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DEVELOPMENT OF A 12 V / 20 Ah ELECTRICALLY RECHARGEABLE ZINC-AIR BATTERY

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This paper reports results obtained at the second stage in our development of a light-weight, low-cost 12 V / 20 Ah zinc-air battery. We successfully developed electrodes having large working areas (up to 200 cm^2), and increased the Zn electrode capacity in order to achieve a high specific energy in the range of 100 Wh/kg for the 12 V / 20 Ah battery. Deep discharge cycles at different currents were carried out for single cells and batteries with nominal capacities of 15 Ah and 30 Ah. For the 12 V / 20 Ah battery a cycle at low rate was performed.

INTRODUCTION

For many applications such as portable electric equipment, integrated PV-systems as well as electric vehicles, the electrically rechargeable zinc-air battery shows very promising properties. Major advantages in addition to its high practical specific energy (ca. 100 Wh/kg) are the low cost of zinc as is anode material, its reversibility in aqueous electrolytes and the low toxicity of the materials used for the battery system [1, 2].

During the last several years different research teams made a great effort to develop components for the electrically rechargeable zinc-air battery. Their studies were mainly fundamental and focused on the development of bifunctional catalysts [3], corrosion-resistant conductive substrates for the oxygen electrode catalysts [4], reversible zinc electrodes, and electrolyte systems to inhibit zinc corrosion, dendrite formation, and shape change during cycling [5].

In contrast to these prior studies, the present research program at the Paul Scherrer Institute aims at demonstrating the feasibility of an electrically rechargeable 12 V / 20 Ah zinc-air battery with a specific energy and specific power in the range of ca. 100 Wh/kg and 100 W/kg, respectively.

In the first stage of this program battery components such as bifunctional oxygen diffusion electrodes and electrically rechargeable zinc electrodes with surface areas of 25 cm^2 and a nominal zinc electrode capacity of 2.5 Ah were developed [6,7]. With $La_{0.6}Ca_{0.4}CoO_3$-activated two-layer gas-diffusion electrodes significant progress has been made in recent years towards the demonstration of a high number of cycles [3, 8]. On the anodic side of the cell the structure of pasted zinc electrodes was optimized by using cellulose additives with a specified fibre length in concentrations of up to 10 wt.% [9]. Compared to conventional electrodes with 1-2 % newsprint [5] as an additive, these zinc electrodes showed extended service life, higher zinc utilization at high discharge rates and higher peak power drain capability [10].

In the second stage of this program, which is reported in this paper, electrodes having large working areas (up to 200 cm^2) were developed. A battery was modularly built up to an open-circuit voltage of ca. 13.5 V and a rated capacity of ca. 20 Ah.

EXPERIMENTAL

Electrode Preparation

Zn electrode. A process for preparing pasted zinc electrodes has been described which involves vacuum filtering of a slurry consisting of ZnO, PTFE, PbO and cellulose [11, 7]. It is successful for smaller electrodes and low production rates. However, for preparing larger pasted zinc electrodes on an industrial pasting device, the consistency of the slurry has to be optimized and adapted to the machine. The water added to the mixture of ZnO (84 wt.%), PbO (2 wt.%) and cellulose fibers (10 wt.%) must not amount to more than approximately 30 wt.%. The stiff ZnO paste obtained can be used for a continuous industrial process as well as for hand-pasting. The two preparation processes are outlined in Figure 1. As described elsewhere [9] the Zn loading of the larger electrodes (>100 mA/cm^2) was increased by a factor of 1.5 to ca. 75 mAh/cm^2. Based on this value a nominal capacity of 30 Ah is attained in a 200 cm^2 cell (the Zn electrode is active on both sides).

Different types of current collector such as 1.3 mm Pb-grids (used for lead-acid-batteries), 0.15 mm expanded lead metal (Exmet), and 1.3 mm Sn-grids were tested in zinc electrodes with bifunctional oxygen-diffusion electrodes as the counter electrode. Concerning the peak power drain capability and available discharge capacity, we found the same performance for zinc electrodes with the two lead current collectors. A markedly lower conductivity resulting in approx. 30 % lower peak power was measured with Sn current collector in the anode. For all further experiments described in this paper 0.15 mm expanded Pb metal current collectors were used for the zinc electrode.

Bifunctional Oxygen-Diffusion Electrodes. The two-layer electrodes were activated with a $La_{0.6}Ca_{0.4}CoO_3$ catalyst that had been synthesized in our laboratory by an amorphous citrate precursor method. The B.E.T. surface area of the catalyst was ca. 15 m^2/g, the particle size was in the range of 1-2 μm. Further details concerning the preparation of the electrodes can be found elsewhere [8].

Battery design. Figure 2 shows the components necessary for assembling a single cell. The zinc electrode was first wrapped in Celgard separator and soaked with the alkaline electrolyte, then positioned between two bifunctional air electrodes each glued into a Plexiglas frame. The cell package was held together by two Plexiglas end-plates. A low-weight polypropylene case was used in order to demonstrate high specific energy data. The 12 V / 20 Ah battery excluding battery case is presented in Figure 3.

The cells were cycled using a computer-controlled system (Kepco electronic load, software LabView etc.). Initially metallic zinc was formed during three cycles at C/25 charge and discharge cycles. For the 200 cm^2 cell the final capacity of metallic zinc in the electrode was 20 Ah, which is two thirds of its nominal capacity. The ZnO remaining in the electrode serves as a reservoir which improves the cyclability of the cell, as already demonstrated for Zn/NiOOH cells [5].

The maximum zinc utilization in the Zn electrodes was evaluated by discharging two thirds of the nominal capacity of the cell at different rates (C/25 - C/2.5) until the cell voltage dropped below 0.7 V. Finally complete discharge to a cell voltage of 0.7 V was performed at 1.25 mA/cm^2, followed by zinc formation at the same current density.

Cycle life tests were performed by cycling one third of the nominal capacity ($C_{nom}/3$) (or 50 % of the metallic zinc). If the voltage limit of 0.7 V mentioned above was reached before $C_{nom}/3$ could be discharged, the recorded capacity was then used as the new capacity for the following charging process, thus the rated capacity gradually decreased. Cycling continued until the rated capacity had dropped below 50 % of its original value (below $C_{nom}/6$).

RESULTS

Scale-up of Zn electrodes and batteries

Discharge Performance. Figure 4 compares the available capacities of 25 cm^2, 100 cm^2, and 200 cm^2 cells, discharged at A) the 24 h rate and B) the 4 h rate. For the 25 cm^2 cell, 100 % rated capacity corresponds to 1.75 Ah, but for the two larger cells (100 and 200 cm^2) the specific capacity was increased to 10.04 Ah and 20.33 Ah of rated capacity. The increase in Zn loading for the larger electrodes resulted in thicker Zn electrodes and a somewhat lower Zn availability. At low discharge rates the activity of the bifunctional oxygen electrodes influences the cell voltages. We found that after an activation period of approx. 100 - 200 h, minor differences in the catalytic activity of the electrodes were noticed in some experiments (not in that of Fig. 4).

Figure 5 a/b illustrates the discharge performance at different rates for batteries with two and five cells in series. Single cell voltages between 1 and

1.25 V were measured for discharge rates between C/25 and C/2. The corresponding values of average power were: for the battery of Fig. 5a, 20 W @ C/2.1, 11 W @ C/4.2, 5.5 W @ C/8.3 and 2 W @ C/25, and for the battery of Fig. 5b, 48 W @ C/2.1, 26 W @ C/4.2, 14 W @ C/8.3 and 4.8 W @ C/25. For the two-cell battery the available capacity gradually decreased with increasing discharge rate, but for the five-cell battery we observed very even discharge performance up to a discharge rate of C/2. However, for both systems the discharge voltages were very stable and the delivered capacities were in the range of 80 % to 95 %. With the high-zinc-loading anodes (C_{nom}=75 mAh/cm^2), low-weight current collectors and a polypropylene housing, a specific energy in the range of 80 - 100 Wh/kg was obtained for the five-cell battery under the discharge conditions described here.

Finally the 12 V /20 Ah battery was built by connecting ten 200 cm^2 cells in series. Figure 3 shows the battery package which was finally built in a polypropylene case of the type usually used for lead acid batteries. Modification were made to the battery case for an air supply provided by two 0.5 W fans. The whole battery package including battery case, electrolyte and air supply system weighs 2.3 kg. 30 % of the battery weight is associated with the pasted zinc electrodes, followed by 24 % for the electrolyte. The air electrodes and the battery case each contribute 14 % of the battery weight.

Figure 6 illustrates the voltages independently measured for each cell during a low-rate charge and discharge cycle of the 10-cell battery. For all ten cells the charging voltages were reproducible at 1.96 V +/- 10 mV. At discharge all ten cells delivered 93 % of the rated capacity (20 Ah) at an average battery voltage of 11.5 V. The corresponding specific energy of the battery amounts to ca. 95 Wh/kg.

Cycle life of a single 200 cm^2 cell. The most time consuming experiments were cycle life tests for all electrode and battery sizes. Scale-up of the electrode size with a simultaneous increase in zinc loading resulted in a lower cyclability, especially at high discharge rates. For the thinner zinc electrodes the longest cycle life was obtained with moderately alkaline electrolyte of 15 % KOH, but the thicker zinc electrodes showed earlier failure due to densification of the anode occurring under these conditions. An improvement of the cyclability was achieved with more highly concentrated KOH (up to 30 %). With 100 cm^2 cells (C_{nom} = 15 Ah) and batteries (with two cells in series) at C/6 charge and C/3 discharge rates, approx. 150 cycles were achieved until the rated capacity dropped to 50 % of its original value. Figure 7 illustrates the very stable charge and discharge voltages during routine cycling over 1250 h for a 200 cm^2 cell with a rated capacity of 10 Ah. During the first 1000 h, 100 % of the rated capacity could be cycled. Afterwards a gradual loss in capacity to the defined endcapacity of 5 Ah was observed.

CONCLUSIONS

The bifunctional oxygen-diffusion electrodes and the pasted Zn electrodes have been successfully scaled up in surface area from 25 to 200 cm^2 and in Zn loading from 50 to 75 mAh/cm^2 (of exposed surface area of the Zn-electrode). At low discharge rates nearly 100 % of the rated capacity of the cells was available during cycling. At the C/2 discharge rate ca. 80 % of the rated capacity of the test-cells was available independently of the size and loading of the Zn electrode. With a 200 cm^2 zinc-air cell a cycle life of ca. 1250 h was demonstrated in C/9 charge and discharge cycles. With a package of ten 20 Ah cells connected in series and mounted in a standard lead-acid battery case a specific energy of ca. 95 Wh/kg was demonstrated at low discharge rate.

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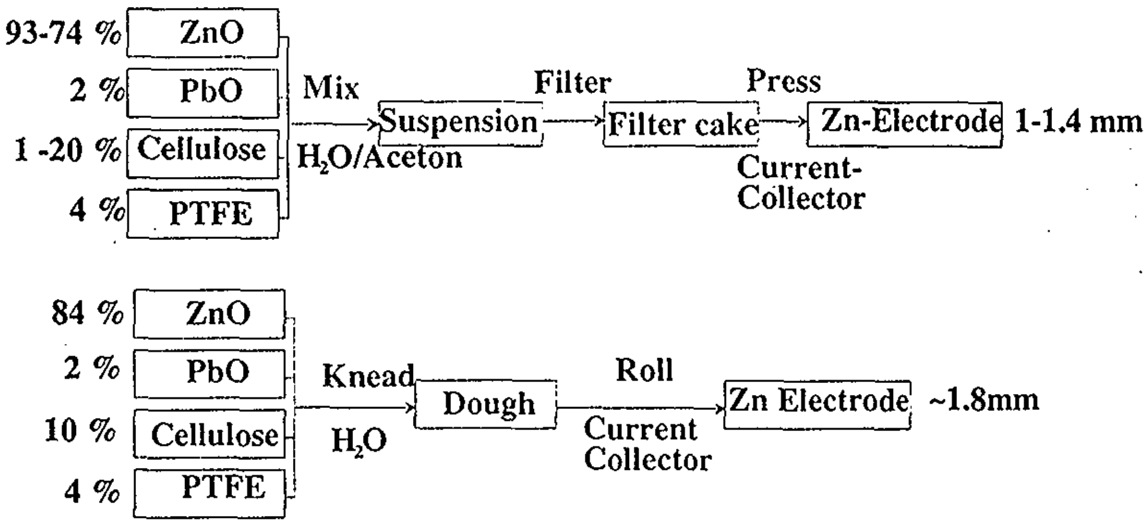

Figure 1 Processes for preparing pasted ZnO electrodes by (a) filtering and (b) pasting on a industrial pasting device.

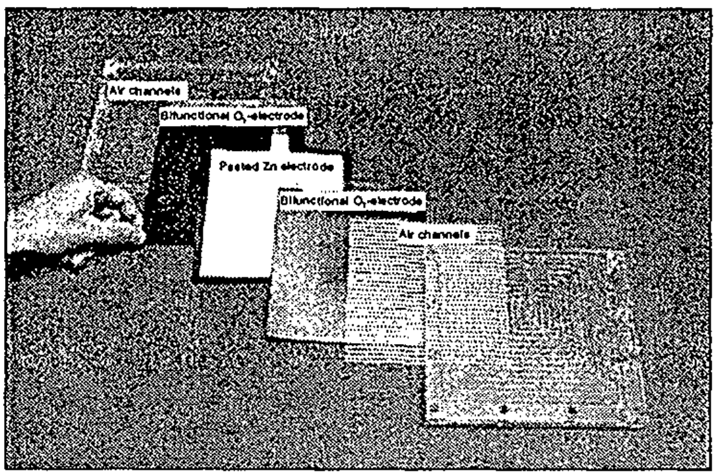

Figure 2 Zn-electrode sandwiched between two bifunctional air electrodes. Corrugated Plexiglas for air distribution and Plexiglas end-plates.

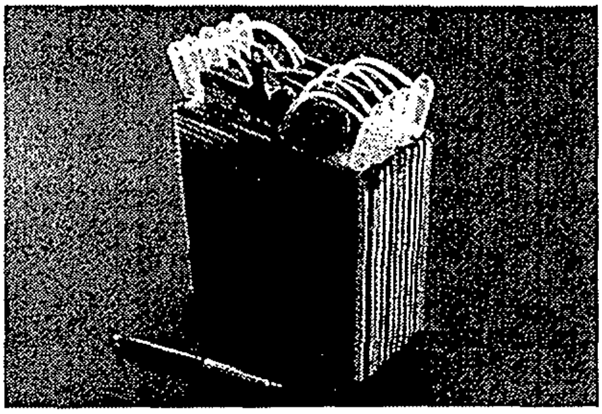

Figure 3 12 V / 20 Ah zinc-air battery (without battery case).

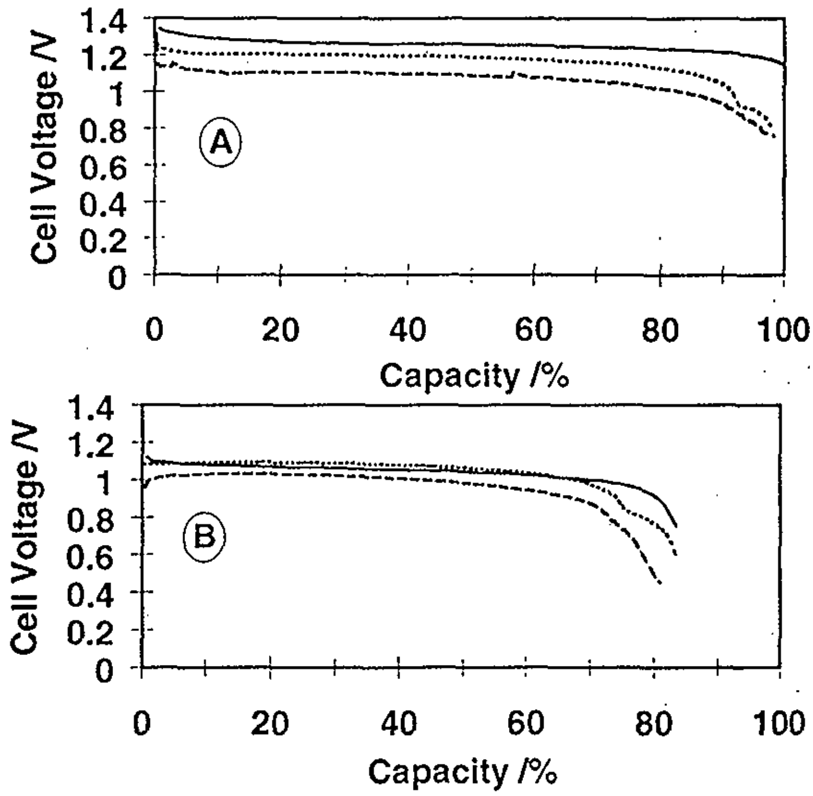

Figure 4 Cell voltage vs. percent capacity delivered by Zn/O_2 - cells: (——) 25 cm^2 Zn electrodes, 1.75 Ah, (- - -) 100 cm^2 Zn electrodes, 10.04 Ah and (— —) 200 cm^2 Zn electrodes, 20.33 Ah. The cells were discharged with A) 2 mA/cm^2 (C/~24) and B) 12 mA/cm^2 (C/~4). Electrolyte: 15 % KOH + 1.5 M KF + $ZnO_{sat.}$

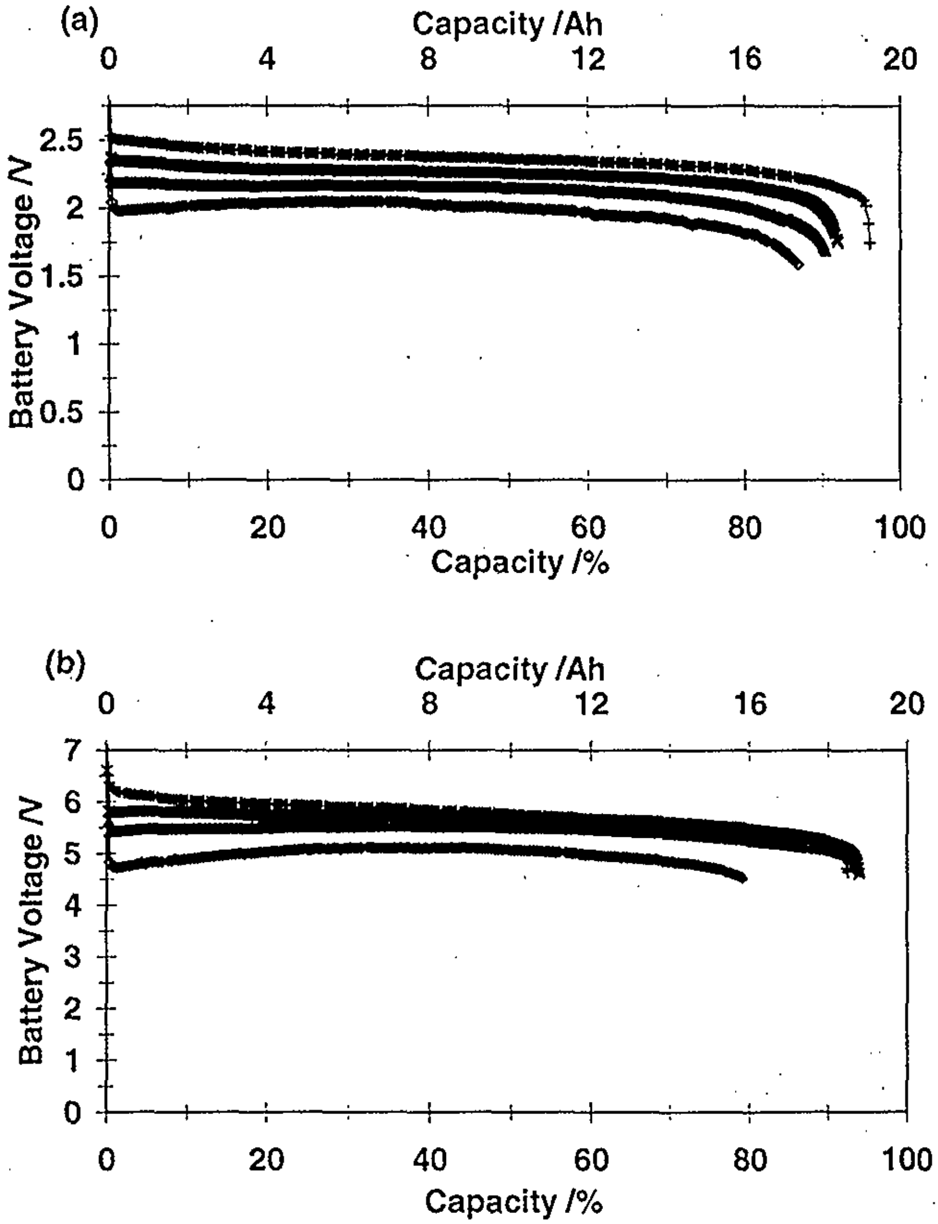

Figure 5 Zinc/oxygen cell voltages and available capacities measured at different rates of discharge for (a) two 20 Ah cells in series; (b) five 20 Ah cells in series. Discharge rates: (+) C/25, (x) C/8.3, (▲) C/4.2, (◆) C/2.1.

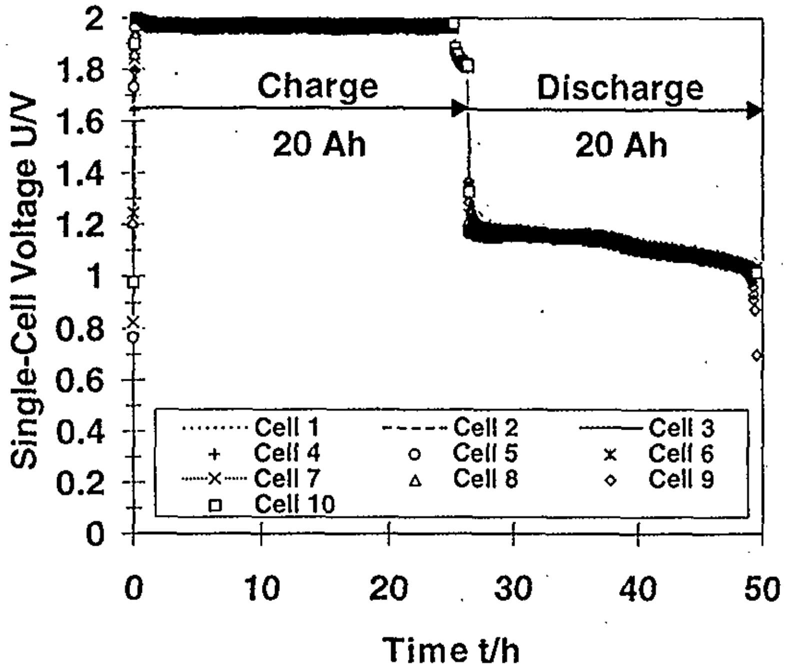

Figure 6 Plot of the single cell voltages individually measured during charge and discharge of the 12 V / 20 Ah Battery.

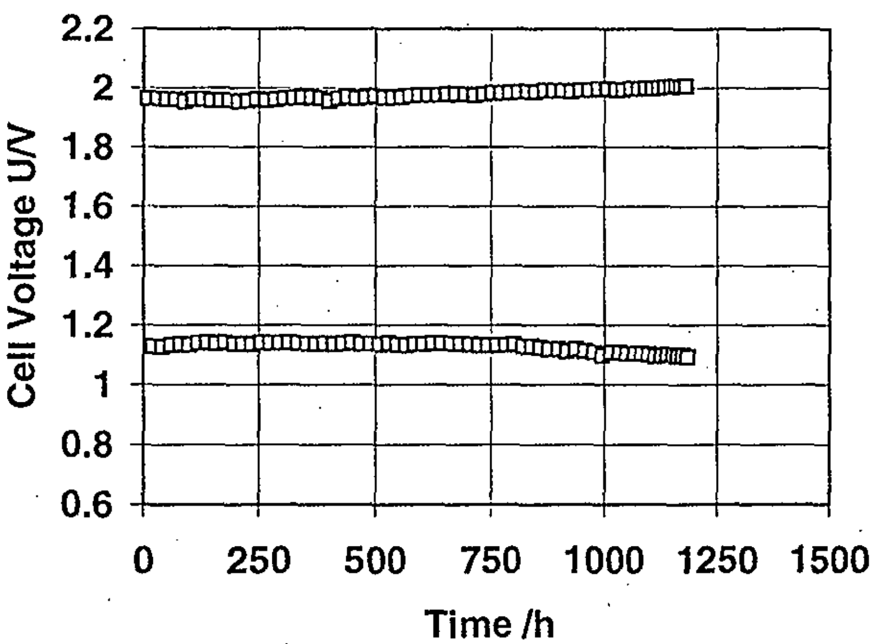

Figure 7 Cycle-life test for a 200 cm^2 zinc-air cell. C/9 charge and discharge cycles. Electrolyte: 30 % KOH, 1.5 M KF, $ZnO_{sat.}$.

Key words: zinc/air battery, pasted zinc electrode, bifunctional oxygen electrode.