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Zn|Al Salt (aq)|MnO$_2$ Galvanic Cell with High Voltage and High Energy Density

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Zn–MnO$_2$ galvanic cells are now widely used. As for the electrolyte of the cell, the following three kinds of electrolytes are added: (1) NH_4Cl, (2) $ZnCl_2$, and (3) KOH [1]. We now report a new Zn|Al salt|MnO$_2$ galvanic cell which shows higher discharging voltages and a higher energy density than the conventional Zn–MnO$_2$ galvanic cells.

In this research we used a galvanic cell as shown in Fig. 1. A mixture of electrolytic γ-MnO$_2$ (40 mg, prepared by Mitsui Mining and Smelting Co. Ltd., commercial code = TAM) and 10 mg of carbon black (Ketjen black EC-DJ 600 [2]) was used as the active material of the positive electrode, and the amount of MnO$_2$ corresponds to a theoretical one-electron capacity of 45 C or 12.3 mA h (one-electron capacity = total charge to reduce Mn^{4+} to Mn^{3+}). Areas of positive and negative electrodes were 1.33 cm^2.

Figure 2 shows discharging curves for Zn|3 M $AlCl_3$(aq)|MnO$_2$, Zn|1 M $AlCl_3$(aq)|MnO$_2$, Zn|1 M $Al_2(SO_4)_3$(aq)|MnO$_2$, and Zn|5 M $ZnCl_2$(aq)|MnO$_2$ galvanic cells at constant electric current (2 mA, 1.5 mA/cm^2). As shown in Fig. 2, the Zn|Al salt|MnO$_2$ galvanic cells show higher initial discharging voltage by 0.2–0.45 V than the commercialized Zn|ZnCl$_2$(aq)|MnO$_2$ galvanic cell. Open circuit voltage of the cells using the aluminum salts were as high as 2.0 V.

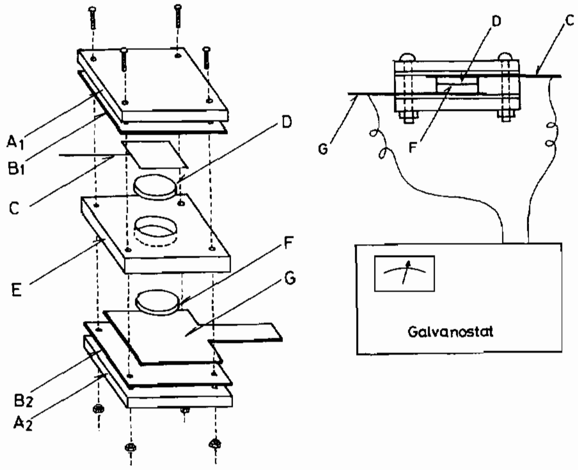

Fig. 1. Structure of the test cell. A: board made of glass fiber-epoxy resin composite, B: silicone rubber, C: collector (Pt plate), D: active material for the positive electrode (γ-MnO$_2$ (40 mg) + carbon black (10 mg)), E: spacer (board made of silicone rubber), F: glass fiber paper with an aqueous 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.

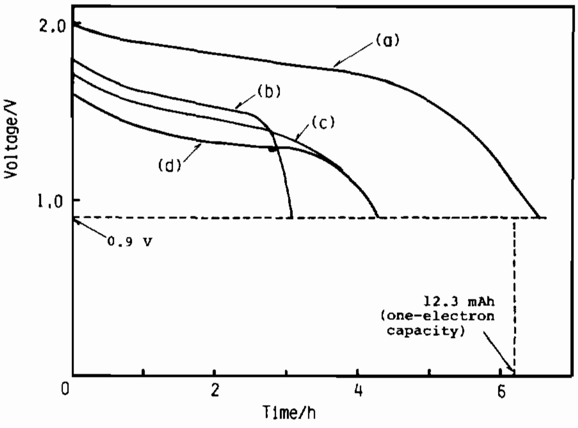

Fig. 2. Discharge curves of the cells shown in Fig. 1. Electrolyte = 2 M $AlCl_3$ (a), 1 M $AlCl_3$ (b), 1 M $Al_2(SO_4)_2$ (c), or 5 M $ZnCl_2$ (d). Closed circuit voltage is shown.

It can be seen from Fig. 2 that use of the aqueous solution of $AlCl_3$ with a higher concentration affords a better discharging performance (*cf.* curves (a) and (b)). When an aqueous solution of $AlCl_3$ with a concentration of 3 M, which is almost a saturated aqueous solution of $AlCl_3$, is used as the electrolytic solution, the cell shows rather flat discharging voltage (curve (a)) with high discharging voltage until about 85% of the one-electron capacity (12.3 mA h or discharging of 6.2 h at 2 mA, see Fig. 2) of MnO$_2$ is discharged. That the cell can be discharged beyond the one-electron capacity suggests partial participation of a two electron reaction ($Mn^{4+} \rightarrow Mn^{2+}$). The Zn|3 M $AlCl_3$(aq)|MnO$_2$ galvanic cell shows an averaged discharging voltage of 1.78 V and energy density of 580 W h/kg of MnO$_2$ when discharged until the discharging voltage (closed circuit voltage) drops to 0.9 V. The energy density is about double the energy density (280 W h/kg of MnO$_2$) of the conventional Zn|5 M $ZnCl_2$(aq)|MnO$_2$ galvanic cell which shows an averaged discharging voltage of 1.34 V (curve (d) in Fig. 2).

Aluminum salts show a buffer effect at the pH region of about 3 as revealed by their pH titration. The buffer effect is considered to be due to the formation of insoluble $Al(OH)_3$

$$Al^{3+} + 3OH^- \longrightarrow Al(OH)_3 \qquad (1)$$

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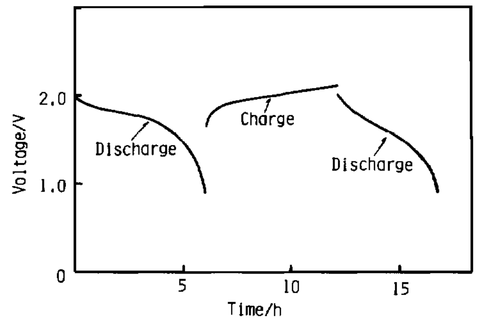

Fig. 3. Charge–discharge curves of the Zn|3 M $AlCl_3$|MnO_2 cell at 2 mA. The cell was initially discharged to 0.90 V, charged for 6 h, and re-discharged.

Since precipitation of $Zn(OH)_2$ starts at the pH region of about 5.5 in the pH titration, electrically non-conducting $Zn(OH)_2$ formed at the negative electrode by the cell reaction,

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

appears to be dissolved in the aqueous solution containing aluminum salts to continue the smooth discharging reaction at the negative electrode. Under these circumstances, the negative electrode reaction (eqn. (2)) will be modified and reactions like

$$Zn + 2/3Al^{3+} + 2OH^- \longrightarrow Zn^{2+} + 2/3Al(OH)_3 + 2e \qquad (3)$$

may be involved in the negative electrode reaction. Actually, measurement of the electrode potential of Zn ($Zn \rightarrow Zn^{2+} + 2e$) in the aqueous 3 M $AlCl_3$ solution showed that it is lower by 0.07 V than the reported electrode potential of Zn (−0.76 V *versus* standard hydrogen electrode).

Another part of the larger discharging voltage of the Zn|3 M $AlCl_3$(aq)|MnO_2 cell than that of Zn|5 M $ZnCl_2$(aq)|MnO_2 cell is attributable to the buffer effect of $AlCl_3$ at a relatively low pH region. It is reported that the electrode potential of MnO_2 increases with a lowering of the pH of the electrolytic solutions with a slope of −0.060 V/pH in a pH region higher than 3 and a slope of −0.118 V/pH in a pH region lower than 3 [3]. Since $AlCl_3$ shows the buffer effect at a lower pH by 2.5 than $ZnCl_2$, it will cause an increase in the electrode potential by about 0.15 V at the buffering region. The 3 M $AlCl_3$(aq) solution before the discharge shows a pH value of about 0, and the high open circuit voltage at the initial stage of discharge seem to be attributable to the high electrode potential of MnO_2 at the low pH value. With start of discharging, the pH value of the electrolytic solution rapidly becomes about 3 due to the formation of $Zn(OH)_2$ (eqn. (2)) and the buffering effect of $AlCl_3$. Partial participation of the two electron reaction ($Mn^{4+} \rightarrow Mn^{2+}$, *vide supra*) may also contribute to the high electrode potential of MnO_2.

Due to the buffering effect of $AlCl_3$ at the considerably low pH region, corrosion of the Zn negative electrode with evolution of H_2 took place besides the negative electrode reaction, reaction (2) or (3). Under such circumstances the Zn|$AlCl_3$|MnO_2 battery is particularly suitable to a water-activated battery [4] which starts to work by adding water to the electrolyte just before use. Addition of ZnO to the aqueous 3 M $AlCl_3$ solution retarded the corrosion of the Zn negative electrode, and the corrosion was virtually inhibited in the aqueous 3 M $AlCl_3$ solution containing a saturated amount (*ca.* 2.5 mol/l) of ZnO.

The Zn|$AlCl_3$|MnO_2 and Zn|$AlCl_3$ + ZnO|MnO_2 galvanic cells are rechargeable as shown in Fig. 3. After charging for 6 h at 2 mA, the Zn|3 M $AlCl_3$(aq)|MnO_2 cell can be discharged for about 4.5 h at 2 mA corresponding to 75% current efficiency. The charge–discharge cycles were repeated. Since the present galvanic cell has a simple constitution and $AlCl_3$ is easily supplied, it may find practical use.

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