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Air gas-diffusion electrodes for operation in magnesium-air cells/NaCl – electrolyte

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Metal-air batteries have attracted much attention for their future potential as clean mobile power sources. However, the study is mainly focused on alkaline electrolyte Zn-air batteries and Al-air batteries. A very few studies on neutral saline Mg-air battery were carried out so far.

Air gas-diffusion electrodes (GDE) for reduction of oxygen from the air are commonly used as cathodes in metal-air systems and fuel cell with alkaline electrolytes. They are also used in electrochemical cells operating with neutral electrolytes: Mg-air cells, Al-air batteries and microbial fuel cells. The electrodes, which are subject of this study, consisted of two layers: hydrophobic and an active one. One of the most important tasks in the development of air gas-diffusion electrodes is to find proper catalysts for the electrochemical reduction of oxygen, which ensures high electrochemical characteristics and long exploitation time. Various non-platinum catalysts, introduced into the active carbon, are studied: cobalt tetramethoxyphenylporphyrine (CoTMPP), VS50–CoTMPP–700 and active carbon with Co and Ni (ACCoNi). Transport hindrances that occur in the catalyst layers are evaluated with potential ΔE vs. current density (i) analysis. The optimal values of the parameters of the overall structure of the electrodes and the optimal composition of the catalyst are found.

Mg-air cells operating with saline electrolyte NaCl-solution are developed and investigated.

Key-words: air gas-diffusion electrodes, catalysts for the electrochemical reduction, CoTMPP, Mg-air cells

INTRODUCTION

As efficient, clean, energy converters, fuel cells and metal-air batteries have attracted much attention in recent years due to the possible energy crisis induced by power demands and the increasing importance of protecting our environment. However at the current stage of technology, high cost is one of the big obstacles hindering the commercialization of fuel cells.

Bidault et al. [1] are given review of the state-of-the-art in gas diffusion cathode development. The overall cell performance and stability is dominated by the behavior of the cathode, leading to a focus of research effort on cathode development. Many publications have discussed the behavior of porous electrodes in alkaline fuel cells. Whereas some authors have focused on specific issues such as current distribution [2], or the degree of catalyst utilization [3, 4], the majority have tried to understand the overall mechanism of operation in the GDE related to the structure; considering factors such as gas diffusion and electrolyte penetration. Several models have been used such as the simple pore model [5], the thin film model [6] or the dual scale of porosity model [7]. In the former, a range of porosities is considered, where macropores are gas filled and micropores are electrolyte filled [8, 9]. Giner [10] listed the limitations of this 'flooded porous electrode' model introducing the concept of 'flooded agglomerates'. The operational mechanism of this structure consists of catalyst particles, which form porous agglomerates 'flooded' with electrolyte under working condition. It has been reported elsewhere that the concept of 'flooded agglomerates' gives a satisfactory explanation for the behavior of Polytetrafluoroethylene (PTFE) bonded gas diffusion electrodes, and is in good accordance with experimental findings [11-14].

Optimizing the cathode performance is essential because it governs the overall performance of the fuel cell. According to Bockris [15] at high current density, 80% of the polarization may be due to the oxygen reduction. The Oxygen Reduction Reaction (ORR) is a complex process involving four coupled proton and electron transfer steps. Several of the elementary steps involve reaction intermediates leading to a wide choice of reaction pathways. The

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exact sequence of the reactions is still not known, and identification of all reaction steps and intermediates, and their kinetic parameters is required, which is clearly challenging. Appleby [16] has reviewed and discussed the issues relating to the ORR in acid and alkaline solution. In acid electrolyte, the ORR reaction is electrocatalytic, as pH values become alkaline, redox processes involving superoxide and peroxide ions start to play a role and dominate in strongly alkali media. The reaction in alkaline electrolytes may stop with the formation of the relatively stable HO_2^- solvated ion, which is easily disproportionated or oxidized to dioxygen. Although there is no consensus on the exact reaction sequence, two overall pathways take place in alkaline media [17]:

Direct 4-electron pathway:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (1)$$

Peroxide pathway or '2 + 2-electron' pathway:

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \quad (2)$$

With:

$$HO_2^- + H_2O + 2e^- \rightarrow 3OH^- \quad (3)$$

The peroxide produced may also undergo catalytic decomposition with the formation of dioxygen and OH^-, given by:

$$2HO_2^- \rightarrow 2OH^- + O_2 \quad (4)$$

Due to the inherently faster kinetics for the ORR in alkaline media, a wide range of catalysts have been studied including noble metals, non-noble metals, perovskites, spinels, *etc*. However, it is important to appreciate that the carbon support plays a role in the kinetics as well as the catalyst supported on its surface, so that in evaluating the performance, it is necessary to assess the loading of the catalyst and the type of carbon used where its hydrophobic properties as well as its surface groupings greatly affect the final hydrophobic structure of the electrode.

Developing non-noble catalysts to replace expensive platinum-based catalysts is one of the major approaches being explored to reduce the cost [18-20]. Among the non-noble catalysts that have been discovered, metalloporphyrin complexes have been investigated for several decades as promising candidates for a fuel cell ORR catalyst.

Oxygen electrocatalysis that J. Lee et al. [21] first defined is considered as the most important phenomenon in almost all electrochemical industries because it is the most sluggish reaction that governs the overall reaction rate in electrochemical cells. In this review, they covered two main areas of oxygen–water electrocatalysis, oxygen reduction to water and oxygen evolution from water. This review will be of value to both electrochemists and other applied scientists interested in this field of electrocatalysis.

In the paper Liu H. et al. [22] described the mechanism and kinetics of oxygen and hydrogen peroxide electrochemical reduction that is catalyzed by an adsorbed CoTMPP on a graphite electrode was investigated using cyclic voltammetry and the rotating disk electrode technique. Carbon particle-based air cathodes catalyzed by CoTMPP were fabricated for metal-air fuel cell application. The obtained non-noble catalyst content cathodes show considerably improved performance and stability.

Catalysts containing mixed Ni-Co oxides prepared by impregnating active carbon with solution of Ni-acetate and Co-acetate and subsequent heat treatment are investigated [23].

Here we present a study on selection of hydrophobic material with optimal physical, chemical and electrochemical characteristics for the gas layer of the air gas-diffusion electrode and investigation and selection of suitable catalyst for the electrochemical reduction of oxygen that occurs on the air gas-diffusion electrode.

EXPERIMENTAL

During the last few years in our laboratories research efforts in the field of Metal-air systems have been directed towards developing a Mg-air battery with neutral chloride electrolyte. The air gas-diffusion electrode is a porous, thin and light tablet, which serves as a wall of the metal-air cell and separates the electrolyte of the cell from the surrounding air. This configuration poses some conflicting requirements to the air electrode: it must be highly porous and permeable for gaseous oxygen and simultaneously the leakage of the electrolyte through the porous electrode must be completely avoided. The electrode must be electrically conductive and must possess enough mechanical strength to withstand the hydrostatic pressure of the electrolyte and the eventual hydrodynamic shocks. The air electrode must contain an active catalyst for electrochemical reduction of oxygen in contact with the electrolyte. Stable operation of the air electrode with time is also needed.

The air gas-diffusion electrode developed in our laboratory [24-30] is a double-layered tablet (thickness ca.1.5 mm), which separates the electrolyte of the cell from the surrounding air. The electrode comprises two layers: a porous, highly hydrophobic and electrically conductive gas layer (from the side of the air) and a catalytic layer (from the side of the electrolyte). During operation oxygen from the atmospheric air diffuses in a gas phase trough the free of electrolyte hydrophobic pores of the gas layer and trough the catalytic layer's hydrophobic zones and reaches the partially flooded with electrolyte catalytic zones in the catalytic layer. Electrochemical reduction is taking place on the three-phase boundary oxygen/catalyst/electrolyte.

Porous hydrophobic material

The hydrophobic gas layer of the air electrode possesses high porosity (0.7-0.9 cm^2/g) enabling effective oxygen transport through this layer. From the experimental porograms measured by both mercury and KOH-porometry, the contact angle Θ_{eff} of the hydrophobic material with water electrolytes is obtained (Θ_{eff}=116° – 118°). Because of this high hydrophobicity, the gas layer prevents completely the leakage of the electrolyte through the electrode. The hydrophobic material possesses relatively high electronic conductivity (1.0 – 2.0 $\Omega^{-1}.cm^{-1}$), which allows the current collection to be achieved through a metal grid pressed on the gas layer of the electrode. In this way the current collector grid is not in contact with the electrolyte and thus corrosion is avoided. This is very important especially in the case when the electrode operates in NaCl-electrolyte.

Catalysts for the electrochemical reduction of O_2

Various carbon-based catalysts are tested in the investigated air gas-diffusion electrodes: active carbon promoted with mixed Co-Ni oxides and catalysts prepared by pyrolysis of active carbon impregnated with some N-4 chelate compounds.

ACCoNi catalyst was prepared as active carbon NORIT NK was impregnated with a solution containing both Co- and Ni-acetates, dried and heat treated at 300° C in open air. VS50-CoTMPP-700 type was prepared while dispersed SiO_2 (VS) was impregnated with a solution of CoTMPP and after removing the solvent and drying, the material was treated at 700° C in argon. Pyrolyzed CoTMPP catalyst is produced by impregnation of a dispersed carbon material with a solution of CoTMPP, drying and subsequent heat treatment in Ar at 800° C.

Several types of experimental Mg-Air cells are tested, differing in their size (working area of the air electrodes used) [31].

RESULTS AND DISCUSSION

Fig. 1 represents a comparison between the polarization curves of the air electrodes and the investigated types of catalysts: pyrolyzed CoTMPP, VS50–CoTMPP–700 and ACCoNi. The measurements were performed in 4M NaCl electrolyte operating both in air and in pure oxygen. The comparison with the polarization curve for the electrodes with CoTMPP catalyst shows that the chelate-promoted electrodes have also better current-voltage characteristic.

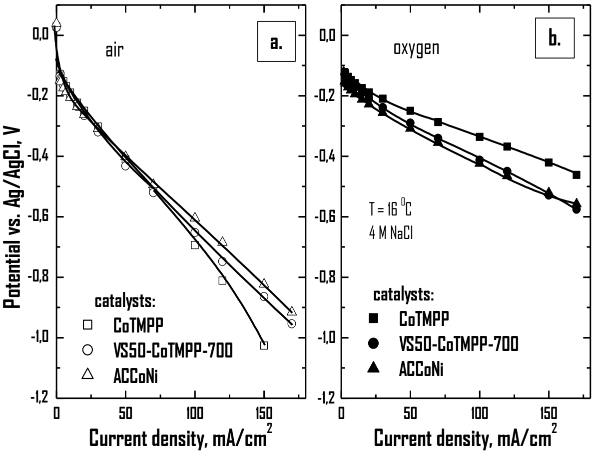

Fig. 1. Current-voltage characteristics of the electrodes with catalysts VS 50 CoTMPP 700, ACCoNi and pyrolyzed CoTMPP, operating in pure oxygen and in air in saline electrolyte.

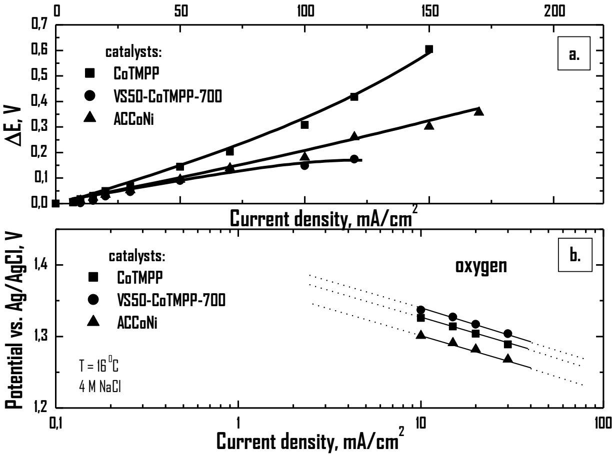

Fig. 2. Comparative methods for diagnostics of the transport hindrances (a) and activity (b) in the electrodes.

The differences in the behavior of the air electrodes with various catalysts is strongly influenced both by the activity of the catalyst used, and also by the hindrances in the transport of the reagent (oxygen) in the porous structure of the catalyst.

Comparative methods for diagnostics of the transport hindrances (Fig. 2a) and the activity (Fig. 2b) in the electrodes are used. The transport hindrances in the air electrodes with the

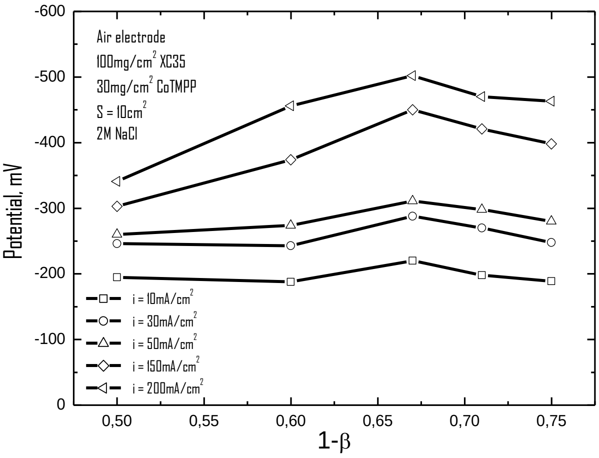

Fig. 3. Current of the air electrode as a function of the catalytic layer content at constant potential.

investigated catalysts are studied by the use of the difference ΔE ($\Delta E = E_{oxygen} - E_{air}$). It is theoretically shown that at low current densities, where the transport hindrances in the porous structure of the air electrode are negligible, the value of ΔE remains constant. At higher current densities the value of ΔE increases with the increase of the current density. This increase is much faster when the transport hindrances in the electrode are more pronounced. From the ΔE-i dependences of the air electrodes with the investigated catalysts, presented in Fig. 2a it can be seen that the transport hindrances in the electrode with catalyst VS50-CoTMPP-700 are comparatively low versus the electrodes with catalysts ACCoNi and pyrolyzed CoTMPP. The activity of the catalysts was compared based on the experimental Tafel plots (Fig. 2b). The more active catalysts are VS50-CoTMPP-700 and pyrolyzed CoTMPP.

One of the main advantages of the developed air electrode is the possibility to vary independently the parameters of its structure: thickness of the gas layer, thickness of the catalytic layer and the ratio catalyst/hydrophobic material in the catalytic layer. One of the important structural parameter of the air electrode is the ratio between the amounts of catalyst and hydrophobic material in the catalytic layer. This ratio is given by the value (1-β), which expresses the amount of the catalyst per unit weight of the catalytic layer. In Fig. 3 the potential at constant current as a function of the ratio (1-β) is presented. At low value (1-β) the amount of the catalyst is low and the potential is also low. With the increases of (1-β) the current density increases and reaches a maximum value. Further increase of (1-β) value results in current density decrease. This is connected with the transport hindrances in the catalytic layer. With the increase of (1-β) the dimensions of the hydrophobic zones in the catalytic layer decrease which results in an increase of the transport hindrances of the gaseous reactant towards the catalytic zones.

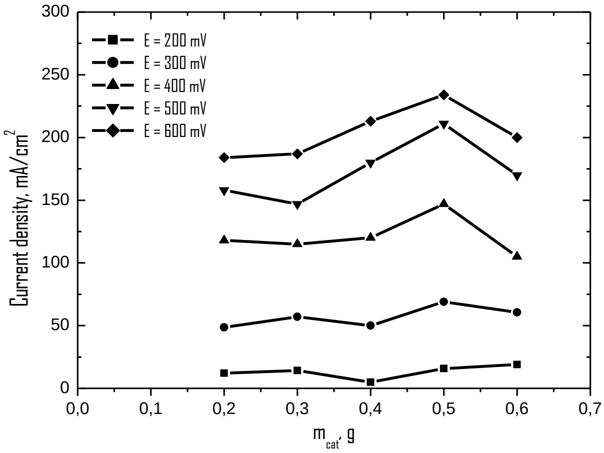

Fig. 4. Current generated from the air electrode at constant potential as a function of the ratio catalyst/hydrophobic material in the active layer.

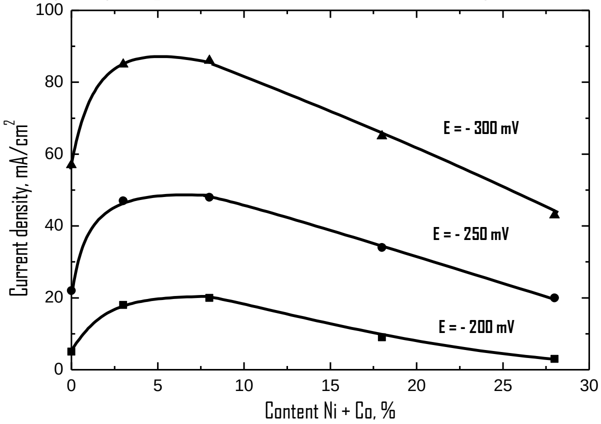

Fig. 5. Optimization of the oxides content in the catalyst ACCoNi.

To investigate experimentally the influence of the active layer thickness, the polarization characteristics of a series of air supplying layers 100 mg/cm^2 XC-35 and corresponding value of catalyst mixture (0,2 g (14%); 0,3 g (21%); 0,4 g (28%); 0,5 g (35%); 0,6 g (41%)) were measured. The dependence of the generated by the electrodes current at constant potential amount of catalyst mixture is studied. Measurements showed, that the optimal value is 0,5 g (35%) catalyst mixture (Fig. 4).

In Fig.5 are presented the current densities of air electrodes measured at constant potential as a function of the content of metal oxides (expressed as a sum of Co + Ni content) in the catalyst. From this figure the optimal content of the mixed Co-Ni oxides in the catalyst is found (ca. 5% Ni + Co).

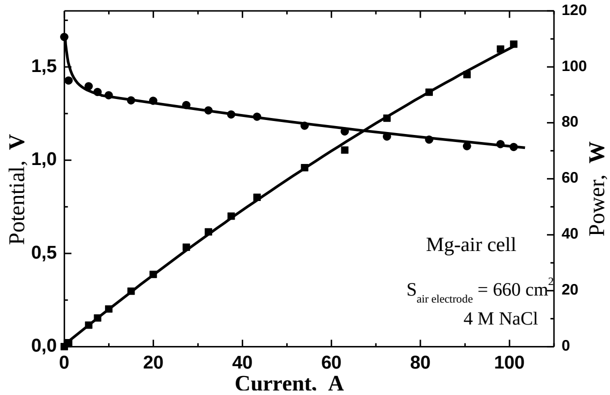

Fig. 6. Current-voltage and power characteristics of the Mg-air cell.

The experiments have shown that high power Mg-air cells can be constructed. In Fig.6 are presented the voltage and the power characteristics of an experimental Mg-air cell: air electrode with pyrolyzed CoTMPP catalyst (total area 660cm^2); Mg – electrode – Mg alloy type MA8M 06; electrolyte - 4M NaCl solution.

The described Mg-Air cells are designed as experimental "mechanically rechargeable cells". Once the magnesium anode has been discharged, it is removed out of the cell together with the electrolyte and new magnesium electrode and fresh saline electrolyte are introduced in it. After this "mechanically recharge" the magnesium-air cell is operational again. The essential feature in this case is that the air electrodes in the cell are used many times. The Mg-air cell can be stored for a long time without electrolyte and without Mg anode. When needed it can be put in operation only by introducing electrolyte and Mg-anode.

CONCLUSIONS

Presented here is a study on selection of hydrophobic material with optimal physical, chemical and electrochemical characteristics for the gas layer of the air gas-diffusion electrode and investigation and selection of suitable catalyst for the electrochemical reduction of oxygen that occurs on the air gas-diffusion electrode. Accordingly, the air gas-diffusion electrodes suitable for operation in NaCl-solution are designed and tested under various conditions. Several carbon-based catalysts for the oxygen reduction reaction were developed.

The performance of the air gas-diffusion electrode is influenced not only by the activity of the catalyst but also by all transport processes taking place in its porous structure. At low current densities, where the transport hindrances in the electrode are negligible low, the value ΔE is practically independent on the current density.

For the CoTMPP catalyst the ratio between catalyst and the amount of the hydrophobic material presented in the catalytic layer is experimentally investigated. The maximum reached value of the ratio is 0,68, which corresponds to catalyst contents of 68% at the active layer.

The investigation of the dependence of the generated by the electrodes current at constant potential amount of catalyst mixture showed optimal value when the amount of catalyst (CoTMPP)/hydrophobic material in the active layer is 35%.

For the ACCoNi catalyst the investigation of the current densities of air electrodes, measured at constant potential as function of the contents of metal oxides, showed that best mixture of Co-Ni oxides in the catalyst is ca. 5% Ni + Co.

The results shows that the Mg-air cells are with substantially increased power output. They could be used as primary and emergency power sources for the residential, commercial and industrial markets. A great advantage of the magnesium-air cells and batteries is the use of the non-toxic magnesium and a non-aggressive salt-water electrolyte and particularly see/ocean water.

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ВЪЗДУШНИ ГАЗОДИФУЗИОННИ ЕЛЕКТРОДИ ЗА ЕЛЕКТРОХИМИЧНИ КЛЕТКИ МАГНЕЗИЙ-ВЪЗДУХ, РАБОТЕЩИ С РАЗТВОР НА НАТРИЕВ ХЛОРИД

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(Резюме)

През последните години горивните клетки и метало-въздушните батерии привличат научно внимание като ефикасни преобразуватели на енергия. За катоди в метало-въздушните електрохимични клетки се използват предимно въздушни газодифузионни електроди (ВГДЕ), върху които протича електрохимична редукция на кислород и се осъществява контакт между електролитния разтвор и газообразния кислород. В литературата често се обсъжда поведението на порести електроди в алкални горивни клетки, но съществуват ограничен брой изследвания за работата на ВГДЕ в неутрален електролит. Цел на настоящото изследване е оптимизиране на ВГДЕ за работа в електрохимична клетка магнезий-въздух с електролит NaCl. Газовият слой е изработен от различни хидрофобирани сажди и е оптимизирана дебелината и количеството въглероден материал в газовия слой на електрода. Изготвени са катализатори за електрохимичната редукция на кислорода на базата на въглеродни материали и различни промотори и са определени електрохимичните характеристики на ВГДЕ с катализаторите: пиролизиран кобалт тетраметоксифенилпорфирин (CoTMPP), VS50 - CoTMPP - 700 и активен въглен с Co и Ni (ACCoNi). Изследвано е влиянието на дебелината на активния слой и съотношението на количествата на катализатора и хидрофобния материал в активния слой върху поляризационните характеристики и транспортните затруднения във въздушните електроди с различни катализатори. ВГДЕ е използван в първична електрохимична клетка магнезий-въздух, която показва добри електрохимични характеристики и работи с нетоксичен магнезиев електрод и неагресивен електролит NaCl.