



Open Access: ISSN 1847-9286

www.jESE-online.org

Original scientific paper

Zeolite based carbon-free gas diffusion electrodes for secondary metal-air batteries

Miglena Slavova✉, Elena Mihaylova-Dimitrova, Emiliya Mladenova, Borislav Abrashev, Blagoy Burdin, Daria Vladikova

Acad. Evgeni Budevski Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 10, Sofia 1113, Bulgaria

Corresponding author: ✉ m Slavova@iees.bas.bg

Received: December 4, 2019; Revised: February 25, 2020; Accepted: February 26, 2020

Abstract

In recent years, secondary metal air batteries have received considerable attention as promising technology for energy storage in combination with renewable energy sources. The oxidation of carbon in conventional gas-diffusion electrodes reduces the life of the secondary metal-air batteries. Replacement of the carbon-based material with zeolite is a possible solution for overcoming this problem which is the aim of this work. Zeolite is a natural or synthetic porous material which provides the necessary gas permeability. The required hydrophobicity of the electrodes is ensured by mixing the zeolite with an appropriate amount of polytetrafluoroethylene following a specially developed procedure. The experiments are performed in a home designed test cell which ensures measurements in both half-cell and full cell configuration. In this study the testing is carried out in 3-electrode homemade half-cell configuration with hydrogen reference electrode. The cell was subjected to cycling at charge/discharge current $\pm 2 \text{ mA cm}^{-2}$ respectively. The obtained results show that the replacement of carbon with zeolite in the gas diffusion layer is a promising direction for optimization of the gas diffusion electrode.

Keywords

Polarization; renewable energy sources; polytetrafluoroethylene; charge/discharge cycling.

Introduction

In order to turn renewable energy sources (RES) into the main energy source it is necessary to store the produced energy, which requires "innovative solutions, next-generation technologies, including potentially revolutionary technologies" [1]. Batteries have an important role in integrating and optimizing the application of RES. One of the directions for new technological solutions is the development of rechargeable metal/air systems. Research in this area paves the way for further industrial production.

Metal-air system is a hybrid electrochemical structure which combines a metal anode and gas-diffusion cathode, similar to that used in fuel cells. Its main advantage is the use of oxygen from the atmospheric air [2]. The development of rechargeable metal-air batteries is a hot topic, due to the advantages of the system to ensure high energy density and capacity at low price [3-5]. However, there are still no effectively operating secondary metal-air batteries which makes this topic attractive for further research, focused on improvements of the recharging, enhancement of durability and reduction of cost [6]. The advantages of the system are: cheapness, non-toxic materials, operation in humid environments and water-based electrolytes, low self-discharge, recyclability, simple construction, long life and "flat" discharge curves [7,8].

The components of the metal-air cell are: metal electrode, alkaline electrolyte, separator, and gas-diffusion electrode (GDE) (Figure 1). The GDE consists of gas-diffusion layer (GDL) which ensures the needed oxygen and catalytic layer (CL) where the oxygen reduction/evolution takes place [6,9]. The classical GDL is made of a carbon-based material and some hydrophobic binding material, most commonly polytetrafluoroethylene (PTFE). An optimization in respect of gas permeability and hydrophobicity is an important step in its preparation. The electrochemical reaction occurs at the triple-phase boundary electrode/electrolyte/gas phase. The active material in GDE is oxygen from the ambient air and thus the air electrode does not "exhaust", *i.e.* it should work until it is mechanically damaged which may be caused by the oxidation of carbon [6]. During discharge, the oxygen reduction reaction (ORR) occurs, while the metal oxidizes and releases electrons which pass through the external circuit. In charge regime the opposite reactions with release of oxygen take place. For rechargeable gas diffusion electrode, a bifunctional catalyst should be used in CL layer. It has to combine good catalytic activity, electronic conductivity, good adhesion towards GDL and mechanical stability.

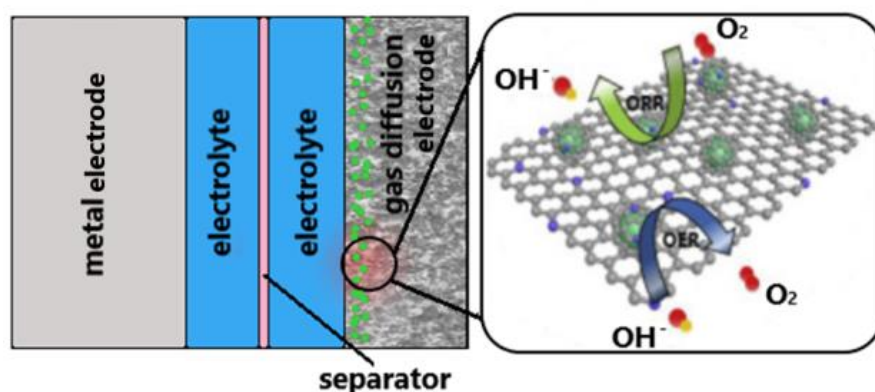


Figure 1. Schematic illustration of rechargeable metal-air system

The main problem with GDE is high electrochemical carbon corrosion during oxygen evolution reaction (OER), which reduces its stability [10-15].

One of the possible solutions is the replacement of the carbon black in GDL with material having similar porous structure as zeolite. There is no information for such replacement in the literature, although zeolites are used in batteries as molecular sieves that can protect metal electrodes from rupture. The zeolite is aluminosilicate with crystalline structure, which forms evenly distributed voids and channels - 20 to 50 %.

The aim of this work is to present innovative zeolite based carbon-free gas diffusion electrodes for rechargeable metal-air batteries. The selected approach replaces the carbon based GDL with the zeolite based one.

Experimental

The zeolite based GDE consists of two layers - porous zeolite based GDL and CL. The replacement of carbon black with zeolite of type clinoptilolite on gas diffusion electrode is described elsewhere [16]. For the preparation of zeolite based GDL, zeolite powder with grain size between 180 μm and 250 μm was mixed with 20-60 % PTFE and hot pressed (0.3 t/cm²) at 250 °C for 3 min. The bifunctional CL is a mixture of 20 wt.% Co₃O₄, 70 wt.% Ag and 10 wt.% PTFE, and its thickness is about 25 % of the total thickness of GDE. The morphological studies were performed using electron microscope JEOL 6390. The electrode working area was 10 cm².

For fast evaluation of hydrophobicity, an empirical “water drop” test was introduced according to which the water drop should stay on the outer GDL surface more than two hours for further testing of the sample (Figure 2a). The second leaking test was performed in the home-made hydrophobicity test cell with electrolyte (6 M KOH) for 100 hours (Fig. 2b).

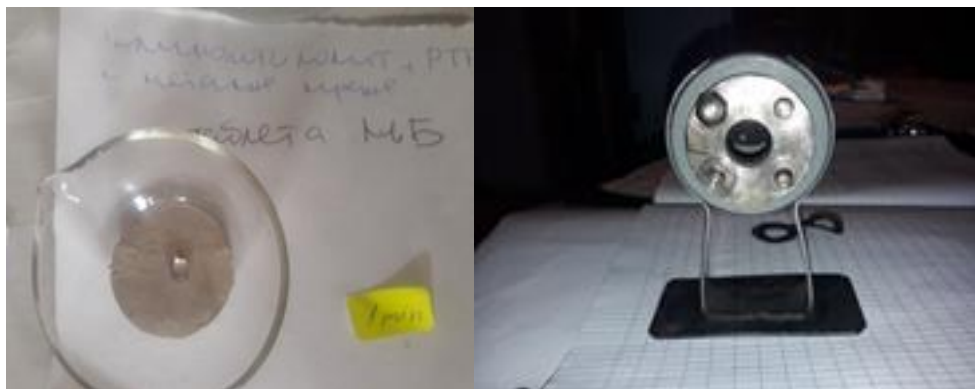


Figure 2. Hydrophobicity testing: a) water drop test and b) real conditions test

For quick evaluation of the sample gas permeability a simple testing system was used which gives more realistic picture reflecting the behavior of the percolating network. The methodology is based on measurements of the pressure P (mm H₂O) dependence on the gas flow, q_{flow} [ml/min], penetrating through porous media [17]. A new characteristic parameter, named permeability resistance R_p (inversely proportional to the permeability) is introduced and the empirical criterion for the investigated system postulated as: the gas permeability should not less than 2.2 (mol / min) / cm² air.

The zeolite based GDEs were electrochemically tested at room temperature in a homemade half-cell configuration with the working electrode area of 1 cm² vs. hydrogen reference electrode (HRE), 6 M KOH as the electrolyte, and mesh of stainless steel as the counter electrode located behind HRE. Volt-ampere curves (VAC) were recorded using a Solartron Schumberger 1820 potentiostat and a Tacussel (Bi-PAD) with a specialized electrochemical program, that allows for potential evaluation within a pre-defined range with a given speed and current flow registered. Charge/discharge tests were performed with an eight channel Galvanostate 54 (PMC). A cyclic condition was employed in the potential range -1.0 V to 2.0 V. The charge time was 45 min, which ensures charging limits from -1000 mV up to 1800 mV, selected in accordance with the further testing of new GDE in full cell configuration with Zn-electrode. The discharge time was 30 min and the charge/discharge current density was ± 2 mA cm⁻². Conditions of the cycling: maximum half-cell voltage limit was 2000 mV; minimum half-cell voltage limit was -1000 mV. VAC results were compared with those for a carbon-based gas diffusion etalon electrode (EE) [16] with the same CL.

Results and discussion

After the replacement of carbon black with zeolite in the classical GDL-recipe, PTFE-fibers net cover the zeolite grains, which is a prerequisite for sufficient hydrophobicity (Figure 3).

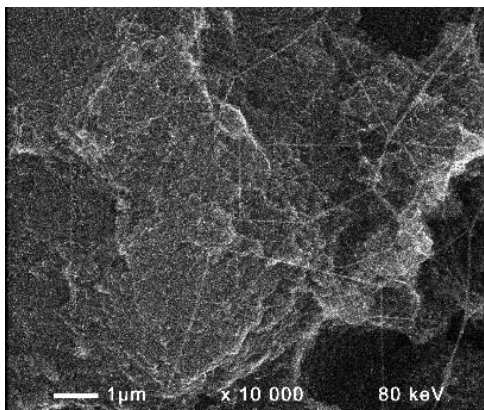


Figure 3. SEM image of zeolite-based GDL with 11 wt.% PTFE

However, samples with the content of PTFE powder above 20 wt. % showed low air permeability and excellent hydrophobicity. The samples with 10 - 20 wt. % PTFE have good gas permeability and mechanical stability, but still insufficient hydrophobicity. For evaluation of the optimal gas permeability, a comparison of the zeolite based and that of the standard carbon based GDL permeability was used [17].

In order to fulfill both requirements, the teflonization procedure was modified and the second generation GDL was developed covering GDL with diluted PTFE emulsion. This impregnation procedure was performed in several cycles which ensured necessary hydrophobicity and gas permeability. The hydrophobicity increased as a result of the stepwise zeolite pores coated with PTFE. This technology was used for preparation of the second generation GDE (sample ZE 1) with bifunctional CL.

Although ZE 1 has similar volt-ampere characteristics as EE until 7 mA/cm² (Figure 4), its durability is low – it operates only several cycles before wetting. For further improvement a third optimization of the teflonization procedure was performed – PTFE powder was replaced with PTFE emulsion. Following this procedure, a third generation GDE was introduced (sample ZE 2).

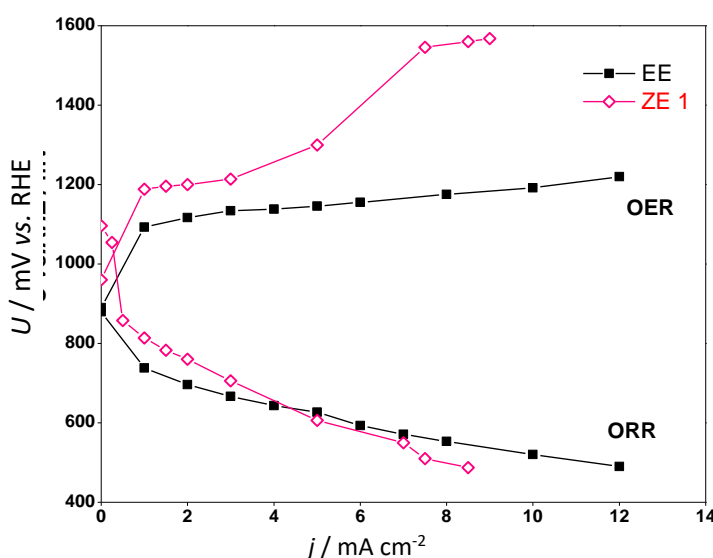


Figure 4. Volt-ampere characteristics during discharge (ORR) and charge (OER) measured on GDE with impregnated zeolite-based GDL (ZE 1) compared with the etalon carbon based GDE (EE)

As presented in Figure 5, the current density of about 2-5 mA/cm² is a promising initial result, which corresponds to the requirements for the final usage of Zn/air batteries in solar farms where they shall operate in combination with other batteries/supercapacitors [6].

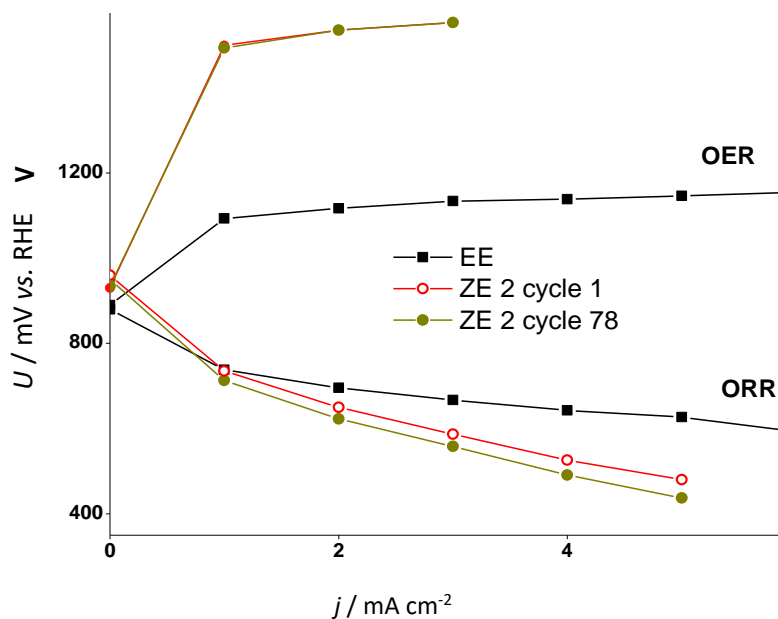


Figure 5. Volt-ampere characteristics on the second generation zeolite-based GDE (ZE 2) during discharge (ORR) and charge (OER) compared with the etalon carbon based GDE (EE)

For durability testing, the charge/discharge cycling was performed and showed a promising result for more than 150 cycles (Figure 6).

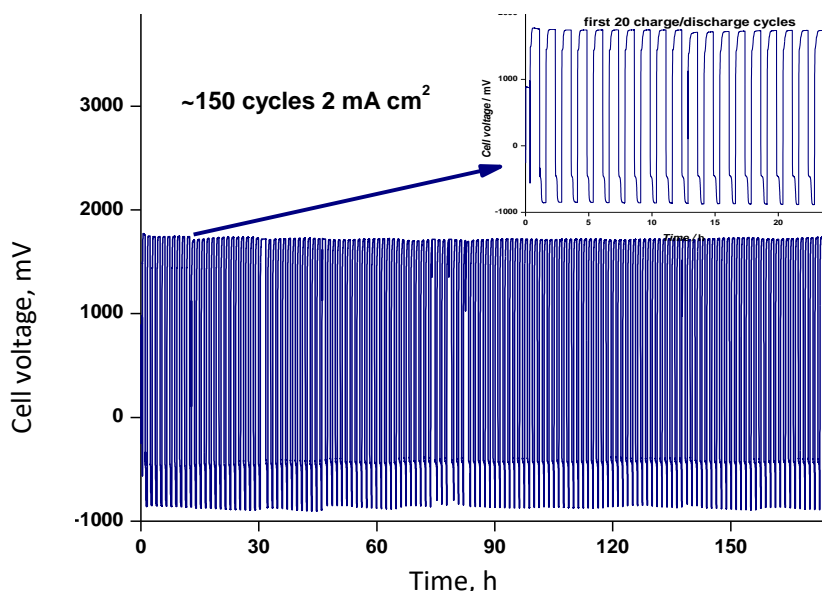


Figure 6. Charge/discharge cycling of the third generation zeolite-based GDE (ZE 2) in half-cell configuration

Conclusions

The first obtained results on the development of carbon free GDE carried out by replacing carbon with zeolite are promising in respect to both – reached current densities and number of cycles. In addition, zeolites are easily available and cheap materials what makes them attractive for replacement of carbon-black in GDL for secondary metal-air batteries.

The next stage of the optimization is focused on further increase of the current density and number of charge/discharge cycles, *i.e.* durability and scaling up.

Acknowledgements: This work was supported by the Bulgarian Ministry of Education and Science under the National Research Programme E+: Low Carbon Energy for the Transport and Households, grant agreement D01-214/2018 and the National Roadmap for Research Infrastructure (2017-2023): Research Infrastructure Energy Storage and Hydrogen Energetics NI SEVE, grant agreement D01-160/28.08.18.

References

- [1] Accelerating Clean Energy Innovation COM (2016) 763 final, http://ec.europa.eu/energy/sites/ener/files/documents/1_en_act_part1_v6_0.pdf (accessed November 15, 20219).
- [2] A. Kaisheva, in: *Portable and Emergency Energy Sources*, Z. Stoynov and D. Vladikova (Eds.), Marin Drinov Academic Publishing House, Sofia, Bulgaria, 2006, p. 301.
- [3] European Strategy for Low-Emission Mobility COM (2016) 501 final; <https://ec.europa.eu/transparency/regdoc/rep/1/2016/EN/1-2016-501-EN-F1-1.PDF> (accessed November 15, 20219).
- [4] P. Gu, M. Zheng, Q. Zhao, X. Xiao, H. Xue, H. Pang, *Journal of Material Chemistry A* **5** (2017) 7651-7666.
- [5] J. Fu, ZP. Cano, MG. Park, A. Yu, M. Fowler, Z. Chen, *Advanced Materials* **29(7)** (2016) DOI: 10.1002/adma.201604685.
- [6] EU funded H2020 project "Zinc-Air Secondary innovative nanotech based batteries for efficient energy storage" – ZAS (GA 646186) (<http://sintef.no/projectweb/zas/>)(accessed November 15, 20219).
- [7] J-S. Lee, ST. Kim, R. Cao, N-S. Choi, M. Liu, KT. Lee, J. Cho, *Advanced Energy Materials* **1** (2011) 34–50.
- [8] Z. Stoynov, D. Vladikova (Eds.), *Portable and Emergency Energy Sources*, Marin Drinov Academic Publishing House, Sofia, Bulgaria, 2006, p. 301.
- [9] G. Zhang, *Journal of Power Sources* **163** (2006) 591–597.
- [10] S. Velraj, J. Zhua, *232nd ECS Meeting Abstracts, MA2017-02*, 1500, National Harbor, Maryland, USA, 2017.
- [11] M. Kar, B. Winther-Jensen, M. Forsyth, DR. MacFarlane, *Physical Chemistry Chemical Physics*, **15** (2013) 7191-7197.
- [12] S. Müller, F. Holzer, O. Haas, *Journal of Applied Electrochemistry* **28** (1998) 895-898.
- [13] O. Haas, JV. Wesemael, in: *Encyclopedia of Electrochemical Power Sources*, J. Garche (Ed.), Elsevier Science Ltd., 2009, p. 384.
- [14] B. Dunn, H. Kamath, J-M. Tarascon, *Science* **334** (2011) 928–935.
- [15] V. Caramia, B. Bozzini, *Materials for Renewable and Sustainable Energy* **3** (2014) 28. <https://doi.org/10.1007/s40243-014-0028-3>
- [16] B. Abrashev, D. Uzun, H. Hristov, D. Nicheva, K. Petrov, *Advances in Natural Science: Theory & Applications* **4(2)** (2015) 65-69.
- [17] E. Mladenova, D. Vladikova, Z. Stoynov, A. Chesnaud, A. Thorel, M. Krapchanska, *Bulgarian Chemical Communications* **45(3)** (2013) 366–370.