Development of Rechargeable Monopolar and Bipolar Zinc/Air Batteries

Stefan Müller(a), Franziska Holzera), Otto Haasa), Christian Schlatterb), and Christos Comninellisc)

Abstract. For the development of a rechargeable zinc-air battery, LiK0.6Ca0.4CoO2, catalyzed (perovskite) bifunctional oxygen electrodes and pasted zinc electrodes were prepared and tested in monopolar zinc/air cells. In addition, a bipolar Zn/air stack was tested using reticulated copper foam as substrate for the zinc deposit. The cells were cycled in moderately alkaline ZnO-saturated electrolytes with KOH as an electrolyte additive. The maximum power as well as the cycle life of the cells was investigated. The differences in porosity of the zinc electrode before and after the long-term test were analyzed using mercury porosimetry.

1. Introduction

In metal/air batteries only the metallic active material has to be stored in the negative electrode, while oxygen is continuously provided to the positive electrode from the ambient air. These cells offer very attractive specific energy and power data. For zinc/air cells, the theoretical specific energy is 1085 Wh/kg, based on the molecular weight of ZnO (658 Ah/kg) and the theoretical cell voltage (1.65 V). Practical values of 90–300 Wh/kg for secondary and primary batteries, have already been demonstrated[1][2].

Since cheap and nontoxic batteries with a high energy density are a prerequisite for electric vehicles, we think that investigation of these batteries will prove very rewarding.

About 25 years ago, GM and other companies gave up their Zn/air battery projects, since their oxygen electrodes had a very short life time and were not bifunctional, i.e., could not be used for the charging process. In fact, the service life of their Zn/air module was only ca. 200 h. In one of their studies, they came to the conclusion that the Zn/air battery would only be interesting for private electric car applications, if the battery could be recharged electrically, but not, if it was recharged mechanically by replacing the Zn electrodes. For an electrically rechargeable Zn/air battery, bifunctional oxygen electrodes and Zn electrodes with minor shape change[3] and no dendrite formation are necessary. More recently, LBL (Lawrence Berkeley Laboratory) developed a pasted zinc electrode with a high cycle life[4], mainly for the Zn/NiOOH battery.

With the pasted Zn electrode, more than 500 cycles could be demonstrated in a Zn/NiOOH battery; moreover, the cycle life of this battery was not limited by the Zn electrode. Shape change, which typically degrades Zn electrodes, was not the major problem in these cells, since they used moderately alkaline ZnO-saturated electrolyte and electrode or electrolyte...

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Abstract. For the development of a rechargeable zinc/air battery, LiK0,6Cao,4Co2O4, catalyzed (perovskite) bifunctional oxygen electrodes and pasted zinc electrodes were prepared and tested in monopolar zinc/air cells. In addition, a bipolar Zn/air stack was tested using reticulated copper foam as substrate for the zinc deposit. The cells were cycled in moderately alkaline ZnO-saturated electrolytes with KF as an electrolyte additive. The maximum power as well as the cycle life of the cells was investigated. The differences in porosity of the zinc electrode before and after the long-term test were analyzed using mercury porosimetry.

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additives (Ca(OH)$_2$ and K$_2$CO$_3$/KF, respectively), which lowers the solubility of the zinc-electrode discharge products and inhibits redistribution of the Zn [4][5].

Recently, Shimizu et al. proposed a bifunctional oxygen electrode using La$_{0.6}$Ca$_{0.4}$CoO$_3$ as a catalyst [6]. Together with LBL, we improved this electrode from the point of view of operation time. This electrode needs corrosion resistant support material for the bifunctional catalyst and a stable catalyst with a good bifunctional activity for the O$_2$ reduction and evolution reaction. On top of the active layer a hydrophobic diffusion layer is necessary to prevent electrolyte leakage. The corrosion rate of the electrode material could be improved considerably using graphitized carbon as a catalyst support material [7]. To achieve a good oxygen electrode potential, the catalyst has to activate the disproportionation reaction of the peroxide being formed at the electrode. Such porous two-layer perovskite-catalyzed diffusion electrodes, which were prepared by the rolling technique, exhibited constant O$_2$ evolution (2 V vs. Zn, 10 mA/cm$^2$) and reduction potentials (1.2 V vs. Zn, 10 mA/cm$^2$) during 1300 h (130 cycles). For the electrodes, ca. 20% La$_{0.6}$Ca$_{0.4}$CoO$_3$ was homogeneously dispersed on graphitized Vulcan XC 72 (B.E.T. = 70 m$^2$/g) [8].

In this publication, we present some results obtained with a monopolar 25 cm$^2$ Zn/oxygen cell and with a bipolar cell stack. In the bipolar battery, the Zn was deposited in and dissolved from a reticulated Cu foam (preplated with a dense Pb-layer). The metal-foam zinc electrode was originally developed by Ross [9]. In contrast to his work, in which he proposed a soluble zinc electrode (formation of Zn(OH)$_4$ during discharge), we worked with an insoluble discharge product. To this end, a moderately alkaline electrolyte in which insoluble ZnO is formed during discharge was applied for the cycling test. For the monopolar cell, as in the Zn/NiOOH cell, a ca. 1-mm-thick pasted Zn/ZnO electrode with a specific charge of ca. 50 mAh/cm$^2$ was used. While in the monopolar cell configuration the zinc electrode is sandwiched between two bifunctional oxygen electrodes, in the bipolar cell arrangement only one cathode faces the anode.

2. Experimental Procedures

The monopolar and bipolar zinc-oxygen test cells are depicted in Fig. 1a and b. The monopolar cell consists of a pasted Zn/ZnO electrode held between two bifunctional oxygen electrodes. The capacity of the 25 cm$^2$ zinc electrode ($\Omega$ = 56.4 mm, thickness ca. 1 mm) was 2.5 Ah (active on both sides). The process for preparing pasted zinc electrodes is outlined in Fig. 2. The electrodes were prepared from a slurry containing 84 wt-% ZnO, 4 wt-% PTFE, 2 wt-% PbO, and 10 wt-% cellulose. To each side of a Pb-plated Cu mesh, the vacuum-filtered slurry was pressed. More details are described in [10]. In addition to ZnO (84 wt-%), the electrode contained a relatively high amount of cellulose (10%). To prevent drying out of the cell, cellulose was used as an internal wick. Dendritic shorting of the cell was prevented by wrapping the Zn electrode in three layers of Celgard 3401 separator (0.02-µm effective pore size, Hoechst Celanese Corp., Charlotte, North Carolina). Each separator layer was heat-sealed. Before the pasted zinc electrodes were mounted in the cell, they were degassed under vacuum and then soaked with electrolyte.

The formation of the Zn on the electrode was realized by charging the electrode with 1.7 Ah (2/3 of the total capacity) at 1.25 mA/cm$^2$ and then discharging it using the same current density, until the cell voltage dropped below 0.9 V. About three formation cycles were performed before the electrode was used for the cycle test. After the last formation cycle ca. 95% of the charging current could be recovered in the discharge cycle. Under regular test conditions, one third of the initial capacity was cycled at C/6 (6 h charge rate) charge and C/3 discharge rates. The computer-controlled system (software: work bench; hard-
3. Results and Discussion

3.1. Complete Discharge of the Monopolar Zinc-Oxygen Cell

To measure the recoverable capacity of a zinc electrode which was previously charged by transforming two thirds of the activated Zn electrode, one third of the initial capacity of (45% KOH + 12 g/l ZnO) to a nominal capacity of 1.5 Ah. After the first charge, the electrolyte was replaced by a 20% KOH containing 1.5M KF and ZnO (saturated). During discharging in this moderately alkaline electrolyte, oxidized Zn precipitates as ZnO on the foam. There was no electrolyte flow during cycling. As with the pasted Zn electrode, one third of the initial capacity of the Zn-Cu-foam was finally cycled at C/2 discharge and C/4 charge rates. Under these operating conditions, the current densities were two times higher than for the monopolar cell.

The bifunctional oxygen electrodes were fabricated by applying the rolling technique. Petroleum-wetted dough consisting of Teflon, graphitized Vulcan XC 72 and La$_2$O$_3$Co$_3$O$_4$ catalyst was rolled in several steps to a thin active layer. A more hydrophobic gas transport layer and the active layer were finally rolled together. One end of the bipolar cell, the more hydrophobic gas transport layer and the active layer were finally rolled together. The current collector, an expanded Ni mesh (Stork Veco, B.V. NL), was pressed on top of the gas transport layer. The assembly was then sintered under pressure at 340 °C and 50 kg/cm$^2$. A detailed report on the preparation and the electrochemical and physical properties of these electrodes has already been published [8].
zinc oxide to zinc, we performed some galvanostatic discharge experiments at 63 mA, 300 mA, 600 mA, 900 mA, and 1200 mA. For all these experiments, the electrode was first charged with 1.615 Ah using a current of 150 mA. In Fig. 3, these discharge experiments are illustrated by plotting the potentials measured vs. a zinc reference electrode against the cell capacity (taking 1.615 Ah as 100%). At very low discharge currents (63 mA) 95% of the zinc was available for the oxidation process. Up to 600 mA, the average Zn electrode polarization was less than 100 mV. At 1.2 A, the overpotential was a bit higher, but still 80% of the Zn was available for oxidation, and more than 50% could be oxidized with an overpotential < 100 mV. These results demonstrate that the battery may be discharged completely. For high cycle life, it is advantageous, however, to use an initial loading of ZnO which is three times the design cycle capacity. The relatively high amount of zinc not involved in cycling improves the conductivity of the electrode considerably. On the other hand, if the electrode is charged until 100% of the ZnO is transformed to Zn, the porosity of the electrode may decrease substantially upon cycling. For routine cycling, a current of 0.3 A and a design capacity of ca. 0.85 Ah were chosen for an electrode with 2.5 Ah capacity. Under these cycling conditions, and taking into account the electrode and electrolyte mass of our laboratory cell combined with an estimated mass for the cell case and hardware (ca. 15% of the complete battery mass), a specific energy of ca. 70 Wh/kg was calculated. Higher specific energy can be obtained, if more than one third of the zinc is cycled, e.g., at low discharge rates two thirds of the zinc can be cycled, and a specific energy of 120–140 Wh/kg should be achievable.

3.2. Long-Term Performance
3.2.1. Monopolar Cell
In Fig. 4, the cell voltages and electrode potentials (vs. Znref) are plotted vs. the cycle number for a cell with an electrolyte containing 15% KOH and 1.5M KF. For the first 100 cycles, the average charging and discharging potentials of this battery were 2.0 V and 1.2 V, respectively. More than 90% of the potential losses in this cell are related to the overpotential at the bifunctional oxygen electrode. Its deviation from the standard potential was ca. 250 mV for the oxygen evolution and 450 mV for the reduction process. The polarization at the Zn electrode was close to 50 mV. The cathodic polarization of the
3.2.2. Bipolar Cell

The end-plates of the bipolar battery were first tested as a single cell; the polarization of the bifunctional oxygen electrode and the zinc electrode vs. Hg/HgO, respectively, are plotted in Fig. 6a against the number of cycles performed. To achieve a homogeneous zinc deposition on the reticulated Cu-foam, the first charging process was performed at limiting current density and high flow rate of the 45% KOH electrolyte. The cycling test of this electrode was then performed with 20% KOH and stationary electrolyte at current densities of 6 mA/cm$^2$ (charge) and 12 mA/cm$^2$ (discharge). The polarization of the zinc electrode slightly increased under these conditions. The conductivities of 45% KOH and 20% KOH are comparable (ca. 500 mS/cm). Thus, the small increase in internal resistance is related to ohmic losses in the zinc foam and its electrical connection to the end plate. In contrast to the bifunctional electrode, which did not change its performance during the next 20 cycles, the zinc electrode exhibited a slightly higher polarization, especially at discharge.

The capacity of the cell dropped below 100% after 100 cycles and remained at 90% for the next 30 cycles. Capacity decay continued during the next 200 cycles. After 350 cycles the capacity had dropped to 50% of the design capacity (0.85 Ah). At this point, a formation cycle at low rate (25 h; 1.25 mA/cm$^2$) was performed. After this formation cycle, the cell delivered again an average capacity > 60%.

The porosity of the zinc electrode was analyzed before and after the cycle test. The average pore diameters were 0.5 and 5 μm for the new and used electrode, respectively. During cycling, the porosity of the pasted Zn-electrode markedly decreased from 65 to 20% (Fig. 5).

Energy efficiency calculations (including overcharge) led to an average value of 45%; at the beginning of the cycle test the energy efficiency was ca. 55%. A small overcharge of ca. 3% was necessary to compensate for zinc corrosion due to hydrogen evolution at the zinc and its recombination at the oxygen electrode. Dendritic shorting was not observed during the long-term test. It seems that any zinc dendrites produced during charging are oxidized in the O$_2$-rich environment.

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By adding two bipolar cells to the system, the theoretical discharge voltage of three cells in series could be experimentally demonstrated, as shown in Fig. 6b. During the charging process small oxygen bubbles were observed at the oxygen electrode, which was not the case in the more compact monopolar cell with pasted Zn electrodes where oxygen was diffusing out of the cell via the porous gas diffusion electrode. The undesirable gas evolution could be responsible for increased polarization at the zinc electrode.

3.3. Specific Peak Power

3.3.1. Monopolar Cell

The maximum power of the monopolar cell was measured at different states of charge. The cell characteristic for a charged (66% Zn) and discharged (33% Zn) cell is depicted in Fig. 7. The conductivity of the zinc electrode slightly decreased during discharging, which is indicated by the slope of the current-potential curves. Thus the maximum peak power of the charged cell was 20% higher than for the discharged one. The calculated specific peak power (based on the same weight assumptions as used for the specific energy calculation) was 160 and 130 W/kg for the charged and discharged monopolar cell, respectively. This specific power is only available for short times (1–2 min).

3.3.2. Bipolar Battery

In Fig. 8 the voltage and power density of a bipolar battery consisting of three cells are plotted vs. the current density. In the bipolar cell design, only one bifunctional oxygen electrode faces each zinc electrode. It is, therefore, more difficult to achieve a high specific power. In addition, this battery was not optimized from the point of view of the weight of the cell components and the porosity of the Cu foam. But if these components are optimized, we estimate that a specific energy of 80 Wh/kg and a specific power of 80–100 W/kg should be achievable.

4. Conclusion

It was successfully demonstrated that the combination of a pasted zinc electrode with \( \text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_{2-\delta} \)-catalyzed bifunctional oxygen electrodes results in a long-life rechargeable battery. 450 charge/discharge cycles were demonstrated for 0.85 Ah zinc/oxygen cells with moderately alkaline electrolytes. A maximum short-time peak power of ca. 160 W/kg was determined for charged cells. The specific energy depends strongly on the discharge rate. At useful discharge rates for electric vehicle application (C/1) the specific energy of the battery is still ca. 60 Wh/kg if only one third of the zinc is cycled. At low current density as applied during the formation cycles (1.25 mA/cm²), the specific energy reaches 120–140 Wh/kg, when two thirds of the zinc are cycled. Densification of the pasted Zn electrode seemed to be the major reason for the loss of battery capacity at high cycle numbers.

The bipolar configuration was successfully demonstrated by applying porous Cu-foams as the matrix for the zinc deposit. A great advantage of the highly porous zinc electrode is its accessibility to electrolyte flow. At periodic service intervals the formation of new, well distributed zinc on the foam is possible by providing flowing highly alkaline electrolyte.

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