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Long-term performance of carbon gas-diffusion air electrodes in saline electrolyte

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1. Introduction

During the last few years in our laboratories research efforts in the field of metal–air systems have been directed towards developing an aluminium–air battery (Alair) with neutral chloride electrolyte. The anode of this battery is an electrochemically active aluminium alloy containing a very small amount of alloying components, developed in the Yugoslav laboratory [1–3], and the cathode is a carbon gas-diffusion air electrode, developed in the Bulgarian laboratory [4–9]. The aluminium anode is placed in between the two air cathodes which make the end walls of the cell. Charging of the battery is carried out by exchanging the aluminium plate and/or the electrolyte in which gelatinous aluminium hydroxide is accumulated during the discharge period.

Since the air cathodes are fixed in the cell walls, which are constituent parts of the cell body, the life time of the cathodes is one of the most important characteristics of the battery.

2. Experimental details

The porous carbon–air electrodes used in these experiments were of the two-layer type: the hydrophobic layer (gas side) and the hydrophilic layer (solution side). The current collector, in the form of a grid, was pressed into the hydrophobic layer. The details of the electrode structure and manufacture can be found elsewhere [10]. The basic catalyst was active carbon Norit NK with a surface area of 600 $m^2 g^{-1}$ (BET). Three additional catalysts, introduced into the active carbon, have also been investigated. These were a mixed cobalt–nickel oxide [6], cobalt phthalocyanine (CoPc) and cobalt tetramethoxyphenyl porphyrin (CoTMPP). The latter was thermally treated at 830° C in an argon atmosphere.

The electrodes had a projected area of 12 cm^2 and their total thickness was about 1 mm.

The experiments were performed in 2 M NaCl and 2 M KCl aqueous solutions at room temperature (25 ± 5° C). The chemicals used were of p.a. purity. A saturated calomel electrode (SCE) was used as the reference electrode.

3. Results

The initial polarization characteristics of the air electrodes used are presented in Fig. 1. The catalytic effects of all the three added catalysts are obvious, CoTMPP being the best catalyst. However, in the life test experiment at a constant current density of 20 $mA\,cm^{-2}$, the electrode catalysed with CoTMPP lost its activity rather quickly, especially during the first 1000 h of operation (see Fig. 2). After that time the catalytic activity of the CoTMPP electrode was worse than that of the active carbon alone. It is surprising, however, that the total life time of the CoTMPP electrode in 2 M NaCl solution was significantly longer than that of the other electrodes. In spite of this, the CoTMPP electrode cannot be considered as a good candidate for the Alair battery with NaCl electrolyte because of the very high polarization during this time (more than 0.4 V).

From Fig. 2 it is also seen that the rate of loss of activity of the other electrodes examined is similar, but the life times of the Co–Ni oxides and CoPc electrodes are somewhat longer

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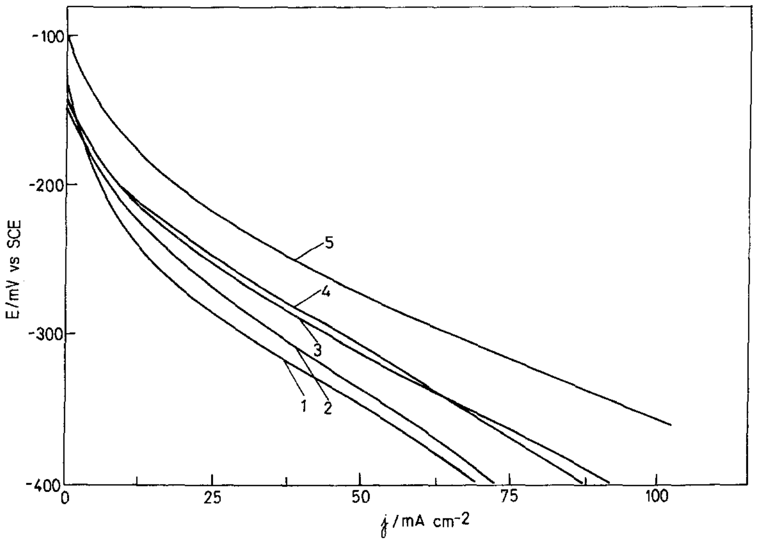

Fig. 1. Initial polarization curves of air electrodes with various catalysts: 1, active carbon Norit NK; 2, active carbon GM (Yugoslavia); 3, Norit NK + Co–Ni oxides; 4, Norit NK + CoPc; 5, Norit NK + CoTMPP.

than those of the electrodes containing no catalyst.

In 2 M KCl the rate of activity loss of the air electrodes was found to be only slightly lower than that in 2 M NaCl. However, a significantly longer life time (by a factor of ~ 2.5) for all of the electrodes was observed in KCl solution. The experiment was stopped after about 10 000 h of operation due to technical reasons and not due to leakage of electrolyte.

In order to eliminate the possible influence of the reaction product, i.e. gelatinous aluminium hydroxide, in the performance of the air electrodes, the life time test was also performed using a graphite anode instead of an aluminium one. The results obtained are presented in Fig. 3. The rate of activity loss is much higher and the life time is much shorter than the case of the aluminium anode.

4. Discussion

It is well known that the catalytic activity of active carbon is due to its various surface functional groups. In the presence of strong oxidizing agents such as H_2O_2, these functional groups

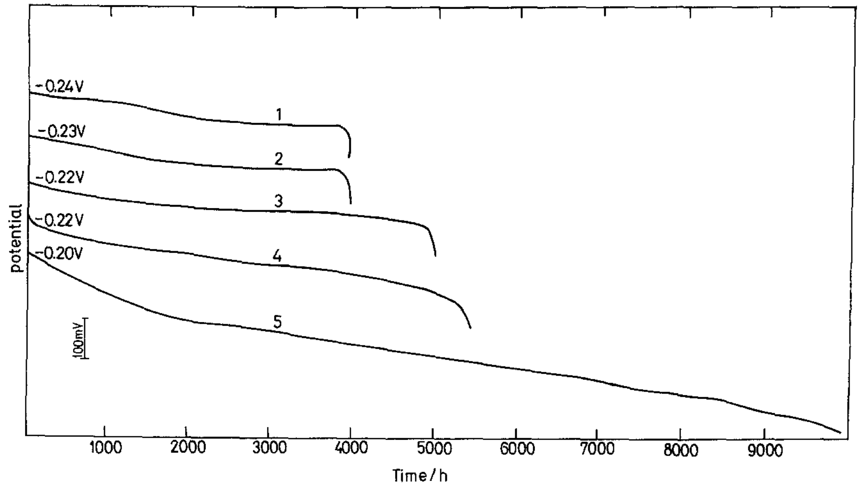

Fig. 2. Potential–time dependence of air electrodes at constant current density of 20 mA cm^{-2} in 2 M NaCl using an aluminium anode; catalysts as in Fig. 1. The initial potential values are indicated in the diagram.

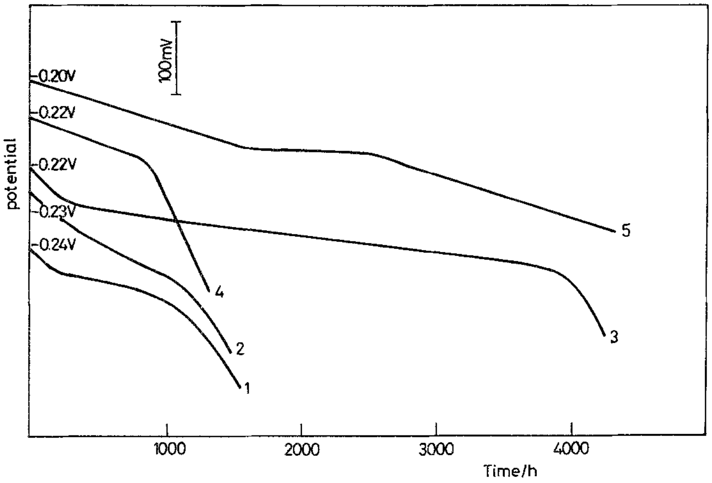

Fig. 3. Potential–time dependence of air electrodes at constant density of 25 mA cm^{-2} in 2 M NaCl using a graphite anode; catalysts as in Fig. 1. The initial potential values are indicated in the diagram.

can be chemically destroyed giving rise to both the lower catalytic activity and lower hydrophobicity. This chemical attack of H_2O_2 has been very well experimentally documented in alkaline solutions at current densities higher than 50 mA cm^{-2} [11]. It seems, however, that during operation of the air electrodes, H_2O_2 does not continuously destroy these functional groups. This conclusion was based on the fact that the rate of activity loss of air electrodes was practically of the same value irrespective of whether or not the electrodes contained a peroxide elimination catalyst, CoTMPP. The life time of the air electrode containing CoTMPP in a very alkaline solution of KOH was, however, an order of magnitude longer than that of the electrode containing no catalyst.

In the case of neutral NaCl solution described in this communication, the life time of the CoTMPP electrode was also significantly longer than that of the other electrodes, although the rate of the activity loss was higher. This means that some other factors were influencing the long-term performance of the air electrodes. One of these could be the low solubility of sodium peroxide. Thus, during operation of the air electrode an increasing amount of sodium peroxide is precipitated inside the porous structure of the electrode. This gives rise to a blockage of the active electrode area and therefore to an increase in local current density, which in turn makes the electrode potential more negative. Furthermore, the precipitation of solid sodium peroxide may destroy the partially hydrophobic structure of the electrode, causing flooding of the pores. Therefore, premature failing of the electrode occurs. The solubility of potasium peroxide is higher than that of sodium peroxide, hence the longer life time of the air electrode is observed.

It should be noted that the life time of air electrodes in alkaline solutions has also been found to be significantly longer in KOH than in NaOH [12]. In the case of neutral chloride solutions the pH of the solution inside the pores of the air electrode is highly alkaline because of the slow diffusion out of the porous structure of OH^- ions generated by the electrochemical reaction, and this accounts for the similarity of the behaviour in the two media.

Finally, a possible but small effect of CO_2, i.e. carbonization of electrolyte inside the pores at the end stage of the electrode operation, may exist.

Contrary to the case of alkaline KOH solution, the very high rate of activity loss of the CoTMPP electrode observed in both NaCl and KCl solutions could be explained by the adsorption of Cl^- ions which block the active sites of the catalyst.

The significantly shorter life times of all electrodes when a graphite anode was used instead of the aluminium anode may be explained by the aggressive attack of highly oxidizing substances, ClO^- and ClO_3^-, formed in the anodic reaction during the operation of the cell.

5. Conclusions

From the experimental results the following conclusions may be drawn.

1. The life time of a gas-diffusion air electrode is significantly longer in 2 M KCl than in 2 M NaCl aqueous solution. This was explained by the higher solubility of potassium peroxide than that of sodium peroxide.
2. The O_2 reduction catalysts, CoTMPP, Co–Ni oxide mixture and CoPC, extend the life time of the air electrode. The magnitude of the extension depends of the catalyst capability to eliminate or to prevent peroxide formation.
3. The life time of the air electrodes additionally catalysed by macrocyclic complexes CoPc or CoTMPP is not determined by the stability of the complexes as often claimed in the literature.

References

[1] A. R. Despić, D. .M. Dražić, M. M. Purenović and N. Ciković, *J. Appl. Electrochem.* **6** (1976) 527.

[2] M. M. Purenović, A. R. Despić and D. M. Dražić, *Elektrokhimiya* **12** (1976) 296.

[3] A. R. Despić and D. M. Dražić, 'Electrochemical Properties of Alloys of Aluminium with Gallium and Phosphorus', Final Report, Laboratory for Electrochemical Energy Conversion, Institute of Electrochemistry, ICTM, University of Belgrade (1982).

[4] A. Kaisheva, S. Gamburzev and I. Iliev, 29th ISE Meeting, Budapest, 1978, Ext. Abstr. p. 100.

[5] A. Kaisheva, *Elektrokhimiya* **15** (1979) 1539.

[6] A. Kaisheva, S. Gamburzev and I. Iliev, *ibid.* **17** (1981) 1362.

[7] *Idem*, *ibid.*, **18** (1982) 1602.

[8] I. Iliev, S. Gamburzev and A. Kaisheva, Fall Meeting Electrochemical Society, Las Vegas, Nevada, 1985, Ext. Abstr. p. 19.

[9] I. Iliev, *Bull. Soc. Chim. Beograd* **48** (Suppl.) (1983) p. S317.

[10] I. Iliev, S. Gamburzev, A. Kaisheva, E. Vakanovva, J. Muchovski and E. Budevski, *Izv. Otd. Khim. Nauki, Bulg. Acad. Nauk.* **7** (1974) 223.

[11] S. Gamburzev. *Elektrokhimya* **19** (1982) 134.

[12] *Idem*, 'Long-time performance of air electrodes' Report on UNESCO Discussion Meeting, 'Electrochemistry of Oxygen and Metal–Air Batteries', May 1983, Pravets, Bulgaria.