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Screening impedance analysis of Zn-air cells

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As a promising technology, zinc-air secondary batteries have gained considerable attention over the past few years. The presented work aims at application of Electrochemical Impedance Spectroscopy (EIS) as a tool to develop new nanostructured and environmentally friendly materials for rechargeable zinc-air cells. The results are obtained on both half- and full-cell configuration during cycling. They ensure electrochemical characterization of the cell and its components (electrodes and electrolyte) in similar state of charge. This offers experimental evidence to determine the rate limiting stages. The accumulated information will be used for further studies and optimization of the zinc-air cell.

Key words: Zn-air cell, Gas diffusion electrode, Zinc electrode, Impedance measurementss

INTRODUCTION

In principle the main advantage of metal-air cells is the use of oxygen from the atmospheric air as a reactant. The air gas-diffusion electrode possesses two advantages over the metal-oxide cathode: infinite charge capacity and low weight independent on capacity. Thus the capacity of metal-air battery is determined only by the amount of active metal, but not by the air electrode. As a result, the specific capacities like gravimetric (Ah/kg) and volumetric (Ah/l) are significantly higher than those for classical electrochemical systems with the same metal anode [1].

Developed zinc–air batteries are traditionally non-rechargeable. Therefore their transition to rechargeable ones is lately becoming a hot topic, due to the advantages of this system to ensure electrochemical storage with high energy density, high capacity and low price [2, 3]. However, there is still not well-performing (long-term) secondary Zn-air battery which makes this technology attractive for intensive research, especially on low-cost materials with improved reversibility and enhanced durability [4].

Battery capacity fading is recognized to happen due to the loss of material properties (for example morphological changes) during cycle life. For the Zn-electrode the shape or the morphology of the zinc particles is of great importance to assure good inter-particle contact and hence, to keep lower internal resistance which improves the electrochemical performance. However, as the electrode surface area increases, the corrosion rate of the zinc electrode generally becomes more significant. The combination of coarse and fine particles or agglomeration of nano-sized zinc/zinc alloyed particles in a meso-porous structure can be regarded as a compromise between high-rate electrochemical performance and self-corrosion [5]. Alloying zinc with other metals (e.g. lead, cadmium, bismuth, tin and indium), or coating the zinc metal with other materials as lithium boron oxide or aluminum oxide are effective approaches. Some additives such as silicates, surfactants and polymers can also efficiently suppress or reduce the rate of hydrogen generation.

In respect to the gas diffusion electrode (GDE) there are two challenges: development of non-precious bifunctional air electrocatalysts for both oxygen reduction and evolution [6, 7] and introduction of carbon-free gas diffusion layer for preventing carbon electrochemical oxidation/corrosion during battery charging (oxygen evolution) [8].

In order to improve the overall reversibility of the zinc-air battery, it is necessary to understand the current limitations, requirements and challenges for each cell component (viz. anode, electrolyte and cathode) and their interaction [9]. It can be achieved by performing electrochemical impedance spectroscopy (EIS) studies. EIS is regarded as one of the most powerful techniques for investigation of electrochemical systems due to its unique capability to separate the kinetics of different steps comprising the overall electrochemical

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process [10]. Since impedance measurements are performed in a large frequency range (about 9 decades), processes with big difference in velocities and time-constants can be monitored, distinguished and evaluated – fast electronic conduction, fast electrochemical kinetics, diffusion and other types of transport limitations, as well as formation and growth of new phases [11, 12].

The aim of this work is to characterize electrochemically a rechargeable zinc-air cell by impedance spectroscopy. It is performed at cell level and to its electrodes during cycling. This feasibility study will be further used for deeper insight in the aging and degradation mechanisms and processes occurring during long-term operation. It will further support the optimization of the zinc-air system.

EXPERIMENTAL

The experiments were performed in a homemade 25 cm^2 test cell which has the possibility to be used as full cell and/or half-cell with three electrodes configuration having Hydrogen Reference Electrode (HRE) (Fig.1) [13].

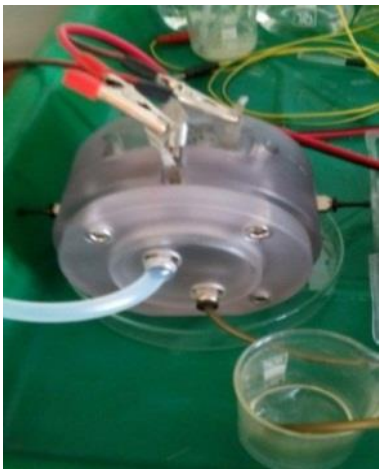

Fig. 1. Homemade Zn-Air test cell.

The Zn electrode was made from a paste prepared by mixing in an optimal ration commercial Zn battery-grade micrometric powder (containing traces of bismuth, indium and aluminum) and ZnO. Both materials are from UMICORE. For improvement of the electrode mechanical stability an improved procedure was introduced. The classical binder carboxymethyl cellulose (CMC) was replaced by PTFE. The discharge capacity of the first cycle in half-cell configuration was used as criterion to define the optimal ratio PTFE:Zn-paste which was found to be 1:5 (Fig. 2). Although it causes about 10 % capacity losses (estimated from nominal and calculated discharge capacity), the PTFE enhances the mechanical stability of the Zn-electrode demonstrated by increasing the number of cycles from 20 when CMC was used to 120 (in full cell configuration). The Zn electrodes were fabricated to provide a capacity of 1000 mAh/g. The active Zn mass was deposited on 9 cm^2 stainless steel mesh and pressed at 250°C with 300 kg/cm^2.

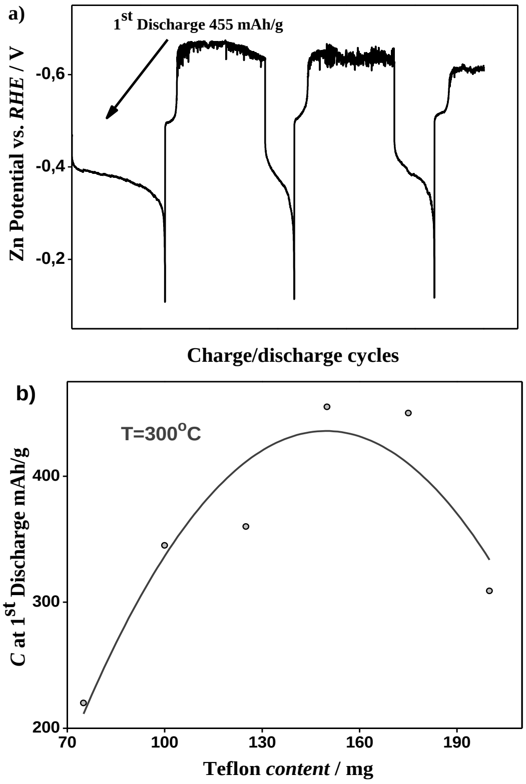

Fig. 2. Zn-electrode: a) voltage profile during charge/discharge cycling at 5 mA/cm^2; b) Initial cell capacity as a function of PTFE content.

An optimized bifunctional GDE which ensures 700 charge/discharge cycles in half cell configuration at current density of 10 mA/cm^2 was used. The GDL was produced from Vulcan XC-72 (Cabot Corp.) which was modified with 60 wt. % Teflon (Sigma Aldrich emulsion) through especially developed procedure. A mixed catalyst with optimized composition of 70 wt. % Ag, 20 wt. % Co_3O_4 and 10 wt. % PTFE which showed excellent performance (Fig. 3) was used as active catalyst layer [14]. The electrode was prepared by hot pressing at 250°C with 300 kg/cm^2 for 3 minutes. The tests were carried out using an optimized formulation (CIDETEC) based on an alkaline electrolyte system [15].

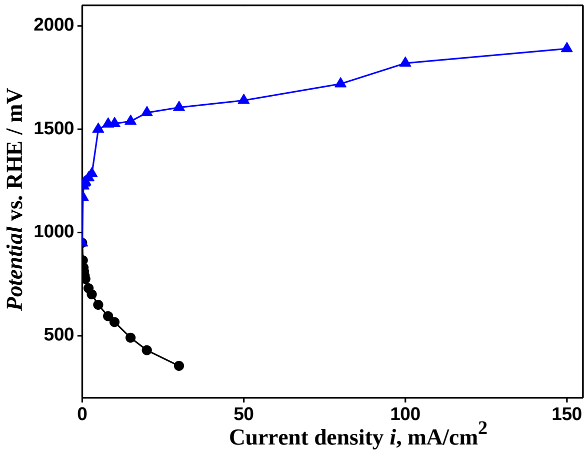

Fig. 3. Charge (▲) and discharge (●) voltages of an optimized bifunctional GDE at different current densities in a homemade 10 cm^2 cell.

The cycling test was performed applying a current density of ±10 mA/cm^2 during 7 h of charge and 6 h of discharge. The cut-off voltages were set at 2.5 V at charge (C) and 0.5 V at discharge (D), respectively (Fig.4) after the first cycles where the C/D voltages were beyond these limits. This situation most likely induced Zn passivation reflected by the subsequent decrease in capacity.

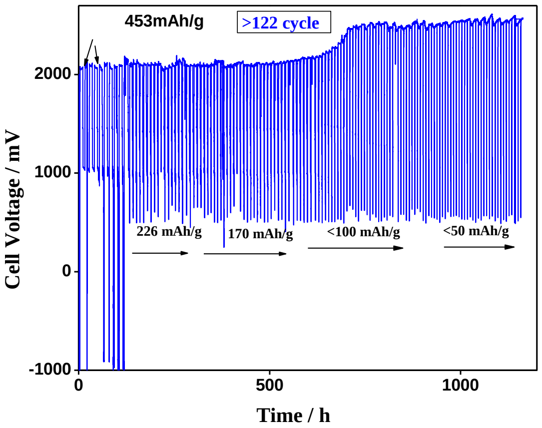

Fig. 4. Long-term cycling of homemade Zn/Air cell at 10 mA/cm^2

The impedance measurements were carried out using a Solartron 1260 Frequency Response Analyzer in the frequency range 1 kHz – 10 mHz with density of 5 points per decade at applied DC current of 10 mA and amplitude of the AC signal of 2.5 mA during both charge and discharge modes. They were performed after the 20th cycle and at the end of the cell life at similar state of charge or discharge for characterization of both the electrodes and cell behavior. For convenience, the impedance measurements of the electrodes were related to the cell voltage, measured before the AC perturbation. Preliminary screening performed before and after the impedance experiments registered insufficient voltage changes, which could be ignored.

RESULTS AND DISCUSSIONS

The volt-ampere characteristic (VAC) is a key feature of any electrochemical power source. It covers the entire operating range and reflects the set of dominant phenomena that govern a process. Thus, VAC gives the main fundamental and simplest description of the cell performance in a given moment of the test. VAC depends on the operating conditions and degradation state. For batteries the state of charge/discharge should be also taken into account. Therefore, at constant working conditions the changes in the VAC may serve as performance indicator to estimate the state of health (SoH) and the degradation rate. For deeper insight into the phenomena and mechanisms the VAC analysis is combined with impedance measurements in selected working points [16].

Fig. 5 represents VAC of the homemade Zn-air cell at a given state during discharge after 20 previous charge/discharge cycles. Generally, the volt-ampere curve has three distinct areas: (*i*) an activation zone at low current (segment I in Fig. 5), followed by (*ii*) a transport zone with linear behavior (segment II in Fig. 5) and (*iii*) a diffusion restriction zone at high current (not presented in Fig. 5). A working point (WP) at 10 mA was selected (triangle in Fig.5) to perform the impedance measurements of the Zn-Air cell in both full- and half-cell configuration. Due to its position in the kink of segments I and II in the voltage-current curve, the measured impedance can ensure information about both the charge transfer, which depends on the electrode catalytic activity, and the transport hindrances.

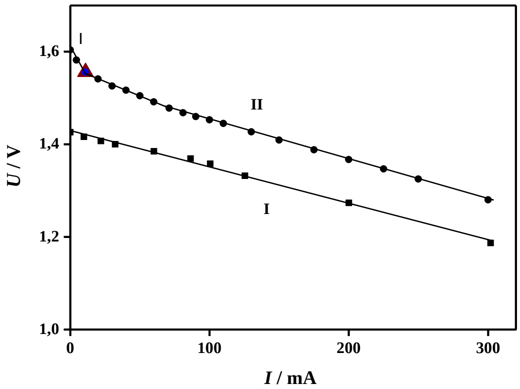

Fig. 5. Volt-ampere characteristic of a Zn-air cell in discharge regime: (●) full cell configuration; (■) half-cell configuration of gas diffusion electrode (GDE).

The VAC of the GDE recorded during discharge shows a linear behavior (Fig. 5.). This is characteristic of electrodes operating under the domination of transport limitations. The VAC comparison with the full cell performance suggests that the activation losses come mainly from the Zn electrode. This hypothesis is confirmed by the impedance measurements presented in Fig. 6.

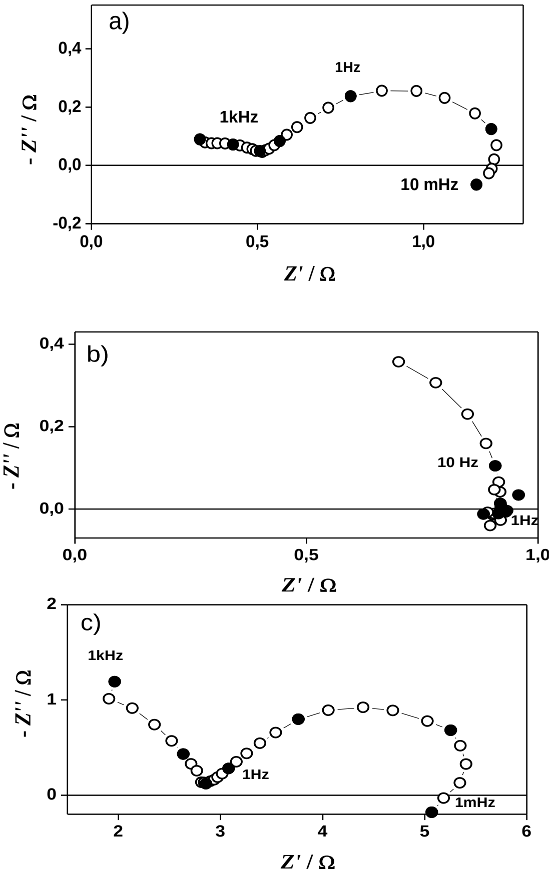

Fig. 6. Impedance diagrams for: a) GDE, b) Zn electrode and c) full-cell during discharge (1,6 V).

The impedance diagram of the GDE (Fig. 6a) is characterized by a well-defined low frequency arch corresponding to bounded transport limitations, while that for the Zn electrode (Fig. 6b) exhibits the domination of the charge transfer semicircle. The impedance of the full cell combines the two characteristic impedance shapes in the high and in the low frequency range, respectively. A significant increase of the resistance is also observed (Fig. 6c). The state of discharge (SoD) influences weakly the anode reaction. The inductive complicated shape in the low frequency range, which is typical for impedance of batteries, usually marks the formation of a new phase [17].

The impedance diagrams for the full cell and for the two electrodes during charge are also well defined (Fig. 7). The charge transfer resistance of the zinc electrode decreases about 3 times, which obviously influences also the cell resistance (Fig. 7b). This asymmetry during charge and discharge may be due to the screening effect of the teflonized anode surface.

The volt-ampere characteristic and impedance measurements in full cell configuration performed at the end of the cell life (after 120 C/D cycles) showed strongly deteriorated behavior (Fig. 8). The resistance registered by impedance was about 10 times higher in comparison to that after the 20th C/D cycle.

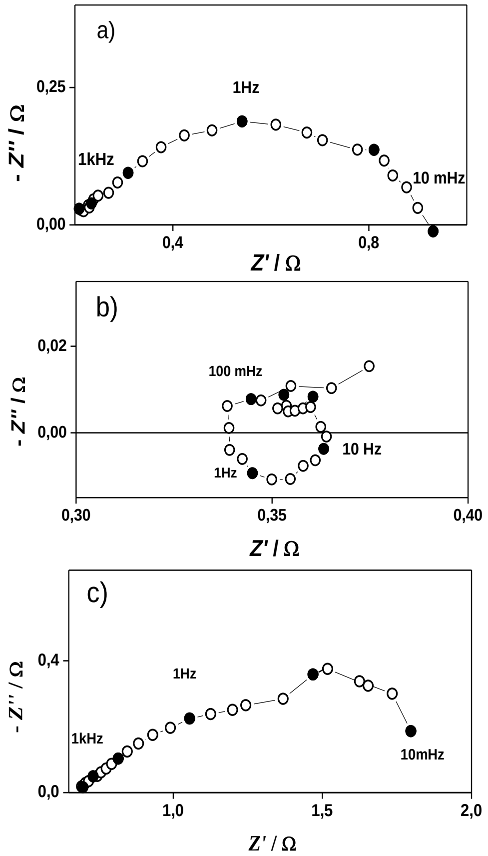

Fig. 7. Impedance diagrams for: a) GDE, b) Zn electrode and c) full-cell during charge (1,9 V).

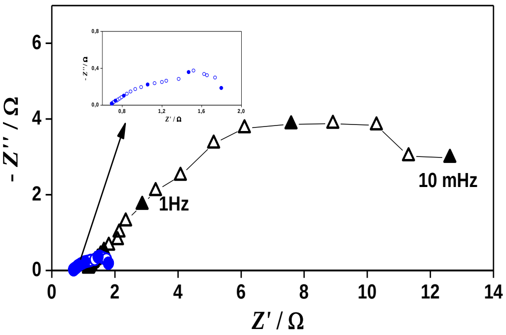

Fig. 8. Impedance characteristics of full cell during charge (about 1,8 V) after the 20th cycle (●) and after the last (120th) cycle (▲).

The subsequent measurement of the Zn electrode failed, due to obviously the entire Zn dissolution and total loss of contacts with the current collector (visually confirmed after opening the cell). It is interesting to note that a lower resistance was registered for the measurements in full cell configuration after the failure of the Zn electrode (Fig. 9), which can be explained with a change of the system, since in practice the Zn electrode was replaced by the stainless steel current collector.

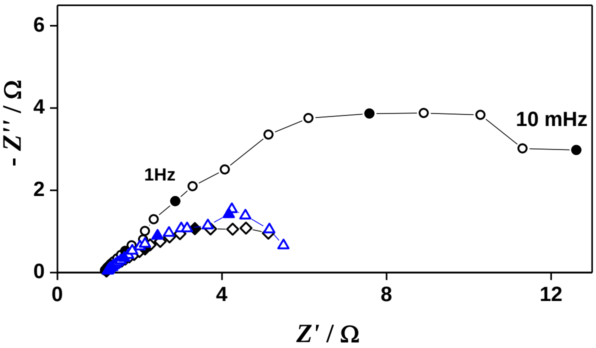

Fig. 9. Impedance of full cell during charge after the 120th discharge: before (●) and after (▲, ♦) the failure of the Zn electrode.

After opening the homemade cell, it could be seen that while the zinc electrode was totally dissolved, the GDE was in good condition (Fig. 10). The replacement of the damaged Zn electrode with a new one and refreshment of the electrolyte ensured more than 50 additional C/D cycles at 10 mA/cm^2.

Fig. 10. Gas diffusion electrode before and after 120 C/D cycles.

CONCLUSIONS

These preliminary results demonstrate the applicability of EIS for performance studies of Zinc-air rechargeable cells. The measurements can be carried out in half-cell and full-cell configuration during charge or discharge. This versatility ensures information about the behavior and influence of the cell components thus determining the rate limiting step and its position in the cell. Comparison of volt-ampere characteristics combined with periodic impedance measurements during battery cycling can bring to a deeper insight into the degradation mechanisms. Getting such knowledge, Zinc-air cells can be further optimized in terms of performance and cycle life.

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СКРИНИНГОВ ИМПЕДАНСЕН АНАЛИЗ НА ЦИНК-ВЪЗДУШНИ КЛЕТКИ

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Като обещаваща технология, вторичните цинк-въздушни батерии спечелиха значително внимание през последните няколко години. Представената работа цели въвеждането на електрохимична импедансна спектроскопия (EIS) като инструмент за разработване на нови наноструктурирани и екологосъобразни материали, подходящи за внедряване в акумулаторна цинк-въздушна клетка. Първите резултати при циклиране са получени при измервания както в конфигурация на полу-клетка, така и на цяла клетка. Те осигуряват електрохимично охарактеризиране на клетката и нейните компоненти (електроди и електролит) при фиксирано състояние на заряд, което позволява експериментално дефиниране на скорост-определящия стадий. Получената информация ще бъде използвана за по-нататъшно проучване и оптимизиране на цинк-въздушната клетка.