

## ON THE PROBLEM OF AGEING OF CARBON-AIR ELECTRODES IN ALKALINE ELECTROLYTES

A. ROLLA, A. SADKOWSKI, J. WILD and P. ZÓLTOWSKI

*Institute of Physical Chemistry of the Polish Academy of Sciences, 01-224 Warsaw (Poland)*

(Received June 30, 1979; in revised form October 7, 1979)

### Summary

The phenomenon of ageing, *i.e.*, the slow deterioration of the performance, of PTFE-bonded, two-layer type, carbon-air electrodes, working in 6, 8.5 and 10M KOH electrolytes has been investigated. The ageing was observed only in the case when carbon dioxide was present in the air supplied to the electrodes. The rate of ageing increased rapidly with the concentration of the electrolyte. For more concentrated electrolyte ( $\geq 8.5\text{M}$ ) the ageing was followed by leakage of the electrolyte through the electrode. The rate of ageing was strongly influenced also by the humidity of the air, and by the porosity of the electrode. An ageing mechanism is proposed.

---

### Introduction

Carbon-air electrodes are components of several electrochemical power systems, *e.g.*, hydrogen/air and other fuel/air fuel cells, primary and secondary metal/air cells. Alkaline electrolytes are often used in these systems because they allow — in contrast to acid electrolytes — the use of carbon electrodes without any additional catalyst.

The wider application of carbon-air electrodes in alkaline electrolytes is hindered at present by two main factors:

- the carbonization of the electrolyte as a result of absorption of  $\text{CO}_2$  from air,

- the ageing of the electrode, *e.g.*, the slow deterioration of its performance, frequently ended by catastrophic collapse.

The problem of ageing was investigated several years ago by Kordesch [1], who emphasized the crucial role of  $\text{CO}_2$  in the process. Recently, a renewed interest in the problem of ageing of carbon-air electrodes has taken place [2, 3]. Based on experiments with such electrodes under a supply of air and oxygen it was suggested that the ageing over several hundred hours under current load is caused by a slow, gradual flooding of

micropores of the active carbon in the electrode, resulting from a decrease of the hydrophobic properties of this material under the influence of hydrogen peroxide produced within the electrode in the course of the electro-reduction of oxygen.

Our observations, in laboratory experiments, of the long-term performance of carbon-air electrodes operating in alkaline electrolytes indicated that factors other than these recently suggested are the most important in the process of electrode ageing. Therefore, it was of interest to undertake some systematic investigation on the influence of several factors including CO<sub>2</sub> content of the air, air humidity, and the presence of H<sub>2</sub>O<sub>2</sub> in the electrolyte, on the ageing of carbon-air electrodes.

## Experimental

The carbon-air electrodes were of the PTFE-bonded, two layer type, similar to electrodes developed by Iliev *et al.* [4, 5]. The back layer was prepared from carbon black and PTFE, and the active layer from active carbon, carbon black and PTFE. If not otherwise stated, no additional catalysts were introduced. The apparent geometrical surface area of the electrodes was 16 cm<sup>2</sup>. The experiments were performed using a one-compartment half-cell arrangement with a nickel counter electrode. The volume of electrolyte was 200 cm<sup>3</sup>. Aqueous solutions of KOH (reagent grade) of concentrations 6, 8.5 and 10M were used as electrolyte. The water losses of the electrolyte, resulting from evaporation through the electrode, were made up by water additions every 24 - 48 h (10 - 20 cm<sup>3</sup>). The electrolyte was changed every 800 h to prevent its excessive carbonization. The experiments were performed at 30 °C.

The electrodes were supplied with unpressurised air of three qualities: ambient laboratory air of about 30% humidity, air free from CO<sub>2</sub> and H<sub>2</sub>O (ambient air purified over KOH pellets), and air of about 90% humidity containing the ordinary concentration of CO<sub>2</sub>. When air of high humidity was used, practically no losses of electrolyte volume were observed.

The electrodes were under continuous d.c. load of 30 or 100 mA. cm<sup>-2</sup> and their current-potential characteristics up to 100 or 200 mA. cm<sup>-2</sup> were measured every few days. The potentials of the electrodes were measured against the reversible hydrogen electrode in the same electrolyte (RHE).

As will be indicated later, in some experiments electrodes with specially increased porosity of the active layer, electrodes with the addition of 3% of MnO<sub>2</sub> (introduced by the method described elsewhere [6]), or electrolyte of technical grade purity were used. In a special series of experiments the water losses from the electrolyte were made up with 30% hydrogen peroxide solution instead of water.

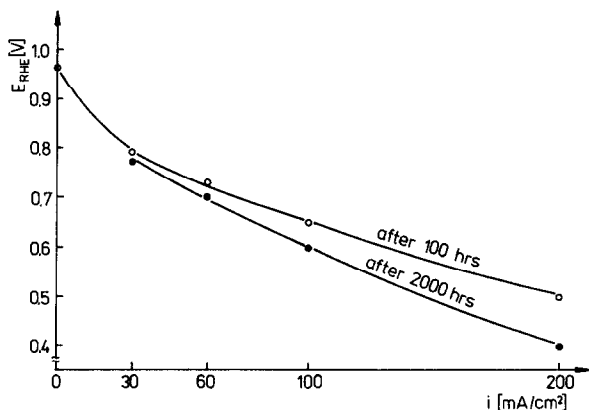


Fig. 1. Current-potential characteristics of the electrode in 6M KOH, supplied with ambient laboratory air, after 100 and 2 000 h under a load of  $100 \text{ mA. cm}^{-2}$ .

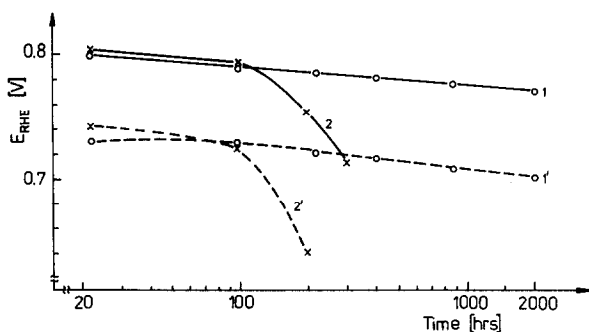


Fig. 2. Potential-time characteristics of electrodes aged at  $30 \text{ mA. cm}^{-2}$ , supplied with ambient laboratory air, in 6M KOH (curves 1, 1'), and in 8.5M KOH (curves 2, 2'); 1, 2 — potentials measured at  $30 \text{ mA. cm}^{-2}$ , 1', 2' — potentials measured at  $60 \text{ mA. cm}^{-2}$ .

## Results

The typical characteristics of the electrode in 6M KOH, under supply of ambient air, after 100 and 2 000 h load of  $100 \text{ mA. cm}^{-2}$  are presented in Fig. 1. The rate of ageing of this electrode was about  $25 \text{ mV}/1\,000 \text{ h}$  for a current density of  $100 \text{ mA. cm}^{-2}$ . When an electrolyte of higher concentration (8.5 or 10M) was used a rapid ageing, as early as after 100 h, was observed, as can be seen in Fig. 2. Moreover, for these concentrated electrolytes, droplets of the electrolyte were observed on the gas side of the electrodes after about 300 and 150 - 200 h, respectively.

In the case of high humidity air, the electrodes in 8.5M KOH withstood not less than 2 000 h without excessive ageing, similar to electrodes in 6M KOH with ambient air supply (see Fig. 1). In 10M KOH droplets on the gas side of the electrode did not appear before 300 h under current load.

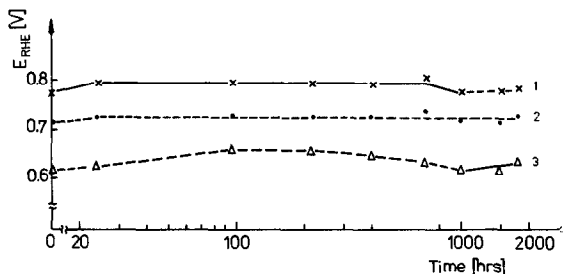


Fig. 3. Potential-time characteristics of the electrode in 8.5M KOH, supplied with air free from  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . During the first 1 000 h the continuous load was  $30 \text{ mA. cm}^{-2}$ , and for the next 1 000 h,  $100 \text{ mA. cm}^{-2}$ . Curves 1, 2 and 3, potentials measured at 30, 60 and  $100 \text{ mA. cm}^{-2}$ , respectively.

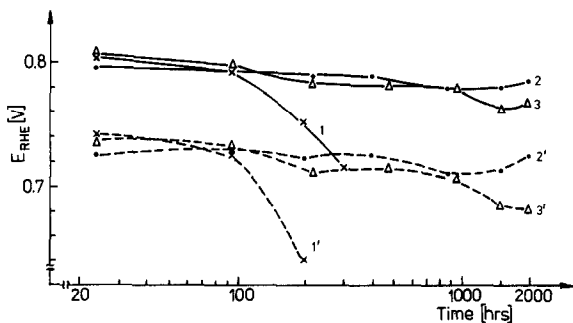


Fig. 4. Potential-time characteristics of the electrodes in 8.5M KOH under continuous load of  $30 \text{ mA. cm}^{-2}$ : curves 1, 1', unmodified electrode supplied with ambient air; curves 2, 2', unmodified electrode supplied with  $\text{CO}_2$ - and  $\text{H}_2\text{O}$ -free air; curves 3, 3', modified electrode supplied with ambient air; 1, 2, 3, potentials measured at  $30 \text{ mA. cm}^{-2}$ ; 1', 2', 3', potentials measured at  $60 \text{ mA. cm}^{-2}$ .

Potential-time characteristics of an electrode in 8.5M KOH supplied with  $\text{CO}_2$ - and  $\text{H}_2\text{O}$ -free air are presented in Fig. 3. This electrode operated under a load of  $30 \text{ mA. cm}^{-2}$  during the first 1 000 h, and thereafter under a load of  $100 \text{ mA. cm}^{-2}$ . These characteristics can be considered as stable over 2 000 h.

The rapid ageing of electrodes in 8.5M KOH supplied with ambient air can be avoided by using electrodes of appropriately increased active layer porosity, as illustrated in Fig. 4. For 10M KOH this method gave no observable improvement.

In other experiments [7], directed to the use of the same carbon electrodes in a secondary metal/air system, in 6M KOH supplied with ambient laboratory air, no long-term ageing during 300 one-day cycles (7 200 h, of which 2 400 h were under a load of  $30 \text{ mA. cm}^{-2}$ ) was observed. Only a transient ageing, dependent on the degree of electrolyte carbonization, was observed, as illustrated in Fig. 5. In these experiments the total volume of the electrolyte was  $32 \text{ cm}^3$  ( $2 \text{ cm}^3$  for each  $1 \text{ cm}^2$  of the electrode external

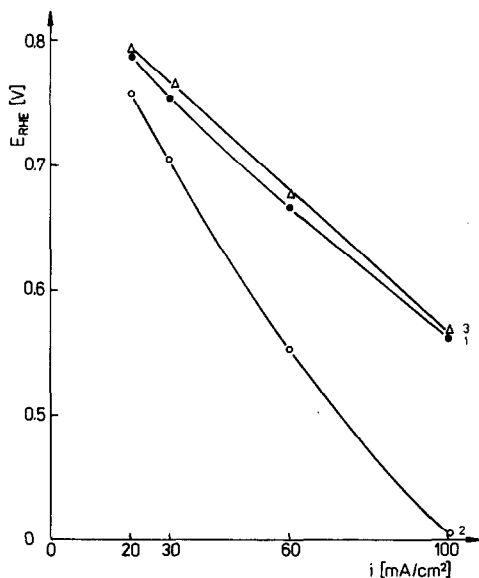


Fig. 5. Current-potential characteristics of the electrode working on a cyclic regime: curve 1, after 129 cycles, 3 cycles after the last change of electrolyte; curve 2, after 193 cycles, 67 cycles after the last change of electrolyte; curve 3, after 200 cycles, 3 cycles after the last change of electrolyte.

surface); after 50 cycles its composition had changed to 0.5M KOH + 3M  $K_2CO_3$ .

Some experiments directed to modify the concentration of hydrogen peroxide in the electrode pores were performed. In one series of experiments electrodes with the addition of  $MnO_2$  to the active layer were used; manganese ions are an effective catalyst for hydrogen peroxide decomposition [8]. These electrodes had the same characteristics as normal electrodes without manganese. In the next series of experiments electrolyte prepared from technical grade KOH, containing heavy metal ions, was used; these ions are also considered to be catalysts for  $H_2O_2$  decomposition [9]. The use of low-purity KOH had no influence on the electrode ageing.

In a further series of experiments, the losses of the electrolyte volume, caused by water evaporation, were made up by additions of about 1.3 - 2.6% of pure  $H_2O_2$  in the total volume of electrolyte. Every time a new addition of  $H_2O_2$  was made, a considerable, but transient, deterioration of the electrode characteristics was observed, as is shown in Fig. 6. The long-term potential-time characteristics during 2 000 h were, however, similar to those measured in normal conditions, *i.e.*, without  $H_2O_2$  additions to the electrolyte.

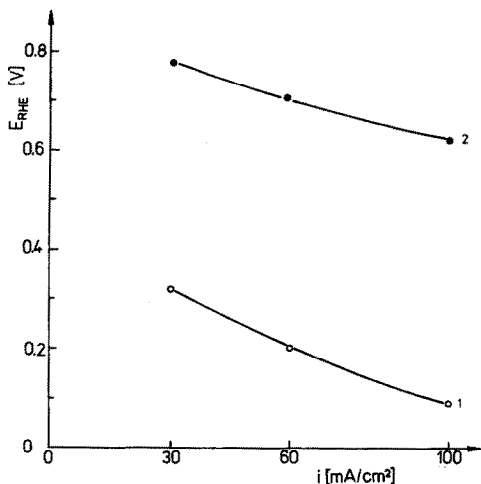


Fig. 6. Current-potential characteristics of the electrode working in the electrolyte with additions of  $H_2O_2$ , 1 h (curve 1), and 5 h (curve 2) after the  $H_2O_2$  addition.

## Discussion

Several processes take place in the pores of the carbon-air electrode in alkaline electrolyte under current load. In the course of the present work we tried to modify the rates of these processes and/or the concentrations of their reactants:

(1) The production of  $OH^-$  ions in the 4- or 2-electron reaction of oxygen reduction; these ions are to some extent washed out into the bulk of the electrolyte in process 5, considered below. The rate of  $OH^-$  production was modified by changing the current density; no influence of the current density, within the limits of 30 - 100  $mA \cdot cm^{-2}$ , on the electrode ageing was observed, Fig. 3.

(2) The production of  $HO_2^-$  ions (or  $H_2O_2$ ) in the 2-electron reaction; the  $H_2O_2$  can chemically attack the electrode material, can decompose spontaneously or catalytically in the pores, or it may be washed out into the bulk of the electrolyte in process 5. An attempt was made to reduce the  $H_2O_2$  concentration in the pores by introducing manganese ions, or by using KOH electrolyte containing heavy metal ions. In other experiments, when  $H_2O_2$  was added to the electrolyte, the  $H_2O_2$  concentration in the pores was markedly increased; a strong transient deterioration of electrode characteristics was observed (Fig. 6). In all these experiments the long-term ageing was not affected.

(3) The absorption of carbon dioxide in the electrolyte; the absorption product can precipitate in the pores or can be washed out into the bulk of the electrolyte in process 5. The absorption was eliminated by supplying the electrodes with air free from  $CO_2$ , and in this case no ageing was observed (Fig. 3). When air containing  $CO_2$  was used, ageing was observed; the ageing was strongly accelerated when the electrolyte concentration was increased (Fig. 2), and restrained when the air supplied was of high humidity.

(4) The transport processes of water between the electrolyte and the air supply; the rate of these processes was modified using air of different humidities. When  $\text{CO}_2$  was eliminated, no ageing was observed, even in the case of dry air (Fig. 3). When  $\text{CO}_2$  was present, increase in the humidity of the air gave a considerable decrease in the rate of ageing of the electrodes.

(5) The transport processes in the liquid phase; the transport of water from the bulk of the electrolyte into the pores, and the transport of hydrogen peroxide and of carbonate ions in the opposite direction. The rate of these processes was modified by changing the structure of the electrode active layer. The modified electrodes, unlike electrodes with normal structure, showed no accelerated ageing in 8.5M KOH (Fig. 4); this modification gave no observable results in 10M KOH. The diminution of the ageing process, observed in experiments directed to the development of the air electrode for secondary metal/air cells, has probably to be ascribed also to modification of the transport processes in the liquid phase.

It follows from our results that the principal factor determining the ageing of electrodes is the presence of carbon dioxide in the air supply to the electrodes. The rate of ageing is influenced by the rate of the transport processes in the liquid phase, and by the concentration of the electrolyte.

These observations suggest the following mechanism for the process of ageing of carbon-air electrodes, leading to electrolyte leakage through the electrode. The carbon dioxide from the air is absorbed by the electrolyte in the electrode at the boundary between the dry layer and the layer soaked with the electrolyte. As a result, carbonate ions are formed. These ions are washed out into the bulk of the electrolyte. If this washing out is slow, potassium carbonate is precipitated in the pores. The degree of hydration of the precipitate depends on the local activity of water, *i.e.*, on the electrolyte concentration and the humidity of the air supplied to the electrodes. The rates of the two competitive processes, of washing out and of precipitation, depend on the porosity of the active layer and on the viscosity of the electrolyte. The viscosity increases considerably with the electrolyte concentration [10] and probably with the carbonate ion concentration. Therefore, the dependence of the viscosity on the KOH concentration is responsible for the dependence of the rate of ageing of electrodes on the electrolyte concentration. The carbonate precipitate blocks some pores, reducing the effective area of the electrode and consequently its potential under current load.

Further, part of the precipitate has no direct contact with the electrolyte, but does have contact with the  $\text{CO}_2$ -containing air. Additional absorption of  $\text{CO}_2$  by the precipitate takes place, with the formation of two molecules of bicarbonate from one molecule of the primary carbonate. The comparison of molar volumes indicates that in this process of bicarbonate formation the volume of the precipitate in the pores is increased. The smaller the hydration of the primary precipitate, the greater is the volume change. The increase of the precipitate volume causes expansion and destruction of the electrode structure, leading in effect to the leakage of the electrolyte through the electrode.

The proposed mechanism is consistent, in general, with the earlier suggestions of Kordesch [1].

## Conclusions

(1) The rate of ageing of carbon/air electrodes increases rapidly when the electrolyte concentration is raised (from 6 - 10M KOH). For electrolytes of high concentration (8.5 and 10M) the relatively rapid ageing is followed by leakage of the electrolyte through the electrode.

(2) The principal factor determining the ageing of electrodes is the presence of carbon dioxide in the air supply to them.

(3) The humidity of the air, and the structure of the electrode active layer have a substantial influence on the rate of ageing of the electrodes supplied with CO<sub>2</sub>-containing air. High humidity of the air, and high porosity of the active layer reduce the rate of electrode ageing.

(4) A suggested role [2, 3] in the ageing rate of the hydrogen peroxide, produced in the oxygen reduction reaction in the pores of the electrode, was not confirmed by this work.

(5) The ageing of the electrodes, and the resulting leakage of the electrolyte through the electrodes is probably the result of the precipitation of carbonates in the pores, and of the increase of the precipitate volume caused by recrystallization into bicarbonate.

## Acknowledgement

This work was carried out under Research Project 03.10, with the financial support of the Central Laboratory of Storage Batteries and Cells in Poznań, Poland.

## References

- 1 K. V. Kordesch, in B. S. Baker (ed.), *Hydrocarbon Fuel Cell Technology*, Academic Press, New York, 1965, p. 17.
- 2 S. Gamburgcev, I. Iliev, A. Kaisheva, G. Steinberg and L. Mokrousov, *ISE 28th Meeting, Druzhba-Varna, 1977*, Ext. Abstr. V. 2, p. 303.
- 3 S. Gamburgcev, A. Kaisheva and I. Iliev, *ISE 29th Meeting, Budapest, 1978*, Ext. Abstr. p. 106.
- 4 I. Iliev, S. Gamburgcev, A. Kaisheva, E. Budevsky, E. Vakanova and I. Muchovsky, *Izv. Otd. Chim. Nauki, Bulg. Akad. Nauk.*, 7 (1974) 223, 233.
- 5 I. Iliev, S. Gamburgcev, A. Kaisheva and E. Budevsky, *Izv. Otd. Chim. Nauki, Bulg. Akad. Nauk.*, 7 (1974) 755.
- 6 P. Zóltowski, D. M. Drazic and L. Vorkapic, *J. Appl. Electrochem.*, 3 (1973) 271.
- 7 A. Rolla, A. Sadkowski, J. Wild and P. Zóltowski, unpublished results.
- 8 W. S. Daniel-Bek, M. F. Minc and O. K. Ritter, *Sb. Rabot po Khim. Istochnikam Toka*, Energia, Leningrad 1968, p. 168.
- 9 J. W. Mellors, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 1, Longmans, London, 1952.
- 10 S. U. Falk and A. J. Salkind, *Alkaline Storage Batteries*, Wiley, New York, 1969.