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Development of an electrically rechargeable zinc air battery for electric vehicles

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Abstract

Zinc air batteries have very high theoretical energy densities, are made of cheap abundant materials, are safe and contain no toxic substances. They are therefore good candidates for electric vehicles. Their major drawback is poor lifetime when cycled due to the bad stability of the air electrode when used to recharge the battery. An alternative oxygen bi-electrode concept has been demonstrated in zinc-air cells with very good stability.

Keywords: zinc air battery, BEV (battery electric vehicle)

1 Introduction

Zinc air batteries have very high theoretical energy densities (> 900 Wh/kg) and are made of cheap abundant materials (zinc, potassium hydroxide, carbon, manganese). The cost of zinc is close to 1 €/kWh based on current zinc prices (around 1000 €/tonne) [1] and the air electrode can be made for as little as 18$/m² for the equivalent of 500 000 vehicles/year [2], which adds around between 4-5 €/kWh to the cost of the battery. Zinc-air batteries could potentially be manufactured at a cost lower than lead-acid batteries, the cheapest technology today.

World resources of zinc are estimated at 300 times greater than those of lithium and therefore pose no threat of resource limitation, even if all vehicles were powered with zinc.

The zinc-air battery is an aqueous system with no toxic or inflammable substances. Zinc is also easily recyclable. They are therefore safe and environmentally friendly.

Commercial primary button cell zinc-air batteries are sold by the millions everyday for hearing-aids. They can have very high energy densities, up to 442 Wh/kg for the Duracell DA675 button cell. The primary zinc-air battery is therefore a mature technology, which is not the case for the secondary, rechargeable variety.

All these properties therefore make them very good candidates for electric vehicles. Unfortunately, their major drawback is the very low lifetime of the battery when recharged electrically. For this reason, nearly all the EV demonstration projects to date have used primary zinc-air batteries which were «recharged» mechanically by replacing the zinc electrode by a fresh one [3].

2 Bifonctional oxygen electrode

Several attempts have been made to develop an electrically rechargeable zinc-air battery using a bifonctional electrode [4]. In this configuration, the air electrode is used both as oxygen reduction electrode and an oxygen evolution electrode. Unfortunately, the two functions are very different and require different electrode morphologies and catalysts.

2.1 Mechanical failure

The oxygen reduction electrode uses a gas, oxygen from the air, as the reactant. It therefore requires a large reaction surface area in contact with both the ionic conductor, the electrolyte, and the current collector, the electrode. This large surface area exposed to the gas ensures that sufficient reactant (oxygen) is fed to the electrode for the electrochemical reaction, to produce the required current. The optimised air electrode has an open porous structure which behaves as a 3D electrode. It is composed of a carbon powder which is shaped into a porous electrode using a hydrophobic polymer such as PTFE. This polymer has two functions : binding together the carbon powder and preventing the electrolyte from flooding the electrode. The electrolyte penetrates the electrode to provide ionic percolation to all reaction sites whilst keeping the porous structure open so that air can also reach the reaction sites. These reaction sites are also called triple phase interfaces because only when the thee phases meet (oxygen, electrolyte, electrode) can the electrochemical reaction take place (fig 1). This optimised electrode structure gives very good results, with current densities as high a 1 A/cm² when used in fuel cells [5].

Negative zinc electrode :
E_0= -1,25 V/ENH

$$Zn + 4OH^- \leftrightarrow Zn(OH)_4^{-2} + 2e^- \qquad (1)$$

$$Zn(OH)_4^{2-} \leftrightarrow ZnO + 2OH^- + H_2O \qquad (2)$$

Positive oxygen electrode :

E_0 = 0,401 V/ENH

$$O_2 + H_2O + 4e^- \leftrightarrow 4OH^-_{(aq)} \qquad (3)$$

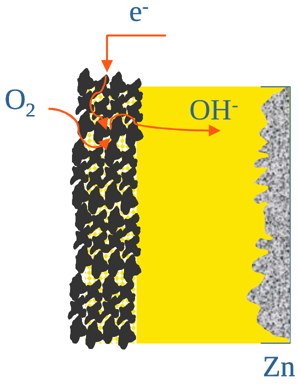

Figure 1 : Air electrode during discharge

During charge, a two phase process is involved at the air electrode/oxygen evolution electrode in which a gas is produced by the reactant in the form of a liquid (eqn 3). The reaction occurs at the interface of a liquid (the electrolyte) and a solid (the electrode) and does not require a high surface area. The fragile 3D open porous structure of the oxygen reduction electrode is not the most appropriate electrode. The tests performed in our laboratories using an air electrode as an oxygen evolution electrode showed that the mechanical integrity of electrode was rapidly destroyed by the gas evolution within the electrode, causing flooding by the electrolyte inside the porous structure (fig. 2).

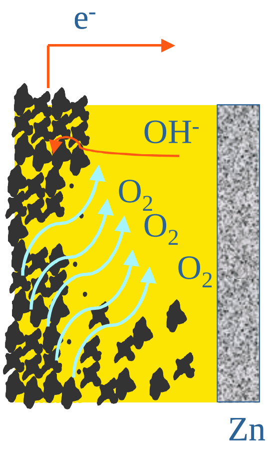

Figure 2 : Air electrode during charge

A stronger 2D electrode is more appropriate for this reaction, such as those used in electrolysers.

2.2 Electrochemical failure

The open circuit cell voltage of the zinc-air cell is typically around 1.5V and drops to 1.2V when in operation in discharge. These potentials are compatible with the air electrodes and do not induce pronounced corrosion or breakdown of the electrode materials. However, the cell voltage needs to be raised to around 2V during the charging process due to the large overpotential of the oxygen evolution reaction. These very high oxidation potentials have two consequences :

(a) MnO_2 which is used as a catalyst is not stable in alkaline solution under these potentials and is oxidised to MnO_4^- which goes into solution [6].

(b) Carbon corrosion by oxidation [7] is accelerated under these potentials

The destruction of the catalyst was confirmed by running UV-Visible spectra of the electrolyte solution at different potentials (fig 3). The spectra clearly show that at potentials higher than 0.4V vs Hg/HgO, the catalyst is not stable and goes into solution

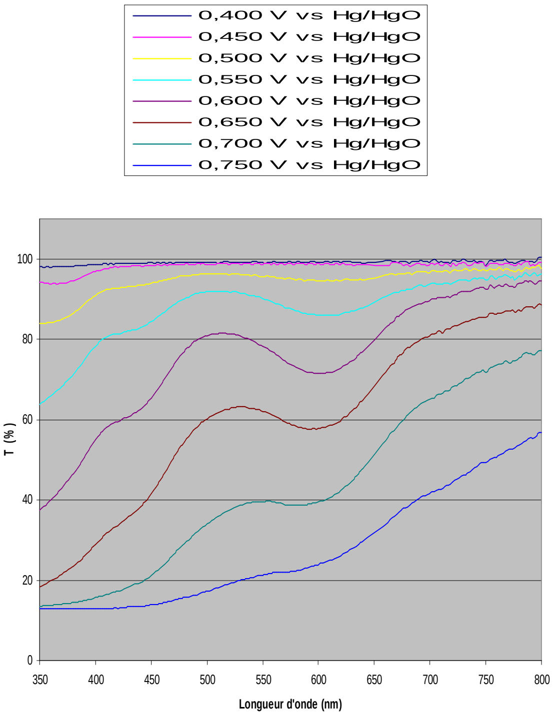

Figure 3 : UV-Vis Spectroscopy of an air electrode containing MnO2 catalyst at different potentials

3 Oxygen bi-electrode

To overcome the problems encountered with a single oxygen reduction/oxygen evolution electrode, a two electrode concept was developed in which the two functions are separated and do not interact with each other. In this concept, a second oxygen evolution electrode is added to the traditional oxygen reduction electrode in the shape of a thin metal grid. To preserve the porous electrode, the oxygen evolution electrode is electrically decoupled during the charge with a simple electronic circuit (fig 4).

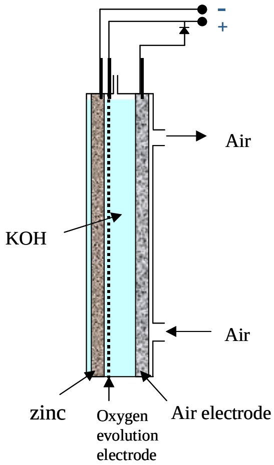

Fig 4 : zinc-air cell with oxygen bi-electrode

Using this concept, cycling tests were performed on half cells with oxygen bi-electrodes composed of a traditional commercial air electrode with MnO_2 catalyst (E4 electrode from Electric Fuel®). The electrodes lasted for more than 3000 cycles with one cycle per hour.

4 Complete Zinc-Air Cells

Full cells using zinc electrodes developed by the company SCPS were built and tested in a symmetrical arrangement in which two bi-electrodes were placed on either side of the zinc electrode (fig. 5). This configuration ensures a more uniform cycling of the zinc within the negative electrode.

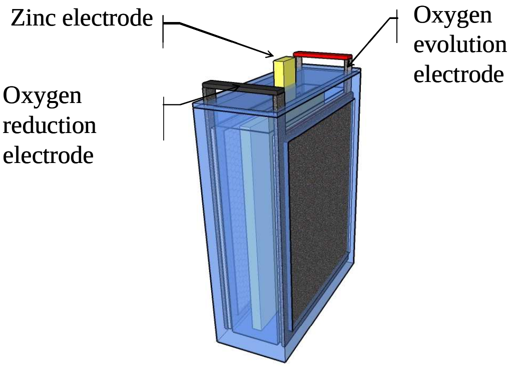

Fig 5 : Zinc-air cell with oxygen bi-electrode

Full cells with 3 Ah zinc electrodes achieved more than 100 full cycles with little degradation. Cells with 6Ah electrodes are now running for more than 1000h at 80% discharge with no degradation to date (fig. 6).

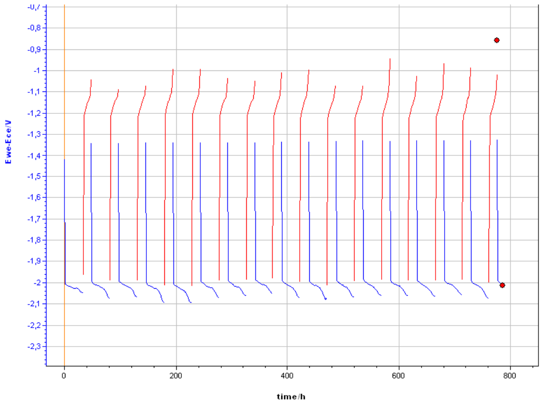

Fig. 6 : Cycling of a complete 6 Ah zinc-air cell

5 Conclusions

The zinc-air battery holds great promise for the electric vehicle as a low cost, high energy density, safe and ecological battery. The primary zinc-air battery is commercial and mechanically rechargeable alternatives have been demonstrated on a large scale on electric vehicles. However, only the electrically rechargeable zinc-air battery really meets the requirements of the EV. The poor cycling stability of the air electrode has been the main limitation in development of the secondary zinc-air battery. An alternative concept has been demonstrated in which the two functions of the oxygen electrode are electrically decoupled in a bi-electrode configuration, which enables each half-electrode to be optimised for their function. This concept has been demonstrated in full cells and has been shown to be stable for more than 1000 hrs to date (the cells are still running). It proves to be a simple and cheap solution for rechargeable metal-air cells which does not compromise its energy density.

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