Rechargeable Zn|ZnSO$_4$|MnO$_2$-type Cells

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Although alkaline MnO$_2$ cells like Zn|KOH|MnO$_2$ are known to show rechargeability to some extent [1–5], there is no detailed report concerning rechargeability of MnO$_2$ cells using neutral or acidic electrolyte. We have recently investigated rechargeability of Zn|ZnX$_n$|MnO$_2$ cells (X = SO$_4$, Cl, NO$_3$, BF$_4$, SiF$_6$, etc.) under various conditions; we find that some of the cells (especially when X = SO$_4$) show good rechargeability when used under appropriate conditions, and we now report the results of the investigation. Since the rechargeable MnO$_2$ cell seems to have some advantages from an industrial viewpoint, the present cell may find practical use.

Figure 1 shows a sketch of a test cell. The active material for the positive electrode (E in Fig. 1) was prepared by mixing 40 mg (0.47 mmol, theoretical one-electron capacity = 45 C) of electrolytic γ-MnO$_2$ (prepared by Mitsui Mining and Smelting Co. Ltd., commercial code = TAM) and 10 mg of carbon black (Ketjen Black) in an agate mortar. An aqueous solution of ZnSO$_4$ (2 mol/dm^3, pH = 3.73) was used as the electrolyte solution. The cell was sealed by pressing the cell from both the sides with silicone rubber (B in Fig. 1) to avoid evaporation of H$_2$O. Use of the cell under both air and Ar gave essentially the same results. The cell was placed in a thermostatted (25 ± 0.3 °C) chamber. Charging and discharging of the cell were performed by using a galvanostat which was controlled by a computer.

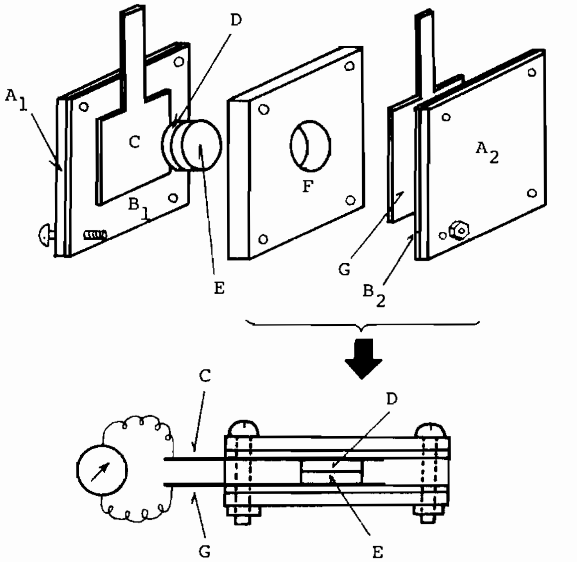

Fig. 1. Sketch of a test cell. A: board made of glass fiber-epoxy resin composite, B: silicone rubber, C: negative electrode (Zn plate), D: glass fiber paper impregnated with an aqueous solution (100 μl) of ZnSO$_4$ (2 M), E: active material for the positive electrode (γ-MnO$_2$ (40 mg) + carbon black (10 mg)), F: spacer (board made of silicone rubber), G: collector (Pt plate). D and E fit the hole (ϕ = 13 mm, area = 1.33 cm^2) of F.

The cell was first discharged at 2.0 mA; the discharging started at 1.56 V (*CCV* = closed circuit voltage) and was stopped after 200 min when *CCV* dropped to 0.90 V. The discharging time of 200 min corresponds to 53% of the theoretical one-electron capacity of MnO$_2$, the percentage value being comparable to that observed with commercial Leclanché type primary MnO$_2$ cells. After the discharging, the cell was charged for 240 min at 2.0 mA and then discharged at 2.0 mA until *CCV* dropped to 0.9 V. Between the charging and discharging a pause time (10 min) was taken.

Figure 2 shows charge–discharge curves thus obtained. The following features of the present secondary cell at the first charge–discharge cycle are seen from Fig. 2:

(1) The cell can be discharged for 180 min corresponding to 75% of current efficiency and to 48% (0.002 × 60 × 180 ÷ 45 × 100 = 48) of the theoretical one-electron capacity of MnO$_2$.

(2) Averaged charging and discharging voltages are about 1.55 V and 1.30 V, respectively. Based on the current efficiency and averaged charging and discharging voltages, the energy efficiency of the secondary cell is calculated as 63% (75 × (1.30/1.55) = 63).

(3) The energy stored in the cell is calculated as 7.8 mWh from the discharging electric current (2 mA), the averaged discharging voltage (1.30 V), and the discharging time: 2 × 1.30 × (180/60) = 7.8. The

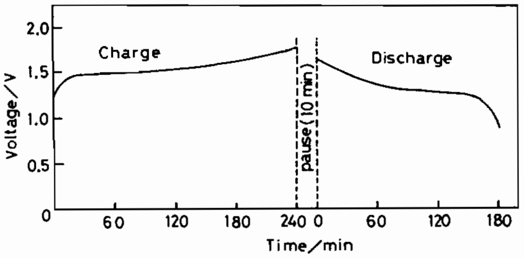

Fig. 2. Charge–discharge curves of the cell shown in Fig. 1. (1st cycle). At 2 mA and at 25 °C.

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energy density calculated based on the energy stored and weights of active material for the positive electrode (50 mg (MnO_2 + Ketjen Black)) and the electrolyte solution (*ca.* 127 mg) is about 44 Wh/kg. Use of a $ZnSO_4$ solution with a higher concentration is expected to give a secondary cell with higher energy density.

(4) The charging voltage remains below 2.0 V through the charging. Therefore, occurrence of electrolysis of H_2O is considered to be negligible.

X-ray diffraction analysis of the active material for the positive electrode revealed formation (or regeneration) of γ-MnO_2 during the charging and consumption of γ-MnO_2 during the discharging.

The charge–discharge cycle can be repeated, and up to the 30th charge–discharge cycle no significant change in the discharging curve was observed (Fig. 3). However, further increase in the number of charge–discharge cycles caused shortening of the discharging time. Repeated experiments indicated that the shortening of the discharging time started at about 30 ± 4th charge–discharge cycle. Use of $Zn(NO_3)_2$, $ZnCl_2$, $Zn(BF_4)_2$, or $ZnSiF_6$, instead of $ZnSO_4$, also afforded rechargeable cells; however, in these cases the charge–discharge performance was not as good as that observed in the case of $ZnSO_4$.

Addition of polymer to the mixture of MnO_2 and carbon black caused a significant change in the charge–discharge curve. For example, use of a mixture of the electrolytic MnO_2 (40 mg), powder nylon-6 (40 mg), and carbon black (Ketjen Black, 20 mg) gave a cell which was suitable for relatively short-period discharging (60 min) and rechargeable more than 120 times without changing of the charge–discharge curves. The secondary cell showed about 93% current efficiency and about 76% energy efficiency. Use of other polymers (e.g., poly(sulfone), copolymer of ethylene and maleic anhydride, poly(phenyleneoxide)) also gave rechargeable cells.

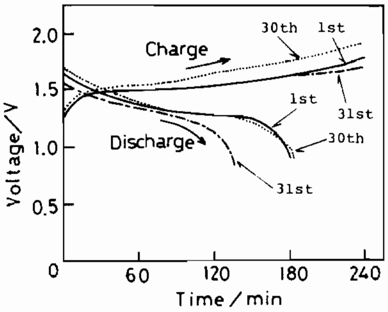

Fig. 3. Charge–discharge curves of the cell shown in Fig. 1. ——: 1st cycle (data from Fig. 1), ·······: 30th cycle, –·–: 31st cycle. At 2mA and at 25 °C.

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