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Effect of bath temperature on electrochemical properties of the anodically deposited manganese dioxide

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Abstract

The effect of bath temperature on the electrochemical properties of electrolytic manganese dioxide (EMD) was studied. EMD was produced by anodic deposition from acidic aqueous solution of manganese sulfate at different bath temperatures in the range of 60–120°C. At temperatures above the boiling point of water, the electrolysis was carried out in an autoclave. The EMD produced at 120°C was of gamma type, identified by X-ray diffraction (XRD). Furthermore, the materials produced at 115 and 120°C were quality-controlled by cycling a sample as cathode mix in small size RAM-cells and by scanning electron microscopy. The results indicated an increase in cyclic charge/discharge performance and an improvement of crystallization conditions of EMD produced at elevated temperature when compared to data of commercially available γ-MnO_2.

Keywords: Electrolytic manganese dioxide; Rechargeable alkaline batteries; Autoclave; Discharge capacity; Electrodes

1. Introduction

Electrolytic manganese dioxide (EMD) is used worldwide as a cathode active material in commercially traded rechargeable alkaline manganese dioxide (RAM^{TM}) cells. The production of EMD having high electrochemical reactivity is one of the greatest problems in the production of rechargeable batteries. Thus, much effort has been directed to synthesizing new structures that exhibit enhanced electrochemical activity.

The nature of the reactants, the pH of the reaction medium, heating temperature and heating duration have dramatic effects on the crystal structure of the phase formed.

It is known that temperature plays an essential role to influence the crystal structure and the physical and chemical properties of MnO_2 [1]. EMDs, produced at low bath temperature such as 60°C, show inferior capacity in comparison with EMDs produced at elevated temperature (96–98°C) [2].

The consequence of the temperature increase is obviously the stabilization of the crystal-structure, which counters itself with volume alteration and collapsing of crystal structures during cyclic charge and discharge of EMD.

It has been reported that not only the applied voltage (should be increased the lower temperature is) but also the anodic current density influence the electrochemical qualities of EMD [3,4]. In practice, energy efficiency for deposition is approximately 40%. The application of higher voltage and energy during deposition of EMD leads to formation and incorporation of soluble 6- and 7-valent manganese species.

It was therefore important to study the influence of elevated electrolysis bath temperature on physical and electrochemical properties of anodically deposited manganese dioxide.

2. Experimental

2.1. Electrodeposition of manganese dioxide

EMD was electrolytically produced in an autoclave at different bath temperatures. The electrolysis was conducted at a current density of approximately 1 A dm^{-2} in 250 ml of 1 M $MnSO_4$ and 0.5 M H_2SO_4 solution. Cell voltage usually floated between 2.3 and 2.4 V. The process took approximately 2.5–3 h per batch. The autoclave was made from aluminum with a volume of 5 l. It was equipped with three valves. Heating was done electrically. The inside temperature of the autoclave, which was measured by means of a

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Table 1
Summary of EMD electrodeposition results

EMD no.	Bath temperature (°C)	Electrolysis cell voltage (V)	Cell pressure (bar)
1 (TOSOH GH-S)	Close to 100	–	1
2	60 ± 1	2.4–2.6	1
3	115 ± 1	2.3–2.5	1.7
4	115 ± 1	3.6	1.7
5	120 ± 1	2.3–2.5	2
6	120 ± 1	2.3–2.5	2.7

thermocouple, was remotely controlled by turning off and on the delivery valves to adjust the desired temperature.

Cell pressure was calculated approximately by application of the Clapeyron formula [5]. A summary of the EMD electrodeposition results is given on Table 1.

EMD deposits were mechanically removed from the anode and washed repeatedly with distilled water. After neutralization with dilute ammonia solution for removal of unoxidized manganous sulfate, the product was ground to pass through a 100 μm sieve. The oxide was washed with distilled water and dried at 100°C to constant weight. The resulting powder was mixed with graphite (Lonza KS44) and acetylene black and compacted to cathode pellets.

2.2. Construction of cells

The electrochemical properties of the EMD were investigated in specifically designed test cells.

These cells could be used several times after opening and replacing separator and electroactive materials. Fig. 1 shows a cross sectional view of the test cell.

The cells were constructed using polymethylmethacrylate (PMMA). They were made up of two main parts, namely, the anodic and the cathodic cap. The front sides of the PMMA were smooth. This provided a gas-tight connection of both parts without using O-rings. All fittings were screwed into position.

At the center of the anodic cap, a brass nail (11 mm) serving as anode current collector, was hot-welded on a brass foil. The brass foil fitted into the threaded hole in the center of the cap.

A graphite can fitted into the threaded hole in the center of the cathodic cap. The graphite can housed the EMD pellet. A copper wire, which was connected to the bottom of the graphite can be used as cathode current collector. Cathode pellet and anode mass were separated by a laminated double-layer separator. When the cell was assembled, the brass current collector rested in the center of the anode mass filling the hole inside the cathode rings.

2.3. Measurements of discharge capacity

A half-cell was used in order to determine the discharge capacity of EMD deposited at 60°C and EMD TOSOH. The reference electrode was zinc and a nickel foil was used as counter-electrode. EMD powder was sieved to a particle size of 100 μm.

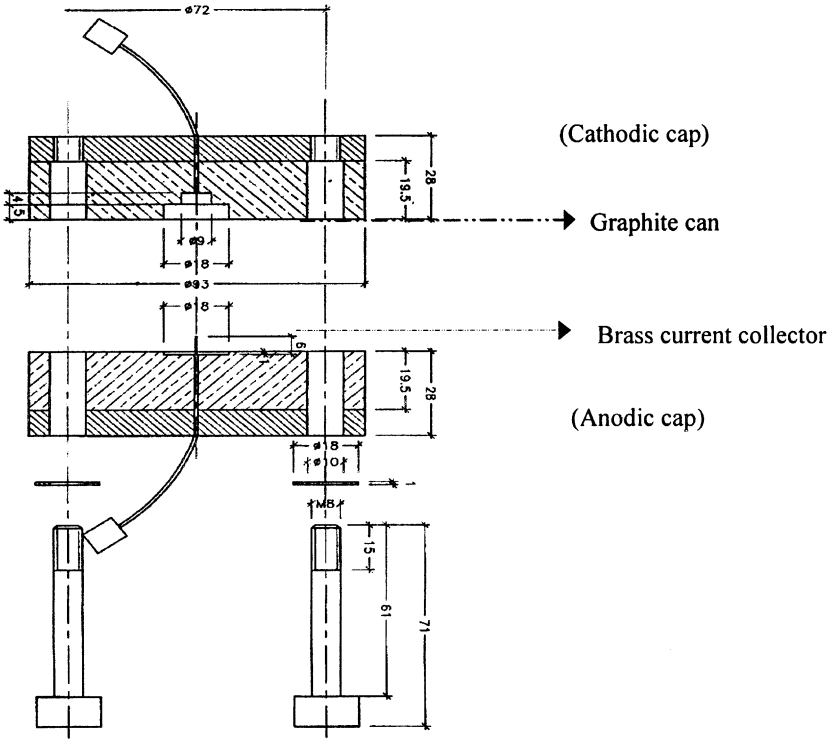

Fig. 1. Sectional drawing (front view) of the test cell (a detailed description is given in Section 2).

The manganese dioxide was pressed on a gold plated brass foil (5 cm^2) at a pressure of 450 kg cm^{-2}. All samples contained 160 mg EMD + 40 mg graphite KS 44. The electrolyte was KOH 9N. Those tests were repeated on samples this time not under pressure.

3. Results and discussion

3.1. Cyclic performance of RAM cells

The positive electrode consists of 360 mg EMD, graphite and additives, which are formed under high pressure (4 tons cm^{-2}) to a cathode ring (pellet). The cathode ring of slightly oversized diameter is inserted into the cavity of graphite can.

Gelled zinc anodes are prepared from zinc powders and additives. The separator is a laminate of a non-woven material and cellophane. The applied electrolyte volume is exactly the same for each cell. The cells are discharged over a 101 Ω resistor. Discharge is stopped at a cut-off voltage (COV) of 900 or 700 mV as given in Table 2.

RAM cells are charged by means of voltage limited taper current charging (VLTC) method to avoid overcharging. Due to voltage-controlled charging to 1.72 V, no overcharge of RAM cells takes place in approved RAM chargers.

The simplified discharge/charge reactions for RAM cells in aqueous potassium hydroxide electrolyte are as follows:

$$\text{Cathode} : MnO_2 + H_2O + e^- \Leftrightarrow MnOOH + OH^- \quad (1)$$

$$\text{Anode} : Zn + 2OH^- \Leftrightarrow ZnO + H_2O + 2e^- \quad (2)$$

$$\text{Overall} : Zn + 2MnO_2 + H_2O \Leftrightarrow ZnO + 2MnOOH \quad (3)$$

The first electron discharge of manganese dioxide proceeds in a homogeneous reaction by the movement of protons and electrons into the lattice, resulting in a gradually decreasing value of x in MnO_x, from $x = 2.0$ to 1.5. The reaction is a reversible conversion of one solid structure (MnO_2) into another (MnOOH). The second electron discharge of manganese dioxide which leads to formation of $Mn(OH)_2$ may progress either in solid phase or in solution. These reactions are regarded as irreversible from the standpoint of recharging γ-MnO_2 [6].

Table 2
Summary of test cells

Cell no.	EMD	Graphite (%)	Cut-off voltage (V)
1	TOSOH	9.5	0.9
2	5	9.5	0.9
3	3	9.5	0.9
4	TOSOH	17.4	0.9
5	5	17.4	0.9
6	4	17.4	0.9
7	5	17.4	0.7
8	3	17.4	0.7
9	TOSOH	17.4	0.7

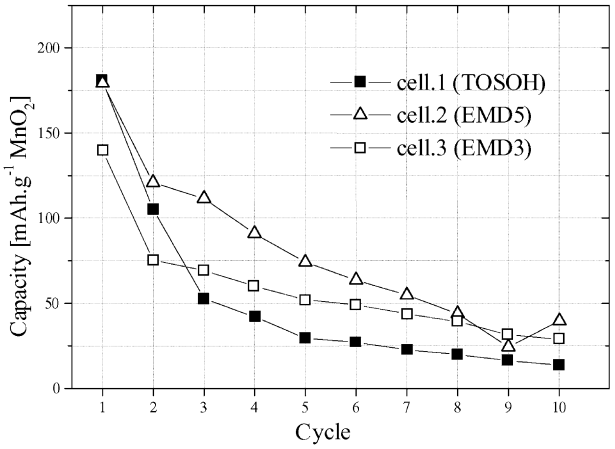

Fig. 2. Discharge performance of RAM cells. A cycle consists of a discharge followed by 3 h charge to a voltage limit of 1.72 V.

Test cells were subjected to various discharge and cycling tests at room temperature (22 ± 2°C) as shown in Table 2. Discharge capacity versus number of cycles were recorded. For a better overview, the cumulative capacities are also represented. The results compared to reference cells made under the same conditions with commercially available γ-MnO_2 (TOSOH GH-S, TOSOH Hellas AIC, Greece, ≤90 μm).

The influence of current density in the process of anodic deposition of EMD (equally effective when done in the autoclave) was investigated by Preisler [7]. Additionally, the impact of graphite quantities in the cathode mix on charge/discharge characteristics of EMD was studied.

Figs. 2 and 3 show that the amount of discharge capacity of cells containing EMD produced at bath temperatures of 115 and 120°C has risen in comparison to cell 1 containing EMD TOSOH. This may be explained by the fact that the anodic overpotential decreases with rising temperature, nucleation rate decreases as well and crystals become larger [8].

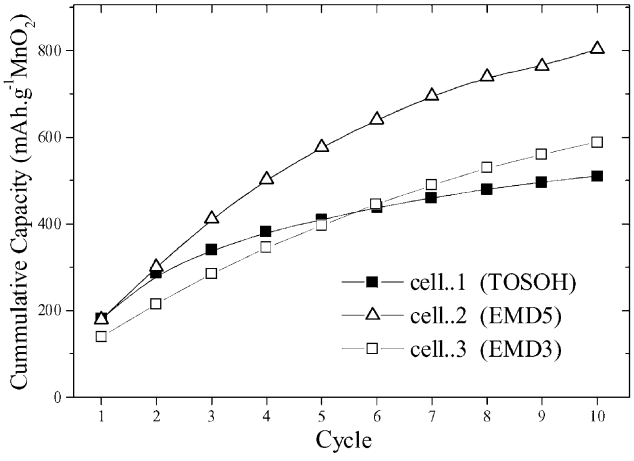

Fig. 3. Cumulated discharge capacity of 1.5 V test cells. Discharge with 45 mA g^{-1} MnO_2 to a COV of 900 mV, charged at 1720 mV for 3 h.

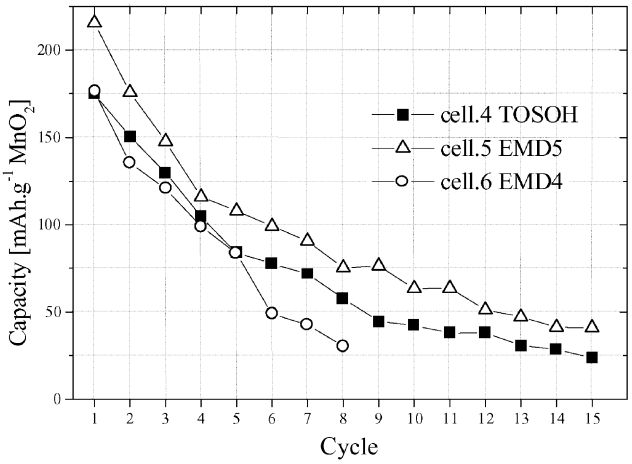

Fig. 4. Discharge capacity of 1.5 V test cells based on EMD4, EMD5, TOSOH as cathode materials. Discharge with 45 mA g^{-1} MnO_2 to a COV of 700 mV, charged at 1720 mV for 3 h.

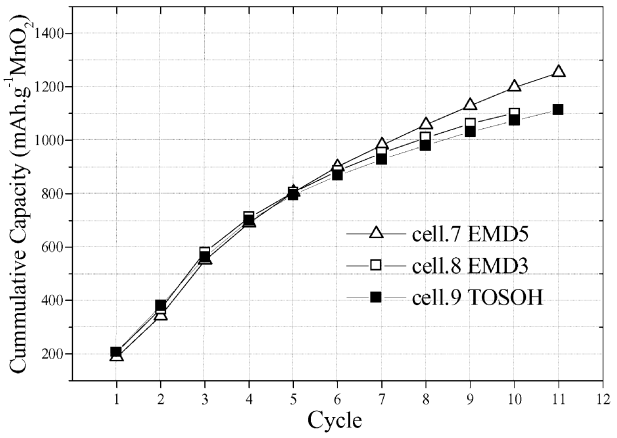

Fig. 6. Cumulative performance of RAM test cells over 11 deep discharge cycles. Discharge with 45 mA g^{-1} MnO_2 to a COV of 700 mV, charged at 1720 mV for 3 h.

Figs. 4 and 5 show that not only temperature but also cell-voltage has dramatic effects on the discharge performance of EMD. The milliampere-hour capacity of EMD (mAh g^{-1} EMD) increases with increasing graphite content. This feature is evident when comparing Figs. 2–5.

Discharge capacity of cell 6 containing EMD4 deposited at 115°C is lower in comparison to the cell 4 containing EMD TOSOH. This is attributed to the application of higher cell-voltage (3.6 V) in the process of anodic deposition of EMD4. Higher cell-voltage results in higher anodic over-potential and this leads to inferior, mossy deposits with low density [9].

Discharge of EMD is accompanied with volume expansion. The lower the COV-value, the more soluble Mn(III)-ions go lost because of volume expansion. The graphite content of cells 6, 7 and 8 is 17.4%, which were discharged to 0.7 V (Fig. 6). The large graphite surface can adsorb the soluble Mn(III) ions. Charge and discharge of these ions can take place on the graphite surface. This ''dissolution–precipitation'' type of mechanism requires a certain amount of electronically conductive surface (graphite!) to work properly [10]. Because of the higher graphite content in cells 7–9 (compared to cells 1–3 in Fig. 3), the difference in discharge capacity of EMD5, EMD3 and EMD TOSOH in the corresponding cells becomes inferior (Fig. 6).

3.2. The effect of mechanical pressure on discharge capacity of EMD deposited at different bath temperatures

For comparison, discharge capacity of standard EMD TOSOH was determined under the same conditions as described in Section 2.3. Graphs 7 and 8 illustrate the strong influence of pressure on discharge capacity of EMD deposited anodically at different bath temperatures (Fig. 7).

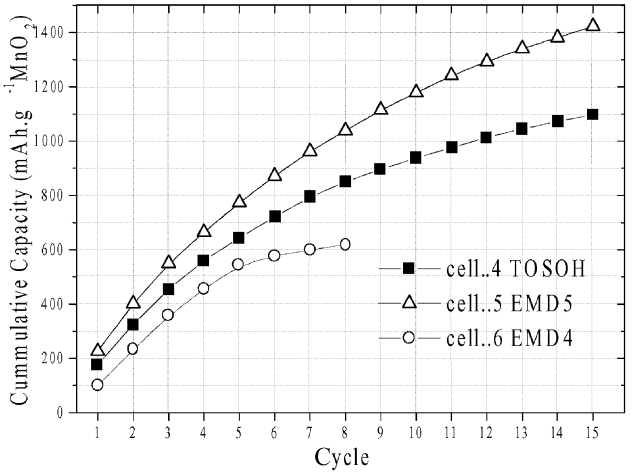

Fig. 5. Cumulative performance of RAM test cells over 15 deep discharge cycles.

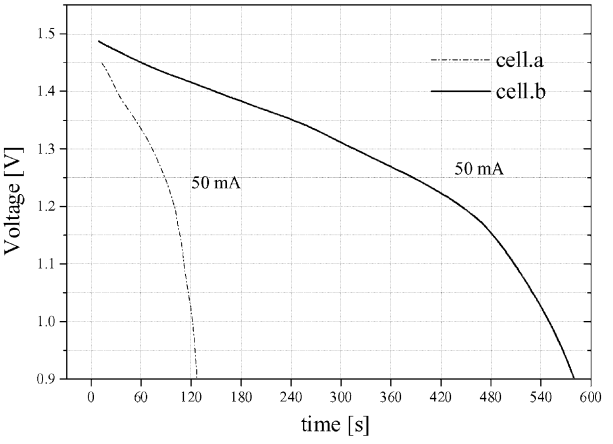

Fig. 7. Discharge–voltage profile of EMD deposited at 60°C (EMD2) at a constant current drain rate of 50 mA. Cell 'a' was not compressed, cell 'b' under pressure of 450 kg cm^{-2}.

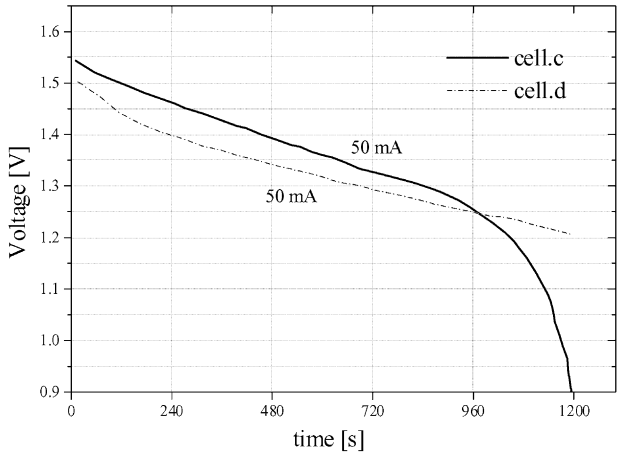

Fig. 8. Discharge–voltage profile of EMD TOSOH at a constant current drain rate of 50 mA. Cell 'c' was not compressed, cell 'd' under pressure of 450 kg cm^{-2}.

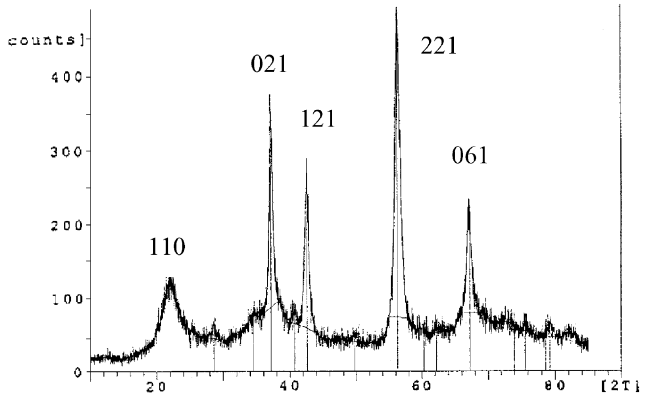

Fig. 9. X-ray diffraction patterns of anodically deposited MnO_2 at 120°C on graphite substrate from a bath containing 112 g l^{-1} $MnSO_4$ and H_2SO_4 1 M.

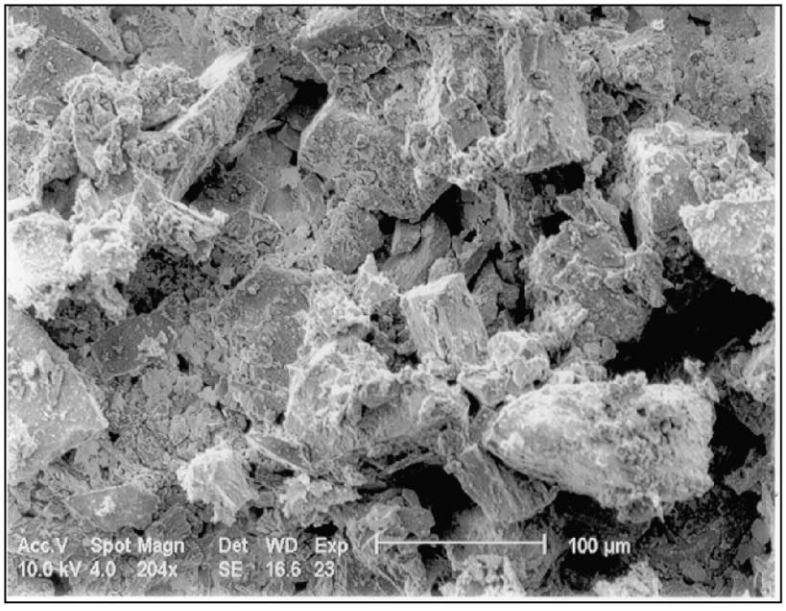

Fig. 10. SEM image of EMD particles produced at 120°C.

The effect of pressure on EMD produced at low bath temperature (60°C) is higher in comparison to EMD TOSOH, which is produced at bath temperature of almost 100°C. This effect can be attributed to higher density and, therefore, better contact of EMD particles produced at higher temperature (Fig. 8).

3.3. X-ray diffraction (XRD) patterns

XRD was used to determine the type of deposited MnO_2 (Fig. 9). The deposit consists of gamma MnO_2. All reflections of manganese dioxide assigned to the gamma modification are in good agreement with those of IC sample no. 2 (IBA Inc., Cleveland, USA).

3.4. Scanning electron microscopy (SEM)

Morphology of EMD particles determined by SEM showed that high temperature induced large EMD crystal particles (Fig. 10).

Investigation results on anodic deposition of EMD showed that EMD deposit morphology depends on bath temperature and anodic current density [7,8].

4. Conclusion

The impact of bath temperature on the electrochemical behavior of EMD used in rechargeable alkaline zinc/manganese dioxide-cells was studied.

High temperature gives rise to high crystallization grade and consequently more structural hardness and better performance in its electrochemical charge and discharge properties.

Obviously, there is a correlation between bath temperature, structural parameters of MnO_2 and the extent of its volume change during discharge.

Lower crystallization grade of EMD leads to facilitated and accelerated volume expansion during discharge and finally to break asunder and a loss of electroactive species in form of soluble manganate ions.

The uptake of ions by the frail structure of EMD in solution can be explained by an adsorption process. Because of the infirm structure of low-temperature produced EMD, it can adsorb many ions like potassium-ions from the solution. The consequence is that the crystal-structure of gamma MnO_2 changes to the electrochemically inactive form [11].

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