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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 alcaline 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 first part focuses on the development of a non-rechargeable zinc/air single fuel cell with a MnO_2 cathode, a polymer membrane (PVA) and a zinc foam anode. The principle of the micro fuel cell is presented in figure 1.

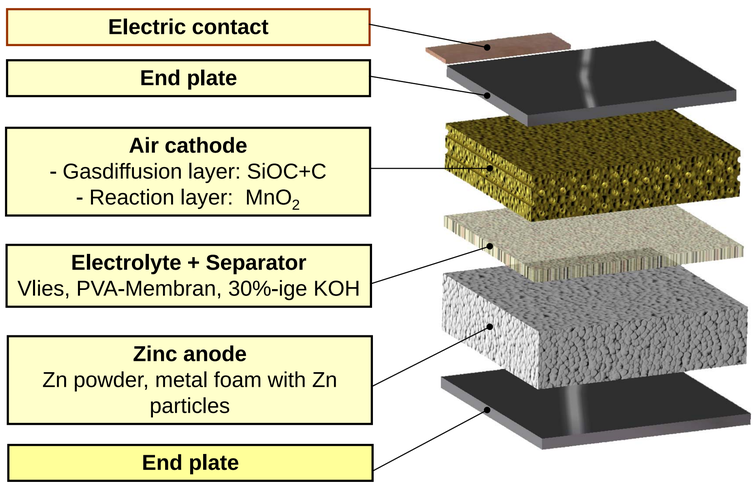

Figure 1: *Principle of the novel zinc/air fuel cell*

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 cell preparation and characterisation is shown in figure 2.

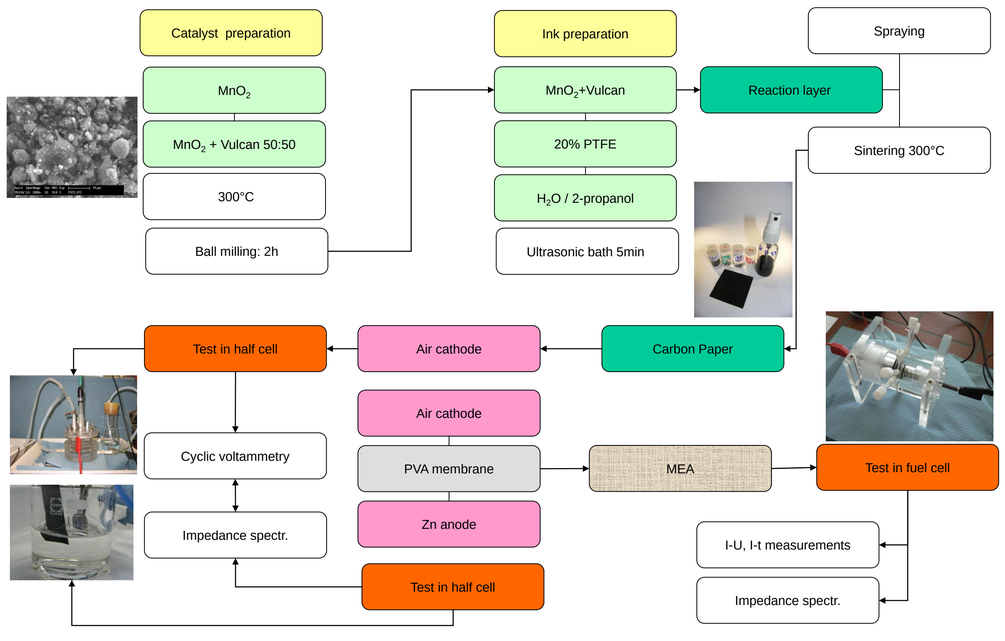

Figure 2: *Preparation and test of the zinc/air micro fuel cells.*

Results

Air cathode

One of the most important challenges consists on avoiding catalyst flooding and electrolyte leak. In commercial cells, this problem is solved by pressing a PTFE membrane together with the gas diffusion electrode. In this project, a thin PTFE layer was incorporated in the GDE. In the case of GDE53, no diffusion limitation was observed compared to the system without PTFE layer (GDE51) during the test in the GDE cell.

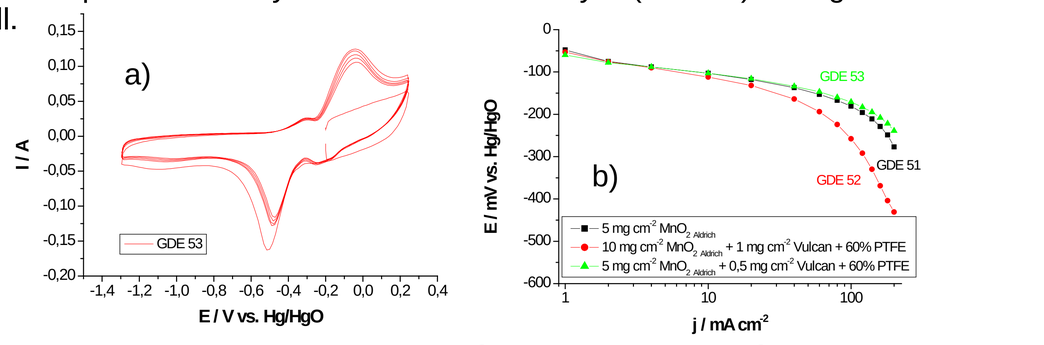

Figure 3: *a) Voltammogramms of 5 mg cm^{-2} MnO_2 + 0,5 mg cm^{-2} Vulcan/60%PTFE in 6 M KOH at 40 mV s^{-1}. b) Activity of different cathodes in the GDE cell with air.*

Zinc anode

The use of a Zn foam as anode material should promote the direct oxidation of Zn to ZnO and suppress the zincate formation. The zinc foam anodes were polarized under half-cell conditions in order to test their electrochemical stability in 6 M KOH (fig. 4). This test should not be confounded with a battery charge/discharge cycle. In this experiment, one anodic charge for oxidation of Zn to ZnO amounts 5-7C, whereas the theoretical charge for 1 g zinc is 2952 C. Zn13 in fig. 4b exhibits the highest corrosion resistance or slowest dissolution rate into the zincate complex during cycling.

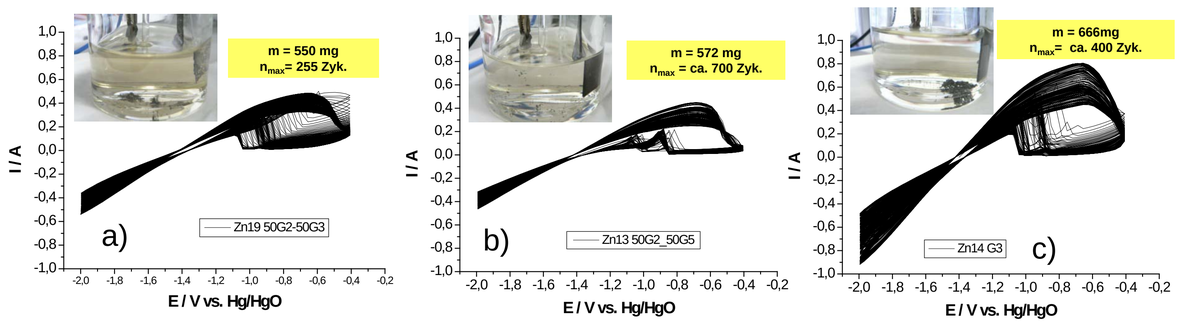

Figure 4: *Cycling test of different Zn foams in 6 M KOH at 40 mV s^{-1}.*

Zinc/air laboratory cell

In the last part of this project, the test of the compounds were carried out in a Plexiglas cell without any tube for electrolyte addition similar to the working conditions of a commercial cell. Some compounds and results are shown in figure 5. The wetting of the zn foams with KOH is still a problem and should be improved.

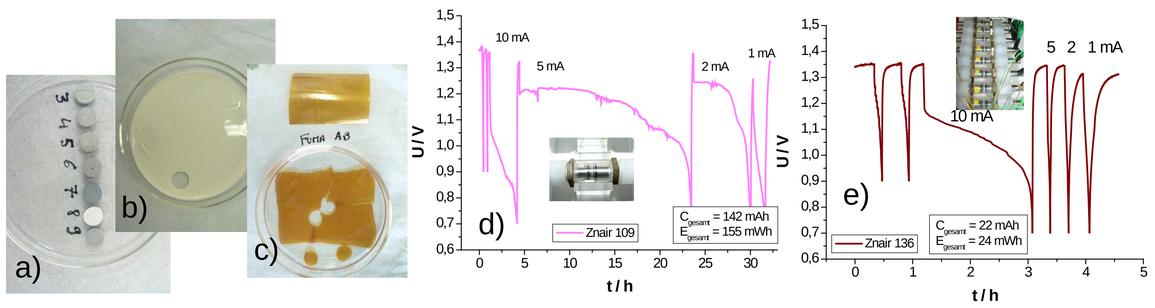

Figure 5: *a) Zinc foams (uni Bremen), membranes b) PVA-TiO_2 (HS Mannheim) & c) Fumapem (fumatech); d) U/t curve of Zn paste/FumapemAB/5mgcm^{-2} MnO_2 & e) Zn foam/PVA-TiO_2/5mgcm^{-2} MnO_2. at different discharge current values.*

Demonstrator

The cell was designed by Würth GmbH and Siegert GmbH for micro-system applications (efm-systems). The ZiluZell demonstrator a) as well as some measure-ments b) & c) are shown in figure 6. The highest capacity was obtained at znair32 with a zinc paste, a PVA membrane and 5 mg cm^{-2} MnO_2 and was about 125 mAh (405 mAh/g_{zinc}).

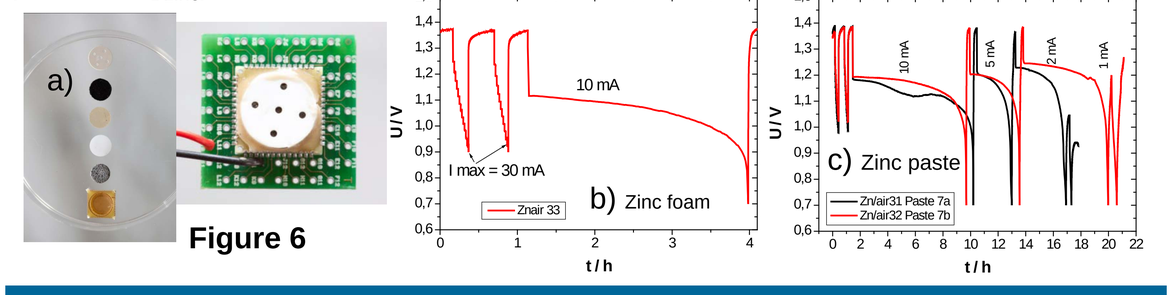

Figure 6

Conclusion & outlook

The feasibility of a non-rechargeable zinc/air fuel cell composed of a zinc foam, PVA membrane and MnO_2 cathode was demonstrated. The chargeability of this system with a bifunctionnal cathode will be investigated in a following project.

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