INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2014) 1–6

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Small fuel cell system with cartridges for controlled hydrogen generation

Robert Hahn*, Andreas Gabler [1], Axel Thoma, Fabian Glaw, K.-D. Lang

Fraunhofer IZM, Gustav-Meyer-Allee 25, 13355 Berlin, Germany

ARTICLE INFO

Article history:
Received 12 July 2014
Accepted 14 November 2014
Available online xxx

Keywords:
Hydrogen generation
Galvanic cell
Gas diffusion electrode
Zinc anode
Fuel cell system control

ABSTRACT

Galvanic cells are investigated which can be used as a hydrogen source for small fuel cell systems. Hydrogen is produced by the reaction of zinc and water in a cell which consist of zinc powder as negative electrode and a hydrogen evolution cathode in form of a gas diffusion electrode. In comparison to a zinc air primary battery the KOH electrolyte contains additional water and the ingress of oxygen is prevented. Therefore, the large energy density of the zinc air battery can be maintained to a great extend while the life time of the system is considerably higher. This is achieved by complete separation of the cell from ambient air.

Based on the material improvements of Zn powders and separation membranes demountable cells of 70 Ah capacity were designed and tested in combination with micro fuel cells. A control algorithm for the hydrogen generation rate were developed and tested, to achieve stable fuel cell performance at lowest possible hydrogen consumption.

The system can be miniaturized and is well suited for mobile and portable power supplies.

Introduction

The main motivation underlying the development of micro fuel cells is the possibility to achieve higher energy densities in comparison to batteries. Hydrogen PEM micro fuel cell technology has been developed extensively over the last two decades. Nevertheless small, portable PEM fuel cells have not emerged on the marked. The two greatest barriers for commercialization of large fuel cells are durability and cost [1]. For small, portable systems it is the lack of a light weight, reliable and low cost hydrogen source. Compressed high pressure gas or liquid hydrogen cannot be used for portable systems. Reversible metal hydrides are still too costly and too heavy. Chemical hydrides require sophisticated peripheral components for hydrogen flow control. The system described here presents three main advantages:

- High energy density – comparable with other hydrogen storage and aproximately twice that of lithium ion batteries,
- High safety in comparison to lithium ion batteries (aqueous electrolyte) and hydrogen storage (hydrogen is produced on demand),
- Practical for miniaturization: besides fuel cell and hydrogen generation cell only valves and the electronic control circuit are required.

* Corresponding author. Tel./fax: +49 30 31472833.
E-mail address: robert.hahn@izm.fraunhofer.de (R. Hahn).
[1] Fraunhofer HHI, Am Stollen 19B, 38640 Goslar, Germany.
http://dx.doi.org/10.1016/j.ijhydene.2014.11.080

The principle of hydrogen generation in electrochemical cells with help of a gas evolution electrode has already been developed decades ago and used in coin type cells [2]. The hydrogen evolution was used for pumping liquids and pasty masses at a low rate as well as other actuator devices. It was at the same time that the gas evolution electrode was developed featuring Raney-nickel as catalyst that is bonded into a nickel mesh mixed with PTFE binder to provide a porous electrode with triple phase boundary [3]. We combined coin type hydrogen cells of this type for the first time with planar micro fuel cells and showed that they can be used as a high energy density source of electricity [4]. The hydrogen rate of these prototypes was adjusted with a shunt resistor. It was shown that full advantage of the hydrogen generation fuel cell system can only be realized if an electronic control circuit is implemented. Thus, here a larger system that consists of 70 A h hydrogen generation cells, micro fuel cell stacks and electronic control circuit was developed to minimize hydrogen losses and study the time dependent performance.

The system is somehow quite similar to the zinc air primary battery. In our case, a different cathode catalyst is used, the electrolyte contains additional water and the ingress of oxygen is prevented. Therefore the large energy density of the zinc air battery can be maintained to a great extend while the life time of the system is much higher compared to zinc air batteries. Long term stability is achieved by complete separation from ambient air. In contrast, zinc air batteries have an operational life time of only several weeks because of the reaction with the ambient atmosphere and dry out of the cell.

Functional principle and experimental setup

The basic principle, energy density

The hydrogen producing cell consists of a gas-generating electrode as cathode, a zinc anode and it is filled with aqueous potassium hydroxide electrolyte (KOH). KOH electrolyte is used since it has a higher conductivity than most other alternatives, it is well established in other batteries with Zn anode (alkaline, zinc air) and it allows the use of non-noble catalysts at the hydrogen evolving cathode.

Hydrogen is produced by the reaction of zinc and water according to equation (1).

$$Zn + H_2O \rightarrow ZnO + H_2 \tag{1}$$

At the cathode water is split into hydrogen and hydroxyl ions which migrate into the zinc anode. At the anode, Zn is not oxidized directly but in a two-step reaction including zincate according to equation (2). The zincate decays into zinc oxide and water returns to the electrolyte (3):

$$2Zn + 8OH^- \rightarrow 2Zn(OH)_4^{2-} + 4e^- \tag{2}$$

$$2Zn(OH)_4^{2-} \rightarrow 2ZnO + 2H_2O + 4OH^- \tag{3}$$

In the reaction, water is consumed since zinc oxide and hydrogen are produced. The amount of the electrolyte required in the cell therefore depends on the amount of zinc incorporated. The volume of electrolyte must therefore be such that after consumption of the quantity of water required for the hydrogen generation sufficient electrolyte remains for stable operation of the cell until the end of discharge. As a result of water consumption, the KOH concentration of the electrolyte steadily increases while the portion of the liquid phase decreases. The volume reduction due to water consumption is partially compensated by the volume increase of the ZnO. The volume difference of the discharged cell in comparison to the fresh one can be calculated from densities of the individual components to be ca. 30%.

The starting KOH concentration is 20 wt% and rises to a value of 40 wt% during complete discharge. This value is still well below the KOH solubility limit of 1120 g/l and represents the concentration range of lowest freezing point [5].

Taking into consideration only the zinc anode and the electrolyte as the components of energy storage, the specific capacity of Zn of 0.82 Ah/g results in a maximum capacity density of 1520 Ah/l and a specific capacity of 533 Ah/g.

Considering the system voltages the energy density can be calculated. During operation, the hydrogen evolving cell stabilizes at ca. 0.2 V while the fuel cell is operated at 0.7 V per cell which results in a sum voltage of 0.9 V. The product of maximum capacity and mean system voltage yields the energy density and specific energy of 1368 Wh/l and 480 Wh/kg respectively. As will be shown later, the complete system can provide approximately 50 per cent of this maximum energy density.

Materials and cell construction

Anode

Various types of Zn powders were fabricated using the mass fabrication technology dedicated to alkaline primary batteries. The most important criteria are low gassing and high power density. The influence of size distribution and shape was already optimized for the use in alkaline and zinc air batteries. It has been found that the addition of fine particles of zinc and grain sized distributions in a relatively small range result in improved electrical characteristics of the battery, particularly an improvement in the maximum discharge rate [6].

The Zn powders were tested with help of small button type hydrogen generation cells. The goal of this investigation was to evaluate if further optimizations towards hydrogen generation cells can be made [7]. Both particle size and alloy content was varied. Mercury-free zinc powders from very high-purity SSHG zinc with particle dimensions in the range of 50 … 500 ppm and several grain size distributions have been tested. The role of metal additions including In, Al and Bi was studied to increase hydrogen overvoltage and prevent corrosive hydrogen generation at the anode. We want to emphasize here on the fact that the suppression of hydrogen generation at the anode has the same detrimental effect as in alkaline or zinc air batteries as it reduces storage time and may lead to deformation of the cell package. Only the hydrogen generated at the cathode can be used by the fuel cell.