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Optimization of the bi-functional oxygen electrode (BOE) structure for application in a Zn-air accumulator

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A novel structure of a bi-functional oxygen electrode (BOE) was developed, which is based on a new technological process of teflonization. The electrochemical oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) were studied in a half-cell configuration, to investigate its charge/discharge characteristics. Both the gas-diffusion layer (GDL) and active layers (AL) of the electrodes were optimized. Preliminary studies of GDLs with different carbon blacks and for different ratios between the PTFE and carbon blacks have shown, that the most stable GDL is produced from Vulcan XC-72 teflonized with 60 % PTFE – TV-60. The innovation regarding the GDL is in the way it is prepared using high-energy mixing, which assures an equal dispersion and intimate contact between the carbon black and Teflon particles. With this GDL an optimization of the AL was performed with respect to both the thickness (amount of catalytic mass – catalyst + PTFE) and the ratio between the catalyst and the binding agent (PTFE). The volt-ampere characteristics and the charge/discharge tests showed that the most suitable catalyst with respect to the stability of the GDE is a mix of Ag and Co_3O_4. The GDE with the above composition reaches more than 700 cycles without a decrease in performance.

Keywords: Me – air accumulator, GDL, electrochemical cell design.

INTRODUCTION

The necessity for energy storage systems is growing due to the fact that today's society is in transition from fossil fuel to clean energy sources. The use of renewable energy sources such as wind and photovoltaic systems requires the availability of cheap and efficient electrochemical systems to store the produced energy for a time when renewable energy production is greater than the energy consumption. Such systems may be metal/air-batteries. This gradual but inevitable process is accelerated by the latest active research on a global scale for the collection, transformation and storage of sustainable energy. Electrochemical systems (batteries, accumulators, etc.) have long been utilized in the conversion and storage of electrical energy [1].

Among the different metal/air systems, the zinc/air system is a relatively mature technology and has the required capacity for energy applications. Its primary batteries have been known to the scientific community since the late nineteenth century. Commercial products began to appear in the 1930s [2]. Both now and in the past because of their use in alkaline fuel cells, the concept of gas diffusion electrodes is important. The optimization and improvement of GDE has been explored since the 1960s. Intensive experimental research has been carried out to improve the design and construction of the gas-diffusion and active-layer electrodes.

Electrically rechargeable metal/air-batteries are very attractive as candidates for an energy storage material, due to their low cost and high stability in an aqueous solution; they are environmentally benign and have a high specific energy density. Concentrated potassium hydroxide solution is the electrolyte of choice for rechargeable metal-air batteries such as the zinc-air and iron-air batteries, because of its high conductivity. Zinc-air batteries, to be more specific, yield an extremely high potential and therefore can be used in alternative energy storage devices. In an alkaline solution Al can corrode more easily than Zn, although Al-air cells have a much greater energy density than zinc-air cells [3, 4]. In addition, Zn has various advantages such as a low cost, is quite abundant, has a low equilibrium potential, is environmentally benign and has a protracted exploitation lifetime [5, 6]. A principal advantage of the alkaline zinc-air batteries is that non-noble metal catalysts can be used for the ORR and OER reactions, as calculated, the specific energy density of Zn-air batteries is 1084 $W\ h\ kg^{-1}$. In order to properly operate these metal-air systems, a bi-functional air electrode is required. Recent advances in bi-functional electro-catalysts for both the ORR and OER provide strong support for the use and development of bifunctional air electrodes (BAE) for metal air batteries [7–12].

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Recently many authors have improved the bi-functional air electrodes applied in Zn/air systems [13–16].

The current work describes our achievements in the development of bi-functional air electrodes. The oxygen reduction reaction occurs at the triple-phase interface, whereas the OER occurs at the two-phase interface [17]. The air electrode is composed of a porous hydrophobic membrane, a catalytic layer and a current collector. These electrodes are leak-proof and conductive, while remaining active and stable at high charge-discharge current densities and have a porous structure to ensure the supply of oxygen. The air electrodes usually contain a catalyst dispersed on a carbon substrate. This mixture is PTFE-bonded and forms the active part of the porous gas-diffusion electrode [18, 19].

EXPERIMENTAL

Air electrode design

The new design of the BOE is comprised of metal oxide-based catalysts. The electrochemical OER and ORR were studied in half-cell configurations to investigate the charge/discharge characteristics. By using a new process of high energy mixing teflonization, an even distribution of the carbon particles was obtained. The BAE is a double-layered structure (Fig. 1) comprised of two layers: a porous hydrophobic carbon black GDL and a semi-hydrophobic AL. The electrode was made using a matrix of a size corresponding to the electrodes produced (1, 10, 25 cm^2). First the GDL is deposited followed by the catalytic layer onto the GDL and then the Ag based current collector is manually placed on top. After that the matrix is closed and hot-pressed at 300 kg cm^{-2} for 1 min at 300°C. The GDL is produced from Vulcan XC-72 (Cabot corp.) which is modified by PTFE (Teflon emulsion, Sigma Aldrich) through a novel technology. The BAE is optimized with respect to both the GDL and the AL. The catalysts used were: (i) a mixture of Ag (Ferro AG, Ag 311), Co_3O_4 (Sigma Aldrich, < 50 nm) and PTFE (3M Dyneon, TF9207Z), (ii) only Ag (Ferro AG, Ag 311) and (iii) only Co_3O_4 (Sigma Aldrich, < 50 nm). The following parameters were studied: (i) catalyst amount, (ii) pressure during production, (iii) electrode thickness, (iv) PTFE amount.

Based on previous experience a catalyst mixed of Ag + Co_3O_4 was used for the AL [20]. The suggested composition of the AL was 70 wt.% Ag + 20 wt.% Co_3O_4 + 10 wt.% PTFE [21].

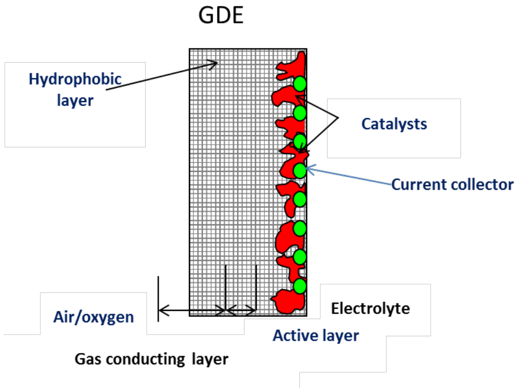

Figure 1. Schematic cross-section of the air gas diffusion electrode.

The amount of catalytic mass was optimized in a three electrode half-cell setup, whereas the Ag/Co_3O_4/PTFE was mixed with a double-knife mill and pressed on a stainless steel gauze (Haver&Boecker, W 0.5 mm, D 0.125 mm, SS type: 1.4306) as the current collector. After pressing at 2.5 bar, a heat treatment was applied at 340°C for 1 hour. The Ag/Co_3O_4 mixture is shown in Fig. 2, the big white particles are the Ag, and the smaller darker particles covering the Ag surface are the Co_3O_4 particles.

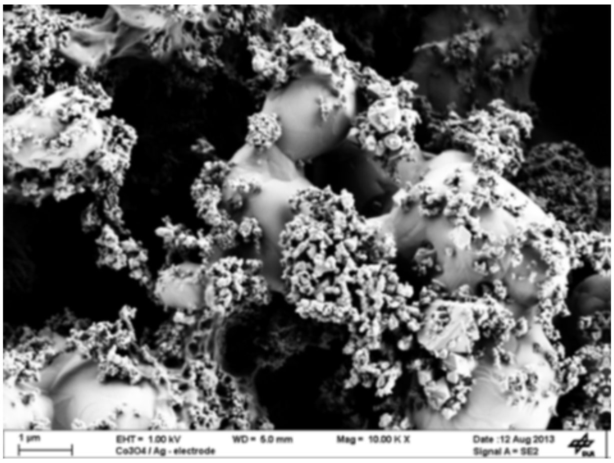

Figure 2. SEM picture of an Ag /Co_3O_4 mixture.

Due to this good coverage of conducting Ag particles with non-conducting Co_3O_4 particles, the performance of the mixture increases the electrochemical performance of the electrode. The thickness of these electrodes is in the order of 400 µm. The current density increased with an increase of Co_3O_4 amount up to 20 wt.%, above 20 wt.% the electric resistivity of the electrode increased by an order of several magnitudes. This is due to blocking of the conducting paths by the Co_3O_4 catalyst particles. This increase in electrical resistivity leads to a decrease in current density. The loading of the optimized electrode is a conductive additive consisting of: 105 mg cm^{-2} Ag, 30 mg cm^{-2} Co_3O_4 and 15 mg cm^{-2} PTFE.

The catalytic properties of the cathode electrodes were determined with the aid of 1, 10 and 25 cm^2 three-electrode cells as described in [22]. The process of ORR and OER was studied in 6M KOH. The counter-electrode was a stainless steel mesh. The reference electrode was a “Gaskatel” reversible hydrogen electrode (RHE). A Solartron 1286 Electrochemical Interface, was used for the galvanostatic measurements.

A minimum of four measurements were made for each result to achieve better reproducibility. Arithmetic averages are presented in the graphs.

The GDE (BOE) were optimized with respect to the catalyst used, electrode thickness and mass ratio between catalysts and binder, varying one parameter at a time and keeping the others constant.

RESULTS AND DISCUSSION

The working electrode (cathode) potential at a fixed current density (i=10 mA cm^{-2}) was selected as a criterion for the quality of the electrode. With this criterion, electrodes with different amounts, resp. ratios of the components were compared to find the optimum composition.

Fig. 3 shows the optimization curves relative to 60% teflonized Vulcan XC-72 in mg cm^{-2} at E (i = 10 mA cm^{-2}), mV *versus* a RHE. From the data obtained, it can be seen that the electrodes containing 50 mg cm^{-2} of 60% teflonized Vulcan XC-72 show the lowest overvoltage for both OER and ORR.

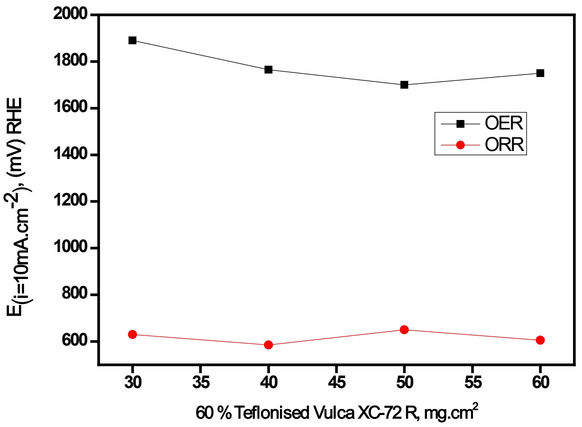

Figure 3. Optimization curve for a quantity of 60 % Teflonized Vulcan XC-72 in mg cm^{-2} at E $_{(i = 10 \text{ mA cm}^{-2})}$, mV *versus* RHE.

The newly developed technological process allowed a high teflonization (up to 60 wt.%) and homogenization of the GDL. By utilizing this process, the diffusion limitation is increased. Hence, the developed GDE is expected to be more stable in alkaline solutions. Nevertheless, in comparison with previous research [20, 23] when using 35 wt.% teflonization the obtained current density was very low, about 30 mA cm^{-2} for the ORR.

The AL catalytic mass in the electrodes is a mixture of the catalyst materials (Ag + Co_3O_4), which was used to fabricate the BOE. The active layers were optimized with respect to both the thickness (amount of catalytic mass – catalyst + PTFE, Fig. 4) and the ratio between the catalyst and the binding agent (PTFE, Fig. 6). Preliminary studies of the GDL with different ratios between the PTFE and carbon black content have shown that the most stable GDL is produced from Vulcan XC-72 teflonized with 60 % PTFE – TV-60. The total amount of TV-60 is 50 mg cm^{-2}. With this GDL as the backbone, an optimization of the AL was performed.

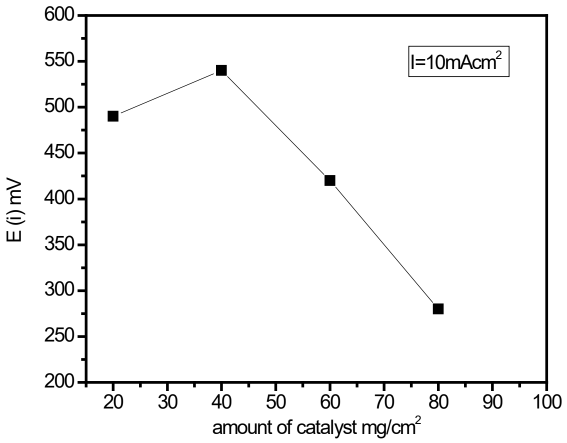

Figure 4. Optimization curve of the catalytic mass amount at a constant ratio for the ORR (catalyst: PTFE) = 80:20.

Shown in Fig. 4 is an optimization curve with respect to the catalytic mass for oxygen reduction at a constant current density i = 10 mA cm^{-2}. From the data obtained it is seen that the electrodes containing 40 mg cm^{-2} have the lowest overvoltage at ORR. The optimization towards OER of the catalytic mass was done following the same procedure. A similar optimal value of AL thickness 40 mg cm^{-2} could be obtained.

Fig. 5 shows an optimization curve in terms of the quantity of Teflon in percent for oxygen reduction at a constant current density of 10 mA cm^{-2}. From the data obtained it can be seen that the electrodes containing 20 wt.% PTFE have the lowest ORR overvoltage. For the OER similar results were observed.

Cobalt oxide and silver were used as catalysts for optimization of the active layer. The dependence of the potential, with respect to the current density, of the OER for Co_3O_4 is shown in Fig. 6. The electrode performs very well for OER, but for the ORR a very low current density (5 mA cm^{-2}) was achieved and the overpotential yield was not good.

The electrode with Ag powder catalyst performed well for the ORR. The anode curve had two characteristic domains with different slopes. The results presented in Fig. 6 are similar to those obtained by Amin *et al.* (2015) [24], where oxidation of Ag to AgO_2 was carried out.

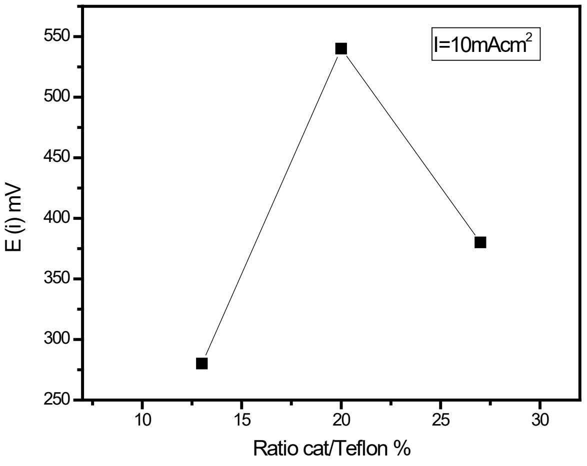

Figure 5. Optimization curve of the ratio for ORR (catalyst – PTFE at a constant catalytic mass amount = 40 mg/cm^{-2}).

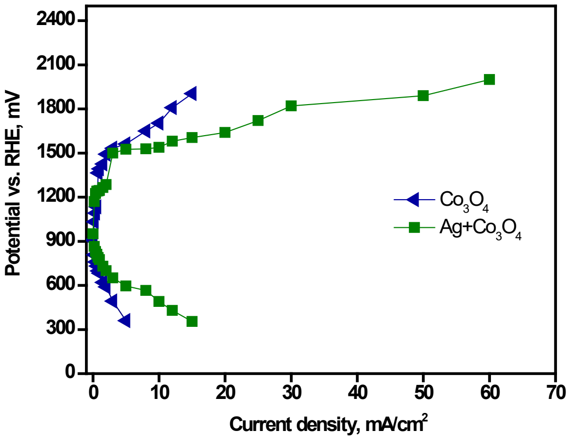

Figure 6. Polarization curves of the electrodes for ORR and OER for catalysts: ■ Ag + Co_3O_4; ▼Co_3O_4. The electrolyte was 6 M KOH at room temperature. The geometrical area of the electrode was 25 cm^2.

Charge/Discharge tests

The behavior of the BOE improves with the addition of Co_3O to the contained Ag catalyst reaching more than 700 charge/discharge cycles. Shown in Fig. 7 are the charge/discharge tests of the electrode containing a GDL – 60% teflonized Vulcan XC-72 – 50 mg cm^{-2} and an AL consisting of 70% Ag + 20% Co_3O_4 + 10% PTFE – 40 mg cm^{-2}. The tests were carried out in a full cell. The area of the working electrode was 25 cm^2. The charge/discharge time was 45/30 min, respectively. The counter electrode in the full cell was a stainless steel mesh.

The electrolyte was 6 M KOH at room temperature. The potential obtained at the OER reached between 1550–1600 mV *vs*. RHE and the ORR potential was 520–600 mV *vs*. RHE.

The results obtained for the volt-ampere characteristics and the charge/discharge tests showed that the most suitable catalyst with respect to the GDE is a mix of Ag and Co_3O_4 which ensures more than 700 cycles.

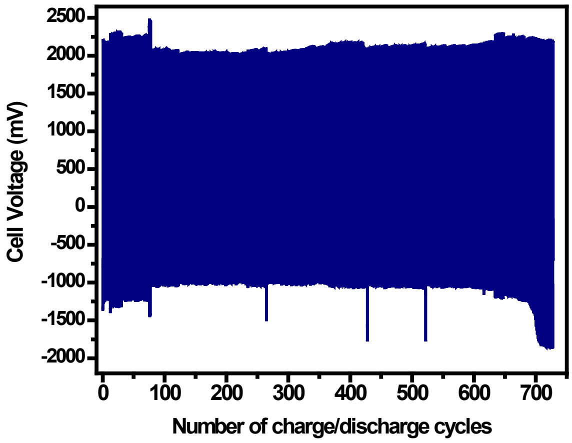

Figure 7. The electrode is comprised of a GDL – 60% teflonized Vulcan XC-72 – 50 mg cm^{-2} and an AL consisting of 70% Ag + 20% Co_3O_4 + 10% PTFE – 40 mg cm^{-2}. The electrode is with a work area of 25 cm^2. The electrode is pressed at P = 300 atm and T = 300°C.

CONCLUSIONS

From the volt-ampere characteristics obtained and the charge/discharge tests carried out it can be concluded that the most suitable catalysts with respect to the GDE are pure Ag and a mix of Ag and Co_3O_4.

By applying this new technological method for the teflonization of carbon blacks from GDL of the electrodes a mix of Ag and Co_3O_4 reached more than 700 charge-discharge cycles, which can be regarded as one of the best reported results. The applied technological approach ensures extremely homogeneous distribution of the basic components for the gas diffusion layer of Teflon on to carbon particles.

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