

Effects of direct and pulse current on electrodeposition of manganese dioxide

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Abstract

The physical and chemical properties of electrolytic manganese dioxide (EMD) are determined predominantly by the conditions employed during the anodic deposition process. There are relationships between deposition parameters, EMD properties and battery performance, as reported in many investigations. This study describes the influence of pulse current and direct current on the electrochemical properties of EMD. The EMD produced at different current conditions is characterized by charge–discharge cycling of various samples in the cathodic mixture of rechargeable alkaline AA cells, whereby the anode composition and the other cell parameters are kept constant. Results have shown that there is a systematic correlation between the pulse parameters and the cycle performance of EMD. The charge–discharge characteristics of test cells indicate an improvement in cycle performance of EMD with increasing duty cycle (i.e. with the approach of pulse current to direct current).

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1. Introduction

With the introduction of rechargeable alkaline MnO₂/Zinc batteries (RAMTM) many attempts were made to increase the possible depth of discharge (DoD) and the number of charge–discharge cycles (cycle-life) as well.

It is well-known that the initial deep discharge of the MnO₂ cathode results in a decrease of cycle-life. To improve the rechargeability of EMD, attempts were made to study the correlation between electrolysis conditions, structural parameters and their influence on electrochemical properties of EMD.

EMD is generally produced by anodic deposition using acidified aqueous solutions of manganese(II)-sulfate as the electrolyte. Since, the dc current density affects the electrochemical properties of EMD [1,2], it was therefore interesting to study how pulse current parameters can influence the charge–discharge characteristics of EMD.

One important feature of pulse electrolysis is the ability to generate high instantaneous current densities and hence very high positive potentials at the anode. The high overvoltage changes the rate relationship of the reactions. Therefore,

pulse current can create a new deposition mechanism [3,4]. There are also many types of agitation that can help replenish ions in the bath along with on–off pulsing.

Investigation of the properties of deposited manganese dioxide, using both pulse current and conventional direct current can lead to a better understanding of the electrocrystallization mechanism.

2. Definitions

Pulse electrodeposition (PED) refers to deposition where the potential or current density is alternated rapidly between two different values. This is accomplished with a series of pulses of equal amplitude, duration and polarity, separated by periods of zero current. Each pulse consists of an ‘on’ time during which potential and current is applied, and an ‘off’ time during which open-circuit potential and zero current is applied. During the portion of the cycle when the current is off, metal ions from the bulk solution diffuse into the layer next to the anode. When the ‘on’ time for the pulse occurs, more evenly distributed ions are available for deposition. A pulsing scheme with one segment ‘on’ at an applied current and another segment ‘off’ at zero current is shown in Fig. 1. An oscilloscope is used to reveal how well the equipment controls the output.

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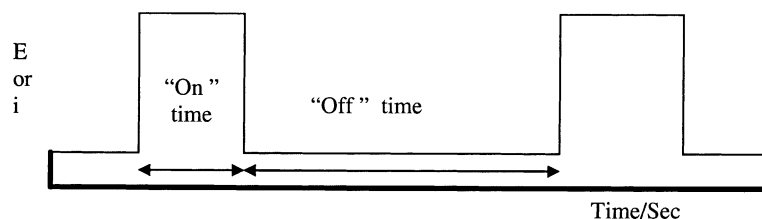


Fig. 1. Shape of pulsing scheme for electrodeposition.

The electrochemical behavior of EMD can also depend on the relative kinetics of these reactions.

From the above reactions, it is obvious that the pH value in the bath is of great importance, since free hydrogen ions play an important role in the deposition mechanism of EMD, which the participation of Mn^{4+} , Mn^{3+} , H^+ , and OH^- [7]. It is equally obvious that both the concentration of manganese ions near the anode and the current density (available electrons) exert an influence on the deposition process. The bath temperature has a large effect on the speed of the reactions and, hence, on the electrochemical of anodically deposited manganese dioxide [8]. In order to obtain comparable results, the experiments reported here were performed at constant temperature.

3. Experimental

The electrolyzer consisted of three lead electrodes (one anode, two cathodes) fixed in a plexi glass support mounted at the cell top (Fig. 2). The electrodes were separated by

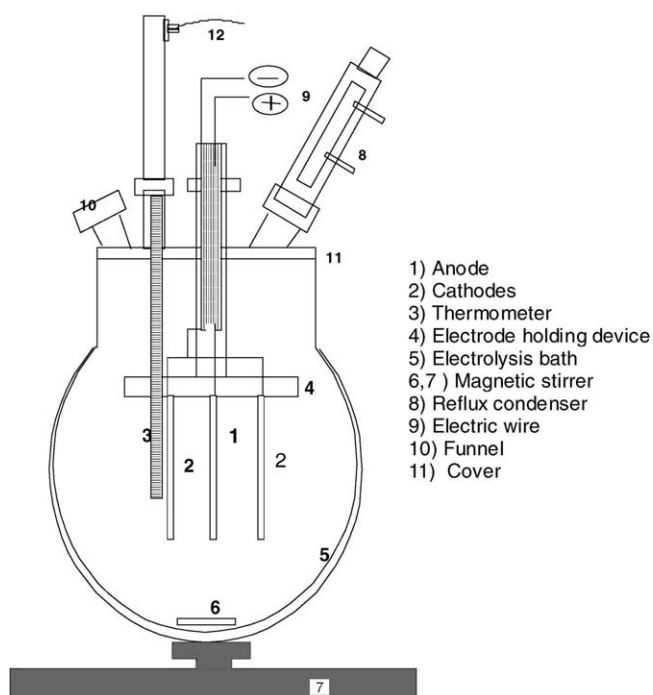


Fig. 2. Device for electrodeposition of EMD.

spacers made of PVC. A four-necked, 3 l, round bottom flask served as the electrolytic bath. The electrodes were immersed vertically in the bath which was maintained at $97 \pm 1^\circ C$. The electrolyte was heated by an electrical heater and the condensate was regained using a reflux condenser made from laboratory glass. A thermometer inserted through the cell cover was used to measure the temperature of the electrolyte. A Teflon-coated magnetic stirrer served to circulate the electrolyte during deposition experiments. Bath composition was: sulfuric acid: 98 g l^{-1} , manganese sulfate: 112 g l^{-1} . EMD was deposited using direct and pulse current. A microcomputer connected to a dc source was used to generate a rectangular pulse voltage signal of desired magnitude, duty cycle, and pulse period. The peak pulse current and the time-averaged dc current during each experiment were monitored.

The electrodeposition of EMD was performed over a range of anode peak current densities from 1.8 to 23.2 A dm^{-2} , a pulse frequency of 9 – 167 Hz , and duty cycles of 4 – 100% . The peak current, 'on' time or 'off' time could be adjusted.

EMD deposits were mechanically removed from the anode and rinsed with water. After neutralization with dilute alkali solution and repeated washing with distilled water and drying, the product was ground and sieved through a wire mesh with a screen opening of $100 \mu\text{m}$.

In this paper, the following abbreviations are used [5]:

- peak current is the maximum current output during the 'on' time, i.e.:

$$\langle i_p \rangle = \frac{\text{peak current}}{\text{anode area}} \quad (1)$$

where i_p is the anode peak current density;

- duty cycle = on time/(on time + off time), in percentage;
- average current = duty cycle \times peak current:

$$\langle \bar{i}_a \rangle = \frac{\text{average current}}{\text{anode area}} \quad (2)$$

where \bar{i}_a is the average anode current density;

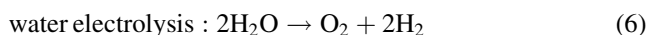
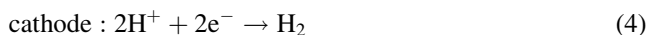
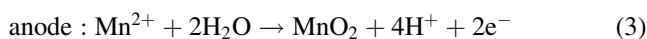
- the sum of 'on' time and 'off' time is the pulse period (T);
- frequency: pulse rate expressed in Hertz, i.e. pulses per second, $1/(\text{on time} + \text{off time})$, assuming neither on time or off time = 0;
- pulse width: time span of 'on' portion of a pulse; pulse width is a function of both frequency and duty cycle.

Table 1
Cathode and anode composition used in AA batteries

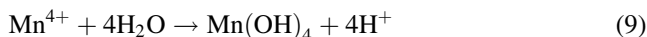
Cathode composition	Deposition (wt.%)	Anode composition	Deposition (wt.%)
EMD	90.0	Zinc	61.5
Graphite	9.2	ZnO	3.4
Acetylene black	0.5	MgO	2.0
		Alfa cellulose	1.0
Polytetrafluorethylene (PTFF)	0.3	Starch (Farinex 273)	1.1
		KOH (12 normal)	31.0

4. Electrodeposition kinetics of EMD

The deposition of manganese dioxide takes place through a number of intermediate steps, as follows [6]:



The mechanism of the electrodepositing reaction of EMD at the anode is:



The resulting powder was mixed with graphite and acetylene black and compacted into cathode pellets (Table 1).

Sample cells (AA size) were assembled using different products. Testing of samples was undertaken with computer-

controlled test equipment. The cells were cycled and compared with standard reference cells made with industrial EMD (TOSOH Hellas, Greece). The cells were discharged through a 3.9Ω resistor with a discharge cut-off voltage of 900 mV. The voltage limited taper current (VLTC) charging method was used to charge cells to 1.72 V. The discharge capacity and the discharge time were recorded.

For each deposition experiment, the total charge Q was measured. This value can, together with the total weight of deposited EMD, be used for calculating current efficiency, θ , i.e.:

$$\theta = \frac{(W_{\text{MnO}_2}/M_{\text{MnO}_2})Fz}{Q} 100\% \quad (11)$$

where F is $96440.4 \text{ C mol}^{-1}$ (Faraday's number); z the differential atomic charge (for $\text{Mn}^{2+}/\text{Mn}^{4+}$, z equals 2); M_{MnO_2} the molar weight of EMD (85.4 g mol^{-1}); W_{MnO_2} the total weight of deposited EMD.

5. Results and discussion

Results showed that different current conditions (direct or pulse) alter significantly the electrochemical properties of EMD. For comparison of results, the average direct and pulse current densities must be equal, or must remain at the same level. There are several reasons for the observed negative effect of pulse deposition or the positive effect of dc on the electrochemical behavior of EMD.

5.1. Current efficiency

The average anode current efficiency for EMD deposition in the range $0.5\text{--}3.75 \text{ A dm}^{-2}$ is given in Fig. 3. Current efficiency data listed in Table 2 show that efficiencies $>90\%$ can be obtained at lower average current densities in the

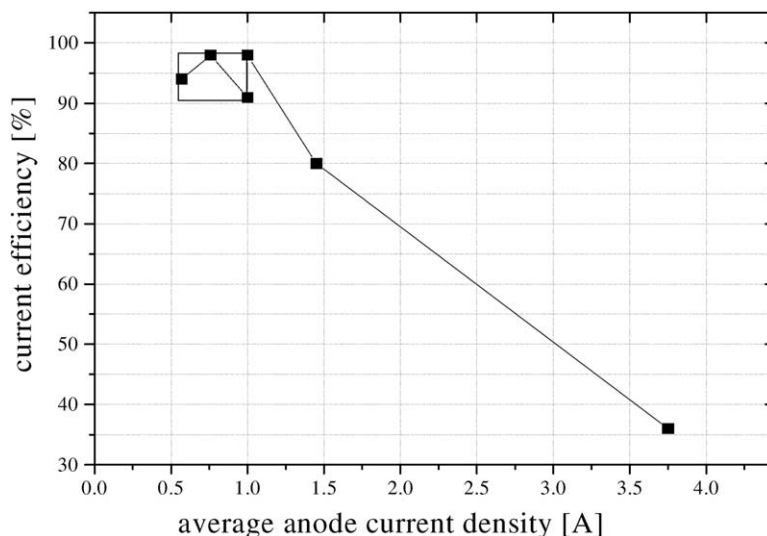


Fig. 3. Decreasing current efficiency with increasing current density.

Table 2
Pulse and dc electrolysis parameters during deposition of manganese dioxide

Cell	1	2	3	4	5	6	7	8 (dc)
Peak current (A)	41.8	18.02	18.2	11.4	18	2.42	2.4–2.6	–
Average current density (A dm ⁻²)	1.8	1.02	1.95	1.9	6.75	0.968	1.77–1.92	–
Anode peak current density I_p (A dm ⁻²)	23.2	10.07	10.08	6.33	10	1.9	1.85–2	–
Average anode current density (A dm ⁻²)	1	0.57	1.08	1	3.75	0.759	1.39–1.51	1
Charge (A min)	1805	1715	1770	1753	1825	1736	1883	–
On time (ms)	0.9	6	6	1	6	40	75	–
Off time (ms)	20	100	50	5	10	60	25	0
Current efficiency (%)	91	94	96	98	36	99	80	95
Duty cycle (%)	4.3	6	10	17	37.5	40	75	100
Frequency	47.8	9.4	17.86	167	62.5	10	10	–
Pulse width	1.912	0.564	1.79	28.3	23.4	4	7.5	–

range 0.5–1.1 A dm⁻². The dc anode current efficiency of the bath is nearly 95%, as anticipated. Generally, the same average current density, I_a is used for comparison between pulse and dc experiments.

Decreasing current efficiency is a consequence of an increase in anode current density. As may be expected, the lowest values are obtained when the average current density is high. At high anodic potentials, oxygen evolution may inhibit the deposition, decrease the current efficiency or may become a competitive reaction for EMD deposition.

Because of higher average anode current density in cell 7 (1.4–1.5 A dm⁻², Table 2), a low current efficiency (~80%) was recorded compared with other cells. This reduced efficiency and the associated average anode current density obviously had no notable influence on the electrochemical behavior of EMD. At higher current densities, the electrolysis of water is activated. In cell 5, with a high average current density of 3.75 A dm⁻², the current efficiency fell to 36%.

5.2. High overvoltage in pulse electrodeposition

For a given time at average current density, the average activation overpotential in pulse electrodeposition is different from that with dc [9,13]. The average activation overpotential versus average dc current density relation can be obtained from a set of empirical polarization data in the form:

$$\bar{\eta}_a = f[\bar{i}_a, T, \Theta] \quad (12)$$

where \bar{i}_a and $\bar{\eta}_a$ denote the average values of current density and activation overpotential at the anode (anodic deposition), T is the pulse period, Θ the duty cycle. For a given electrolyte system and a pulse current with a fixed duty cycle and pulse period, function f is determined from experimental measurements of the polarization.

A high instantaneous current density is used in pulsed electrodeposition. It is therefore important that the conductivity of the electrolyte is maintained at a high level to allow the peak pulse current to be completely effective, otherwise IR drop and cell overvoltage will become very high. During 'on' time, because of the higher activation energy required

for gas evolution reactions or of the inadequate conductivity of the EMD electrode, an excess in voltage will be necessary to attain the desired peak current. This can affect the composition and, therefore, the electrochemical quality of EMD.

The energy of formation of the EMD grain nucleus depends on the electrode overpotential [10,11]. A large electrode overpotential favors nucleation through a decrease in the energy of nucleus formation.

Thus, reduction in grain size is possible with a short 'on' time combined with high peak current densities. Under these conditions, the number of nuclei increases, the crystallites become smaller and the contact or adhesion between particles is impaired.

Many investigations have shown that using dc for deposition fills the pores non-uniformly [12]. Dies can positively affect the electrochemical behavior of EMD with respect to electrolyte penetration. Pulse electrodeposition can produce uniform and dense fine-grained deposits [13] with reduced porosity. Accordingly, the passage of electrolyte or ion transport in the EMD crystal becomes impeded. This results in EMD with inferior electrochemical behavior.

In addition, due to the presence of a higher voltage compared with dc, the deposition of metal impurities is favored. Metallic impurities in electrodeposited samples can originate from impurities in the chemicals used for the bath, inclusions of electrolyte, and contamination from external impurities or electrode materials. The deposition of impurities depend on the duty cycle and is more likely with pulse electrodeposition than with the dc counterpart.

5.3. Duty cycle

The deposition rate in the pulse technique is governed by the pulse current and other parameters such as 'on' time and 'off' time. At a given peak current, the relationship of the last two parameters (duty cycle) determines the average current density.

'On' time has a significant influence on current distribution and grain size. After a strong pulse, when the electrolyte in the vicinity of the electrode is depleted in cations, material

supply occurs in the ‘off’ time during which adsorption and desorption phenomena can occur. The ‘off’ time also allows the diffusion of reaction products (e.g. H^+) that can adversely affect the electrodeposition reaction.

Despite the use of the same anode peak current density in cells 2, 3, 5 (Table 2), the cycle performance of EMD is changed. In fact, the peak current (or anode peak current density) is not the only crucial option for the diffusion-controlled process. Rather, the percentage (duty cycle) of peak rating, or the average current determines the diffusion-controlled mechanism and hence the electrochemical behavior of EMD.

Results show that at a low average anode current density ($0.5\text{--}1.5\text{ A dm}^{-2}$), the duty cycle alone controls the charge–discharge characteristics of EMD (cf. cells 6, 7 and 2, 3, Table 2).

With high peak current but small duty cycles, the process runs at a low average current (cell 1). In this case, depletion of the concentration of metal ions at the electrode surface cannot occur and the process does not become diffusion-controlled [14–16]. Thus, degradation of the characteristics with a low average current regime may have compositional [17], morphological or crystallographic causes. General trends of increasing AA cell capacity with increasing duty cycles in the low current density regime are shown in Figs. 4 and 5, i.e.:

Cell	Duty cycle (%)	Cycle performance
7	75	>
6	40	>
4	17	>
3	10	>
2	6	>
5	37.5	>
1	4	>

Clearly, cell 5 is an exception in this sequence. Electrolysis in cell 5 was carried out under a high average anode current density (Table 2). This impairs the electrochemical properties of the EMD since the deposition becomes diffusion-controlled.

Another consequence of a decreasing duty cycle would be uneven deposit distribution. Generally, pulsing will influence deposit distribution more than dc electrodeposition [18]. For the same amount of charge, pulsing will increase thickness in the high current density areas compared with dc. This shows that the local current density in pulsed electro-deposition can be very different and no homogeneous current distribution is present.

5.4. Average anode current density

At a high average anode current density, the rate of electrodeposition is greater than that of the transport of ions to the electrode. After that time, the concentration of metal ions in the vicinity of the anode is reduced to the extent that the process becomes diffusion-controlled. Diffusion effects only become important, however, when the concentration of reacting species at the electrode surface is zero.

In particular, the anodic ‘on’ time and the average anode current density control the diffusion layer thickness and the transition time of the deposition process [19,20]. The thickness is proportional to the ‘on’ time and therefore, allows control of the grain size. The transition time (t) is the time for the concentration of reacting species at the electrode surface to drop to zero and is inversely related to pulse current density (i_a), i.e.:

$$t = \frac{(nF)(2C)(2D)}{2(2i_a)} \quad (13)$$

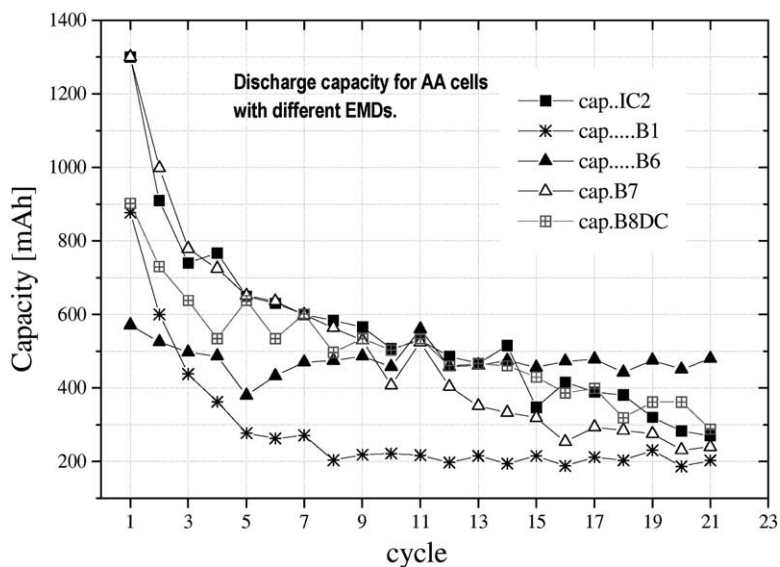


Fig. 4. Discharge capacity of 1.5 V RAM cells based on EMD cathode materials produced under different pulse and dc electrolysis conditions. Discharge at $30\text{ mA g}^{-1}\text{ MnO}_2$ to cut-off voltage of 900 mV, charged at 1700 mV.

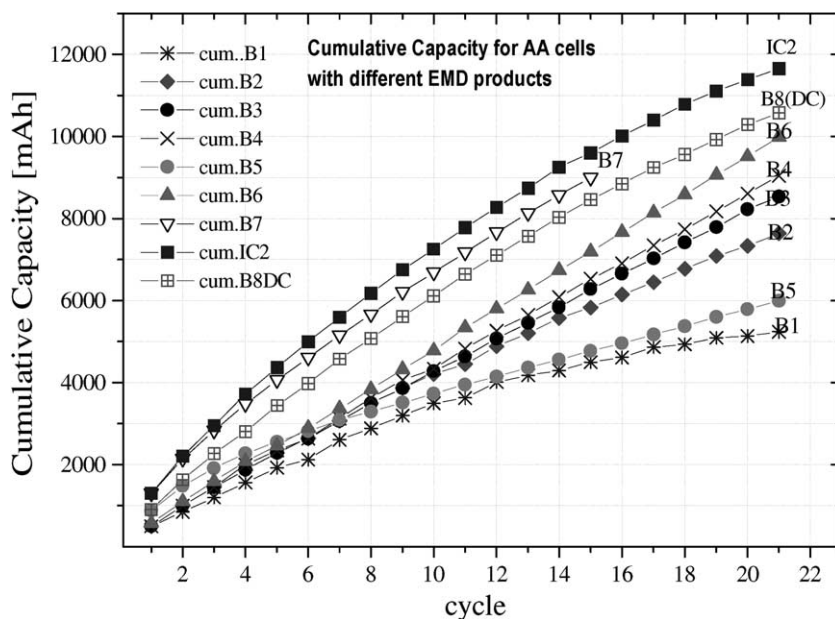


Fig. 5. Cumulated discharge capacity of RAM cells.

where the number of electrons (n), the diffusion coefficient (D), Faradays constant (F), and the reactant concentration (C) are all constants. Consequently, when the pulse ‘on’ time is much longer than the transition time, that is for a high anode current density, diffusion effects have a significant influence on the current distribution and on the electrochemical properties of EMD (cell 5, Table 2).

Mass transport limitations result in a depletion of metal ions at the electrode surface. This lowers the reaction rate and also results in accumulation of reaction products and oxygen evolution. The latter could become the dominant process, especially in the case of pulsed deposition. Therefore, bubbles might be incorporated into the deposit and inhibit homogeneous deposition and cause preferential deposit growth. In this regard, the influence of temperature must also be considered. In general, a high temperature increases the deposition rate and current efficiency by enhancing diffusion. This, in turn, causes enhanced crystallinity and grain growth of the deposit. In order to obtain comparable results in this work, the temperature was held constant at 97 ± 1 °C.

5.5. pH

According to the induced mechanism, generation of hydronium ions is an inherent part of EMD deposition. Since the overpotential can be influenced by the pH value, an optimum pH value is required to minimize the overpotential of deposition process. Thus, the solution pH can influence the physical and chemical properties of the deposit and local pH change can result in a shift of complexation equilibria during EMD deposition [21,22].

It was identified that galvanostatic pulsing with a long relaxation time can manage the local pH change [23]. Under

test condition, we have not observed any positive effect of pulse current on electrochemical properties of EMD in this regard. An interpretation would be that pH alteration is not a significant factor for EMD properties in the experimental approach adopted in this work.

6. Conclusions

The electrochemical properties of electrodeposited EMD are governed by a number of pulse parameter. Pulse electrodeposition changes the cycle performance of EMD deposits and the charge–discharge characteristics are influenced by the duty cycle and the anode current density I_a . At comparable low average anodic current density, direct current can be used to give improved cycle performance of EMD compared with pulse electrodeposition. Generally, pulse parameters, bath composition, and structure and chemical properties of deposits are not independent of each other [24]. Further investigation of the composition, morphology, crystal characteristics and the mechanism of structure formation of EMD particles is necessary using various pulse parameters.

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