

Optimized zinc electrode for the rechargeable zinc–air battery

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For the development of a long-lived, electrically rechargeable zinc–air battery the structure and wettability of pasted zinc electrodes were optimized. Pasted zinc electrodes containing 1 to 10% cellulose but having almost the same nominal capacities were prepared and tested in zinc/oxygen cells. The effect of discharge rate on cell voltage and delivered capacity, as well as the maximum power, were measured. Furthermore, cell charge–discharge behaviour and cycle life were examined. After different times of operation, the porosity and the pore size distribution of the pasted zinc electrodes were measured by means of mercury porosimetry. The cycle life and peak power drain capability of the Zn/oxygen battery could be substantially improved by the addition of 10 wt % cellulose to the pasted zinc electrode.

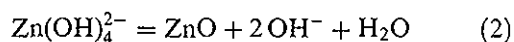
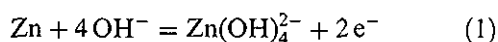
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1. Introduction

Zinc–air batteries, because of their high specific energy, environmental compatibility and low-cost materials, have long been considered to be potentially attractive as power sources for electric vehicles.

The key tasks in the technical realization of an electrically rechargeable zinc–air battery are the development of an efficient, long-lived, bifunctional oxygen diffusion electrode and the development of a zinc electrode which shows no significant shape change and no dendrite formation during cycling. Concerning the development of bifunctional oxygen electrodes significant progress has been made in demonstrating a long service life. With metal oxides such as $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ [1] in combination with graphitized Vulcan XC 72 a cycle life of approx. 3000 h in zinc/oxygen cells has already been demonstrated in our laboratory [2].

The concept of the rechargeable zinc electrode is based on the formation of insoluble ZnO in the pasted electrode that can be reduced to metallic zinc during the charging process. The following two consecutive reactions take place at the zinc electrode during discharge:



The charge transfer reaction (1) yielding zincate is followed by the precipitation of solid ZnO (2). Shape changes, which typically degrade the Zn electrode, can be diminished by reducing the solubility of the Zn electrode discharge product in the electrolyte. Lower solubility can be achieved by using moderately alkaline ZnO-saturated electrolytes and electrolyte additives such as K_2CO_3 . With Zn/NiOOH cells more

than 500 cycles were demonstrated using this electrolyte [3]. However, the electrolyte system developed for the Zn/NiOOH system is not feasible for zinc–air batteries. The CO_3^{2-} additives lead to crystallization of $\text{K}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$ in the pores of the bifunctional oxygen diffusion electrode [4]. Apart from shape change, the major problems are densification and passivation of the zinc electrode [5]. The formation of passivating layers may occur in parallel with the precipitation of ZnO during discharge [6]. The solution inside the porous electrode can be depleted of hydroxide ions due to the limited transfer of OH^- ions across the separator and reaction zone. Increasing the size of the electrolyte reservoir (electrolyte outside the pores but within the compartment) helps to overcome this problem. However, a large electrolyte reservoir can promote shape change, which leads to limited cycle life of the zinc electrode. In order to reduce the passivation of the zinc electrode induced by pore plugging, the porosity and the pore size distribution of the electrode must be improved.

The goal of this work is to optimize and stabilize the pore structure of the zinc electrode and improve its wettability in order to avoid pore plugging and to enhance zinc utilization during discharge. The improved pore structure leads to better ion mobility and greater OH^- -concentration in the pores. Introducing Zn electrode additives such as hydrophilic and chemically stable cellulose is a strategy to keep the electrode wet and porous over long operating periods. Cellulose is highly hygroscopic and tends to swell in aqueous solution. The zinc/oxygen cell must be designed so as to tolerate the increase in volume of the zinc anode caused (i) by swelling of the cellulose and (ii) by the density difference between the charged zinc and discharged ZnO electrode, respectively.

2. Experimental details

The pasted zinc electrodes were prepared from an aqueous slurry containing ZnO, PTFE (Teflon 30 N dispersion, Dupont, NL), traces of PbO (to suppress hydrogen evolution) and cellulose. The amount of cellulose was varied between 1 and 10 wt %. The vacuum-filtered slurry was applied in consecutive layers to both sides of a lead-plated copper screen ($\phi = 56.4$ mm) and compressed to a final thickness of 1.2 to 1.4 mm. The electrodes were dried in air, first for 12 h at ambient temperature, then for 4 h at 110 °C. Dendritic shorting of the cell was prevented by three layers of Celgard 3401 separator (0.02 μ m effective pore size, Hoechst Celanese Corp., Charlotte, North Carolina, USA) wrapped and individually heat-sealed around the zinc electrodes. The pasted zinc electrodes were degassed under vacuum and then soaked with electrolyte before being mounted into the cell. The electrolyte consisted of 3.2 M KOH + 1.5 M KF and was presaturated with ZnO.

The zinc electrodes described were tested in monopolar cells of 2.5 Ah nominal capacity. A schematic presentation of such a cell is given in Fig. 1. It consisted of a pasted 25 cm² zinc electrode held between two bifunctional oxygen diffusion electrodes. Its effective surface area was 50 cm² (two sides). A Zn wire reference electrode ($E(\text{Zn}_{\text{ref.}}) = -1.338$ V vs Hg/HgO) was used for measuring the individual electrode potentials. The preparation of the La_{0.6}Ca_{0.4}CoO₃-catalysed bifunctional oxygen diffusion electrode is described elsewhere [7]. The cells were cycled using a computer-controlled system (Akku-Lab II, Bettschen Elektronik AG, Switzerland). The cells were initially subjected to two formation cycles at low rate. This zinc formation process was realized by charging the Zn electrode with 1.7 Ah (2/3 of the nominal capacity) at 64 mA and then discharging it using the same current until the zinc electrode reached a potential of >450 mV vs Zn_{ref.}. Under regular test conditions only 1/3 (approx. 0.8 Ah) of the nominal capacity was used. Even then an attractive specific energy (approx. four times those of the lead-acid battery) can be obtained in a practical cell. The cells were cycled at

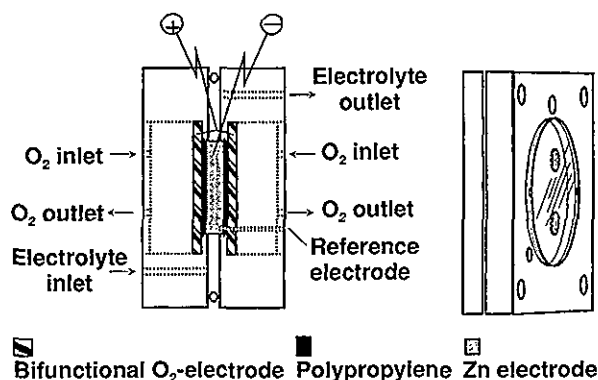


Fig. 1. Schematic view of the Zn/O₂ cell. Electrolyte inlet/outlet are only used for filling the cell. During cycling there was no electrolyte flow through the cell.

constant current (150 mA charging and 300 mA discharging current). Between each half cycle, the cells were exposed to a 12 min open-circuit period. The discharge-process was stopped when polarization of the zinc electrode exceeded 300 mV (vs Zn_{ref.}) before it had been discharged to $C_{\text{nom}}/3$. The discharge capacity recorded was then used as the new capacity for the following charging process. Cycling continued until the cell capacity had dropped below 50% of its original value. The experiments were carried out at ambient temperature (approx. 25 °C).

After the experiment was completed the cell was disassembled and post mortem analysis of the pasted zinc electrodes consisted of either (i) pore size distribution or (ii) determination of the amount of electrochemically inactive metallic zinc was performed. (i) The pasted zinc electrodes were several times vacuum-impregnated with distilled water which was reextracted from the electrode so as to remove the KOH. The pore size distribution of the dry electrodes was calculated from the intrusion curve obtained with a Hg porosimeter (Pore Sizer 9320, Micromeritics, Belgium). The pore size distribution of the electrode was not affected by the applied rinsing technique described above. A new electrode had the same pore distribution as determined by Hg porosimetry both before and after this procedure. (ii) Completely discharged Zn electrodes were immersed in HCl (approx. 20%), and the amount of hydrogen evolved at the electrodes was measured volumetrically.

3. Results and discussion

Figure 2 illustrates the pore size distribution in new pasted zinc electrodes containing 1%, 5% and 10% cellulose. The porosity measurements of these pasted zinc electrodes showed consistent values in the range

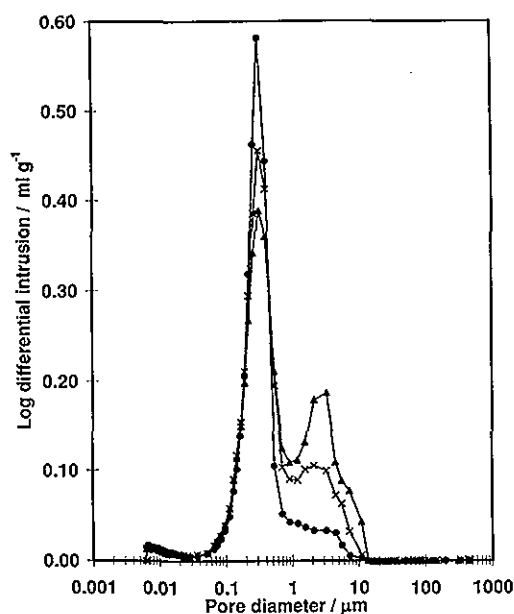


Fig. 2. Pore size distribution of new pasted zinc electrodes with (●) 1, (×) 5 and (▲) 10 wt % cellulose.

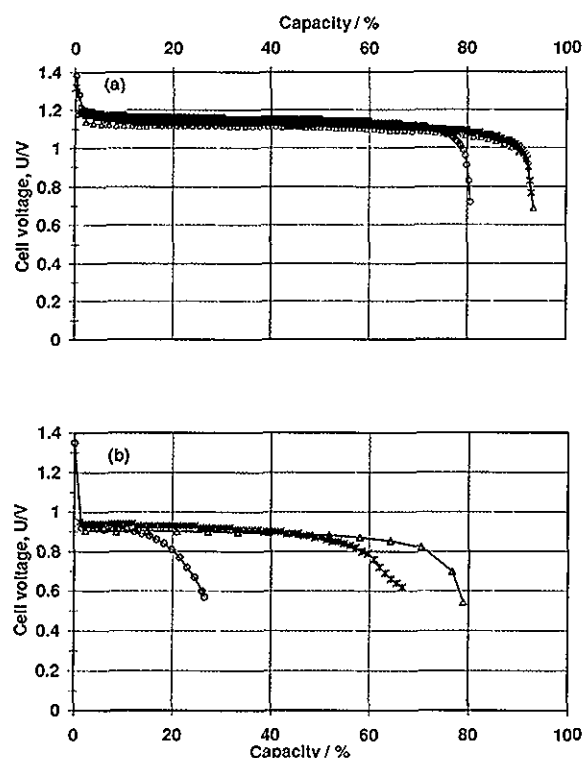


Fig. 3. Zinc/oxygen cell voltages versus discharge capacity (100% \approx 1.7 Ah) measured at discharge currents of (a) 0.3 A (\sim C/6) and (b) 1.2 A (\sim C/1.5) for two cells with pasted zinc electrodes containing (O) 1%, (x) 5% and (Δ) 10% cellulose fibres.

47 to 49%. The main part of the pores are in the range 0.1 to 1 μ m. However, for higher amounts of cellulose in the pasted Zn electrode the pore size distribution is shifted to larger pores (1 to 10 μ m).

The amount of cellulose in the pasted zinc electrode has an important impact on the zinc utilization at high discharge rates. The zinc/oxygen cell voltages, obtained during discharge at 300 mA (a) and 1200 mA (b) are presented in Fig. 3 for zinc electrodes containing 1%, 5% and 10% cellulose. For these discharge experiments the rated capacity of the cells was about 1.7 Ah. The formation of ZnO during discharge presumably occurs in a receding front from the electrode surface toward the current collector. While at low discharge rates OH^- diffusion into the electrode does not limit the capacity of the cell, at high discharge rates pronounced differences in zinc

utilization were measured depending on the amount of cellulose present in the zinc electrodes.

The initial capacity ($C_{\text{nom}}/3$), the electrode thickness, the maximum number of cycles, and the cycle life (until 50% of the initial capacity was reached) is presented in Table 1 for pasted zinc electrodes containing 1%, 5% and 10% cellulose fibers. Figure 4 shows the capacity (100% is equal to the initial cycled capacity of approx. 0.8 Ah) against the cycle number for three representative examples of these zinc electrodes with different cellulose concentrations. The life time of the electrodes was improved by a factor of five to ten by increasing the amount of cellulose in the paste. While for the 1% cellulose electrode the capacity continuously dropped after a few cycles, the 10% cellulose electrode showed both a more stable and a higher capacity over a larger number of cycles.

Figure 5 shows the porosity change and densification of the zinc electrode occurring during cycling. Pasted zinc electrodes exposed to KOH showed a shift of the medium pore size to larger diameters compared to the measurements discussed in Fig. 2. Swelling of the electrode is one explanation for this behaviour. During the first 10 cycles the porosity

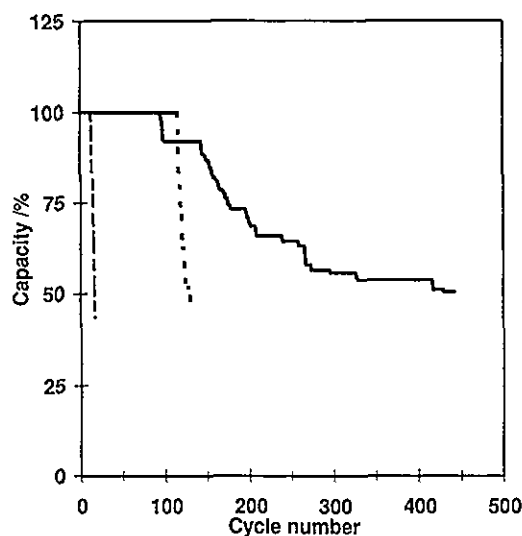


Fig. 4. Capacity (100% \approx 0.8 Ah) decrease as a function of the cycle number for Zn/O₂ cells with pasted zinc electrodes containing: (---) 1%, (.....) 5% and (—) 10% cellulose.

Table 1. Initial cycled capacity, electrode thickness, number of cycles and cycle life (until 50% of the initial capacity was reached) of Zn electrodes containing 1%, 5% and 10% cellulose fibre additives

Charge and discharge current are 150 and 300 mA, respectively

Electrode type	Electrode no.	Cellulose content/wt %	Initial cycled capacity/Ah	Electrode thickness/mm	Number of cycles	Cycle life /h
A	1	1	0.823	0.98	22	185
A	2	1	0.853	0.95	16	100
B	1	5	0.854	1.30	77	631
B	2	5	0.860	1.28	129	1195
C	1	10	0.866	1.45	259	2175
C	2	10	0.785	1.23	264	1974
C	3	10	0.835	1.34	443	2917

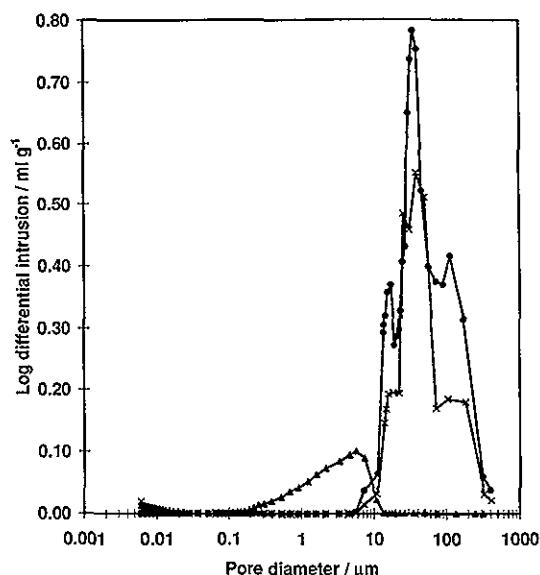


Fig. 5. Pore size distribution of pasted zinc electrodes with 10% cellulose measured after different cycle numbers: (●) 10 cycles, (×) 50 cycles and (▲) 450 cycles.

decreased from 53% to 40% while the pore size distribution remained almost the same. After 450 cycles the porosity had decreased to 15% and the pore size distribution had changed completely with an almost complete loss of the larger pores. SEM pictures of zinc electrodes cycled in Zn/NiOOH batteries showed an accumulation of metallic zinc towards the center of the electrode paralleled by a loss in porosity [8]. Lower electrode porosity results in limited zinc utilization owing to earlier depletion of hydroxide ions within the zinc electrode.

The amount of nonactive metallic zinc present in the anode after the last discharge in the cycle life test was approx. 1.2 Ah. At a discharge current < 300 mA (e.g., at a current similar to that applied during the formation cycle) the electrodes could be discharged to a final nonactive capacity of 0.3 Ah of metallic zinc.

Figure 6 illustrates the gains in cell voltage and power obtained with a pasted zinc electrode containing 10 wt % cellulose, relative to electrodes with lower cellulose contents. The oxygen electrode potentials vs Zn_{ref} measured for the three cells showed similar polarization behaviour. Cellulose builds electrolyte channels through the zinc paste which improve the electrolyte transport. In addition, passivation of the electrode is prevented at very high discharge currents (e.g., for peak power drain conditions) since the porous structure of the electrode is not completely blocked.

4. Conclusions

The average pore size of pasted ZnO electrodes containing 1–10% cellulose, 4% PTFE and 2% PbO is shifted towards larger pore diameters with in-

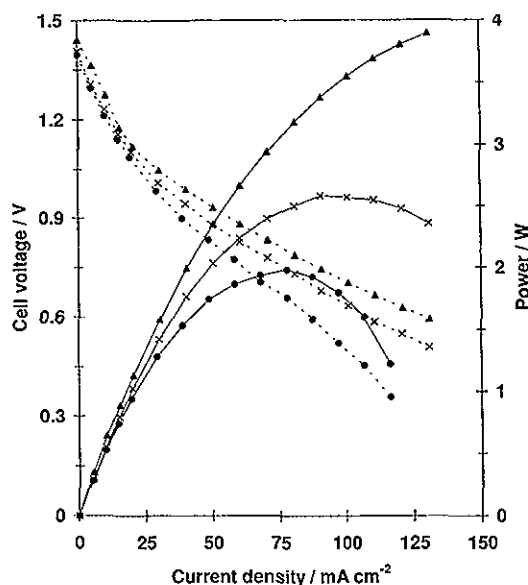


Fig. 6. Voltage (---), current density and power (—) delivered by Zn/O₂ cells with pasted zinc electrodes containing: (●) 1%, (×) 5% and (▲) 10% cellulose. Zn electrode surface area: 50 cm² (two sides of the electrode are active).

creasing cellulose content. The change in porosity which occurs during cycling can be diminished by using pasted Zn electrodes with higher cellulose content. With 10 wt % cellulose as a pore builder and internal wick, the cycle life of the pasted zinc electrode could be increased by a factor of five to ten. In addition the optimization of porosity and wettability of the zinc electrode led to a higher peak power drain capability.

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