

Citric acid as electrolyte additive in aqueous Magnesium-Air battery used in Antarctic climate

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Introduction

The magnesium-air electrochemical system has a high specific weight energy of 6200 W kg^{-1} , employs aqueous electrolyte and the source and end products of the electrochemical reaction are harmless for the environment – Mg and Mg(OH)_2 . The system is able to work at temperatures below $0 \text{ }^\circ\text{C}$. These characteristics make it an attractive ecological energy source in the context of green energy and green recycle economy.

Magnesium possesses high negative electrochemical potential (-2.37 V vs. SHE), high electrochemical equivalent (2.2 Ah g^{-1}), is widespread in Earth's crust and low weight. It is thermodynamically unstable in aqueous solutions. The Pourbaix diagram shows that in acid and neutral environment, magnesium dissolves with the formation of Mg^{2+} , while in alkalic environment it is covered by a insolvable layer of Mg(OH)_2 (solubility $0.00064 \text{ g.100 ml}^{-1}$ at $25 \text{ }^\circ\text{C}$) and passivates at $\text{pH} > 12$. For this reason, the magnesium-air electrochemical system is practically irreversible, and a secondary electrochemical element cannot be realized with this system. It is however possible to realize a mechanically rechargeable magnesium-air battery where the magnesium electrode and the foul electrolyte are replaced mechanically.

The corrosion of magnesium and its alloys in sea water is widely investigated [1,2]. In presence of chloride ions, the corrosion is significantly enhanced [3 - 6], resulting in disintegration of the passive Mg(OH)_2 film. Mg(OH)_2 falls down into the electrolyte as a slimy mass, increasing the ohmic drop and obstructing the access of fresh electrolyte to the electrode surface.

The aim of the present paper is to introduce citric acid as an additive to the electrolyte, to optimize the performance of the magnesium electrode and to check the working capacity of the battery under polar conditions.

Experimental

Magnesium samples of 99,99% purity (Merck), and commercial grade magnesium alloy AZ63 have been used in this study. Laboratory electrochemical tests - Tafel plot (TP), Potential Electrochemical Impedance Spectroscopy (PEIS), Open Circuit Voltage (OCV) and Chrono Potentiometry (CP) are carried out with a potentiostat SP 50e of the firm BioLogic SAS (France). OCV is measured 30 seconds after stabilizing the potential 1 mV h^{-1} . PEIS is carried out in the frequency range 2 Hz to 200 kHz with a signal amplitude of 10 mV . Tafel plots are measured thereafter in the range $\pm 250 \text{ mV}$ from OCV.

A magnesium foil of 99,99% purity and dimensions $10 \times 3 \times 0.15 \text{ mm}$ is used as a working electrode, the counter electrode was a platinum foil with 35 mm^2 surface area. Ag/AgCl was used as a reference electrode. The electrolyte was 3.5 M aqueous solution of NaCl with addition of 10 g dm^{-3} citric acid or without additive for control.

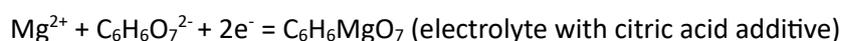
Chronopotentiometry was done in a customer design magnesium-air cell, drafted for the AWG meteorological station. It involves a cylindrical rod of magnesium alloy AZ63, a Ag/AgCl reference electrode and a gas diffusion counter electrode with a surface area of 45 cm^2 and CoTMPP catalyst [7]. The electrolyte is 3.5% NaCl, corresponding to the average salinity of the world Ocean, since the AWG station was designed to work with sea water in the polar regions. The cell current was increased stepwise from 0 to 400 mA. The first step is 5 mA for 10 minutes, all subsequent steps have a duration of 5 minutes - 15 mA, 24 mA, 50 mA, 100 mA, 150 mA, 200 mA, 250 mA, 300 mA, 350 mA and 400 mA. The electrochemical tests were analyzed by means of EC-Lab 11.43 software (BioLogic SAS).

The performance of the magnesium-air battery with 10 g dm^{-3} of citric acid added was checked under real polar conditions, where it served as a as power supply for the Antarctic Weather and GPS logger

(AWG) recording meteorological station of the Bulgarian Antarctic station at Livingstone Island, which measures continuously geolocation coordinates, temperature, illumination, altitude, pressure, and voltage of each cell. The battery for AWG consists of three cells, containing two AZ63 electrodes each. The weight of each magnesium rod is 38 g, including the current collector.

Results and discussion

The electrochemical reactions occurring on the magnesium electrode are as follows:



Open circuit potential (OCP) against an Ag/AgCl reference electrode was measured for samples of pure magnesium and AZ63 alloy in electrolyte with citric acid additive and compared to data for a reference electrolyte without the additive. OCP shifting of 190 mV in negative direction is observed for pure magnesium and of 90 mV for AZ63 alloy. This negative shift is due to the lower pH value of the electrolyte after addition of citric acid. The smaller shift by the alloy is naturally due to zinc and other admixtures in it.

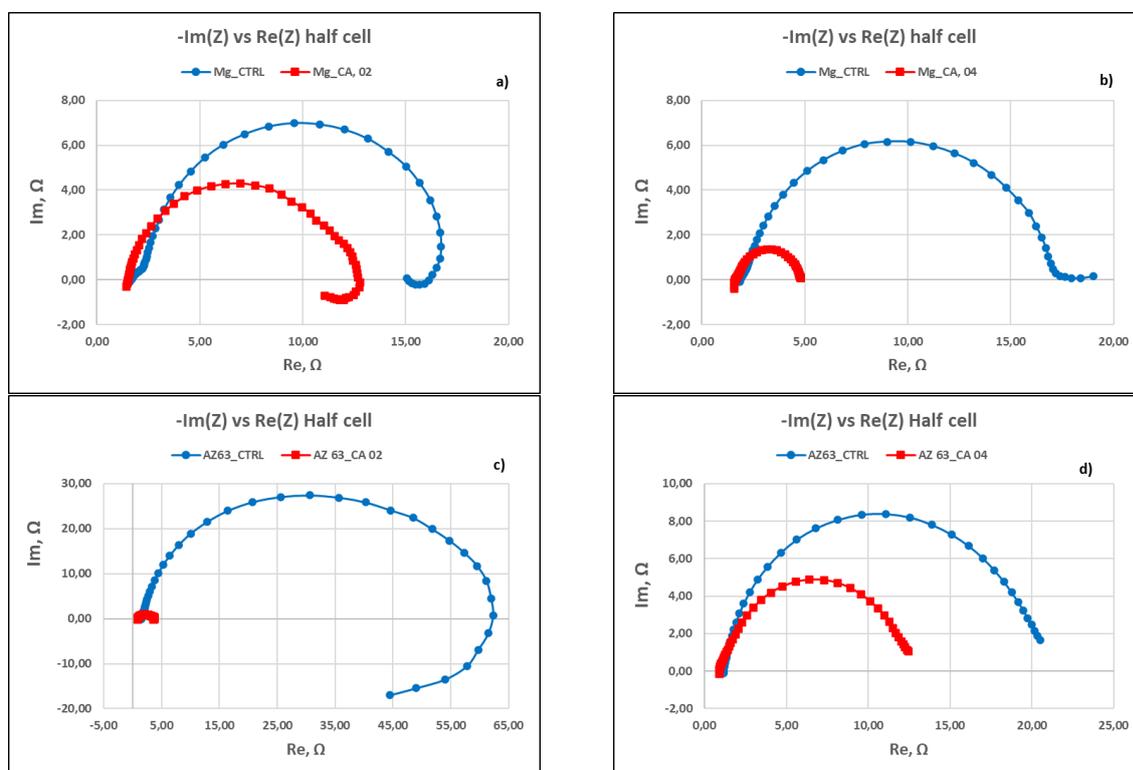


Fig. 1. Impedance spectra of 99,99% magnesium foil, (a,b) and AZ63 alloy (c,d) in electrolyte with (red) and without (blue) citric acid additive .

The electrochemical impedance of magnesium and AZ63 are shown in Fig. 1. The pure magnesium sample in reference electrolyte reveals two semicircles and small capacitive loop, indicating the presence of two phases, i.e. formation of an oxide film. The spectrum recorded in electrolyte with citric acid additive shows a single semicircle, because no oxide film is formed on the magnesium surface. It may be concluded that the use of electrolyte with additive reduces the charge transfer resistance and the capacitive behaviour. The ohmic resistance is also reduced, due to the better access of the electrolyte to a clean metal surface. All of this favours a higher rate of the electrochemical reaction and enhanced energetic features of the system. Similar behaviour is observed also with the magnesium alloy AZ63.

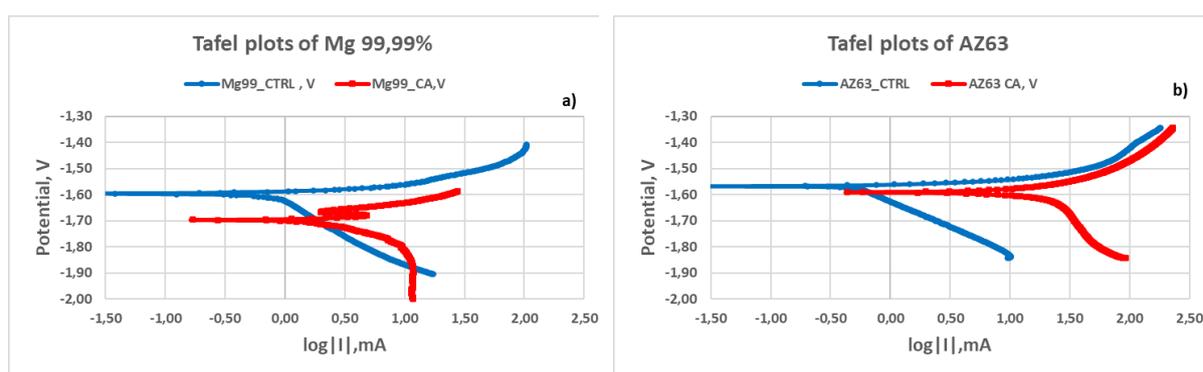


Fig. 2 Tafel plots of 99,99% magnesium foil, (a) and AZ63 alloy (b) in electrolyte with (red) and without (blue) citric acid additive.

The Tafel plots of 99,99% magnesium foil and AZ63 alloy in electrolyte with and without citric acid additive (Fig. 2) reveal that the rates of cathodic and anodic reaction become equal when the additive is applied. The corrosion potential shifts in negative direction and the corrosion current increases. The main electrokinetic parameters derived from the Tafel plots are summarized in Table 1. The exchange current density is directly related to the rate of the electrochemical reaction. The samples studied in reference electrolyte show different slope of the Tafel lines. The higher value of the cathodic Tafel constant b_c indicates that the reaction proceeds with cathodic control, eventually the oxygen reduction reaction, provoking dissolution of magnesium. For the samples studied in electrolyte with additive, there is a smaller difference in the values of anodic and cathodic Tafel constants.

Table 1 Main electrokinetic parameters derived from the Tafel plots

Parameter	Mg in NaCl	Mg in NaCl+Add	AZ63 in NaCl	AZ63 in NaCl+Add
b_c , mV	521	341	246	554
b_a , mV	64	138	40	166
i_{corr} , μ A	1350	4457	687	21718
E_{corr} , V vs. Ag/AgCl	-1.59	-1.69	-1.56	-1.59

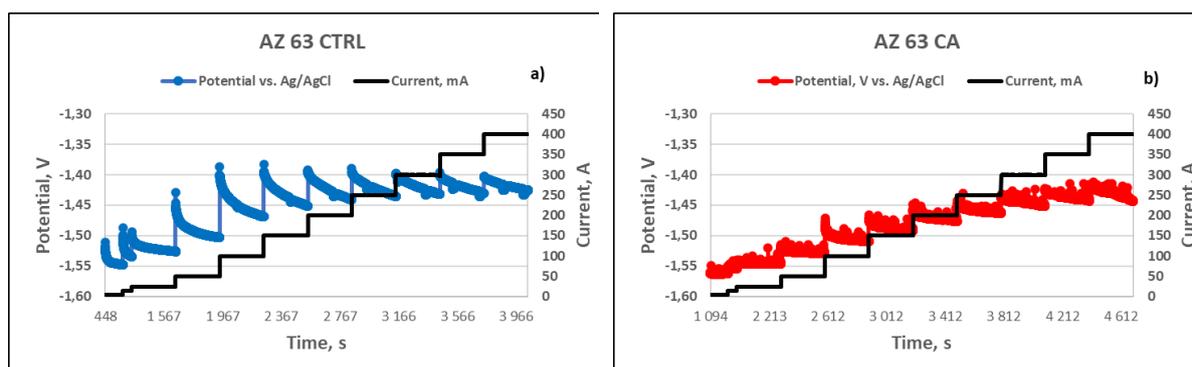


Fig. 3. Chronopotentiometric study of the AZ63 alloy

The magnesium alloy AZ63 has been chosen for the field tests under polar conditions. It is seen from Fig. 3 that the polarisation at high current density is lower in electrolyte with additive (b) compared to that in reference electrolyte (a). The gas diffusion electrode appears to be the limiting factor at higher current density.

An important part of the study is the testing of the system under arctic conditions. The recording weather station (Antarctic Weather and GPS logger - AWG "Alissa"), used by the 31st Bulgarian Antarctic expedition to Livingstone Island was powered by 3 magnesium-air cells "OXYMET". The use of citric acid additive stabilized the cell voltage and prolongs the life of the system due to the dissolution of $Mg(OH)_2$. It should be noted that the reduction of $Mg(OH)_2$ influences favourably both the magnesium anode and the gas diffusion electrode.

An excerpt of data, recorded by the AWG in the field is given in Table 2.

Table 2. Data from Antarctic Weather and GPS logger of the Bulgarian Antarctic Station at Livingstone Island.

Antarctic Weather and GPS logger - AWG "Alissa", powered by "OXYMET" - an ecological Magnesium-Air battery, design & development: Iliyan Popov, Boris Shirov						
GPS Lat.	GPS Lon.	Cell 1, V	Cell 2, V	Cell 3, V	Luminance, %	Temperature, °C
-62.64	-60.37	1.12	2.1	3.06	4.97	9.2
-62.64	-60.37	0.9	1.93	3.26	4.96	9.22
-62.64	-60.37	1.04	1.8	3.15	4.97	9.4
-62.64	-60.37	1.04	2.12	3.13	4.96	9.6
-62.64	-60.37	0.95	1.96	3.35	4.97	9.65
-62.64	-60.37	1.18	2.23	3.15	4.97	9.88
-62.64	-60.37	1.17	2.12	3.4	4.97	9.81
-62.64	-60.37	0.98	2.16	3.34	4.97	9.9
-62.64	-60.37	0.98	1.96	3.14	4.97	9.97
-62.64	-60.37	1.06	1.9	3.29	4.96	10.02
-62.64	-60.37	1.13	2.1	3.63	4.96	10.06
-62.64	-60.37	1.14	2.15	3.25	4.97	9.96
-62.64	-60.37	1.07	2.4	3.59	4.97	10.08
-62.64	-60.37	1	2.12	3.15	4.96	10.1

-62.64	-60.37	1.04	2.15	3.22	4.97	10.14
-62.64	-60.37	1.16	2.34	2.95	4.96	10.17
-62.64	-60.37	1.07	2.2	3.2	4.97	10.21
-62.64	-60.37	1.14	2.39	3.33	4.97	10.22
-62.64	-60.37	1.09	2.16	3.27	4.96	10.24

Summary

In the present paper, citric acid is introduced as an additive enhancing the performance of the magnesium-air electrochemical system working with saline electrolyte or sea water. Electrochemical tests show reduction of the insoluble magnesium hydroxide, decreasing of polarisation and passivation of anode, reduction of the difference negative effect and increasing the cell OCP. Citric acid favours also the work of the gas diffusion electrode. Practical application of the ecological system magnesium-air is demonstrated with the improved electrolyte at the Bulgarian Antarctic Station at Livingstone Island.

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