tanase and Yuguchi, 2013).

Cathode: $2MnO_2 + 2H^+ + 2e^- \rightarrow Mn_2O_3 \cdot H_2O$ (2MnOOH)
$E^o = 0.980$ V   (8)

Anode: $Zn \rightarrow Zn^{2+} + 2e^-$
$E^o = -0.763$ V   (9)

Total: 0.980 - (-0.763) = 1.743 V   (10)

Table 1: Open circuit voltage (OCV) of samples

Commercial	Standard		
R6PNB	HCl 0.00 mL	HCl 0.03 mL	HCl 0.06 mL
1.642 V	1.783 V	1.851 V	1.906 V

From the table, the OCV of a commercial battery shows 1.642 V, and it is about 0.1 V lower than that of a theoretical one. This is caused by self-discharge, and reaction products will interfere with the reactions shown above. On the other hand, a standard battery shows almost the same voltage as the theoretical one, and HCl added samples showed more than 1.85 V and it is even higher than that of the theoretical one. One of the reasons to be considered is that pH decreasing by HCl addition will change standard electrode potential and increase voltage, as shown below. E (H^+/H_2) is standard electrode potential, R is gas constant, T is Kelvin temperature, and F is Faraday constant.

$$E (H^+/H_2) = - (2.303\, RT/F) \times pH \qquad (11)$$

At 25°C, RT/F = 25.69 mV. The above equation can be changed as follows:

$$E (H^+/H_2) = - 59.16\, mV \times pH \qquad (12)$$

This result indicates that one unit of pH decreases; electrode potential will rise to about 59 mV (Atkins, 1995).

3.4 Current density of cells

Figure 3 shows the relation between current density and discharge time of the cell.

In this experiment, the anode area of commercial battery and the handmade dry battery are not the same. The commercial battery has few times larger anode area than hand-
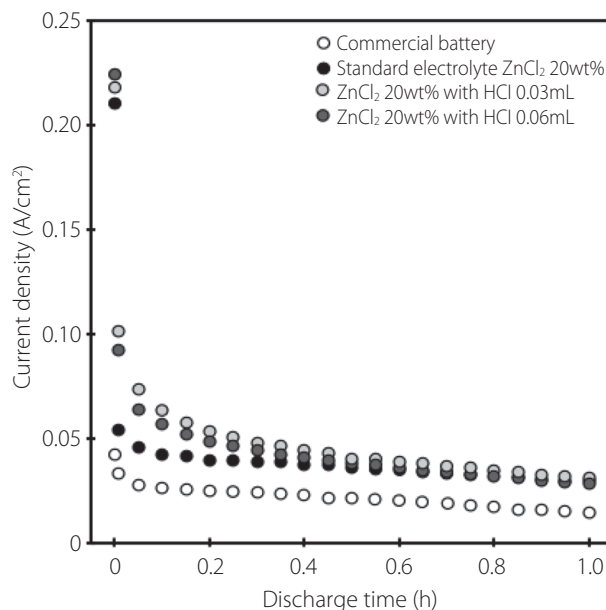

Figure 3: Relations between current density and discharge time

Note: Commercial battery is made by Panasonic and all others are hand-made dry batteries.

made dry battery. For better comparison, the current density was calculated and each cell was compared with the commercial battery. Every cell shows decreasing current density with increasing discharge time. The current density of the standard electrolyte cell shows higher than that of the commercial cell. Because the structure of the cell was the same, this result is attributed to the concentration of $ZnCl_2$ in the electrolyte. The 0.03 mL HCl added cell showed the highest current density in all time regions. On the other hand, 0.06 mL HCl added cell does not show a higher current density at all. This result indicates that there is above optimum for HCl amount. The existence of the above optimum may be attributed to the reaction product of ZnO and $Zn(OH)_2$. These products on the anode are an interference factor of redox reaction.

3.5 Cell resistance

Figure 4 shows the relation between current density and voltage. Inclination of each graph shows resistance of the cell. The results show that resistance of the commercial cell is 4 times or more higher than that of the handmade dry cell.

The sample with HCl addition in electrolyte showed completely the same behavior as the standard sample. These results may be attributed to the concentration of $ZnCl_2$ in the electrolyte.

4. Conclusions

In this paper, it is showed that $ZnCl_2 \cdot 4Zn(OH)_2 \cdot H_2O$ in the electrolyte will generate an aqueous solution. This substance
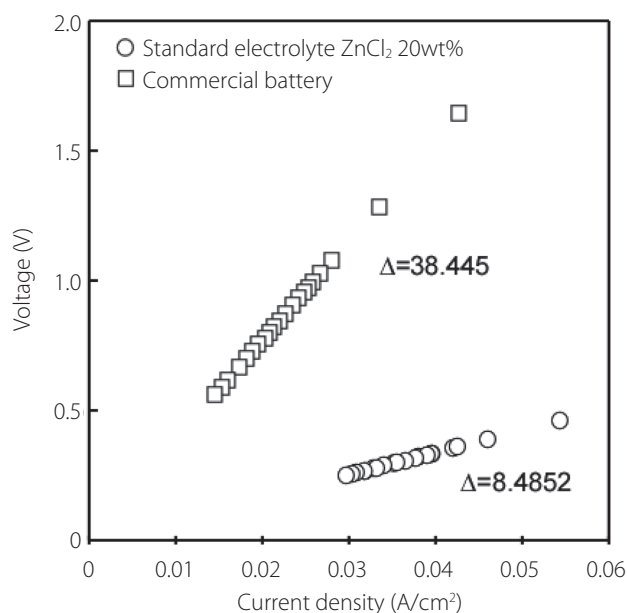
Figure 4: The cell resistances of commercial battery and standard electrolyte dry battery

Note: The relation between voltage (V) and current density (A/cm$_2$) makes cell resistance (V/[A/cm^2] = Ωcm^2 (13)). Delta donates cell resistance.

also generates a redox reaction at the anode and it interfers with the anode reaction. HCl addition is effective for decomposing $ZnCl_2 \cdot 4Zn(OH)_2 \cdot H_2O$ and also rises current density with OCV. However, there is above optimum for HCl concentration. One of the reasons which can be considered is that HCl addition will form ZnO and $Zn(OH)_2$ on the anode Zn plate. The anode reaction will be obstructed by these reaction products. Relations between XRD result of anode, pH of electrolyte, and electrolyte composition are very complicated. These relations will be ascertained for future investigation.

Acknowledgement

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