DECHEMA FORSCHUNGSINSTITUT

Chemical Technology

Development of a zinc/air fuel cell

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Introduction

The recent advances in micro electro-mechanical systems and in downsizing of electronic compounds lead to the development of a new generation of sensors and actuators. These systems often require an autonomous energy supply that has to be miniaturized as well. Because of its high theoretical energy density, low toxic properties and attractive price, the zinc/air fuel cell is an interesting candidate. However, large scale commercialisation of this system is hindered by inherent drawbacks of the zinc electrode, such as poor reversibility, low energy efficiency, shape change and dendrite formation during the charging process. Moreover, the activity of bifunctional catalysts for oxygen reactions and the resistance of gas diffusion electrodes (GDE) towards carbonate poisoning have to be improved.

Electrode reactions

The electrode reactions for the zinc/oxygen system in high concentrated alkaline solution (pH 14) are listed below followed by the calculation of the theoretical maximal capacity of 1g zinc:

	Discharging process	**Charging process**
Cathode:	$0{,}5\ O_2 + H_2O + 2e^- \rightarrow 2\ OH^-$ (+ 0,4 V)	$ZnO + H_2O + 2\ e^- \rightarrow Zn + 2\ OH^-$
Anode:	$Zn + 4\ OH^- \rightarrow Zn(OH)_4^{2-} + 2\ e^-$ (-1,25 V)	$2\ OH^- \rightarrow 0{,}5\ O_2 + H_2O + 2\ e^-$
	$Zn(OH)_4^{2-} \rightarrow ZnO + 2\ OH^- + 2H_2O$	

Overall reactions: $Zn + 0{,}5\ O_2 \rightarrow ZnO$ (+1,65 V) $\qquad ZnO \rightarrow Zn + 0{,}5\ O_2$

Specific capacity: $Q = (m/M) * z * F = 819\ mAh\ g_{Zn}^{-1}$

Objectives

Five research institutes and five companies are involved in this project that aims at the development of a new type of zinc/air fuel cell (www.ziluzell.de). The last part of this project focused on the development of a electrically rechargeable zinc/air single fuel cell with a $La_{0.6}Ca_{0.4}CoO_3$ cathode, a polymer membrane (PVA) and a zinc foam/paste anode. The principle of the micro fuel cell is presented in figure 1.

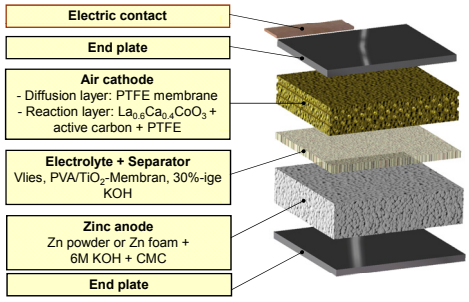

Figure 1: *Principle of the novel zinc/air fuel cell*

Experimental

The main work of the KWI in this project deals with the electrochemical characterization of the electrode materials in a half-cell, the development of reaction layer for the air electrode and the test of the different compounds in a laboratory fuel cell. The electrochemical characterization was carried out by using cyclic voltammetry and chronopotentiometry methods. The flow chart of the catalyst, ink and cell preparation and characterisation is shown in figure 2.

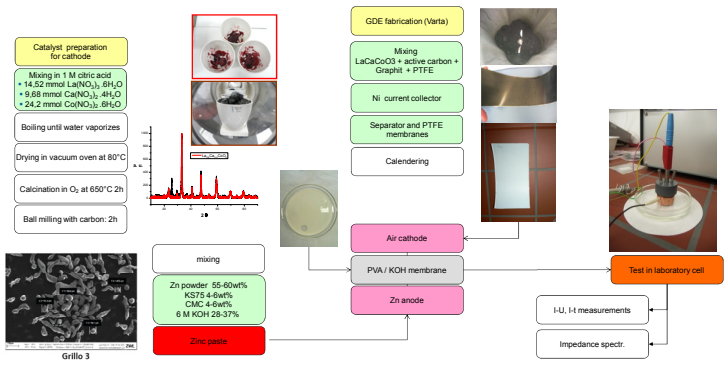

Figure 2: *Preparation and test procedure of the zinc/air micro fuel cells.*

Results

Characterisation of the air cathode in the half-cell

Prior the test in fuel cell, the gas diffusion electrode was tested towards oxygen reduction reaction (ORR) in a flow cell. At 50 mA cm^{-2}, the potential difference between oxygen reduction (discharge) and oxygen evolution (charge) at $La_{0.6}Ca_{0.4}CoO_3$ is large and amounts about 925 mV (see Fig. 3).

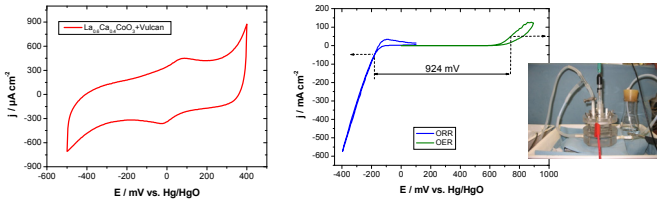

Figure 3: *CV of 0,5 mg cm^{-2} $La_{0.6}Ca_{0.4}CoO_3$-Vulcan (1:1)/ TCP (left) in 6 M KOH / N_2 at 40 mV s^{-1} and (right) in 6M KOH / air at 5 mV s^{-1} and 25°C.*

Tests in the laboratory cell

One important challenge consisted on optimise the laboratory cell for long-term experiments in a way to prevent any electrolyte leak. The best results (17 cycles) were obtained with a paste containing 55% Zn, 4% KS75, 6% CMC and 35% 6M KOH, a Celgard separator and a perovskite-based bifunctional oxygen cathode.

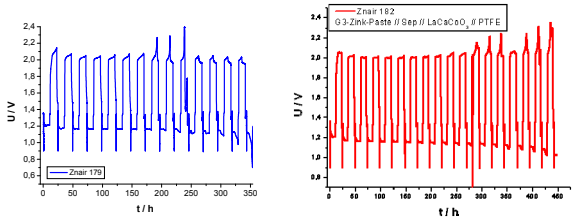

Figure 4: *Discharging/charging behavior of an electrically rechargeable zn/air battery*

Zinc/air button cell

In the last part of the project, an intensive cooperation with Varta Microbattery was planed in order to develop a rechargeable zinc/air button cell. Several compounds were tested such as zinc foam (Uni Bremen), PVA membran (HS mannheim) and bifunctional air cathode (Varta, DECHEMA).

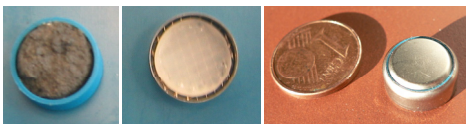

Figure 5: *from left to right; zinc foam anode, air cathode with PVA/TiO_2-membran and assembled Zn/air button cell.*

The best results were obtained with a Zn paste, a commercial separator and the bifunctional air electrode (Fig. 6). After measurement, however, a brown colored layer was observed close to the air holes that is obviously due to active carbon dissolution.

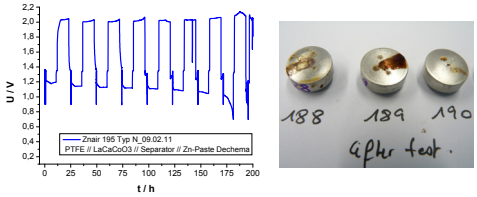

Figure 6: *Left: 8 discharge/charge cycles of a button zinc/air cell with a zinc paste, Celgard separator and $La_{0.6}Ca_{0.4}CoO_3$/active carbon air electrode.Right: Zn/air cells after test*

Conclusion & outlook

The feasibility of a rechargeable zinc/air fuel cell composed of a zinc paste, a commercial separator and a bifunctional cathode was demonstrated in the laboratory cell. The corrosion resistance of the air electrode should be improved. Further experiments with a zinc foam and a PVA/TiO_2 membrane have to be carried out.

BMBF and project partners are thanked for financial support and excellent cooperation, respectively.