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A new Zn | $AlCl_3$ | MnO_2 galvanic cell suitable to water-activation

T. YAMAMOTO, T. SHOJI

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

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The Zn | 3 M $AlCl_3$(aq) | MnO_2 galvanic cell gives an open circuit voltage (OCV) of 2.0 V. When the cell is discharged at constant current (1.5 mA cm^{-2} or 50 mA g^{-1}), its discharge curve shows a relatively flat portion in the region 2.0–1.6 V and the cell has an energy density of 550 Wh (kg of $MnO_2)^{-1}$ with a discharge capacity of 330 mA (kg of $MnO_2)^{-1}$, these values being about 2 times and 1.5 times, respectively, larger than those of the Zn | 5 M $ZnCl_2$ | MnO_2 cell. The cell also shows good discharge behaviour at higher electric currents (for example 9.5 mA cm^{-2} or 240 mA g^{-1}), and the advantages of the Zn | $AlCl_3$ | MnO_2 cell over the Zn | $ZnCl_2$ | MnO_2 are clear at the higher discharge currents. The high discharge voltage, energy density, and discharge capacity of the Zn | $AlCl_3$ | MnO_2 cell are attributed to the strong buffering effect of $AlCl_3$ at pH ~ 3. Due to this buffering effect, the electrolytic solution causes gradual corrosion of the zinc and, consequently, the cell is suited to water-activation.

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1. Introduction

High power and high energy, water-activated galvanic cells such as Mg–AgCl(+Ag) [1], Mg–$CuSO_4$(+C), and Mg–Cu_2Cl_2(+C) cells have been developed mainly for emergency uses [2]. We now report a new Zn | $AlCl_3$ | MnO_2 water-activated galvanic cell. The positive and negative electrode materials, as well as the elecrolyte in the cell, are stable against oxygen in air and the cell shows high energy density and high power density.

2. Experimental details

2.1. *Materials*

Commercially available zinc plate (99.99%), anhydrous aluminium chloride, zinc chloride, and zinc oxide were used. Electrolytic γ-MnO_2 (commercial code = TAM, particle size: below 44 μm, 90%; below 74 μm, 99%) and carbon powder (Ketjen black EC-DJ 600) were kindly donated from Mitsui Mining and Smelting Co. Ltd. and Lion Co. Ltd., respectively. Distilled water was used.

2.2. *Measurement*

pH titration of $ZnCl_2$ and $AlCl_3$ was carried out using a TOA pH meter HM-7A. Discharging and charging of the cell were carried out at room temperature (~25° C) and controlled by a Hokuto Denko Potentiostat/Galvanostat HA-301 or Hokuto Denko Charge/Discharge Unit HJ-201B. Fig. 1 shows a sketch of the test cell. Measurements were carried out at room temperature (~25° C) unless otherwise noted. The active material of the positive electrode was obtained by grinding a mixture of γ-MnO_2 (40 mg) and carbon powder (10 mg) in an agate mortar.

3. Results and discussion

Figure 2 shows discharge curves for Zn–MnO_2 galvanic cells using 3 M $AlCl_3$(aq), 1 M $AlCl_3$(aq), 1 M $Al_2(SO_4)_3$(aq), and 5 M $ZnCl_2$(aq) as the electrolytic solution. In the experiment to give the data shown in Fig. 2, 40 mg of MnO_2 corresponding to one-electron capacity ($Mn^{4+} \longrightarrow Mn^{3+}$) of 12.3 mAh was employed. It is seen from Fig. 2 that the 3 M aqueous solution (almost a saturated solution) of $AlCl_3$ affords very high discharge voltage (2.0 – 1.6 V) until about 85% of the one-electron capacity, and an averaged discharging voltage of 1.67 V is obtained on discharge to 0.9 V. That the cell can be discharged beyond the one electron capacity, as shown in Fig. 2, indicates partial participation of a two electron process ($Mn^{4+} \longrightarrow Mn^{2+}$).

Because of the high discharge voltage and high utilization of MnO_2, the Zn | 3 M $AlCl_3$(aq) | MnO_2 galvanic cell gives an energy density of as high as 550 Wh (kg of $MnO_2)^{-1}$. The energy density is about double the energy density (280 Wh (kg of $MnO_2)^{-1}$) of the conventional Zn | 5 M $ZnCl_2$(aq) | MnO_2 galvanic cell ((d) in Fig. 2). The discharge capacity (330 Ah/(kg of $MnO_2)^{-1}$) of the Zn | 3 M $AlCl_3$(aq) | MnO_2 cell is about 1.5 times larger than that of the Zn | 5 M $ZnCl_2$(aq) | MnO_2 cell. When an aqueous solution of $AlCl_3$ and Al_2SO_4 (1 M, almost a saturated solution) with lower concentration of Al^{3+} (1 and 2 M, respect-

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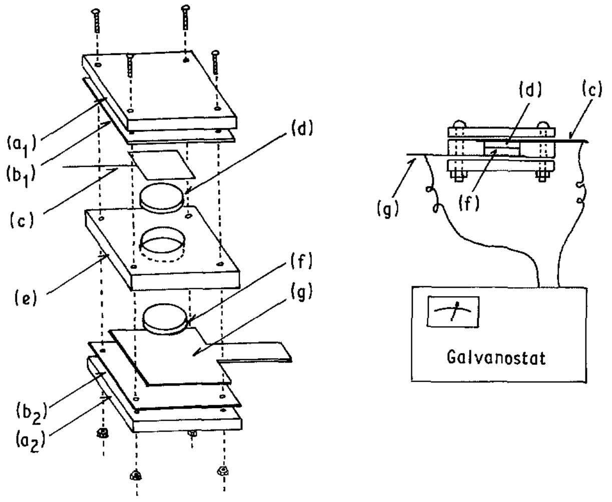

Fig. 1. The test cell. (a) Glass fibre epoxy resin composite board, (b) silicone rubber, (c) collector (Pt plate), (d) active material for the positive electrode (γ-MnO_2 (40 mg) + carbon black (10 mg)), (e) spacer (board made of silicone rubber), (f) glass filter paper with an aqueous electrolytic solution (200 μl), (g) negative electrode (Zn plate). (d) and (f) fit the hole (ϕ = 13 mm, area = 1.33 cm^2) of (e).

ively) are employed as the electrolyte, the Zn-MnO_2 cell also shows higher discharge voltage than the cell using the aqueous solution of 5 M $ZnCl_2$. However, in these cases, use of the electrolytic solutions does not lead to an increase in the discharge capacity.

The high energy density and high discharge capacity of the Zn | 3 M $AlCl_3$(aq) | MnO_2 cell, as well as the fact that $AlCl_3$ is quickly dissolved on addition of water, indicate that the cell is suitable as a water-activated cell.

The high discharge voltage of the cell appears to be due to a strong buffer effect of $AlCl_3$ in the pH region of ~3 as revealed by its pH titration curve (a) shown in Fig. 3. Fig. 3 also shows a pH titration curve of $ZnCl_2$, and it is seen that $AlCl_3$ shows the buffer effect at lower pH than $ZnCl_2$ (curve (b) in Fig. 3). The buffer effect is considered to be due to the very low solubility of $Al(OH)_3$, and the buffer effect at about pH = 3 ($[OH^-]$) = 10^{-11} M) corresponds well to the solubility product of $Al(OH)_3$, $K_{sp} = [Al^{3+}][OH^-]^3 = \sim 1 \times 10^{-33}$ M^4 [3].

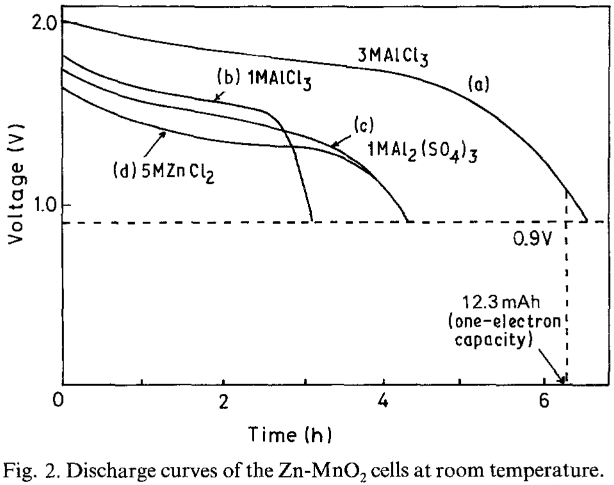

Fig. 2. Discharge curves of the Zn-MnO_2 cells at room temperature. Electrolytic solution: 3 M $AlCl_3$ (a); 1 M $AlCl_3$ (b); 1 M $Al_2(SO_4)_3$ (c); 5 M $ZnCl_2$ (d) at a constant current of 2 mA.

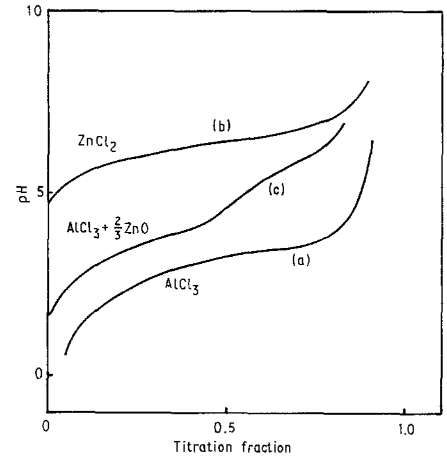

Fig. 3. Titration curves of $AlCl_3$ (a) and $ZnCl_2$ (b) at room temperature. 3 M $AlCl_3$ and 2 M $ZnCl_2$ aqueous solutions were titrated with an aqueous solution of NaOH. In the case of (c), an aqueous solution containing 3 M $AlCl_3$ and ZnO (2 mol l^{-1} s, dispersed in the solution as fine particles) was titrated with NaOH.

As judged from the titration results, electrically non-conducting ZnO, which is formed at the negative electrode by the cell reaction

$$Zn + 2OH^- \longrightarrow Zn(OH)_2 + 2\,e^- \qquad (1)$$

and starts to precipitate in the region of pH ~5.5, appears to be dissolved in the electrolyte solution containing 3 M of $AlCl_3$ to continue the smooth discharge reaction at the negative electrode. In the presence of $AlCl_3$, the negative electrode reaction, Equation 1, is modified and reactions such as

$$Zn + \tfrac{2}{3}\,AlCl_3 + 2OH^- \longrightarrow ZnCl_2 + \tfrac{2}{3}\,Al(OH)_3 + 2\,e^- \qquad (2)$$

seem to be involved in the negative electrode reaction. Actually, the electrode potential of Zn ($Zn \longrightarrow Zn^{2+} + 2\,e^-$) in the aqueous 3 M solution of $AlCl_3$ was lower by 0.07 V than the reported electrode potential of Zn (−0.76 V with respect to SHE).

Another part of the large discharge voltage of the Zn-MnO_2 cell using $AlCl_3$ as the electrolyte is attributed to the buffer effect of $AlCl_3$ on the electrode potential of MnO_2. It is reported that the electrode potential of MnO_2 increases with decreasing pH with a slope of −0.059 V/pH in the pH region higher than 3 and with a slope of −0.118 V/pH in the pH region lower than 3 [4–6], that is:

$$\Delta E/\Delta(\mathrm{pH}) = -0.059\ (\mathrm{pH} \geqq 3),$$
$$\Delta E/\Delta(\mathrm{pH}) = -0.118\ (\mathrm{pH} < 3).$$

Since $AlCl_3$ shows the buffer effect at a pH lower than ~3 than $ZnCl_2$, this leads to an increase in the electrode potential of about 0.2 V in the buffering region. The aqueous 3 M $AlCl_3$ solution before the discharge shows a pH of ~0, and the high discharge voltage of the cell in the initial stages of discharge is attributed to the high MnO_2 electrode potential at the low pH value.

When the discharge starts, the pH of the electrolytic solution tends rapidly to ~3 due to the formation of

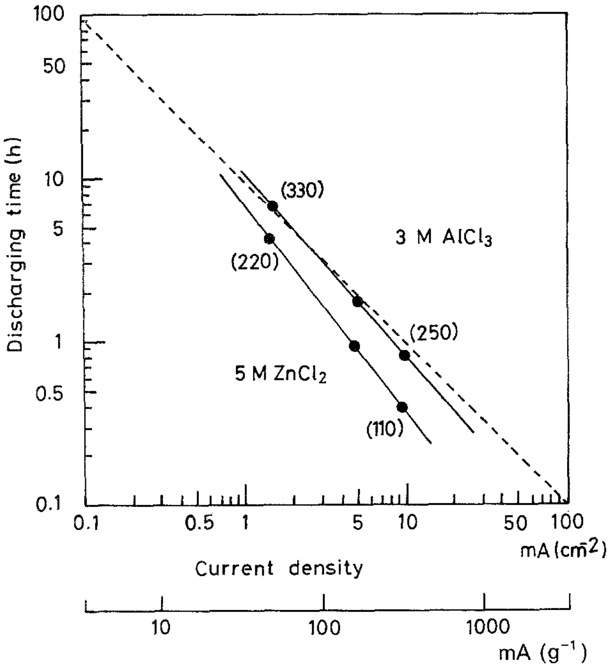

Fig. 4. Relation between discharge current density and discharge time obtained by using the cell shown in Fig. 1. The figure in the parentheses shows the discharge capacity in Ah (kg of MnO$_2$)$^{-1}$.

Zn(OH)$_2$ by the cell reaction (Equation 1) and the AlCl$_3$ buffer effect. Partial participation of the two electron reaction (Mn^{4+} $\longrightarrow$ Mn^{2+}) may also contribute to the high discharge voltage of the cell.

Figure 4 shows the relation between discharge current density and energy density for the Zn | 3 M AlCl$_3$(aq) | MnO$_2$ cell. As shown in Fig. 4, the cell using 3 M AlCl$_3$(aq) shows high discharge capacity even at large discharge current (as high as 320 mA g^{-1}), again revealing that it is suitable as a water-activated cell. At a discharge current of 9.5 mA cm^{-2} or 320 mA g^{-1}, the Zn | 3 M AlCl$_3$(aq) | MnO$_2$ cell affords about 2.4 times larger a discharge capacity than the Zn | 5 M ZnCl$_2$(aq) | MnO$_2$ cell.

Because of the buffering effect of 3 M AlCl$_3$ in the low pH region, corrosion of the zinc negative electrode with evolution of H$_2$ takes place besides the negative electrode reactions, Equations 1 and 2, although the rate of evolution of H$_2$ is much slower than that observed for the zinc plate in dil. H$_2$SO$_4$. Table 1 summarizes results of corrosion tests of the zinc plate in various aqueous electrolytic solutions. As seen in Table 1, zinc is not stable in the 3 M aqueous solution of AlCl$_3$, indicating that the present cell is particularly suitable as a water-activated cell but not as a dry cell. Addition of ZnO retards the corrosion (Nos. 2 and 3 in Table 1), however this is associated with lowering of the discharge voltage, discharge capacity, and energy density as shown in Fig. 5.

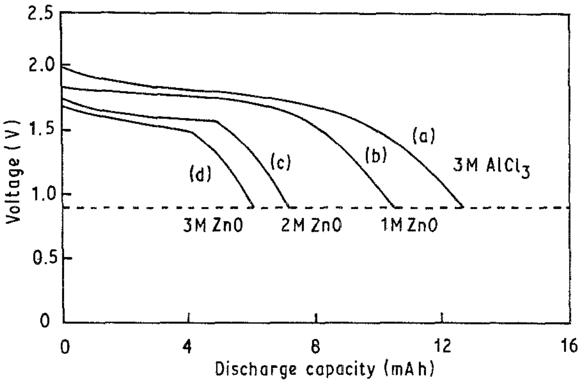

Fig. 5. Effect of ZnO on the discharge curve. ZnO was added to the aqueous solution of 3 M AlCl$_3$. Amount of ZnO/AlCl$_3$ (mol/mol); 0 (a); 1/3 (b); 2/3 (c); 3/3 (d).

The Zn | AlCl$_3$(aq) | MnO$_2$ cell is rechargeable as shown in Fig. 6. After charging for 6 h at 2 mA (1.5 mA cm^{-2}), the Zn | 3 M AlCl$_3$(aq) | MnO$_2$ cell can be discharged for about 4.5 h at 2 mA. The charge-discharge cycle can be repeated.

4. Conclusions

As described above, the Zn | AlCl$_3$ | MnO$_2$ cell has the following features: (1) The cell shows high open circuit voltage (OCV = 2.0 V) and closed circuit voltage (CCV = 2.0–1.6 V), which are comparable to those observed for a conventional water-activated cell using magnesium (for example, Mg–AgCl(+Ag) (OCV = 1.6 V, CCV = 1.5 – 1.1 V) and Mg–CuSO$_4$ (OCV = 2.1 V, CCV = 1.7 – 1.3 V) cells [2]; (2) The cell shows a high discharge capacity of 330 Ah (kg of MnO$_2$)$^{-1}$. 1 Ah discharging of the cell requires active materials of 4.25 g (1.22 g of Zn and 3.03 g of MnO$_2$), whereas 1 Ah discharge of the Mg–AgCl cell requires active materials of 5.80 g (0.45 g of Mg and 5.35 g of AgCl); (3) The cell has high energy density of 550 Wh (kg of MnO$_2$)$^{-1}$; (4) The cell is usable at relatively large discharge current; (5) The cell uses non-expensive and non-toxic materials. Since AlCl$_3$ has a large heat of dissolution in water (ΔH = ~330 kJ mol^{-1}), addition of cold water is possible to start the discharge of the cell. Due to these advantageous points, the cell

*Table 1. Corrosion of zinc plate in various solutions**

No.	*Electrolyte solution (aq)*	*Concentration (M)*	*Additive (mol/mol of AlCl$_3$)*	*pH† before*	*pH† after*	*Weight loss of zinc (mg)*
1	AlCl$_3$	3.0	none	−0.3	0.0	240
2	AlCl$_3$	3.0	ZnO 1.0	0.7	0.7	3.2
3	AlCl$_3$	3.0	ZnO 2.0	1.4	1.4	negligible
4	AlCl$_3$	2.0	none	0.8	0.9	37
5	AlCl$_3$	1.0	none	1.9	1.9	1
6	ZnCl$_2$	5.0	none	3.1	3.2	negligible

*Zinc plate (10 × 10 × 3 mm) was dipped into the electrolyte solution (12 ml) at about 25° C. Weight loss of zinc was measured after 12 h.
†pH values of the electrolyte solution before addition of the zinc plate and after measurement of the corrosion, respectively.

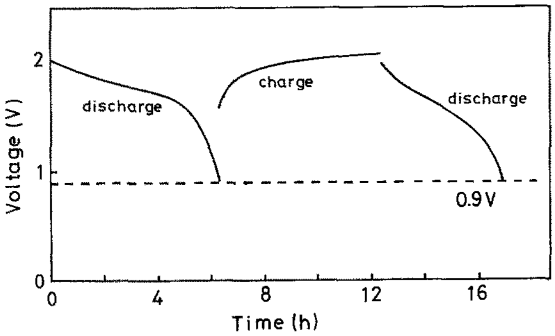

Fig. 6. Charge–discharge curves of the Zn | 3 M $AlCl_3$ | MnO_2 galvanic cell at a constant electric current (1.5 mA cm^{-2}) at room temperature. After initial discharging to 0.9 V, the cell was charged for 6 h and discharged without pause time.

may find practical uses. In a practical cell, $AlCl_3$ or $AlCl_3 \cdot 6H_2O$ will be held in a porous separator.

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