

Environmentally-clean Mg-air electrochemical power sources

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The main aim of this work is investigation, development, and implementation of electrochemical systems of the Mg-Air type with salt electrolytes. The fulfilment of this primary aim will result on one hand in the construction of a comparatively simple and easy to use emergency power source, and on the other, in the development of demo models for training and popularization of the technology for obtaining of ecologically-clean energy.

This research covers:

- Selection of a hydrophobic material with optimal physical, chemical and electrochemical characteristics for the gas layer of the air gas-diffusion electrode;
- Research and selection of a suitable catalyst for the electrochemical reduction of oxygen that occurs on the air gas-diffusion electrode;
- Characterization of various Mg alloys as potential anode material in the Mg-Air system;
- Selection of a non-aggressive salt electrolyte with high ionic conductivity, operational stability, and comparatively low corrosion activity. Design and test of apt constructions for emergency and demo Mg-Air cells.

Key-words: Mg-air cells, air gas-diffusion electrodes, environmentally-clean energy

INTRODUCTION

In the recent years a significant worldwide attention has been paid to the development of new types and novel generations of Electrochemical Power Sources. The interest is mainly due to the extensive search for efficient and ecologically-friendly renewable power sources. The needs for autonomous supply and quick reaction in emergency situations predetermine the extensive use of Chemical Power Sources (CPS) in almost every technical field. Many different types of Metal-Air batteries, like primary, reserve, electrically or mechanically rechargeable battery configurations, have been explored and developed over the last decades. Several metals such as Li, Ca, Mg, Al, Zn, Fe, etc, have been considered for use in the Metal-Air batteries. [1].

Generally the Metal-Air power source comprises of an air gas-diffusion electrode and a metal anode separated by electrolyte. The Metal-Air elements can be viewed as hybrid systems. Their metal anode works as the anodes in the conventional Me/MeO elements, while the cathode operates as a fuel cell. The electrochemical

reduction of oxygen upon an inert air electrode, which is thin and light, results in significantly higher values of the specific characteristics (Wh/kg and Ah/kg) of the Metal-Air element, compared to those, exhibited by conventional elements with an identical metal electrode. The development of Metal-Air systems, operating with non-aggressive, safe and environmentally-friendly salt electrolyte (NaCl, KCl, sea water and others), is of immense practical importance. Despic et al. [2] were the first to investigate Al-Air batteries using physiological electrolytes. Promising results were obtained with primary Al-Air cells in NaCl solution [3]. Despite the good characteristics of the Al in the system, some unsolved problems remained. These problems are related to the high internal resistance of the electrolyte, the formation of a gel of Al hydroxide, and the anode passivation, which made the cleaning of the cell difficult.

The concept of cells, working with sea water, is well-known and has been covered by a number of patents [4–10]. Cells with high energy density and sea water electrolyte involved the use of alloys of the Mg-Hg-Ga type [11]. Shinohara et al [12] reported on the development of a system with sea water for practical application in deep water tanks. The advantages, according to [13], are high energy density, low price, and long storage potential. A joint research project between DGA/BEC (France) and FFI (Norway) focused on the design of autonomous vehicles, powered by semi-fuel cell

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with oxygen as an oxidant, sea water as an electrolyte, and Mg as fuel [14].

Promising results have been obtained with Magnesium-Air cells. The Mg-Air system possesses a number of significant advantages. The use of salt electrolyte is of immense importance for preservation of the environment. The Mg-Air cells are ecologically clean, Mg is non-toxic, no toxic substances are generated during the operation, and the salt electrolyte is chemically non-aggressive. What is more, the Mg-Air cell has practically unlimited storage life. The salt electrolyte can be removed from the cell storage and when necessary, it can be put back, thus making it instantly operational. All of the above, along with the good electrochemical characteristics and the comparatively low price, turns the Mg-Air cell into a very suitable emergency electrochemical power source not only to suit our every-day life needs, but also for application in both, the commercial and the industrial fields. The fact that all components of the cell are harmless and safe, makes the Mg-Air system suitable for demonstration aims (children included) in school labs, for training of students, for specialized university courses, etc.

The Magnesium-Air cell is a conventional electrochemical cell, containing one or two flat air gas-diffusion cathodes, and a magnesium anode, placed in NaCl-solution as an electrolyte. The air gas-diffusion electrode for Metal-Air cell separates the electrolyte from the surrounding air. The electrode, developed in the IEEC, is a double layer tablet, consisting of a porous hydrophobic layer and an active layer, containing porous catalyst. A special highly hydrophobic, electrically conductive material is used to form the gas layer of the electrodes [15, 16].

One of the most important tasks in the development of air gas-diffusion electrodes is to find proper catalysts for the electrochemical reduction of oxygen, which ensures high electrochemical characteristics and long exploitation time of the electrodes. In this respect, the development of non-platinum catalysts for the electrochemical reduction of oxygen is of great interest. Various porous catalysts are tested in air gas-diffusion electrodes, operating in saline electrolytes. The carbon-supported pyrolyzed macrocycles show good oxygen reduction reaction (ORR) activity in alkaline electrolytes, and are currently used in mechanically rechargeable Metal-Air batteries [17–23]. One popular non-noble air cathode is based on cobalt and iron tetramethoxyphenylporphyrine (CoTMPP and FeTMPP). CoTMPP has higher electrochemical

stability and promotes the two-electron ORR pathway, while FeTMPP has inferior ORR activity and promotes direct four-electron oxidation. The stability of the metal macrocyclic complex depends on the metal, and it decreases accordingly: $\text{Co} > \text{Fe} > \text{Mn}$. One common approach to combine the advantages of a more stable CoTMPP and a more ORR active FeTMPP is to fabricate a mixture, FeTMPP/CoTMPP [24]. The ORR activity increases due to the formation of a face-to-face structure, accelerating the destruction of the O–O bond in the oxygen molecule [25–28]. The effect of heat treatment on the N4-chelate stability increase, discovered by Jahnke et al. [29] in 1976, is currently a very popular method for increasing the stability of Co/FeTMPP-based catalysts.

The silver is a typical O₂ reduction catalyst, and has a reasonable high catalytic activity for O₂ reduction, competitive to platinum in alkaline electrolyte [30].

Catalysts, containing mixed Ni-Co oxides, prepared by impregnating active carbon with solution of Ni-acetate and Co-acetate and subsequent heat treatment, are investigated [31].

EXPERIMENTAL

Catalysts, based on different kinds of active carbons, used as carriers, were investigated.

Four types of additional catalysts, introduced into the active carbon, were studied.

VS50–CoTMPP–700 type was prepared while dispersed SiO₂ (VS) was impregnated with a solution of CoTMPP, and after removing the solvent and drying, the material was treated at 700 °C in argon.

Pyrolysed CoTMPP catalyst is produced by impregnation of a dispersed carbon material with a solution of CoTMPP, drying and subsequent heat treatment in Ar at 800 °C. The pyrolysis in Ar of the pure compound of CoTMPP, results in a hard, glassy-like product that practically could not be used as catalyst, so that the presence of a highly dispersed carrier in the production of catalyst seems indispensable. During the heat treatment, the CoTMPP-molecule is decomposed and the pyrolysis residual products are formed in the porous structure of the carbon support and are responsible for the observed high electrochemical activity of the catalyst.

ACCoNi catalyst was prepared by impregnation of the NORIT NK active carbon with a solution, containing both, the Co- and the Ni-acetates, dried and heat treated at 300 °C in open air.

Magnesium possesses a comparatively high

energy density and low specific gravity; its price is not very high, so it could be used as a primary anode in metal-air systems. Sheets of Mg or magnesium alloys are used as anodes in the developed Magnesium-Air cells. The behavior of the air gas diffusion electrode is investigated in a half-cell arrangement, when operating in solutions of NaCl with different concentrations.

RESULTS AND DISCUSSION

Air Gas-Diffusion Electrode

The air electrode, used in the magnesium-air cell, is a double layer electrode, consisting of a gas layer made from a hydrophobic carbon/PTFE material and a catalytic layer, made from mixture of catalyst and the same hydrophobic material.

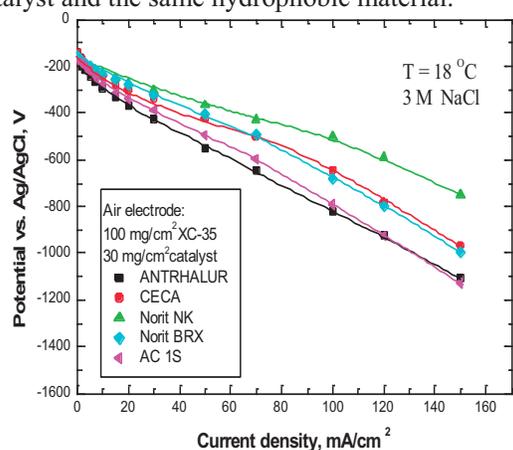


Fig. 1. Polarization curves of air electrodes with different types active carbon catalysts

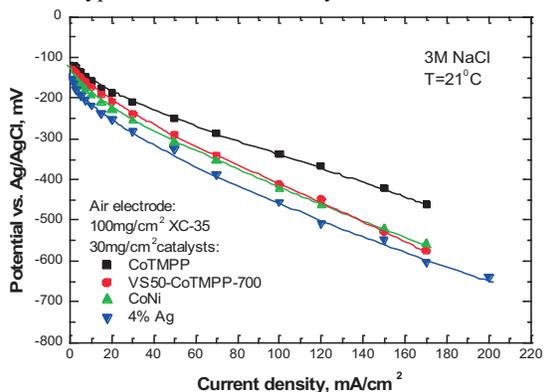


Fig. 2. Polarization curves of air electrodes with different catalysts in 3 M NaCl

Fig. 1 shows the polarization characteristics of air gas diffusion electrodes in 3 M NaCl with catalysts from different kinds of active carbon. It is seen that pure active carbon can be used as catalyst in air electrodes in saline solutions, but the polarization of the electrode in this case is quite high. On the other hand, the active carbon is

suitable to be additionally activated with some suitable compounds.

Four types of catalysts were used for the catalytic layer: pyrolyzed CoTMPP, VS50-CoTMPP-700, active carbon with Co and Ni (ACCoNi), and AC with 4 % Ag. Fig. 2 represents a comparison between the polarization curves of the air electrodes and the investigated types of catalysts when operating in 3 M NaCl. The comparison with the polarization curve for the electrodes with CoTMPP catalyst shows that the chelate-promoted electrodes have also better current-voltage characteristic.

The behaviour of one and the same electrode with a pyrolyzed CoTMPP catalyst, is investigated in a half-cell arrangement, when operating in

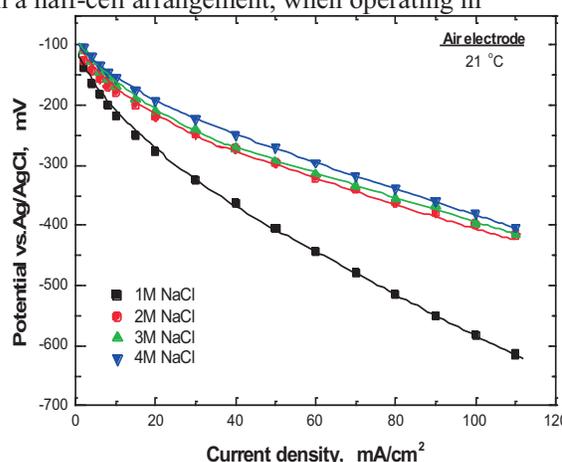


Fig. 3. Current-voltage curves of the air-electrode operating in NaCl solution with different concentrations.

solutions of NaCl with different concentrations (Fig. 3). The difference in the obtained curves, in this case, is probably and mainly due to the difference in the conductivity of the NaCl solution of different concentrations $k = 0,074-0,217 [\Omega^{-1} \cdot \text{cm}^{-1}]$.

Magnesium anodes

Several types of magnesium alloys are tested: pure Mg (99,99 %), MgAM60 (94 % Mg, 6 % Al), MgAM50 (95 % Mg, 5 % Al), MgAZ91(90 % Mg, 9 % Al, 1 % Zn), and MA8M06 (~ 97 % Mg, 0,2 % Fe, 0,12 % Zn, 1,3 % Mn, 0,01 % Si, 0,12 % Al). The testing of the different magnesium anodes is performed in Mg-Air cells with two air electrodes with pyrolyzed CoTMPP catalyst ($S = 65 \text{ cm}^2$). The electrolyte is 3 M NaCl. Fig.4 illustrates a comparison between the current-voltage characteristics of the investigated Mg-Air cell and the different Mg-anodes. The

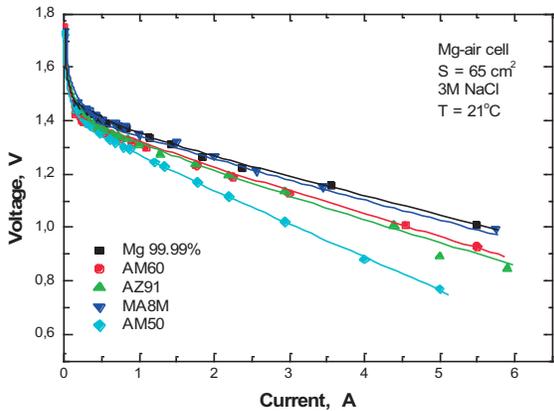


Fig. 4. Current-voltage of the Mg-Air cells with different Mg-anodes.

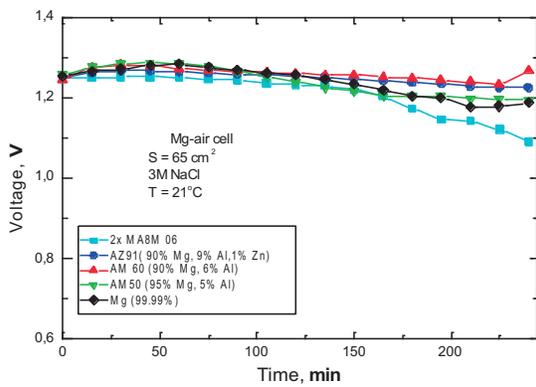


Fig. 5. Discharge curve of Mg-Air cell ($S = 65 \text{ cm}^2$) with different Mg-anodes.

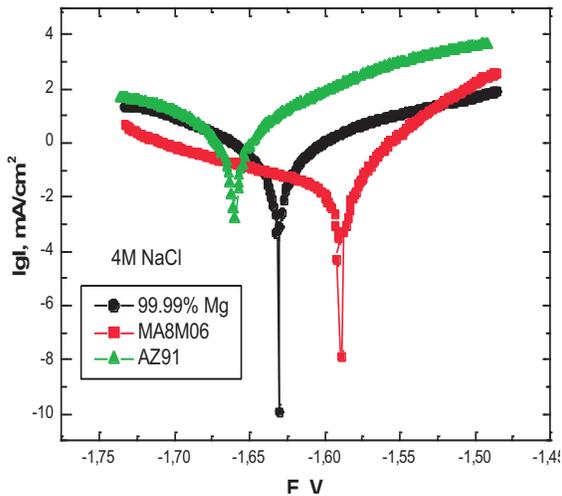


Fig. 6. Polarization curves of Mg alloys and pure magnesium in 4M NaCl.

comparison of the data shows that the Mg 99.99 % and the MA8M, which is produced especially to be used in water activated batteries, are the most suitable materials to be used as anodes. The discharge curves at 0.6 Ω constant load of the

magnesium-Air cells and different anodes are compared in Fig.5.

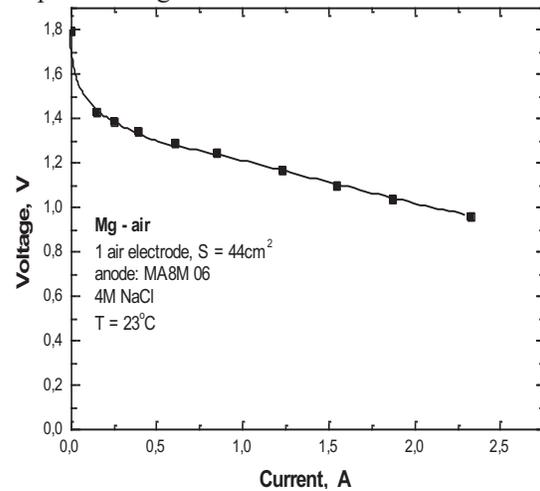


Fig.7. Current-voltage curves of Mg-Air cell ($S = 44 \text{ cm}^2$).

Corrosion investigations on various types of magnesium alloys were carried out in order to optimize the performance of the mechanically rechargeable Magnesium-Air cells. The behavior of AZ 91 and MA8M 06 alloys in respect to pure Mg was under investigation. The experiments were conducted in aqueous solutions of 4M NaCl and the results are shown in Fig.6. It is obvious that corrosion stability increases in the following order: AZ91 < Mg < MA8M. The corrosion stability is described by the corrosion potential shift towards more negative values and the corrosion rate, expressed by the corrosion current.

Experimental Mg-air cells

Several types of experimental Mg-Air cells are tested, differing in size (working area of the air electrodes used) [32].

Fig. 7 presents the current-voltage characteristics of the magnesium-air cell with one air electrode ($S = 44 \text{ cm}^2$). Magnesium MA8M 06 is used. It is covered with a protective current conductive sheet from the side opposite to the air electrode. The discharge curve of this cell at constant load ca.0.6 Ω is presented in Fig.8.

The investigated magnesium-air cells are constructed as experimental mechanically rechargeable cells. Once the magnesium anode has been discharged, it is removed out from the cell together with the electrolyte, and a new magnesium electrode and fresh saline electrolyte are introduced in it. After this mechanical recharge, the magnesium-air cell is operational again. In this case the essential feature is that the air electrodes in the

cell are used many times. Investigation of both, the current-voltage characteristics and the power curves

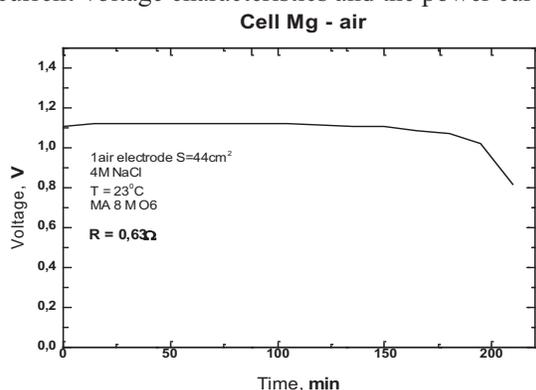


Fig. 8. Discharge curve of Mg-Air cell ($S = 44\text{cm}^2$) at constant load $0,63\ \Omega$.

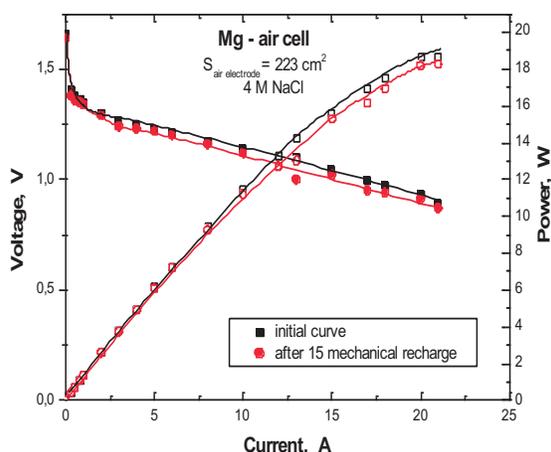


Fig. 9. Current-voltage and power characteristics of the Mg-Air cell ($S = 223\ \text{cm}^2$): initial and after 15 mechanical recharge.

of one and the same Mg-air cell, are performed after its mechanical recharge. The cell comprises of two air electrodes with a catalyst from pyrolyzed CoTMPP (total working area of 223cm^2), and Mg anodes from the MA8M06 alloy are used. 4M NaCl solution is used as electrolyte. The initial current-voltage curve and the current-voltage curve after 15 mechanical recharges of the same Mg-Air cell are presented in **Fig. 9**. It is seen that currents up to 20 A could be obtained from this cell at voltage higher than 1 V. The specific power of this cell is ca. 20 W/kg. The results show also that the Mg-Air cell can be recharged mechanically several times without any significant loss in its performance.

More powerful Mg-Air cell with a total working area of the air electrodes of $440\ \text{cm}^2$ and $660\ \text{cm}^2$ are designed and investigated. They can be used as emergency energy sources.

CONCLUSIONS

Magnesium-Air cells, operating with non-aggressive electrolyte, are developed. Air gas-diffusion electrodes, suitable for operation in NaCl-solution, are designed. Various carbon-based catalysts for the ORR are tested. Magnesium alloys suitable for use as anodes in Mg-Air cells are found.

The current-voltage and the power characteristics of various types of magnesium-air cells are investigated. The results show that the mechanically rechargeable magnesium-air cell with a NaCl-electrolyte is a prospective energy source.

The Mg-air cells are of substantially increased power output. They could be used as primary and emergency power sources for the residential, commercial, and industrial purposes. It should be noticed again that the magnesium-air cells are safe and employ environmentally friendly salt-water electrolyte, therefore, they can be used at school laboratories for experiments and demonstrations.

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ЕКОЛОГИЧНИ ЕЛЕКТРОХИМИЧНИ ИЗТОЧНИЦИ НА ЕНЕРГИЯ МАГНЕЗИЙ – ВЪЗДУХ

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(Резюме)

Основна цел на работата е разработване и реализиране на електрохимични системи Магnezий-Въздух със солеви електролити, които са подходящи за употреба като аварийни източници на енергия и демонстрационни модели за обучение и популяризиране на технология за получаване на екологично чиста енергия.

За реализиране на основната цел са решени следните основни задачи:

- избор на хидрофобен материал с оптимални физични, химични и електрохимични характеристики за газовия слой на въздушния електрод;
- изследване и подбор на подходящ катализатор за електрохимичната редукция на кислорода, протичаща върху въздушен газодифузионен електрод;
- охарактеризиране на различни Mg сплави като аноден материал;
- избор на неагресивен електролит и сепаратор;
- проектиране, изработване и тестване на аварийни и демонстрационни клетки Магnezий-Въздух.