

Development and Tests of Cell Components for a 12 V/20 Ah Electrically Rechargeable Zinc/Air Battery

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Abstract

This contribution describes our research and development efforts towards the demonstration of a lightweight and low-cost 12 V/20 Ah electrically rechargeable Zn/air battery with a specific energy in the range of 90-120 Wh/kg.

In this work, we successfully developed pasted zinc electrodes with nominal capacities of 30 Ah and active electrode areas of 200 cm². The La_{0.6}Ca_{0.4}CoO₃-activated bifunctional O₂ electrodes were scaled up from active areas of 25 to 200 cm². Deep discharge cycles at different currents as well as peak power performance measurements were carried out for monopolar multicell zinc/O₂ and zinc/air systems.

Introduction

The most promising results for electrically rechargeable metal/air systems have been achieved with Zn/air systems. Their high theoretical specific energy of 1085 Wh/kg, based on the specific capacity of ZnO (658 Ah/kg) and the theoretical cell voltage (1.65 V), in combination with further advantages such as low price and environmental compatibility of all components make the zinc/air system a very attractive candidate for traction applications. Several different concepts were recently described for systems that are either mechanically [1] or electrically [2] rechargeable. Mechanically rechargeable systems require additional infrastructure, therefore, electrically rechargeable Zn/air systems are preferred for consumer applications such as electric vehicles and portable devices. Practical specific energies in the range of 90 Wh/kg have been reported for electrically rechargeable Zn/air batteries [3].

Recently many investigations have focused on enhancing the cycle life of the components of rechargeable Zn/air cells. Significant progress has been made concerning the cyclability of the system by utilizing pasted zinc electrodes [3-5], low zinc solubility alkaline electrolytes [5],

cellulose additives in the pasted zinc electrodes [6,7], and metal oxide catalysts dispersed on graphitized carbon for the bifunctional oxygen diffusion electrodes [8].

Experimental

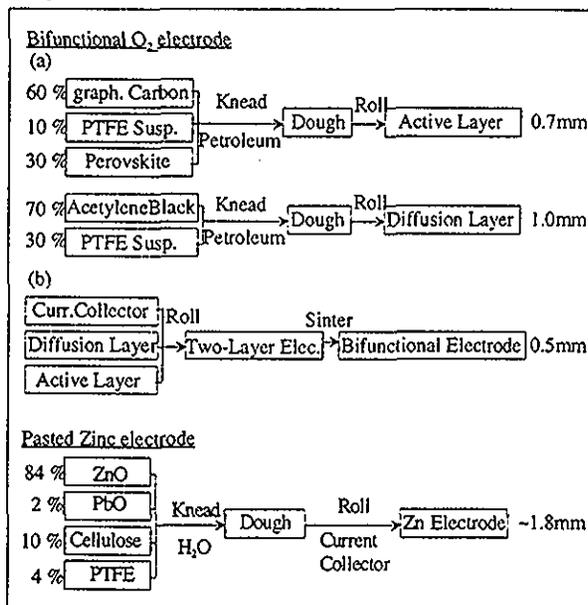


Figure 1: Process for the preparation of bifunctional O₂ electrodes and pasted Zn electrodes.

Our project concerns the scale-up of the electrodes and the improvement of peak power and the discharge capability of the Zn/O₂ and Zn/air battery [7]. We increased the electrode area of our bifunctional oxygen diffusion electrodes as well as the pasted zinc electrodes from 25 cm² to 200 cm². On the cathodic side of the cell, differently prepared catalysts and thermally treated graphitized carbon were evaluated in the bifunctional oxygen diffusion electrode [7]. On the anodic side of the cell, the structure and the wettability of the pasted zinc electrode have been improved, and thus the peak power and the discharge capability of the cells have been enhanced considerably [6,7].

The $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ -activated bifunctional oxygen-diffusion electrodes were prepared by a calendaring and rolling process [8], while the Zn electrodes were prepared by applying an aqueous paste of zinc oxide, cellulose fibers (Technocel 2500, Cff, Mönchengladbach, Germany), traces of lead oxide, and PTFE binder to a lead current collector, as depicted in Figure 1.

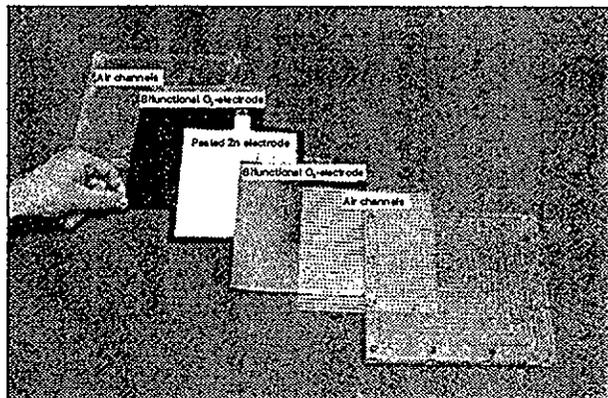


Figure 2: The photo shows the components necessary for assembling a single 200 cm^2 Zn/air cell with a nominal capacity of 30 Ah.

The electrodes were tested in the same formation as depicted in Figure 2. The components were fixed between two Plexiglas plates. This filter press type cell allows an easy modular assembly of batteries. The pasted zinc electrode, wrapped in three layers of Celgard 3401 separator ($0.02\text{ }\mu\text{m}$ effective pore size, Hoechst Celanese Corp., Charlotte, North Carolina), were held between two bifunctional oxygen electrodes, which are covered by a polypropylene wick. A corrugated plastic sheet was placed on the gas side of the oxygen electrode to achieve a homogeneous distribution of oxygen (or air) over the whole electrode area. The electrolyte used was a 30 % KOH solution (w/w) saturated with ZnO and containing 1.5 M KF.

Zinc was formed by charging 2/3 of the nominal capacity at a low current ($\sim C/24$) and afterwards discharging the cell at the same current until the cell voltage dropped below 0.7 V (Figure 3). The formation process was repeated 2 - 3 times. The charged cell (2/3 of the nominal capacity) was then used for deep discharge cycles or for evaluation of peak power performance.

Deep discharge experiments were performed at different discharge rates. In each battery the cell voltages were monitored individually. The batteries were discharged at constant current until

one of the cell voltages dropped below 0.7 V. After reaching the voltage limit the batteries were discharged completely at low current and afterwards charged again to 2/3 of their nominal capacity.

The values of peak powers at different depths of discharge were calculated from current-voltage curves measured for Zn/O₂ as well as Zn/air batteries. The experiment was performed galvanostatically by subsequently increasing the current every 60 s and simultaneously measuring the corresponding voltage.

Results and Discussion

Formation cycles of Zn/air batteries

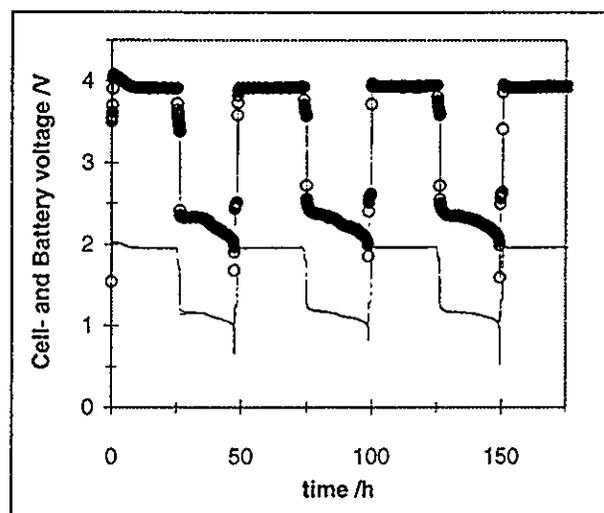


Figure 3: Single cell voltages (-) and battery voltage (o) of two cells connected in series during the first three formation cycles of the Zn/air battery. Two thirds (20 Ah) of the nominal capacity of the zinc electrodes were charged and discharged at C/25.

Figure 3 illustrates the zinc formation process in a Zn/air battery consisting of two cells connected in series with a nominal capacity of 30 Ah. Two thirds of the nominal capacity are charged and discharged at C/25. The coulombic efficiency increased from 85 % in the first to 96 % in the last cycle.

The charging voltage of the Zn/air battery is very stable at around 4.0 V and the discharge voltage drops during discharge from 2.5 to about 1.9 V. Indications for completion of the formation process are the higher and more stable discharge voltage of the last cycle as compared to the first and the increased coulombic efficiency.

Discharge capabilities of Zn/air systems

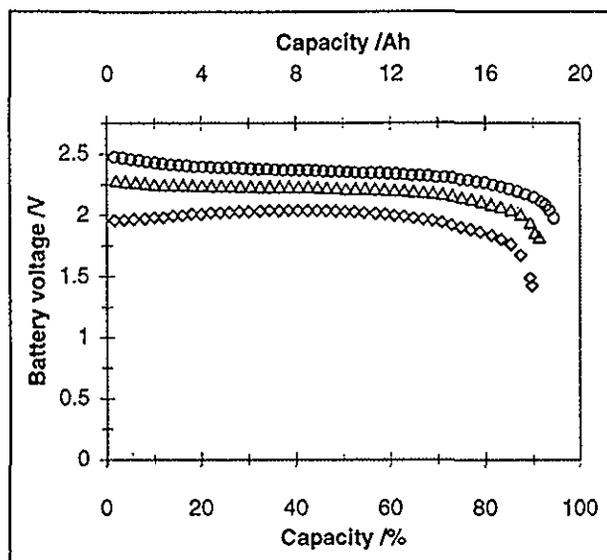


Figure 4: Deep discharge performance of Zn/air batteries consisting of two cells connected in series, at different discharge rates: (\diamond) C/2.1, (Δ) C/8.3 and (\circ) C/25. The batteries were charged to 2/3 of their nominal capacity (20 Ah).

Figure 4 shows the discharge capability of a 200 cm² Zn/air battery (two cells connected in series) at different rates of discharge. The battery had been charged to a capacity of 20 Ah. At a discharge rate of C/2.1, 90 % of the charged capacity was delivered by the battery, and at lower discharge rates 96 % of the capacity were obtained. The discharge voltage is very stable over a long period of discharge; only at the end of the discharge process is a drop in battery voltage detected. The average power delivered by the Zn/air battery was 20 W at C/2.1, 5.5 W at C/8.3 and 2 W at C/25.

The calculated specific energy of a complete Zn/air battery is based on the following weights of the components:

Component	Measured Mass [g]
Zn electrode	70
Electrolyte	55
O ₂ electrode (2 pieces)	40
Frame	15
Gas distributor	10
Battery (2 cells, 3 distributors)	390

The mass of a two-cell battery is 390 g. Specific energies of 90, 105 and 115 Wh/kg were calculated for C/2.1, C/8.3 and C/25 discharge rates, respectively.

Peak power performance of Zn/air and Zn/O₂ batteries

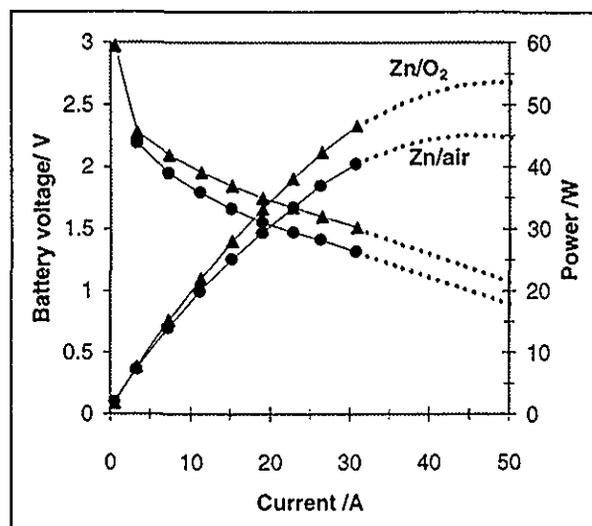


Figure 5: Current-voltage and current-power curves of a (\blacktriangle) Zn/O₂ and a (\bullet) Zn/air battery. Both batteries had two cells connected in series and a nominal capacity of 30 Ah. The Zn/O₂ battery was charged to 17.7 Ah (59 %), the Zn/air battery to 20 Ah (67 %).

The peak power performance of 200 cm² Zn/air and Zn/O₂ batteries is shown in Figure 5. The batteries had two cells connected in series, and they were charged to 59 % (Zn/O₂) and 67 % (Zn/air) of their nominal capacity of 30 Ah. A peak power of 45 W could be demonstrated for the Zn/air, and one of 55 W could be demonstrated for the Zn/O₂ system. The specific power is estimated to be 115 W/kg for the Zn/air and 140 W/kg for the Zn/O₂ system.

The achieved peak power is not only a function of oxygen partial pressure (oxygen or air) but also of the charge state of the battery. Figure 6 shows this effect of the charge state of a Zn/air battery. The battery was measured at degrees of charging of 67 %, 48 % and 32 %. The increased amount of ZnO, and therefore the decreasing amount of Zn in the pasted zinc electrode leads to a decrease in conductivity, which is indicated by the change of slope in the current potential curve. The specific power of the Zn/air battery is reduced from

115 W/kg to approx. 90 W/kg when the charge state is lowered from 67 % to 32 %.

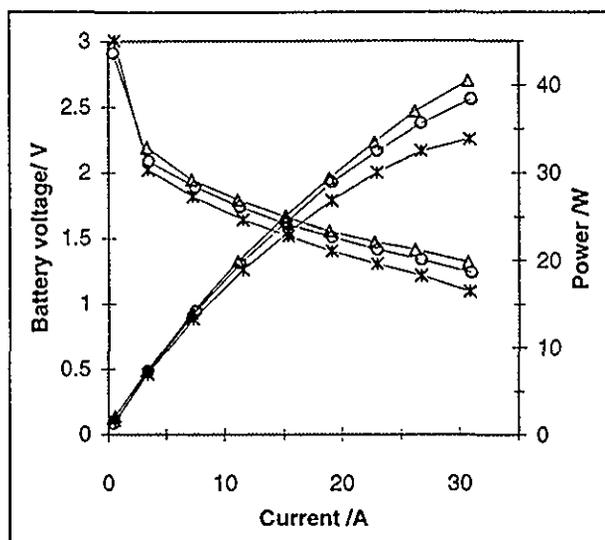


Figure 6: Current-voltage and current-power curves of a Zn/air battery with two cells connected in series and a nominal capacity of 30 Ah. The battery was charged to (Δ) 67 %, (O) 48 % and (*) 32 % of the nominal capacity.

Conclusion

Electrodes, pasted zinc electrodes, and bifunctional oxygen electrodes were successfully manufactured in active areas of 200 cm². The combination of La_{0.6}Ca_{0.4}CoO₃-activated bifunctional O₂ electrodes and pasted zinc electrodes was successfully demonstrated in sandwich-type two-cell batteries.

The deep discharge capability of the Zn/air battery was almost independent of the discharge rate. Between discharge rates of C/25 and C/2.1 the discharge capability decreased slightly from 96 to 90 %, while the average battery voltage decreased from 2.35 to 2.0 V. Based on the weight of the cell components a specific energy of 90 Wh/kg can be calculated for a C/2.1 discharge rate, and values of 105 Wh/kg for C/8.3 and 115 Wh/kg for C/25.

Peak powers of 55 W and 45 W were demonstrated for a Zn/O₂ and a Zn/air battery with two cells connected in series. The lower the charge state of the battery, the lower will be the peak power. Based on the weight of the cell components, specific peak powers of 115 W/kg and 140 W/kg were calculated for the Zn/air and the Zn/O₂ battery, respectively.

Acknowledgments

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