Sea water magnesium fuel cell power supply

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HIGHLIGHTS

- Hydrogen is produced reproducibly in galvanic sea water cell by anodic dissolution of magnesium.
- Use of hydrogen evolving Raney nickel cathodes with gas separation membrane.
- Complete hydrogen generation fuel cell power supply demonstrated.
- Advantages of magnesium AZ31 alloys demonstrated.
- 1200 Wh/kg, 3000 Wh/l electricity achieved from magnesium alloy sheets as the fuel.

ARTICLE INFO

ABSTRACT

An environmentally friendly magnesium fuel cell system using seawater electrolyte and atmospheric oxygen was tested under practical considerations for use as maritime power supply. The hydrogen rate and therefore the power density of the system were increased by a factor of two by using hydrogen evolution cathodes with a gas separation membrane instead of submerged cathodes without gas separation. Commercial magnesium AZ31 rolled sheet anodes can be dissolved in seawater for hydrogen production, down to a thickness below 100 μm thickness, resulting in hydrogen generation efficiency of the anode of over 80%. A practical specific energy/energy density of the alloy of more than 1200 Wh/kg/ 3000 Wh/l was achieved when coupled to a fuel cell with atmospheric air breathing cathode. The performance of several AZ31 alloy anodes was tested as well as the influence of temperature, electrolyte concentration and anode − cathode separation. The excess hydrogen produced by the magnesium hydrogen evolving cell, due to the negative difference effect, is proportional to the cell current in case of the AZ31 alloys, which simplifies system control considerably. Stable long-term operation of the system was demonstrated at low pressures which can be maintained in an open-seawater-submerged hydrogen generator.

1. Introduction

In response to the need for improved electrochemical energy storage in mobile, stationary and portable applications, magnesium has recently attracted new interest [1] as an anode material due to its high discharge activity, large capacity and small environmental impact. Magnesium has a negative standard electrode potential of −2.37 V (vs. SHE) which is more negative than for zinc and aluminum. At 2.205 Ah/g, the Faradaic capacity of magnesium is significantly higher than that of zinc. Its specific weight is lower than that of aluminum and about 25% of that of zinc. Thus magnesium has the potential for very high energy density and light-weight batteries.

Mg anodes are active in neutral aqueous electrolytes that contain chlorine or other aggressive ions; thus the most important applications of magnesium anodes so fare are seawater activated batteries and dissolved-oxygen seawater batteries that were developed several decades ago. In these applications some of the mayor drawbacks of magnesium battery anodes like the high self-discharge rate and electrode clogging with reaction products (deposition of $Mg(OH)_2$ at the Mg surface) can be handled. On the other hand, technologies for closed battery systems and secondary batteries based on Mg anodes, such as magnesium-air [2] or magnesium-ion [3] batteries are still in their infancy, but promise a huge market potential.
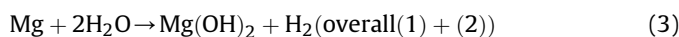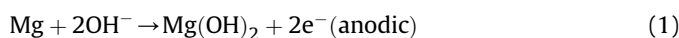
Dissolved-oxygen batteries with Mg anodes have been developed for deep-water applications [4,5] and proven for long time operation. Due to the low oxygen concentration in the sea water, corresponding cathodes have a much larger surface than the magnesium anode. In practical constructions, the distance between anode and cathode is relatively large which results in high cell impedance and low current capacity. Aluminum anodes have already been considered for operation of cathodes in the hydrogen generation mode [6]. In case of hydrogen evolution cathodes the current density is increased by one order of magnitude if the separation between anode and cathode is kept at a constant low distance during the discharge process, but the operating cell voltage is very low (0.1 … 0.4 V). Therefore in the hydrogen evolution mode, the power density can be increased but the energy density is low due to the low cell potential. Most of the energy is represented by the produced hydrogen which is released into the sea.

On the other hand previous work indicates that a practical energy density near that of metal air batteries can be achieved at a moderate power density if both the electrical power and the hydrogen of a hydrogen evolving cell are used in combination with a fuel cell [7–9]. Portable power supply demonstrators in the 1–4 W range [7] and power supplies with milliwatt output for sensor applications [9] were tested. A similar approach was investigated for aluminum hydrogen generation cells [10,11]. Hydrogen and electricity production in these closed cells shows promising results, and additional studies are required to further develop this concept. For instance, neither the influence of continuously increasing electrolyte concentration during the discharge due to water consumption, nor the performance at higher currents and high hydrogen pressure is not fully understood [12].

In this study, we combine the well proven magnesium sea water discharge performance in the hydrogen evolution state, with hydrogen utilization in a fuel cell [13], into a magnesium fuel cell system. In contrast to dissolved-oxygen batteries, here the high oxygen concentration of the air can be combined with the high hydrogen generation rate of magnesium in sea water. Due to the infinitely large electrolyte reservoir, reaction products are continuously flushed from the cell and the electrolyte concentration remains constant, leading to long term stable operation.

Power supplies of this type can on the one hand only be used near sea level, but on the other hand they provide advantages over other types of batteries in high energy density and low environmental impact. Possible applications are sea based remote sensors and signal buoys as well as auxiliary electrical power supplies for sailing boats and leisure activities. Further developments may lead to larger applications like power generation for submarine systems in combination with additional oxygen sources or large storage applications in combination with magnesium recycling.

The main reactions of the hydrogen evolution cell are:

$$Mg + 2OH^- \rightarrow Mg(OH)_2 + 2e^- (anodic) \tag{1}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- (cathodic) \tag{2}$$

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2 (overall (1) + (2)) \tag{3}$$

In addition to the main reactions according to equations (1)–(3), a self-discharge reaction or hydrogen side reaction results in additional hydrogen evolution directly at the anode or inside the electrolyte. Impurities in the magnesium alloy anode may lead to local corrosive hydrogen evolution directly at the metal alloy according to (3) at a rate rH2-corr. In case of Mg anodes additional

hydrogen evolution reaction occurs as a function of the applied potential which is called the negative difference effect (NDE) as discussed in section 3.2. It is assumed that the anodic reaction does not only lead to bivalent Mg^{2+} ions according to (1) but also to univalent magnesium ions Mg^+ [17]. Thus hydrogen can be produced from a chemical reaction according to equation (4) as well.

$$2Mg^+ + 2H_2O \rightarrow 2Mg^{2+} + 2OH^- + H_2 (chemical) \tag{4}$$
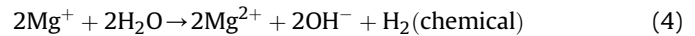
Therefore, the resulting hydrogen rate r_{H2} is the sum of the cathodic $r_{H2\text{-}cat}$ (1) and the chemical $r_{H2\text{-}chem}$ (4) and corrosive reaction as indicated in equation (5).

$$r_{H2} = r_{H2-cat} + r_{H2-chem} + r_{H2-corr} \tag{5}$$

The overall reaction of the hydrogen production inside the hydrogen evolution cell and the fuel cell reaction with ambient oxygen is shown in equation (6). As the water and oxygen are available in unlimited amounts from the sea and ambient air respectively, energy density calculation can be made which considers only the Mg alloy as energy supply.

$$2Mg + 2H_2O + O_2 \rightarrow 2Mg(OH)_2 \tag{6}$$
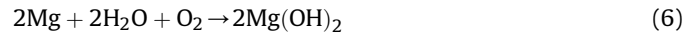
The basic concept of the magnesium hydrogen fuel cell system is shown in Fig. 1.

The galvanic hydrogen generation cell is submerged in the seawater electrolyte. The planar magnesium anode is arranged between two gas diffusion electrodes with hydrogen evolution cathode catalyst and gas separation membranes. Additional hydrogen which is generated directly at the anode or inside the chamber can be collected at the middle hydrogen connecting port. The reaction cell has openings at the bottom for sea water exchange and removal of reaction products. The collected hydrogen is fed into the anode of a fuel cell above sea level which uses the ambient air for cathode supply. The hydrogen evolution cells are connected in parallel as they are all in contact with the same electrolyte. The current of the hydrogen cell is controlled by the DC/DC converter to produce adequate hydrogen flow which is required for the fuel cell operation. The maximum hydrogen pressure is low and depends on the submersion depth of the hydrogen evolution cell. Therefore the fuel cell must be optimized for low pressure operation.

2. Experimental

The experiments are divided into two stages. First, the general influence of material parameters, temperature and electrolyte concentration was investigated in a small flow cell were the catalyst cathode was directly incorporated into the electrolyte flow (Fig. 2a). Here, the Mg anode represents one sidewall of the flow cell. Therefore it is not possible to fully dissolve the anode. The discharge is stopped at the moment of the first occurrence of a hole which results in electrolyte leakage. Second, a larger cell was designed with two cathodes on both sides of the Mg anode to study the influence of different Mg alloys and test the hydrogen evolution gas diffusion electrodes (GDEs) with hydrogen separation membrane which were previously developed for the zinc hydrogen evolution cells [7] (Fig. 2b). The separation between anode and cathodes was varied by using anodes of different thickness.

The hydrogen of the small cell was extracted at the outlet of the electrolyte storage container. Most of the hydrogen of the larger flow cell was extracted in the hydrogen collection chambers behind the gas separation membranes of the cathode GDE on both sides. The hydrogen which was produced at the anode and inside the