Development and characterization of a zinc/air micro 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 actuors. These systems often require autonomous energy supply systems 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 commercialization of this system is hindered by inherent drawbacks of the zinc electrode, such as poor reversibility, low energy efficency, 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

Cathode: $0{,}5\ O_2 + H_2O + 2e^- \rightarrow 2\ OH^-$ (+ 0,4 V)
Anode: $Zn + 4\ OH^- \rightarrow Zn(OH)_2^{4-} + 2\ e^-$ (-1,25 V)
$Zn(OH)_2^{4-} \rightarrow ZnO + 2\ OH^- + 2H_2O$

Charging process

$ZnO + H_2O + 2\ e^- \rightarrow Zn + 2\ OH^-$
$2\ OH^- \rightarrow 0{,}5\ O_2 + H_2O + 2\ e^-$

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.

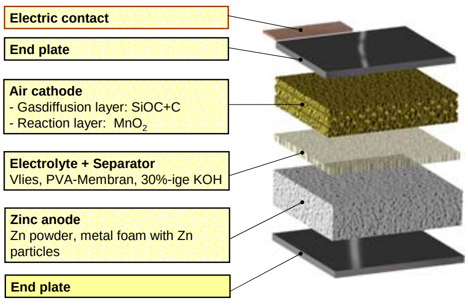


Figure 1: *Principle of the novel zinc/air fuel cell*

Experimental

The main work of the KWI der Dechema 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 cells used in this work can be seen in figure 2.

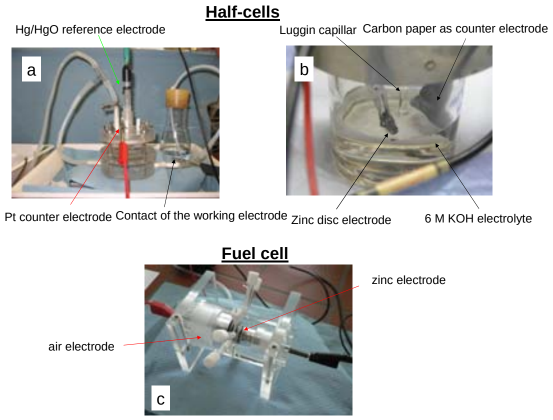
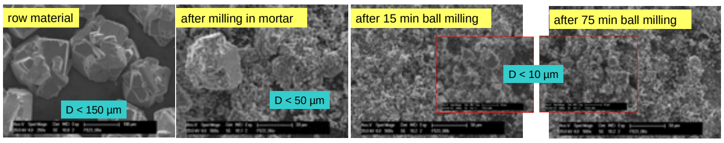
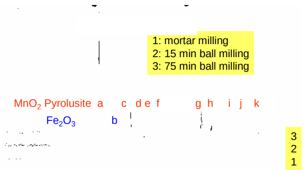


Figure 2: *Half-cells for the test of a) gasdiffusion electrodes and b) zinc electrodes. c) Laboratory cell for the test of the zinc/air micro fuel cells.*

REM pictures and XRD measurements

Commercial MnO_2 powders were purchased by Sigma Aldrich, Riedel de Haen and Merck and milled in order to get smaller MnO_2 particle size. The results of REM and XRD investigation of the Riedel de Haen sample are shown in figure 3 .





- particle size diameter was reduced down to 10 µm after 15 min ball milling.
- Iron oxide contamination due to the steel iron balls increased with growing milling time.
- RDX spectra of the Riedel de Haen sample revealed a crystalline structure that was identified as pyrolusite (β-MnO_2)

Figure 3: *REM and XRD investigations of MnO_2 powder (Riedel de Haen).*

Half-cell and fuel cell measurements

The results of the characterization with the voltammetry method of the MnO_2 on Toray carbonpaper (Riedel de Haen) are shown in figure 4.

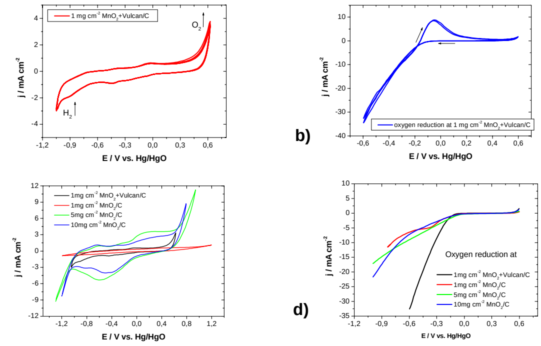


Figure 4: *CVs of GDEs in half-cell at different MnO_2 loadings in a) & c) 6 M KOH at 40 mV s^{-1} and in b) & d) 6 M KOH + O_2 at 5 mV s^{-1} and 25 °C.*

- Higher activity of carbon vulcan containing MnO_2 system for oxygen reduction.
- Poor increase of catalytic activity of MnO_2 with higher manganese dioxide loading.

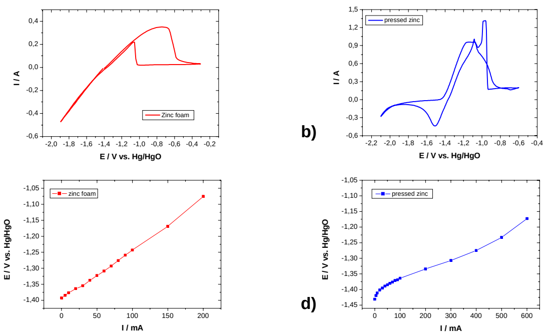


Figure 5: *cyclic voltammogramms and U-I curves of a) & c) a zinc foam and b) & d) a pressed zinc disc electrode in 6 M KOH at 40 mV s^{-1}.*

- Higher oxidation current values measured at the pressed zinc electrode at 100% DOD

First measurement has been carried out in the laboratory fuel cell with a pressed zinc anode, a celgard separator polymer membrane and a Pt/C air cathode

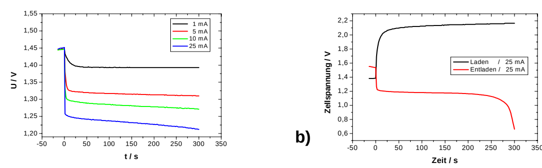


Figure 6: *U-t curves of the zinc/air fuel cell during a) discharging and b) charging and discharging.*

- The fuel cell works. However, passivation of the zinc anode was observed after 250 sec

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