

New advances on bipolar rechargeable alkaline manganese dioxide–zinc batteries

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Abstract

Bipolar rechargeable alkaline manganese dioxide–zinc (RAM) batteries are produced in the laboratory. These are obtained through minimizing the passivation problems associated with the zinc electrode, which is considered to have a limiting effect on the charge–discharge cycle performance. To overcome this, different tin alloys are employed in the zinc negative electrode (anode). A relationship is observed between the tin alloying elements, as current-collectors, and gas evolution during the cycling. A copper–tin–zinc ternary alloy (trademark: Optalloy) displays better corrosion resistance and a higher hydrogen overvoltage, when used as the anode current-collector.

To increase the electrochemical reversibility and electronic conductivity of the anode mass, porous zinc is treated with Optalloy. This is to obtain a modified zinc electrode, which is found to be effective in terms of raising the cycle performance of the bipolar RAM batteries. Moreover, optimum electrical contact between the electroactive materials and the conductive carbon-filled polyethylene matrix is achieved through coating graphite on the cathode as well as electroless plating of copper on the anode side. It is evident that copper acts as an underlayer for the current-collector.

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Keywords: Rechargeable alkaline manganese dioxide–zinc batteries; Bipolar electrodes; Carbon-filled polymer; Optalloy

1. Introduction

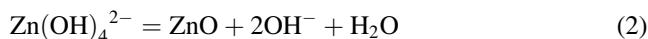
Apart from economical and environmental considerations, one of the factors that is effective in determining the success of a battery system is the energy content with respect to unit weight and volume [1,2]. In order to maximize the power output of a cell, methods for reducing the internal resistance of the electrode and minimizing ohmic (IR) losses must be employed [3,4]. High-performance batteries require large cross-sectional areas, homogeneous current distribution and uniform utilization of the electrode active materials [5]. Proper design of thin bipolar electrodes can meet such requirements.

Attempts have already been made to realize the concept of bipolar of rechargeable alkaline manganese dioxide–zinc (RAM) batteries [6–8]. To date, several obstacles such as electronic contact resistivity, electrolytic bridges between adjacent sub-cells, zinc corrosion and gassing have prevented attainment of this objective.

The zinc electrode, due to its high energy per unit volume and high hydrogen overpotential is a very suitable negative (anode) active-material for use in aqueous electrolytes. The electrochemical reaction of the zinc electrode in a battery proceeds *via* the following dissolution–precipitation reaction [9]:



An independent chemical decomposition of zincate may also occur to form a passive film of zinc oxide, i.e.



The high solubility of ZnO in KOH solution leads, in turn to a redistribution of active materials and a non-uniform deposition of zinc during the recharge. This results in a reduction in the geometric area and a shape change [10]. Other problems are the formation of dendrites and the development of inter-electrode short-circuits.

Many attempts have been made to improve the cycle-life of zinc electrodes [11–15]. It has been found that some organic and surface active agents can eliminate dendrite

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growth [16,17]. Other additives such as graphite and metal powder can act as electronic contacts between the zinc particles [18,19]. Some of these may cause passivity, gassing and/or lowering of the specific energy [20].

Therefore, suitable materials are those with good electrical conductivity, adequate mechanical stability, and inertness to electrochemical reactions. Employment of these materials may serve to optimize the current distribution and avoid different local current densities, which may cause dendrite growth and/or redistribution of zinc particles [10].

Polyalloys have been developed to provide the required specific coating properties and are generally obtained *via* depositing several layers. In this work, a physicochemically suitable ternary alloy composed of copper:tin:zinc (55:25:20) is used in the zinc anode. Optalloy is a trademark of Werner Flühmann AG, Dübendorf, Canton Zürich, Switzerland. The electrodeposited layer is bright, silver-white in appearance and has high resistance to tarnish and abrasion. It is well known for its hardness, good conductivity, and good electrochemical properties. Optalloy shows a specific low electric resistance of $40 \mu\Omega \text{ cm}^{-1}$ [21]. It acts like a noble metal with an open-circuit voltage (OCV) of about -700 mV more positive in comparison with some binary tin alloys. Moreover, a very thin sheet of this alloy, of the order of $2\text{--}4 \mu\text{m}$, can meet all usual corrosion test requirements.

Application of Optalloy in the zinc anode demands a unique distribution on the microscopic scale. This is to obtain good electrical and mechanical properties. Therefore, electrodeposition of Optalloy was carried out on a porous zinc electrode, in order to obtain a modified zinc electrode. With these precautions, the operational parameters, especially the current profile during cycling exerts less influence on the expected cycle-life. Nevertheless, these have not been many studies of the possible usage of Optalloy in electrochemical systems.

Using a plastic matrix instead of metals leads to a considerable reduction in battery weight [8]. Kordesch conducted pioneering studies on the use of plastic-carbon compounds in the construction of bipolar electrodes [22], and the work was continued by other workers [23,24]. Through the use of conductive plastics with fillers, like graphite and soot, many technical and environmental problems are reduced or eliminated. Good electrical contact between the anode mass and the conductive polyethylene (PE) matrix can be achieved by using electroless copper as an underlayer for the current-collector. The most important properties of the chosen pre-metal used are its adhesivity to substrate and its non-porous structure. Both of these seem to be fulfilled when electroless copper is employed [25]. An electrodeposited thin layer of Optalloy as the current-collector on electroless copper serves to prevent the direct contact of copper and zinc. In this work, electrodes composed of zinc gel and MnO_2 discs are serially stacked in order to make bipolar RAM batteries.

2. Materials and methods

2.1. Electrodeposition of binary and ternary tin alloys and preparation of modified zinc anode

Typical bath formulations and operational parameters used to obtain copper–tin–zinc (55:25:20) and tin–zinc (98:2) deposits on a pure zinc foil are listed in Table 1. Manufactured foils (9 cm^2) were used as anode current-collector in the C-size (LR-14) RAM cells.

In order to produce modified zinc, a porous zinc deposit was prepared with around 12 A dm^{-2} . This was obtained using a saturated alkaline zincate solution. The chemically modified zinc was prepared through direct dipping of a porous zinc electrode in Optalloy electrolyte, using a dual-bath technique. The procedure was performed repeatedly with a few minutes residence time, in each bath. After the electroplating, the plated samples were thoroughly rinsed in running distilled water. This treatment eliminated cross-contamination between the solutions. The transfer operation was carried out rapidly in order to avoid any surface passivation. Films of Optalloy formed on the external surface as well as on the inner surface of the porous zinc. The analysis of the modified zinc resulted in 1.25 wt.% of copper and 0.55 wt.% of tin. This corresponded to 2 to 2.5 wt.% of Optalloy in the zinc–Optalloy composite.

2.2. Measurement of corrosion of anode current-collector in C-size RAM cells

A gasometric method was used to measure the rate of hydrogen evolution. Tin, brass, Optalloy and tin–zinc alloy were investigated as to their corrosion behaviour and their quality as anode current-collectors. The materials in the form of rectangular strips of uniform size were used as anode current-collectors in C-size, mercury-free, RAM batteries.

Table 1
Electrolyte composition and operational parameters used for electroplating of Sn–Cu–Zn and Sn–Zn alloys

Material	g l^{-1}	
Optalloy		
CuCN	3	
Na_2SnO_3	2	
$\text{Zn}(\text{CN})_2$	1.4	
KCN	42.55	
KOH	19.8	
K_2CO_3	23.03	
Sn–Zn alloy		
ZnCN	4.5	
NaOH	5	
NaCN	28	
Operational parameters	Optalloy	Sn–Zn
Current density (A dm^{-2})	0.5	1
Bath temperature ($^\circ\text{C}$)	45	RT

The battery was fitted in the hollow space of a pressure cell which was equipped with a pressure sensor [26]. All cells were overcharged at 2 V and discharged through a 1.2 Ω resistance to a cut-off voltage of 0.9 V. The extent of corrosion of each sample was measured at various temperatures, namely, at 25 °C for the first four cycles and at 45 °C for the fifth cycle.

2.3. Cyclic voltammetry

Cyclic voltammograms for brass, tin and Optalloy were obtained in 40% KOH. The solution was saturated with zincate ions. A three-electrode cell assembly was used with a Hg/HgO reference electrode and a large platinum foil as the counter electrode. Polarization experiments were performed by means of TACUSSEL PJT 35-2 potentiostat in the range -1100 to -1900 mV at a constant scan rate of 10 mV s^{-1} . Three successive scans were recorded and compared for each sample.

2.4. Construction of polymer matrix and bipolar batteries

Polyethylene conductive foils, with a thickness of 2 mm and a specific resistance of $\rho = 2 \Omega\text{cm}$ were supplied by the Zipperling Company, Hamburg, Germany. Due to the poor adhesion of electroactive materials to the plastic matrix, conductive PE foil cannot be directly used as a current-collector. In order to obtain an effective adhesivity, the plastic foil was processed with two different preparation procedures. In the first process, the cathodic face of the polymeric foil was coated with graphite, using an optimized temperature in the range $100\text{--}110$ °C and a pressure of 6 t cm^{-2} . Then back-side metallizing of the PE foil was applied before the subsequent electroplating (Fig. 1). The surface pretreatment of the PE plastic included: cleaning, roughening, activating, and electroless copper plating. The roughening process was done with a mixture of sulfuric acid (240 g l^{-1}) and chromic acid (350 g l^{-1}) in a temperature range of $65\text{--}70$ °C. The plastic foil before and after

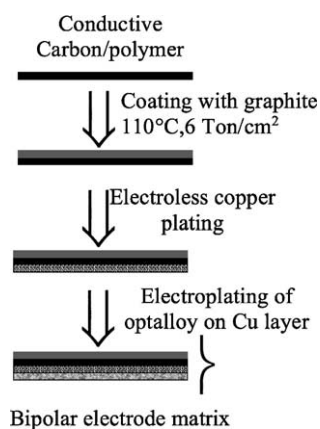


Fig. 1. Schematic representation of coating process of bipolar electrode matrix.

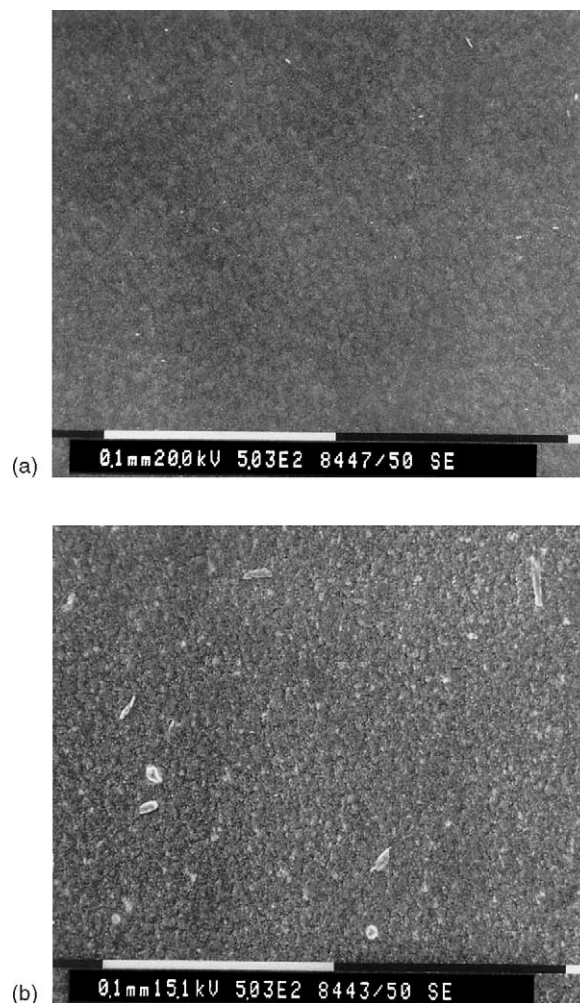


Fig. 2. Conductive polyethylene foil: (a) before surface pretreatment; (b) after surface roughening.

pretreatment in acidic media is shown in Fig. 2a and b, respectively. The PE was activated and then immersed in a commercial electroless plating bath for 5 min [27]. The electroless copper layer provided an adherent conductive base for subsequent plating. To avoid contact corrosion of the zinc–copper couple, the surface of the thin copper layer was plated with Optalloy. This was prior to the addition of the zinc anode gel. The multilayer plastic matrix was finally covered with a layer of graphite (on the cathode side). A thin layer of Optalloy, deposited on electroless copper layer, acted as an anode-current-collector (Fig. 1). The matrix of the bipolar electrodes was cut into circles of 18-mm diameter. Two Teflon washers were fixed on both sides of the matrix. The washers were 1.5 mm in thickness, with an external diameter of 18 mm and an internal diameter of 13 mm. The two washers provided the necessary space for fixing and keeping both the cathodic disc on the graphite, and the anodic gel on the Optalloy surface.

The anode components consisted of zinc powder (amalgamated (Hg: 1.4 wt.%) or modified), ZnO (4.86 wt.%), MgO (2.86 wt.%) and carboxy methyl cellulose (2.68 wt.%).

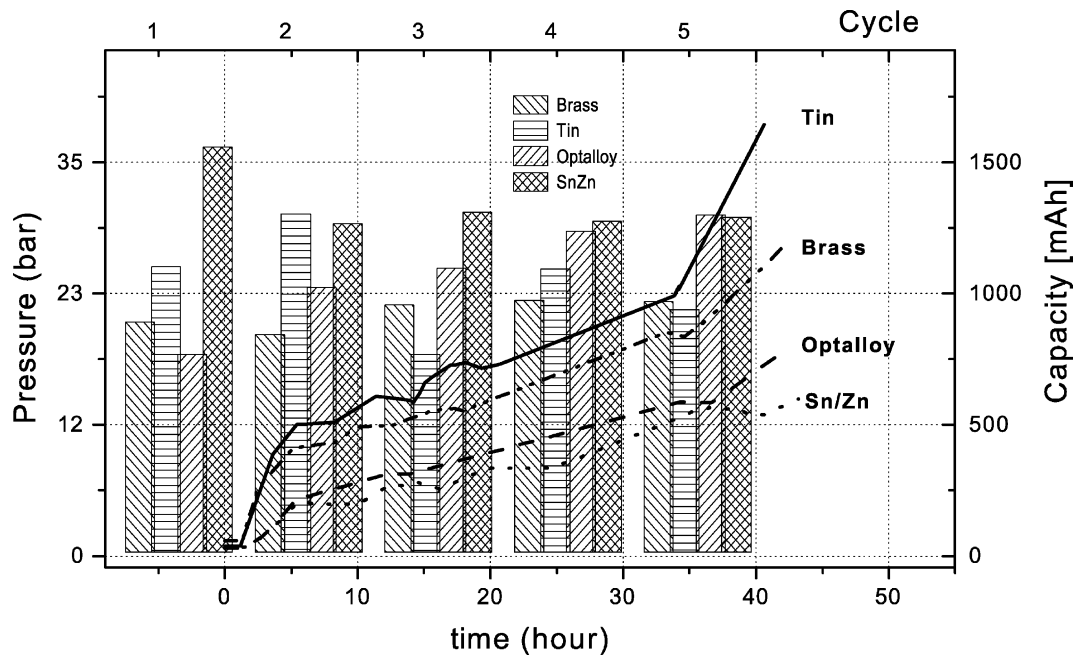


Fig. 6. Change in pressure of hydrogen evaluated on brass, tin, Optalloy and Sn–Zn alloy (98:2) as anode current-collectors (used in C-size RAM cells) as function of time. Also, plots of capacity vs. charge–discharge cycle number are shown.

cycles are also shown. Initially, the pressure shows a plateau, where H_2 is slowly evolving and being absorbed by the auxiliary electrode [30]. When the cell becomes fully charged, a steep pressure increase occurs until charging ceases. This is mainly due to O_2 evolution from the anode which rapidly oxidizes the zinc electrode. Hence, the pressure appears to be somewhat decreased.

The surface morphology and the passage of current through the current-collector are both associated with the emergence of corrosion products [31]. Scanning electron microscopy (SEM) shows that the microstructural surface of the Sn–Zn alloy is comprised of spheres of various dimensions (Fig. 7). By contrast, Optalloy appears completely different with a rather smooth surface structure (Fig. 8).

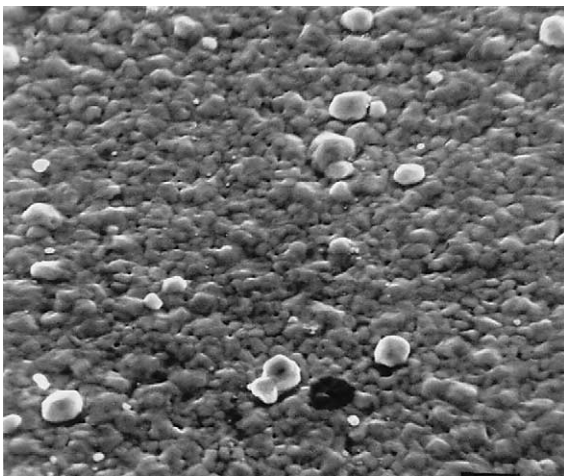


Fig. 7. Scanning electron micrograph of Sn–Zn alloy (98:2) deposited on zinc substrate.

Corrosion occurs on the Sn–Zn current-collector during cycling (Fig. 9). The increasing deposits of zinc and zinc oxide at the edges of the rectangular Sn–Zn current-collector (zone 2 in Fig. 9) are indications of the diversity of current densities at the surface. The corrosion process will intensify at locations with high current densities. The shape change on this electrode is evident by the bulging of the electrode surface at the edges.

The decrease in capacity with cycle number could be directly related to a progressive increase of corrosion (Fig. 6). The reason for the somewhat higher initial capacity may be due to the higher active surface-area of the current-collector. This is due to its rough surface morphology. After the first three cycles, the cell with binary Sn–Zn alloy

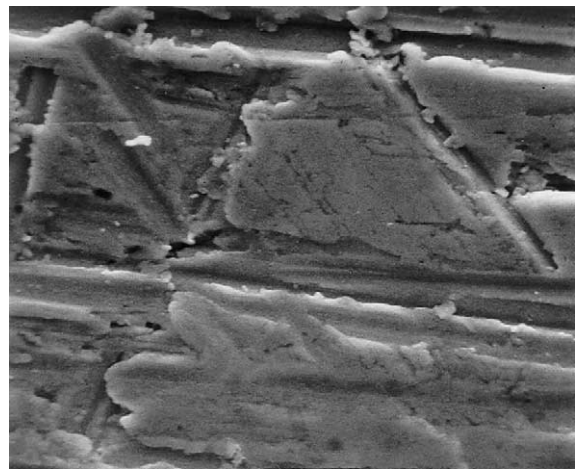


Fig. 8. Scanning electron micrograph of Optalloy deposited on zinc substrate.

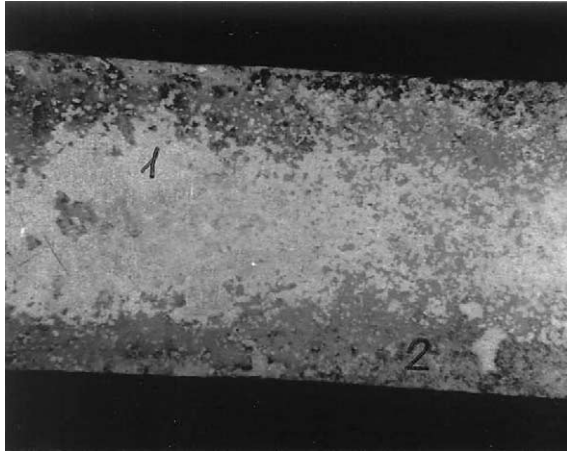


Fig. 9. Sn-Zn current-collector after charge–discharge cycling test with increasing deposit of zinc and zinc oxide at edges (zone 2).

exhibits a discharge capacity which is similar to that of the cell with Optalloy. The latter shows an increasing capacity with cycling. This may be attributed to its anti-corrosion behaviour. No apparent evidence of corrosion is observed on the Optalloy surface. This is in contrast to the corrosion found on the Sn–Zn current-collector (Fig. 9). Thus, Optalloy was selected for producing a modified zinc anode for use in bipolar batteries (Section 3.3).

3.2. Cyclic voltammetry

Cyclic voltammetric curves display an anodic current peak at around -1320 mV (Figs. 10 and 11). This corresponds to zinc dissolution and precipitation of ZnO. A cathodic peak appears around -1450 mV, and is related

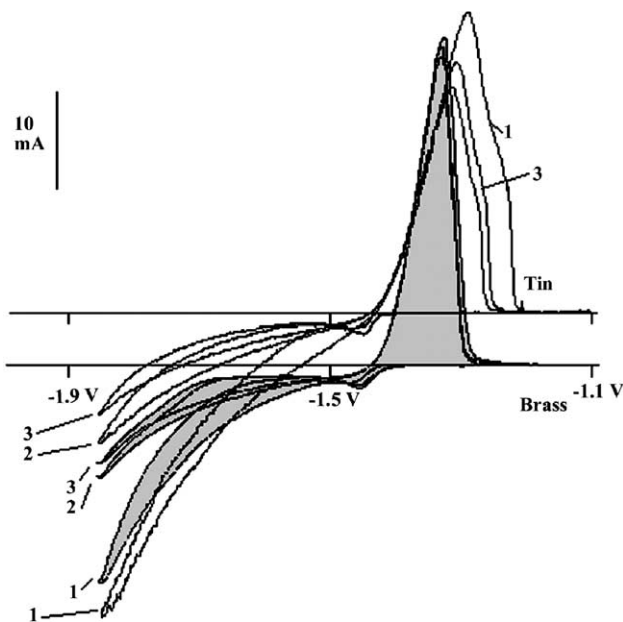


Fig. 10. Cyclic voltammograms for zinc reactions in 9M KOH saturated with zincate using tin and brass electrodes.

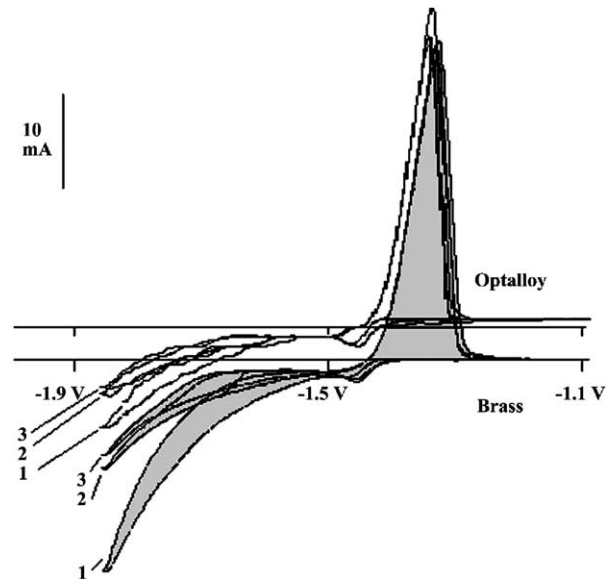


Fig. 11. Cyclic voltammograms for zinc reactions in 9M KOH saturated with zincate using Optalloy and brass electrodes.

to the reduction of the accumulated $\text{Zn}(\text{OH})_2$ and/or ZnO formed during the anodic half-cycle. These compounds remain on the electrode surface and are not dissolved in the electrolyte. With cycling the cathodic peak shifts towards more negative potentials and the current diminishes. This is due to the mass transport limitation of zincate species [32]. Finally, current increases due to the evolution of hydrogen.

Zinc depositions at the tin electrode appear strongly linked to hydrogen evolution on the first cycle (Fig. 10). In fact, hydrogen evolution competes significantly with the metal deposition. The broadening of the zinc oxidation peak, as well as the gradual decrease in the peak-current intensity on the subsequent cycles, indicate a marked passivation of the tin electrode in alkaline medium. Furthermore, while the position of the cathodic peaks remains unchanged, the anodic peaks are shifted to positive values. The difference between the reduction and the oxidation peaks on the tin electrode appears to be greater than that on the brass electrode. This suggests that the reactions become more irreversible on tin.

The cyclic voltammetric curves for the Optalloy show more persistent cycle behaviour (Fig. 11). In the anode region, the current due to the dissolution of zinc continues without any large modification. It appears that the difference between the cathodic and the anodic peaks on Optalloy is less than that on brass. It is therefore concluded that the degree of reaction reversibility is somewhat higher on Optalloy. Gas evolution on zinc is less than on brass or tin. The hydrogen overpotential is raised to about 50 mV on Optalloy compared with brass (first sweep of Fig. 11). In other words, Optalloy may be used as a substitute for mercury as a means to decrease zinc corrosion in the RAM batteries.

3.3. Cycle performance of bipolar batteries with amalgamated and/or modified zinc anodes

The polarization curves (Fig. 12) and cumulative capacity (Fig. 13) of a test battery, with an amalgamated zinc anode (BAZ) show a rather poor cycle performance. Such a cell typically has an open-circuit voltage of 6.30 V and a short-circuit current of 5 A. A relatively higher cycle performance is displayed by a test battery with the modified zinc anode (BMZ) (cf. Figs. 12–15). This is attributed to the difference between the anodic compositions. Apparently BMZ enjoys a higher electrical interface contact. The battery has an open-circuit voltage of 6.25 V and a short-circuit current of 7 A. The higher cycle performance of BMZ suggests that microscopic distribution of the conductive alloy contributes to a more homogeneous current distribution in the anode mass. Electrical cross-linking of the anode mass may result when

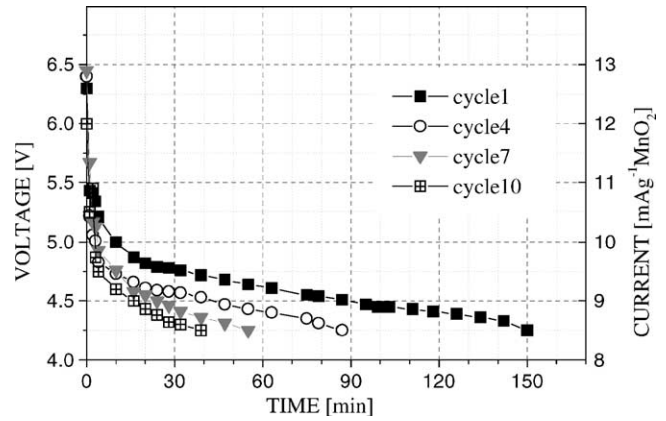


Fig. 12. Polarization curves for bipolar battery with amalgamated zinc anode and brass current-collector. Battery charged at $10 \text{ mA g}^{-1} \text{ MnO}_2$ to end voltage of 6.9 V. Discharge is continuously performed with a 500Ω load to a cut-off voltage of 4.25 V.

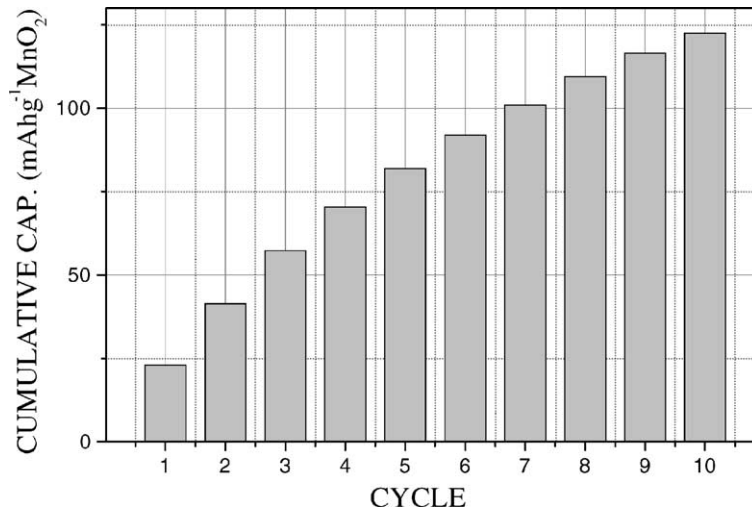


Fig. 13. Cumulative capacity of bipolar battery with amalgamated zinc over 10 cycles.

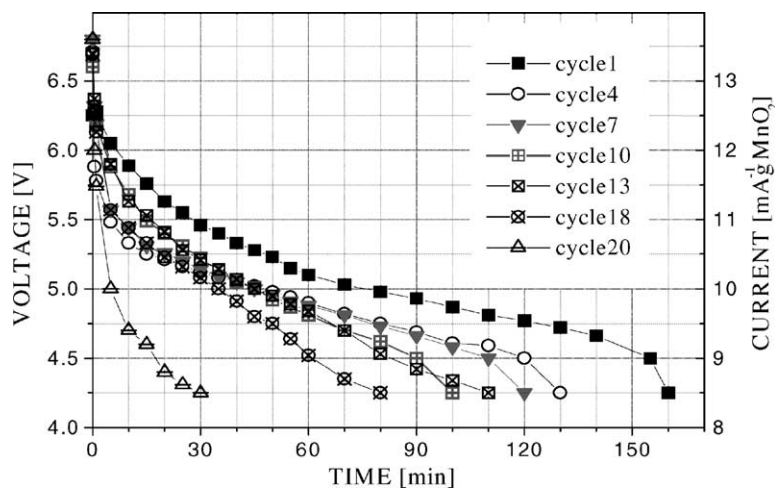


Fig. 14. Polarization curves for bipolar battery with modified zinc anode and Optalloy current-collector. Battery charged at $10 \text{ mA g}^{-1} \text{ MnO}_2$ to end voltage of 6.9 V. Discharge is continuously performed with a 500Ω load to a cut-off voltage of 4.25 V.

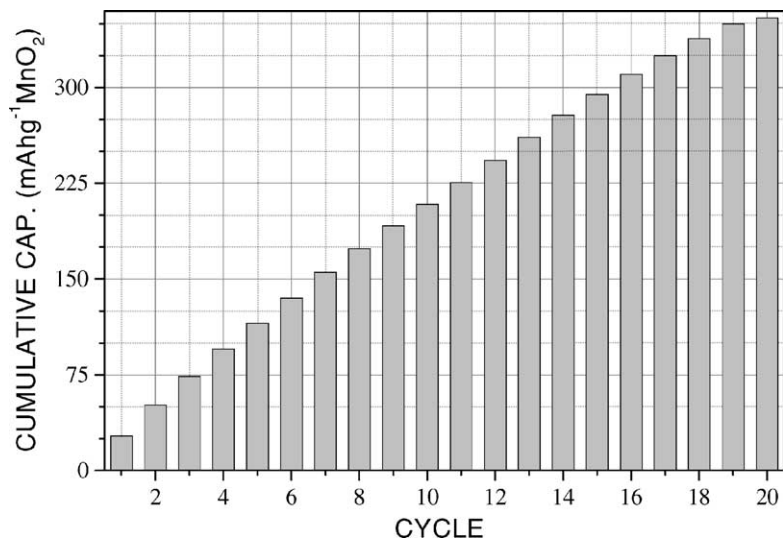


Fig. 15. Cumulative capacity of bipolar battery with modified zinc anode.

Optalloy is used. This may inhibit a possible dendrite formation. It is evident that the higher the rate of discharge, the more is the non-uniformity of the extent of oxidation in the direction normal to the current-collector [32]. This phenomenon is expected to be more pronounced in less-conductive media. The discharge process ends when the extent of oxidation of the layer which directly adjoins the surface of the current-collector reaches a critical value where its conductivity drops sharply. At this point, the internal layers of the active mass may still contain a high degree of unreacted zinc, and there is no substantial electronic contact between them. Along with the known phenomena of passivity and the reduction in porosity of the active mass, this could induce the inferior cycle performance observed with BAZ.

The electrochemical performance of the electrodes is determined by several factors, which include the kinetics of the electrochemical reactions and the rate of mass-transfer of species to the electrode surface [33]. During discharge, where the surface energy is depleted, reaction rates become dependent on the chemistry and ion diffusion within the active layer. The efficiency of the electrokinetic parameters depends on the maintenance of the porous nature of the anode gel. This porosity improves the utilization of the active mass. Therefore, porous electrodes with proper mechanical strength are employed to increase the specific surface-area of the electroactive materials. A better mechanical strength between the entire part of the anode active-material and the current-collector provides another justification for the higher cycle performance of BMZ. It may be concluded that the use of Optalloy is responsible for the above phenomenon and/or for the solidification of the anode mass, through which the shape change of the anodic active material is prevented.

The BMZ displays good performance for the first 18 cycles, but suddenly deteriorates on subsequent cycles. This may occur through leakage.

4. Conclusions

Without stabilizing and/or conductive effects, the activity of the anode mass in bipolar RAM batteries simply diminishes during charge–discharge cycling. Results obtained to date demonstrate the beneficial effects of Optalloy as a current-collector for bipolar batteries. This is mainly due to its hardness, noble characteristics, and good corrosion resistance. In particular, the relatively high hydrogen over-potential on Optalloy leads to a decreased level of gassing. Hence, Optalloy treated zinc anodes can be successfully used to decrease the rate of gas evolution. This resolves the problem of overcoming zinc passivation with an acceptable efficiency, and enhances the cycle performance of bipolar RAM batteries.

Further development of such batteries requires optimization of (i) the electrochemical characteristics, especially the development of a homogeneous current distribution in the active mass, (ii) the electrode matrix, (iii) the operational conditions.

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