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Thin-film zinc/manganese dioxide electrodes based on microporous polymer foils

P.A. Barbic [a], L. Binder [a,*], S. Voss [a], F. Hofer [b], W. Grogger [b]

[a] Institute of Chemical Technology of Inorganic Compounds, Technical University Graz, Stremayrgasse 16, A-8010 Graz, Austria
[b] Research Institute of Electron Microscopy, Technical University Graz, Steyrergasse 17, A-8010 Graz, Austria

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Abstract

Thin-film electrodes allow manufacturing of flat batteries of variable design which can be used for the development of smaller electric appliances. Substituting the metal carrier by conductive plastics leads to a considerable reduction of battery weight. Usually the electroactive materials are deposited onto the surface of the carrier. A significant improvement of the originally poor adherence between polymer foil and electroactive layers can be achieved by mechanical (surface roughening) or chemical (etching) pretreatment. Another way to form extremely thin electrodes having a thickness in the range of some ten micrometers is reported here. First, a metallic layer is deposited onto one surface of a 25 μm thin porous polypropylene foil. Subsequently, the electroactive materials are electrolytically deposited into the pores of the metallized foil providing the required conductive connection through the plastic matrix by themselves. In this case the flexibility of the polymer has a positive influence on the problem of volume change of manganese dioxide during charging and discharging, respectively, because the plastic provides flexible 'mechanical struts' which act as a 'binder' and therefore prevent increasing internal resistance due to contact problems. Assembling a zinc filled polymer and a manganese dioxide filled one in such a way that both metallic back-layers are in contact, a thin bipolar zinc/manganese dioxide electrode can be obtained.

Keywords: Thin-film electrodes; Rechargeable alkaline manganese dioxide cells; Microporous electrodes

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1. Introduction

An important advantage of thin-film electrodes is a better performance than in customary (standard) cells because of a larger contact area between anode and cathode, a better utilization of the electrochemically active materials [1] and shorter diffusion paths. Substituting the metal carrier by conductive plastics lead to a considerable reduction of battery weight (factor 10 to 12 using the Celgard® foil mentioned below compared with sheet brass). The aggravating disadvantages of using plastics as carrier for the electroactive materials are their low conductivity and their lack of adherence to the electroactive layers. Usually the electroactive materials are deposited onto the surface of a conductive (metal or conductive polymer, respectively) carrier. A significant improvement of the originally poor adherence between polymer foil and electroactive layers can be achieved by mechanical (surface roughening) or chemical (etching) pretreatments [2,3]. Using plastics with conductive fillers, like graphite and/or soot incorporated in the polymer, demands an intermediate layer between the carbon-filled polymer and zinc to prevent formation of hydrogen gas by anodic zinc corrosion, which is enhanced in the presence of carbon in any modification.

Attempts to use intrinsically conductive polymers like polypyrrole as carrier materials need special precautions and manufacturing processes because most of these polymers are insoluble and brittle. Thus further treatment is hardly practicable. The advantage of intrinsically conductive polymers compared with 'filled' plastics is that an intermediate layer between carrier and zinc could be avoided.

Each of the above mentioned polymers must comply with the demands of electrolytical deposition of the electroactive materials (e.g., 90°C, 1 mol/l sulfuric acid bath, anodic polarisation for deposition of manganese dioxide) as well as with the requirements of battery operation using 9 mol/l potassium hydroxide as cell electrolyte.

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[*] Corresponding author

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The achievable resistance of these materials (plastics with conductive fillers and intrinsic conductive polymers) is naturally not comparable to that of metal carriers but it is sufficient for thin foils in bipolar arrangements.

Another very promising method to form extremely thin electrodes having a thickness in the range of some ten micrometers is shown in this outline: First, a metallic layer —which serves as current collector—is deposited onto one surface of a 25 μm thin porous polypropylene foil [4,5]. Subsequently, the electroactive materials are electrolytically deposited into the pores of the metallized foil providing the required conductive connection through the plastic matrix by themselves [3,6]. In this case the flexibility of the polymer has a positive influence on the problem of volume change of manganese dioxide during charging and discharging, respectively, because the plastic provides flexible ‘mechanical struts’ which act as a ‘binder’ and therefore prevent increasing of the internal resistance due to contact problems. Assembling a zinc filled polymer and a manganese dioxide filled one in such a way that both metallic back-layers are in contact, a thin bipolar zinc/manganese dioxide electrode can be obtained.

2. Experimental

2.1. Preparation of the single-side-metallized polypropylene foil Celgard®-2402

For electrochemical applications adhesion of the metal layer even in aggressive electrolyte solutions is required. For that reason classical vapor phase metal deposition methods are not acceptable as the membranes dry out and shrink in a vacuum.

The metallization of the polypropylene foil (PP-foil) Celgard®-2402 is a modified commercial coating process [4,5].

In this process the metals are deposited within the microporous structure and on the surface of the PP-foil. A well-adherent metal layer at the substrate Celgard®-2402 results which is mechanically anchored in the pores by metallic ‘roots’. The penetration depth of the metal layer can be controlled by the added surfactants in the electroplating baths.

Two steps are necessary for the electroless metallization. In the first step the surface of the PP-foil is catalytically activated by finely dispersed palladium crystal nuclei. After activation the substrate is electrolessly coated with the corresponding metals copper or palladium (Fig. 1).

While copper was used as negative current collector, only palladium seemed to be usable as positive because of the conditions during electrolytic deposition of manganese dioxide (temperature: 88–93°C, sulphuric acid bath and anodic polarisation). After electroless metallization the two originally attached layers of the Celgard®-2402 foil were pulled apart to achieve two single-side-metallized polymer layers.

2.2. Preparation of the thin-film electrodes

These single-side-metallized PP-foils can be used as thin-film electrodes in rechargeable alkaline zinc/manganese dioxide (RAM™) batteries. The electroactive materials, zinc and manganese dioxide, respectively, were electrochemically deposited in the pores of the single-side-metallized and moistened PP-foil by means of pulse electrolysis. A schematic production process is shown in Fig. 2.

2.2.1. Preparation of the thin-film zinc electrode

To improve the chemical stability of the copper current collector tin was deposited into the pores of the Celgard® foil under the following conditions:

Anode	tin (99,999%)
Cathode:	metallized Celgard®-foil with copper as current collector
Electrolyte:	105 g/l $K_2[Sn(OH)_6]$ 17.6 g/l KOH (85%) 1 ml/l Triton X-100 (a non-ionic surfactant to moisten the pores of the Celgard®)

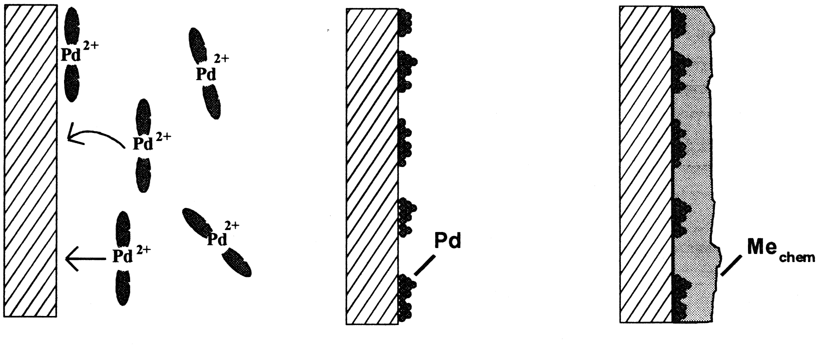

Fig. 1. Electroless metallization of the thin porous PP-foil Celgard®-2402.

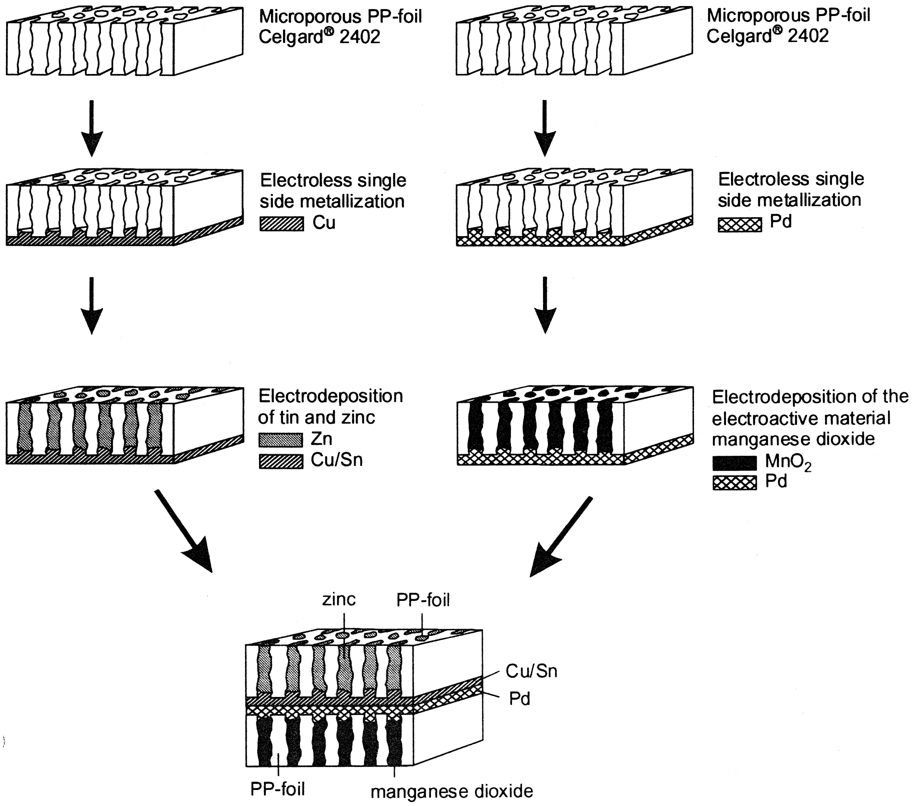

Fig. 2. Production-process of the bipolar thin-film zinc/manganese dioxide electrodes.

Pulse electrolysis	average anodic current density: $15\ mA/cm^2$ average cathodic current density: $6\ mA/cm^2$ pulse timing: 50 ms on, 500 ms off time: 5 min, 70°C

After cooling down to room temperature and washing with distilled water the zinc deposition was performed under the following conditions:

Anode	metal sheet of zinc
Cathode	metallized Celgard®-foil with copper and deposited tin as current collector
Electrolyte	13,8 g/l $ZnCl_2$ 105 g/l KOH (85%) 1 ml/l Triton X-100
Pulse electrolysis	average cathodic current density: $2\ mA/cm^2$ pulse timing: 10 ms on, 100 ms off time: 5 h, room temperature

2.2.2. Preparation of the thin-film manganese dioxide electrode

The deposition of manganese dioxide was performed under the following conditions:

Anode	metallized Celgard®-foil with palladium as current collector
Cathode	Pb
Electrolyte	112 g/l $MnSO_4 \cdot H_2O$ 98 g/l H_2SO_4 conc. (97%) 1 ml/l Triton X-100
Pulse electrolysis	anodic current density: $3\ mA/cm^2$ pulse timing: 50 ms on, 500 ms off time: 1 h, 90°C

After washing with distilled water the electrodes were assembled to batteries. Berec (contains a layer of cellophane) was used as separator. Cell electrolyte was 9 mol/l KOH.

3. Results and discussion

To check the degree of filling of the pores scanning electron microscope (SEM) photographs and analyses were made from a cryosection at the research institute of electron microscopy (FELMI). They proved an entire filling of the pores and a 5–10 μm thick surplus layer on the surface (Figs. 3 and 4).

It was shown that stirring of the electrolyte had a significant improving influence upon the completeness of filling compared to an unstirred electrolyte in spite of the fact that the surface of the deposited layer was much more regular at the optical level. This was explained by obstructing the pores with small particles which were deposited

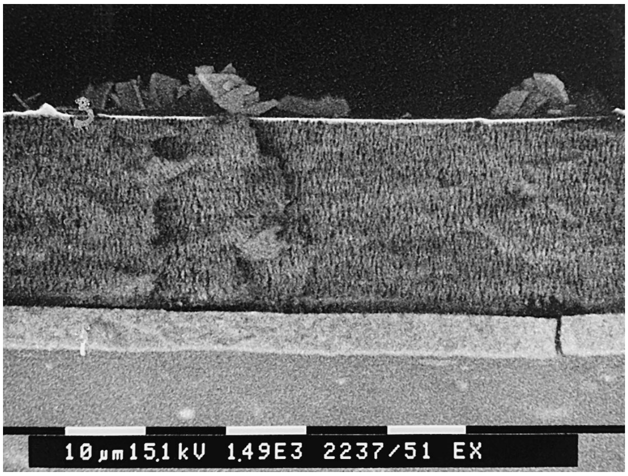

Fig. 3. SEM-shot of a sectional view of a PP–manganese dioxide electrode. (Cryosection, magnification: 1490×). (1) Manganese dioxide on the surface of the porous PP-foil, (2) manganese dioxide within the pores, (3) Palladium layer as current collector (bright line in the upper area of this figure).

onto the surface in unstirred conditions whereas the larger and more coarse particles deposited in stirred conditions are leaving passages for the electrolyte through the surplus layer on the surface.

X-ray diffraction was used to confirm that γ-MnO_2 was deposited (Fig. 5).

The separator between cathode and anode must provide enough capacity to store the electrolyte (KOH) and prevent the growth of zinc dendrites from the zinc anode to the cathode during charging. Thus, one side of such a separator should be made of a non-porous material like cellophane.

Studies on the DC-behaviour of Celgard®-based zinc/manganese dioxide cells showed a rather high corrosion rate of the copper current collector and KOH leakage.

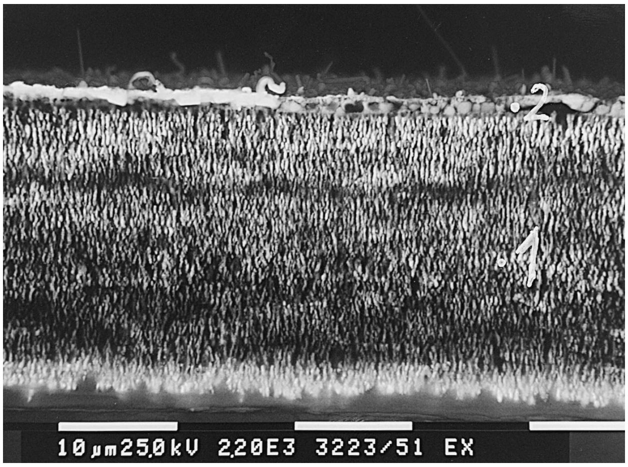

Fig. 4. SEM-shot of a sectional view of a PP–zinc electrode. (Cryosection, magnification: 2200×). (1) zinc within the pores, (2) the bright line in the upper area of this figure represents a copper–tin alloy as current collector.

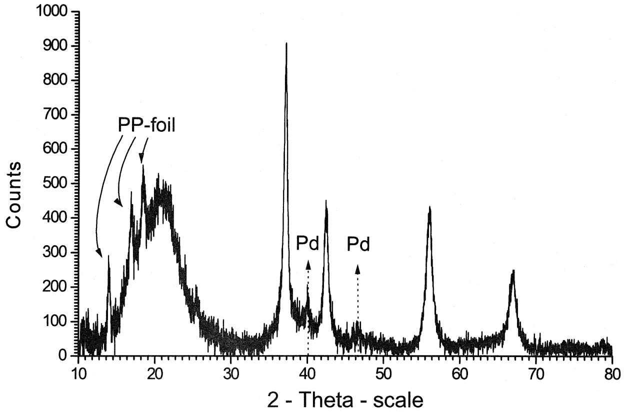

Fig. 5. XRD-spectrum (after background correction) of MnO_2 deposited into the pores of a Pd-metallized Celgard®-foil shows a γ-MnO_2. Start: 10.000°, End: 80.000°, Step: 0.020°, Step time: 20.0 s, room temperature.

The potassium hydroxide takes part in the anodic electrode reaction. Therefore, KOH leakage affects adversely cycle life as well as shelf life of the battery and had to be minimized. Unfortunately, the porous structure of the polymeric carrier increases the property of KOH to creep into every crevice. Thus, the edges of the electrodes were pasted very well using an epoxy resin.

Cells without and with bipolar electrodes (cell-stacks) were investigated in respect of their behavior during charging and discharging. Using computer-controlled galvanostats which provided exactly the same charging/discharging conditions in each cycle, statements on the cycle life of these batteries were obtained. Discharge was stopped at a COV (cut-off-voltage) of 900 mV (without bipolar unit) and 1800 mV (with one bipolar unit), respectively. After discharging had finished the cell was charged potentiostatically with 1700 mV (without bipolar unit) and 3400 mV (with one bipolar unit) for 3 h. Thereafter, discharge was performed again. The measurements are based on a three-electrode-arrangement (Zinc was used as reference electrode). Thus, the advantage was that each electrode behavior can be checked. But this demand increased the above mentioned problem of KOH leakage. Even the insertion of a very thin sheet metal of zinc enclosed in separator material between anode and cathode introduced a ‘good’ opportunity for cell-leakage.

To achieve a more corrosion resistant current collector for the anodic side (copper will oxidize when zinc is completely dissolved during discharge) a thin tin layer was deposited before zinc deposition. FELMI analysis showed that there was no individual tin layer but tin diffused into the copper layer. Using this copper–tin alloy as current collector the cycle life of assembled cells not only increased from average four to average 20 cycles, but, at least for the first four cycles, the cumulated capacity on discharge almost doubled from 2.4 mA h to 3.9 mA h. (Figs. 6 and 7). Due to the oxidation of the less corrosion resistant copper, a current collector layer made of this

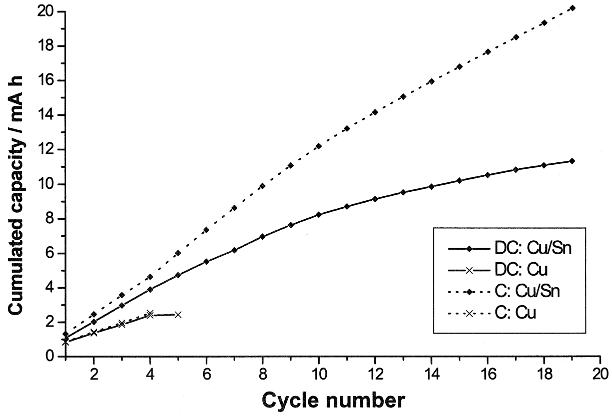

Fig. 6. Cumulated discharge (DC) and charge (C) capacity of a 1.5 V cell based on porous polypropylene carrier dependent on the current collector (discharged with 3 mA, charged at 1700 mV for 3 h, 9 cm^2 electrode surface).

material disintegrates easily. Therefore, parts of the negative electrode cannot be recharged again, causing less capacity in the next discharge cycle.

An external reinforcement of these cells had a significant influence on the OCV and CCV (closed circuit voltage), respectively, because the polymer itself is not as stable as metallic carriers. Consequently, contact problems will appear, particularly if the internal pressure increases due to, e.g., zinc corrosion. Thus, a stable casing is needed to press the cell-stack together.

First attempts were made to achieve thin-film bipolar electrodes by assembling these electrodes in such a way that their metallized sides stick together (Fig. 2).

To succeed in the assembly of functioning RAM™ (rechargeable alkaline manganese dioxide) cell-stacks based on bipolar electrodes, it is very important that each electrode used in one stack has equal geometry, equal capacity and has been produced under equal conditions because otherwise one cell within the stack will be discharged more deeply than the others and thus will be irreversibly damaged. Assembling of the bipolar electrodes requires an electronically conductive connection from the zinc side to the manganese dioxide side. The influence of certain conductive adhesives between the two 'half-electrodes' on the cell-behavior must be considered as well. Fig. 8 shows the discharge curves of the first two discharge cycles of a Celgard®-battery with one bipolar electrode. The capacities were 0.9 mA h during the first discharge and 0.3 mA h during the second one.

The discharge-time and the capacity of the second discharge cycle are much lower than that of the first one. In Fig. 8 it can clearly be seen that one unit was discharged more deeply than the second one. Thus, this deeply discharged unit was damaged irreversibly. Even during potentiostatical charging at 3400 mV this unit was slightly discharged. In the near future it must be checked whether or not there exists a corrosion current within the copper/tin/palladium current collector layer if the electrolyte (9 M KOH) diffuses into it.

A significant disadvantage of the microporous Celgard® foil used as carrier for the electrochemical active materials is the low porosity of only 38%. Thus, several different materials were investigated to replace that foil: Dexter and Berec foils, both used as battery separators, could not be metallized in an 'electroless' procedure: During this metallization the former one became black and the cellophane foil of the latter one peeled off.

A part of a Gore-Tex® foil based on PTFE showed only a bad activation behavior during the first step of metallization.

A different material called PolyHIPE (a microporous material developed at Unilever and Los Alamos National Laboratories, produced through the formation of a high internal phase emulsion (HIPE) of water-in-oil and subsequent polymerization of the oil phase which contains styrene and divinylbenzene) offers an extremely high

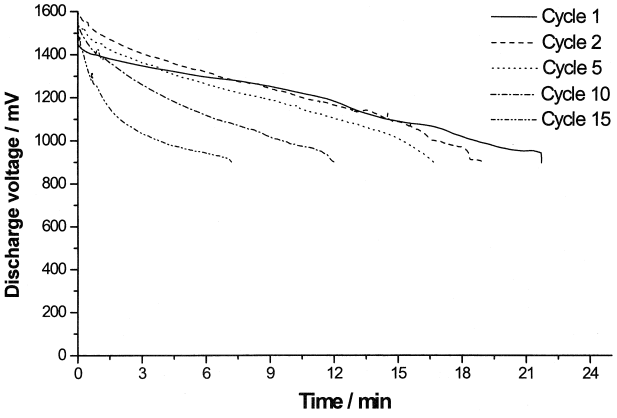

Fig. 7. Discharge curves for a zinc/manganese dioxide cell with Celgard®-foils as carriers (Discharge current: 3 mA, electrode surface: 9 cm^2).

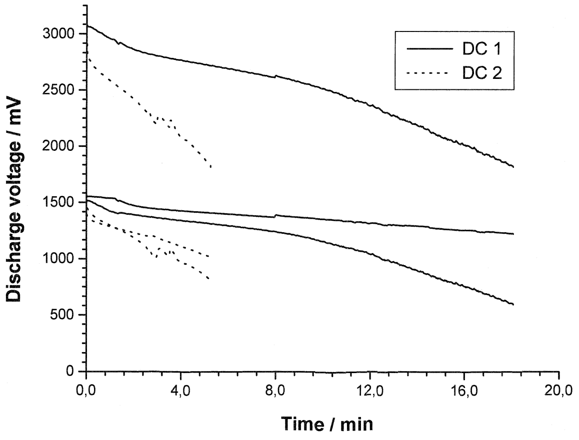

Fig. 8. Discharge voltage vs. time of a cell based on Celgard® carrier (load: 3 mA discharge current, 9 cm^2 electrode area) of the first two cycles. The plots at 3000 mV represent the voltages of the whole stack, those at 1500 mV represent the voltages of the individual cell-units.

voidage (up to 97%) [7] But this material could not be metallized in an 'electroless' manner.

4. Conclusions

In rechargeable arrangements the current collector has a decisive influence on the cycle-life of batteries. Good conductivity and adherence to the electroactive materials as well as an inert behavior under oxidative and reductive conditions, respectively, are the most important demands on current collectors in that case.

To increase the chemical stability of the current collector on the anodic side (zinc electrode) a copper–tin–zinc alloy will be investigated and compared with the copper–tin alloy which has been used recently.

To achieve higher currents the area of the electrodes has to be expanded. In this case problems with the mechanical stability of the polymer during the deposition of manganese dioxide (90°C) must be expected. Larger areas will bulge more easily because of a larger thermal expansion and deposition of manganese dioxide will become more and more irregular. These problems can be minimized, e.g., using mechanical support strutting.

Acknowledgements

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