Development and characterization of a zinc/air micro fuel cell

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Funded by BMBF, Framework: „Mikrosysteme 2004-2009“
Project: ´“Zink/Luft-Mikrobrennstoffzelle-ZiLuZell“
Period: 01.10.2008 – 30.09.2010

Bundesministerium für Bildung und Forschung

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 have 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 gasdiffusion 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: $Zn + 4\ OH^- \rightarrow Zn(OH)_2^{4-} + 2\ e^-$ (-1,25 V)	$2\ OH^- \rightarrow 0{,}5\ O_2 + H_2O + 2\ e^-$
$Zn(OH)_2^{4-} \rightarrow ZnO + 2\ OH^- + 2H_2O$	
Overall reactions: $Zn + 0{,}5\ O_2 \rightarrow ZnO$ (+1,65 V)	$ZnO \rightarrow Zn + 0{,}5\ O_2$

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.

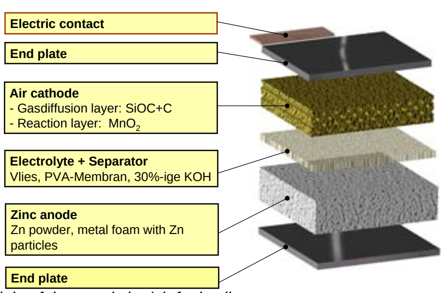

Figure 1: *Principle of the novel zinc/air fuel cell*

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.

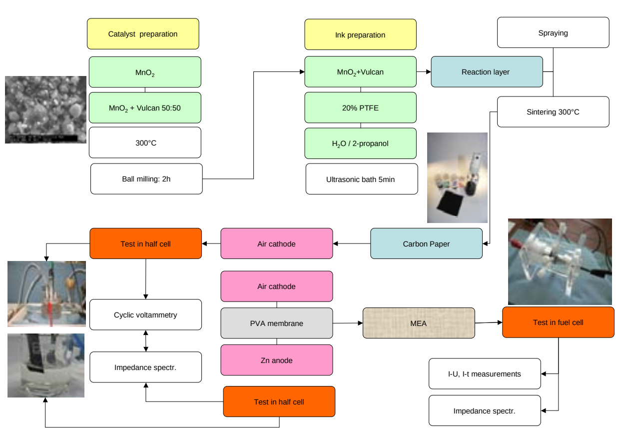

Figure 2: *Preparation and test of the zinc/air micro fuel cells.*

REM, XRD and Hg porosimetry analysis

Commercial MnO_2 powders (Sigma Aldrich, Riedel, Tronox and Merck) were mixed with carbon vulcan to increase electronic conductivity and milled in order to get smaller MnO_2 particle size. The influence of the pore builder concentration (decane) on the structure of Zn foam anodes (Uni Bremen) was investigated. The results of the different analysis are shown in figure 3.

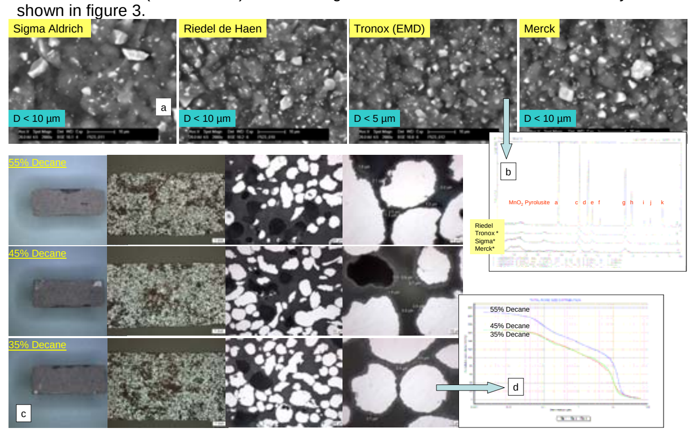

Figure 3: *a) REM pictures anb b) XRD analysis of commercial MnO_2/Vulcan mixtures (1:1 wt%). C) Light microscope and d) Hg porosimetry analysis of different zinc foams.*

- particle size diameter of MnO_2 was reduced down to 10 µm after 2 hours ball milling.
- very good zinc particle interconnection through thin ZnO layer (grey layer)
- high porosity was achieved for the zinc foam with 55vol% Decane

Half-cell and fuel cell measurements

The activity of MnO_2/Vulcan GDEs toward oxygen reduction was tested in the half-cell and compared to that of Pt and the bifunctional catalyst $LaCaCoO_3$.

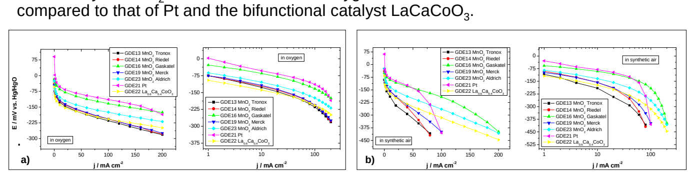

Figure 4: *U-I characteristic of different commercial MnO_2/Vulcan GDEs in a) pure oxygen and b) synthetic air at 25 ° C. Catalyst loading of all the samples (except commercial Gaskatel electrode) was 0.5 mg cm^{-2}.*

- High activity of all MnO_2 systems for oxygen reduction was observed.
- Gaskatel electrode performance closed to that of Pt.

Different anode, electrolyte and cathode materials (developed by other project partners such as HS Mannheim (PVA membran) and Brüggemann (zinc paste)) were tested in the zinc air laboratory fuel cell. The most important results are listed below:

Figure 5: *Summary of the tests in the zinc/air fuel cell*

Conclusions

- High activity of all MnO_2-Vulcan(1:1) systems for O_2 reduction in the half-cell was found.
- A specific capacity of about 400 mAh per gram zinc has been measured by a discharge current value of 5 mA (electrode diameter 13mm) in the fuel cell.
- Power and energy density of the cell is strongly depending on the available pore volume of the Zn foam that limits the ionic mass transport during the reaction
- The feasibility of a non-rechargeable zinc/air fuel cell on the basis of a Zn foam anode, PVA membane & MnO_2/Vulcan cathode has been demonstrated for the first time.
- Further works will focus on the electrically rechargeable system with $LaCaCoO_3$ as bifunctional cathode material and on the CO_2 capture

The authors thank BMBF for financial support (Förderkennzeichnen 16SV3661) and all the project partners for excellent cooperation.