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Zinc–manganese dioxide galvanic cell using zinc sulphate as electrolyte. Rechargeability of the cell

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The discharge capacity of the Zn|$ZnSO_4$(aq)|MnO_2 galvanic cell increases with increase in the concentration of $ZnSO_4$; use of a 2 M aqueous solution of $ZnSO_4$ gives 65% utilization of MnO_2. When the cell is charged after discharging, X-ray diffraction analysis of the positive electrode material indicates regeneration of γ-MnO_2 during the charging. Repeated charging and discharging under various modes reveals that the cell is rechargeable more than 30 times. When the cell is charged to 1.70 V and discharged to 0.9 V, the cell shows about 100% coulombic efficiency with an average discharging voltage of about 1.3 V (energy efficiency = 83%) and 57% utilization of MnO_2. The cell is rechargeable after discharging to 0 V.

1. Introduction

Zinc–manganese dioxide galvanic cells using zinc chloride or potassium hydroxide as the electrolyte are now widely used and several papers have reported that the alkaline cell Zn|KOH|MnO_2 shows rechargeability [1–5]. However, zinc–manganese dioxide galvanic cells using other neutral or acidic electrolytes have attracted much less attention compared with the commercialized Zn–MnO_2 galvanic cells. By choosing a simple zinc compound, $ZnSO_4$, as the electrolyte of the Zn–MnO_2 galvanic cell, we have investigated discharging and charging behavior of the Zn|$ZnSO_4$|MnO_2 cell under various conditions and found that the cell shows good discharging behavior and is rechargeable. We now report results of the investigation focused mainly on the rechargeability of the cell. Some results have been published in communication form [6].

2. Experimental details

2.1. *Materials*

Highly pure (99.99%) zinc plate (thickness = 0.3 mm) purchased from The Japan Lamp Industrial Co. Ltd or zinc plate (thickness = 0.3 mm) produced by Mitsui Mining and Smelting Co. Ltd was used as the negative electrode. Both kinds of zinc plate gave essentially the same result. The following electrolytic manganese dioxide was donated from Mitsui Mining and Smelting Co. Ltd:

Code	Particle size	
	below 44 μm	below 74 μm
TAM for acidic medium	90%	99%
TAD for acidic medium	70%	94%
TASV for alkaline medium	60%	90%

GR grade electrolyte (zinc sulphate, zinc hexafluorosilicate, etc.) was purchased from Koso Chemical Co. Ltd, Takahashi Pure Chemicals Co. Ltd or Hashimoto Chemical Co. Ltd. Cation exchanging membrane (commercial code = Selemion CMV, ASV and DMV) was donated from Asahi Glass Co. Ltd.

2.2. *Cell discharging and charging*

The electrolytic manganese dioxide and carbon powder (Ketjen black (commercial code of Akzo Co. Ltd)) was ground in an agate mortar, and the cell shown in Fig. 1 was constructed using the mixture thus obtained; a zinc plate, electrolytic solution, a separator (filter paper made of glass fiber (Toyo Roshi Co. Ltd commercial code GA-100)) and a platinum plate (collector). Charging and discharging of the cell were controlled by a Hokuto-denko Charge–discharge Unit HJ-201B or a combined set of a galvanostat (Hokuto-denko Model HA-301) and a computer (NEC Model PC-8001/II) with an interface. Charging and discharging the cell under N_2 gave essentially the same results as those obtained by charging and discharging under air, indicating that the effect of air on the cell is negligible.

X-ray diffraction analysis and fluorescent X-ray analysis of the positive electrode material were performed using Phillips Model PS-1051 and Horiba Model MESA-1130 machines, respectively.

3. Results and discussion

3.1. *Primary cell*

Figure 2 shows discharging curves of Zn|$ZnSO_4$(aq)|MnO_2 (TAD, see Experimental details) and Zn|$ZnCl_2$(aq)|MnO_2 cells at constant electric current (2 mA corresponding to 50 mA g^{-1}). When the Zn|$ZnSO_4$|MnO_2 cell with a 2 M aqueous solution of

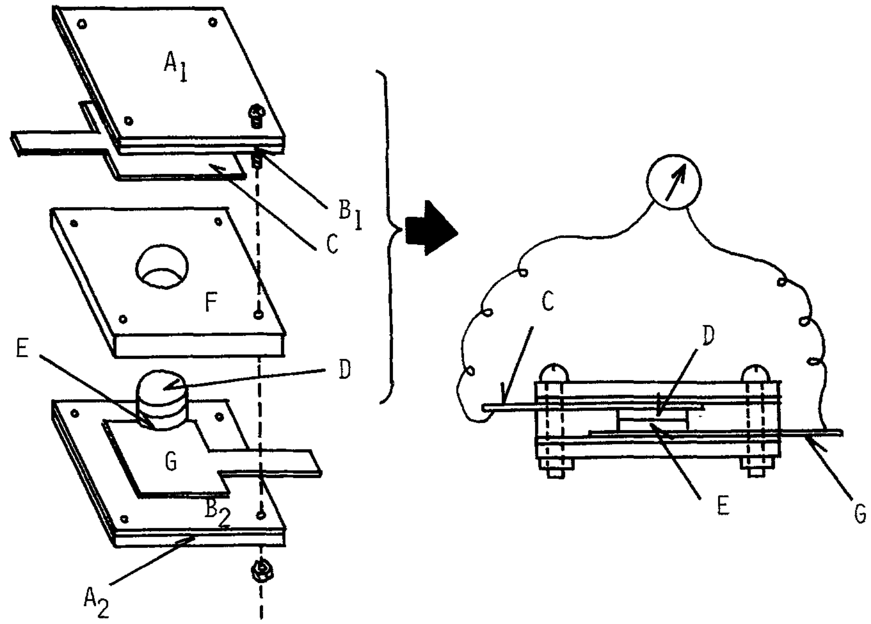

Fig. 1. Structure of the test cell. A: Glass-epoxy resin end plate; B: silicone resin plate; C: platinum plate (collector); D: positive electrode material (MnO_2 40 mg + ketjen black 10 mg); E: glass fiber mat (filter paper from Toyo Roshi Co. Ltd) impregnated with 200 μl of electrolytic solution; F: silicone resin spacer plate; G: zinc plate. D and E fit in the hole (ϕ = 1.3 cm) of F.

$ZnSO_4$ ((d) in Fig. 2) was discharged to 0.9 V, the cell gave 65% utilization of MnO_2.

$$\% \text{ utilization} = \frac{\text{coulomb obtained}}{(\text{mol of } MnO_2) \times 96500} \quad (1)$$

Although the value is lower than the value observed for the $Zn|ZnCl_2|MnO_2$ cell with a 2 M aqueous solution of $ZnCl_2$ ((e) in Fig. 2), the cell shows a discharge capacity of 84% of the discharge capacity of the $Zn|ZnCl_2|MnO_2$ cell. The discharge capacity suggests that the $Zn|ZnSO_4|MnO_2$ cell also may be useful as a practical Zn–MnO_2 cell.

Use of TAM (*cf.* Experimental details) as MnO_2 gave a similar value for the utilization of MnO_2, however use of MnO_2 synthesized for alkali media (TASV) gave lower utilization of MnO_2 (*cf.* 38% on discharging to 0.9 V).

3.2. *Secondary cell*

After the discharging described above, the $Zn|ZnSO_4|MnO_2$ galvanic cell was charged at constant current (2 mA 40 mg^{-1} of MnO_2). The discharging and charging curves are shown in Fig. 3.

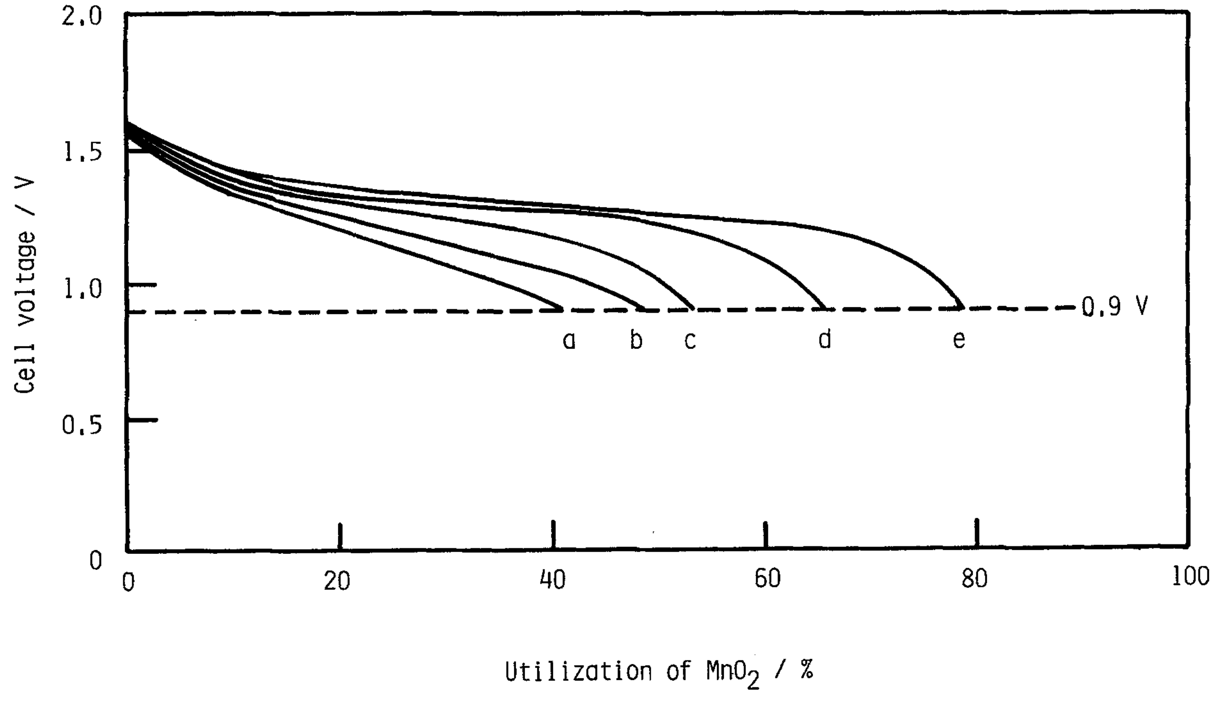

Fig. 2. Discharge curves of $Zn|ZnSO_4|MnO_2$ and $Zn|ZnCl_2|MnO_2$ galvanic cells at 25° C and constant electric current (2 mA). Electrolytic solution = 0.25 M $ZnSO_4$ (a), 0.50 M $ZnSO_4$ (b), 1.0 M $ZnSO_4$ (c), 2.0 M $ZnSO_4$ (d) and 2.0 M $ZnCl_2$ (e) in water. MnO_2 = TAD (40 mg).

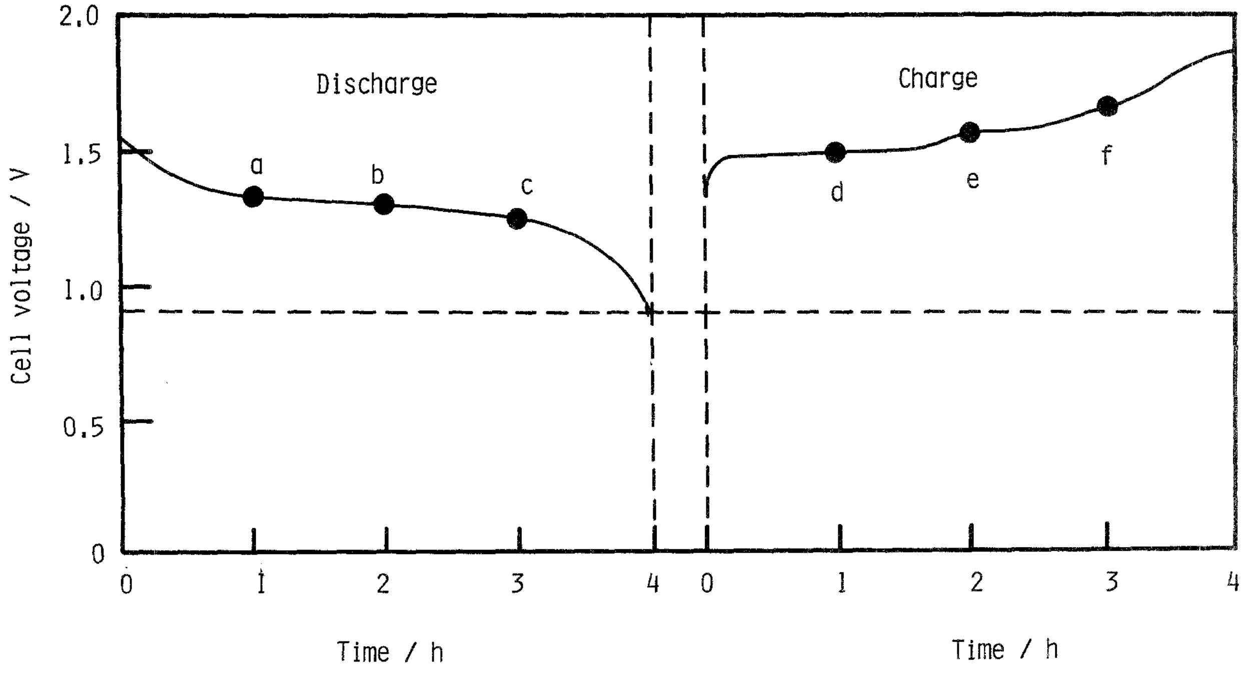

Fig. 3. Discharging and charging of Zn|2 M $ZnSO_4$(aq)|MnO_2 (TAD, 40 mg) at 25° C and 2 mA.

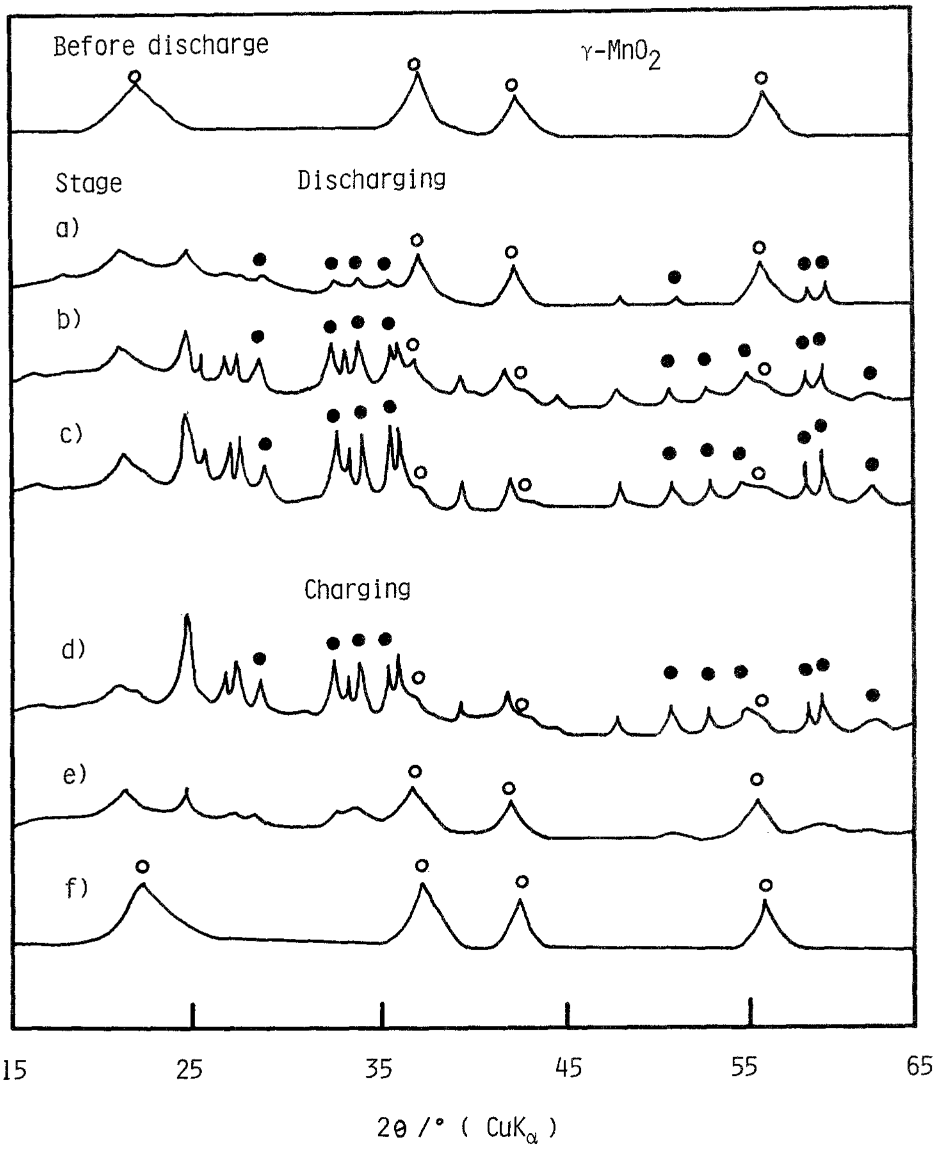

Fig. 4. X-ray diffraction pattern of the positive electrode material at stages a–f shown in Fig. 3. The positive electrode material was rinsed repeatedly with H_2O and dried under vacuum. The signals ○ and ● are assigned to γ-MnO_2 and hetaelorite ($ZnO \cdot Mn_2O_3$) or hausmannite (Mn_3O_4), respectively.

Figure 4 shows X-ray diffraction patterns of the positive electrode materials at discharge stages a, b and c and charge stages d, e and f in Fig. 3. As the discharging proceeds, the γ-MnO_2 signal is weakened whereas signals assigned to hetaelorite ($ZnO \cdot Mn_2O_3$) [7] and/or hausmannite ($MnO \cdot Mn_2O_3$) [8] grow, indicating that Mn^{4+} is reduced to Mn^{3+} (and possibly partly to Mn^{2+}) in the discharge. Fluorescent X-ray analysis of the positive electrode material indicated that zinc was taken into the positive electrode material during the discharging and the amount of zinc increased roughly linearly with discharge time.

On the other hand, during the charging, γ-MnO_2 was regenerated as shown in d–f in Fig. 4. The regeneration of γ-MnO_2 during charging prompted us to investigate the usability of the present cell as a secondary cell.

Figure 5 shows the first charge–discharge cycle of the cell at constant electric current (2 mA corresponding to 50 mA g^{-1} in the cell shown in Fig. 1); before the first charging the cell was discharged to 0.9 V at 2 mA (*cf.* Fig. 2). In Fig. 5, charging for 4 h corresponds to about 65% utilization of γ-MnO_2. After 4 h charging, the charging voltage (closed circuit voltage (CCV)) became 1.84 V and the average charging voltage was 1.65 V. The charged cell showed an open circuit voltage (OCV) of 1.76 V.

The discharging at 2 mA constant current in Fig. 5 started at 1.62 V and after 3.0 h the CCV dropped to 0.9 V with an average discharging voltage of 1.30 V. The discharging time of 3.0 h corresponds to 49% utilization of MnO_2, and the charge–discharge curve gives a coulombic efficiency of 75% and an energy efficiency of 59% (75% × (1.30 V/1.65 V)). The charge–discharge cycle shown in Fig. 5 can be repeated 20–30 times. The discharging time remained 2.5–3.0 h until the 20–25th charge–discharge cycle, and after the 30th cycle the discharging time began to decrease rather steeply. Loss of water from the electrolytic solution by evaporation or physical or chemical changes of the positive electrode material (e.g. crystal structure of MnO_2 and chemical composition of the positive electrode material) accounts for the shortening of the discharging time. Sometimes formation of zinc dendrites was observed and this may also be responsible for the shortening of the discharging time.

Curves b and b′ in Fig. 6 show a new charge–discharge cycle which was obtained with another controlled charging and discharging mode; the cell was charged to 1.70 V (instead of 4 h (charging mode shown in Fig. 5)) at 2 mA and discharged to 0.9 V at 2 mA. When the charging was stopped at 1.70 V, the cell showed about 100% coulombic efficiency as shown by curves b and b′ (the 10th cycle) in Fig. 6, suggesting that γ-MnO_2 was regenerated effectively under mild charging conditions. The current efficiency at the 10th charge–discharge cycle (curves b and b′) was somewhat higher than 100%, suggesting that some MnO_2, which was not used in the previous discharging, participated in the discharging. This type of effect was more apparent in the first charge–discharge cycle (a and a′ in Fig. 6). In Fig. 6, the curve b gives an average charging voltage of 1.57 V, whereas the curve b′ gives an average discharging voltage of 1.35 V.

The charge–discharge cycle shown by curves b and b′ in Fig. 6 can be repeated, and change of the charge–discharge profile with cycle number is shown by curves a–e and a′–e′ in Fig. 6. As shown in Fig. 6, the Zn|$ZnSO_4$|MnO_2 cell was rechargeable more than 25–30 times. The elongation of the discharging time in the early charge–discharge cycles may be due to better mixing of MnO_2 and the electrolytic solution with increasing number of the charge–discharge cycle. At the 15th charge–discharge cycle (curves c and c′), the discharging curve gives 3.5 h charging time (7.0 mAh 40 mg^{-1} of MnO_2, corresponding to 56% utilization of MnO_2) with an average discharging voltage of 1.35 V. The capacity of the cell began to decrease after about the 25th cycle. X-ray diffraction analysis of the

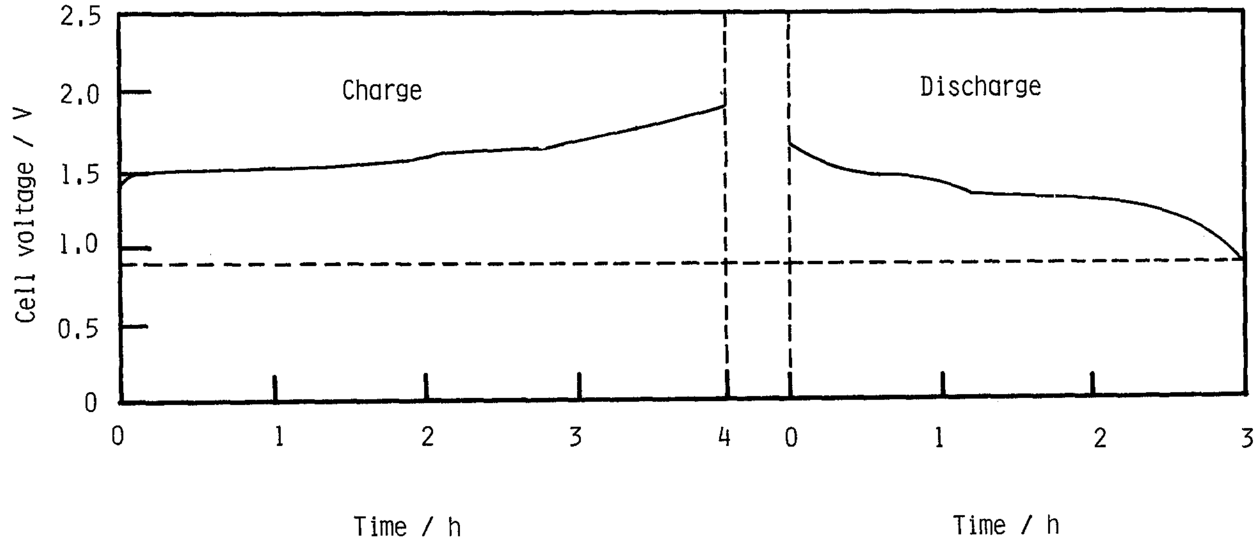

Fig. 5. Charge–discharge profile of the Zn|$ZnSO_4$|MnO_2 (TAD, 40 mg) cell at room temperature (*ca* 25° C) and at 2 mA. The cell was charged for 4 h and discharged to 0.9 V.

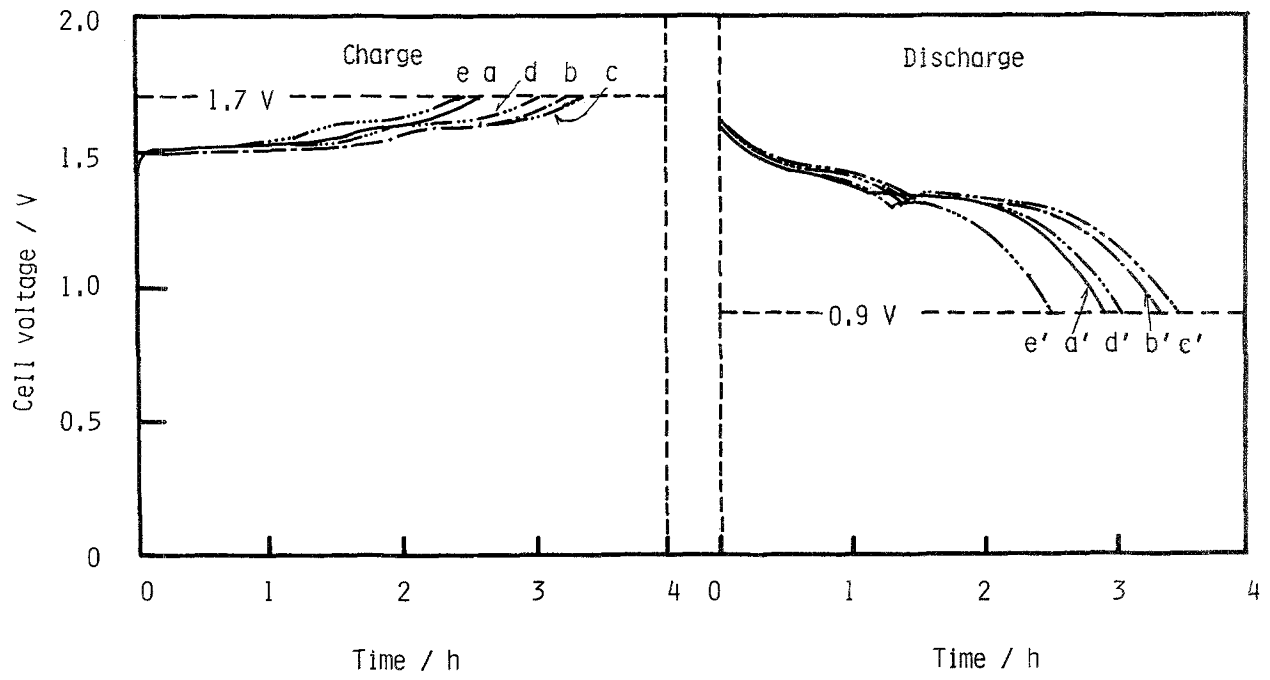

Fig. 6. Controlled charge–discharge profile of the Zn|$ZnSO_4$|MnO_2 (TAD, 40 mg) cell at room temperature (*ca* 25° C) and at 2 mA. The cell was charged to 1.70 V and discharged to 0.9 V. (a and a′): 1st cycle; (b and b′): 10th cycle; (c and c′): 15th cycle; (d and d′): 20th cycle; (e and e′): 28th cycle.

positive electrode materials recovered after the 40th charging showed regeneration of some γ-MnO_2. However, the X-ray diffraction pattern showed many small uncharacterized peaks (especially a relatively strong peak at $2\theta = 18.4°$ (CuK_α)) indicating that the chemical composition of the positive electrode was considerably changed after the 40 charge–discharge cycles.

Other Zn|Zn salt(aq)|MnO_2 type cells (Zn salt = $ZnCl_2$, $Zn(NO_3)_2$, $Zn(PF_6)_2$, $ZnSiF_6$) were also rechargeable to some extent, however their discharging capacities were lower and rechargeability of the cells was not as good as the rechargeability of the Zn|$ZnSO_4$|MnO_2 cell. For example, when the Zn|2 M $ZnCl_2$(aq)|MnO_2 (TAD, 40 mg) cell was charged for 4 h at 2 mA under the same charging conditions as those shown in Fig. 5, the cell gave a discharge time of 2.6 h at the first charge–discharge cycle. However, in the case of this cell, the discharge time dropped steeply with the number of charge–discharge cycles: the discharge times for the 2nd, 3rd and 4th cycles were 1.2, 0.13 and 0 h, respectively. Similar charging and discharging behavior for the Zn|$ZnCl_2$(aq)|MnO_2 cell tested under somewhat different conditions was reported [9]. Use of $Zn(NO_3)_2$ as the electrolyte gave similar results. A Zn|2 M $ZnSiF_6$(aq)|MnO_2 cell was rechargeable more than 30 times, however its current efficiency remained about 25–30% through the repeated charge–discharge cycles.

The superiority of using $ZnSO_4$ as the electrolyte in the Zn–MnO_2 secondary cell seems to be related to the fact that the electrolytic γ-MnO_2 is most effectively produced in aqueous media containing SO_4^{2-} [10]. Cyclic voltammetry for Mn^{2+} in 1 N H_2SO_4(aq) (electrode = Pt) showed good reversibility of the oxidation and reduction of Mn^{2+} and Mn^{4+}, but similar voltammetry in 1 N HCl(aq) did not show such reversibility. A Zn|2 M $(NH_4)_2SO_4$|MnO_2 (TAD) galvanic cell also showed fairly good rechargeability (in this case the term ‘rechargeability’ is mainly concerned with rechargeability of the positive electrode, and the zinc negative electrode seemed to be consumed during the repeated charge–discharge cycle) up to the 10th charge–discharge cycle with about 80% current efficiency when the charge and discharge depth was not high (% utilization of MnO_2 = 15–20).

In the charge–discharge cycle shown in Figs 4–6, the cell was discharged to 0.9 V, and similar repeated charging and discharging were carried out even when the cell was deeply discharged to 0 V in the discharging stage.

When the charging and discharging levels were lower (% utilization of MnO_2 = 16%, charging and discharging at 2 mA for 1 h per 40 mg of MnO_2 and discharging to 0.9 V), the charge–discharge cycle of the Zn|$ZnSO_4$|MnO_2 cell was repeated more than 170 times with slight change of the charge–discharge profile with the number of the cycle. Insertion of a cation or anion exchange membrane between the positive and negative electrodes gave a Zn|$ZnSO_4$|cation or anion exchanging membrane|$ZnSO_4$|MnO_2 galvanic cell. This cell showed similar rechargeability as that of the Zn|$ZnSO_4$|MnO_2 cell. Use of mixtures of water and alcohols (methanol or ethanol, water : alcohol = 90 : 10 (v/v)) instead of water for the solvent to dissolve $ZnSO_4$ gave further Zn|$ZnSO_4$|MnO_2 secondary cells, which showed essentially the same charge–discharge profiles as those observed with the Zn|$ZnSO_4$|MnO_2 secondary cell using water as the solvent.

As described above the Zn–MnO_2 cell using $ZnSO_4$ as the electrolyte showed good discharging behavior.

γ-MnO_2 was regenerated during charging of the cell and consequently the cell was rechargeable. In view of its simple structure, the stability of zinc in aqueous $ZnSO_4$ and the inexpensive nature of the materials, this cell may find practical application.

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