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Polarization effects in a porous air cathode due to the influence of the anode in an alkaline air-metal cell

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Experiments in 6 N KOH at room temperature with air–zinc and air–cadmium cells show clearly that the anodes have an influence on the polarization of the porous air cathode. The electrolyte volume is also found to have an effect. At a constant load of 30 mA/cm^2 the polarization curve for oxygen reduction at the air cathode was, depending on cell arrangement, shifted by up to about 150 mV in the direction of more negative values compared to that measured in the half-cell. Moreover, in some cases, this negative shift was followed by a smaller positive one. These effects are discussed in terms of the concentration of HO_2^--ions, which are produced by Berl's reaction mechanism, and of the potential and the surface state of the anode.

1. Introduction

The porous air-diffusion electrode, capable of operating on air at ambient temperature and pressure with a time-stable position of the three phase (gas/electrolyte/electronic conductor) reaction zone, has meant an important development step in the area of fuel cells and primary and secondary metal–air batteries. During the research and development phase, the electrochemical properties of this electrode are usually studied in half-cell arrangement. When the air cathode is inserted in practical cells some additional effects show up which are connected to the type of anode used. The electrochemical processes in the porous system of the air cathode are thereby often markedly influenced by the working conditions of the anode. Up till now two main phenomena of this kind have been described and discussed in the literature; the influence of hydrazine on the resulting mixed potential of the cathode [1], and the influence of methanol on the reactions of the HO_2^--ions [2].

Both these studies, however, deal with effects from anodes consisting of liquid fuels, while there seems to be no work published which treats the influence of a metal anode. In order to obtain information on the mutual influence of the electrodes in an air–metal cell we have studied in some detail the behaviour of our air electrode when working in half-cells and in complete cells with a zinc or cadmium anode.

2. Experimental

The air electrodes used were two-layer air-diffusion electrodes [3, 4] with a diameter of 31 mm and a thickness of 0·8 mm. They consisted of an active layer of a mixture of active carbon (Norit) and teflon and a gas layer, prepared by pure teflon on the gas side. A nickel mesh in the active layer was used as current collector.

The air electrode was leak-proof sealed in a window frame constituting a part of one wall of the plastic (Lucite) cell. On the opposite wall of the cell a nickel plate was mounted which served as counter-electrode in the half-cell experiments. The distance between the air cathode and the nickel counter-electrode was about 30 mm. In all experiments 6 N KOH was used as electrolyte. Porous zinc anodes were prepared from zinc oxide powder, mixed with HgO and teflon binder [5]. The electrode size was 30 × 28 mm^2. The zinc anodes were wrapped in four layers of non-woven nylon separator and were reduced in 6 N KOH at the current density of 10–16 mA/cm^2. The cadmium anodes were cut to 30 × 26 mm^2 from NIFE sintered-type cadmium electrodes.

Electrode potentials were measured with a pH-meter (Radiometer PHM 26) by means of a Luggin capillary with the tip placed 4 mm from the electrode surface in half-cell measurements, and between the cathode and anode (electrode distance was always 5 mm) in the complete cell experiments. The reference electrode was a Hg/HgO electrode in the same solution. This Hg/HgO reference electrode in 6 N KOH is +38 mV versus the normal hydrogen electrode.

The air electrodes were first run in half-cells at 30 mA/cm^2 for more than 100 hours. An external power source was included in the circuit to provide a constant current. The conditions in the porous air cathode were then quite stabilized and this was reflected in a steady electrode potential. Immediately before the zinc or cadmium anode was inserted in the cell the current was interrupted for a short time and the electrolyte renewed in order to avoid effects from its carbonization. The constant cathodic current densities used were 30 mA/cm^2 and 15 mA/cm^2.

New zinc anodes were used for each experiment, while the cadmium anode consisting of a package of several plates was charged outside the cell between each experiment with this anode.

3. Experimental program and results

1, 2 or 3 zinc anodes were used in the same cell, the internal volume of which was 10 cm^3. The electrolyte volume was thereby decreased with the increased number of anodes. The actual capacity of each zinc anode was about 1 Ah. The discharge current was kept constant with a cathodic current density of 30 mA/cm^2. The change of potential of the air electrode from its initial stable value and the zinc anode potential measured during the discharges are shown in Fig. 1 as a function of used anode capacity in per cent of its actual capacity.

With one zinc anode or a package of several cadmium anodes, the cell volume was reduced step-wise. The potentials were measured at each cell volume as decribed above when the cathodic load was 30 mA/cm^2 and 15 mA/cm^2. The results with zinc anodes are shown in Fig. 2 and 3 and with the cadmium anode in Fig. 4 and 5 respectively.

4. Discussion

In the half-cell experiments oxygen is evolved at the nickel counter electrode when its potential exceeds about 0.5 V.

At the air cathode, atmospheric oxygen reacts according to Berl's reaction mechanism [6], i.e.

$$O_2 + H_2O + 2e^- \rightarrow OH^- + HO_2^- \qquad (1)$$

HO_2^--ions are produced at this cathode and most of these are then catalytically decomposed on the electrode:

$$HO_2^- \rightarrow OH^- + 1/2\ O_2 \qquad (2)$$

The oxygen thus formed is reduced again according to reaction (1). At higher cathodic loads, especially with thin air cathodes working without metal catalysts, there might be considerable losses of HO_2^--ions. The reason for this is that HO_2^--ions migrate to the counter-electrode where, at the relatively high positive potential of the nickel-plate, they are easily oxidized:

$$HO_2^- + OH^- \rightarrow O_2 + H_2O + 2e^- \qquad (3)$$

The oxidation (3) will stop if the potential of the electrode partner is shifted to more negative potentials. This will happen when a cadmium or a zinc anode is used, in which case the potentials become 1·3–1·8 V more negative. Hence, the concentration of HO_2^--ions in the electrolyte will increase. The cathodic process at the interface is then retarded and the cathode potential will shift to more negative values. When, however, the concentration of HO_2^--ions increases,

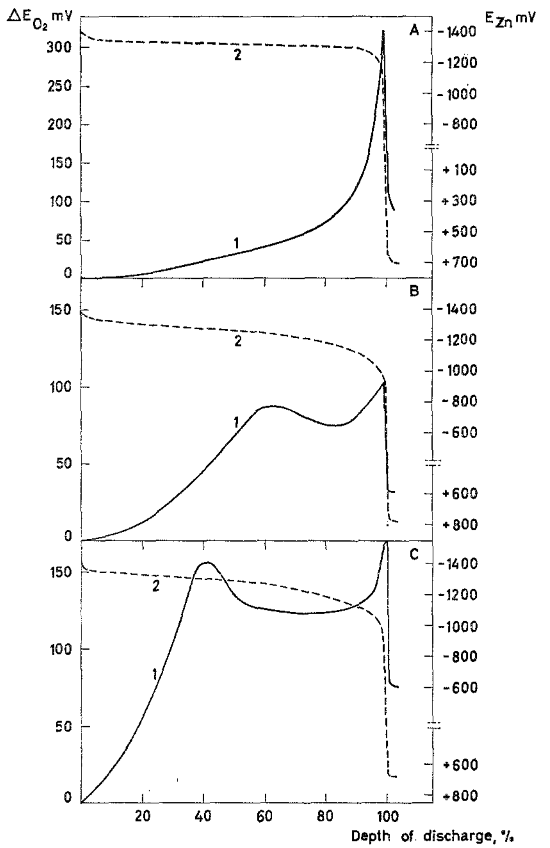

Fig. 1. The change in potential of the air cathode (curve 1) from its initial stable value, and the zinc anode potential (curve 2) during discharge with a 30 mA/cm^2 constant cathodic current density. Number of Zn anode plates: A, 1 plate; B, 2 plates; C, 3 plates. Electrolyte volume: A, 8·7 ml; B, 7·4 ml; C, 6·1 ml.

the catalytic decomposition of HO_2^--ions, according to reaction (2), will also increase, and this acts as an additional source of oxygen. If the HO_2^--concentration becomes high enough this 'oxygen effect' will dominate and the electrode potential will again rise to more positive values.

The electrochemical reaction of HO_2^--ions at the anode can be explained in terms of chemisorbed oxygen formed on the surface of the metal anode by the heterogenous decomposition of HO_2^--ions [8, 9]:

$$M-HO_2^- \rightarrow OH^- + M-O \qquad (4)$$

followed by reduction of the chemisorbed oxygen at the sufficiently negative anodic potential

$$M-O+H_2O+2e^- \rightarrow M+2OH^- \qquad (5)$$

This reaction of HO_2^--ions is retarded as an oxide layer is formed during the discharge of the anode. The concentration of HO_2^--ions will thus increase during the discharge period and will affect the air cathode potential as already discussed.

By changing the ratio between the amount of zinc and the volume of electrolyte, the part of the zinc anode surface which was covered with an oxide layer was varied. This is clearly seen in Fig. 1. When at first the HO_2^--ions easily reach the anode surface which is free from oxide, the potential of the cathode is shifted to more negative values. The absence of any change in the potential of the zinc anode to more positive values can be interpreted as an effect of incomplete surface-coverage by an oxide layer. The anode potential is more negative than 1·3 V until about 85% discharge. When, however, the

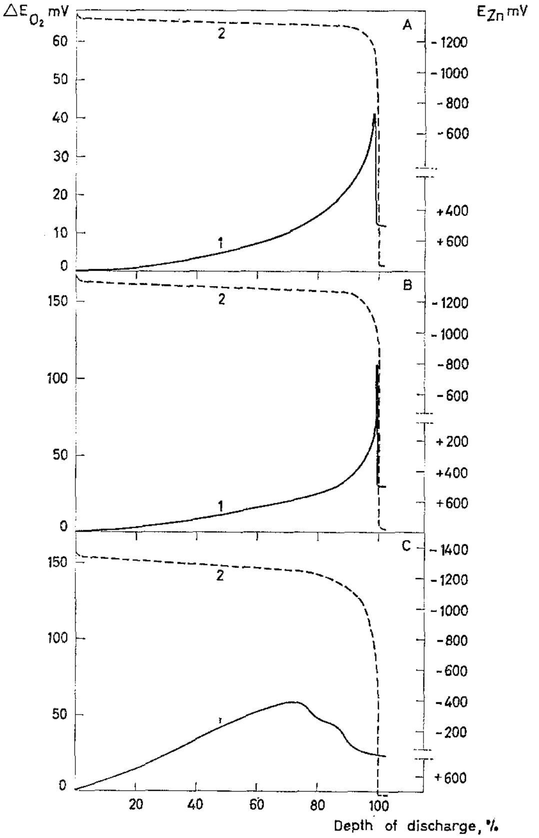

Fig. 2. The change in potential of the air cathode (curve 1) and the zinc anode potential (curve 2) during discharge with a 30 mA/cm^2 constant cathodic current density. (The cell volume was reduced step-wise.) Electrolyte volume: A, 25 ml; B, 15·1 ml; C, 4·2 ml.

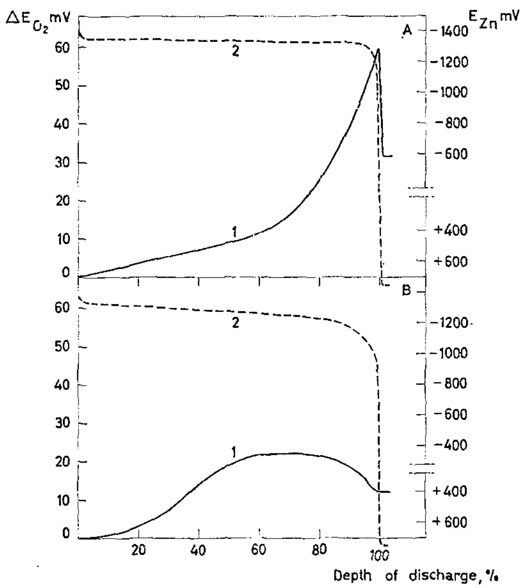

Fig. 3. The change in potential of the air cathode (curve 1) and the zinc anode (curve 2) during discharge with a 15 mA/cm^2 constant cathodic current density. (The cell volume was reduced step-wise.) Electrolyte volume: A, 17·5 ml; B, 3·5 ml.

easy access of HO_2^--ions to oxide-free surface areas is reduced, the HO_2^--ions concentration may increase to the level where the 'oxygen effect' enters. Then the HO_2^--ions serve as an additional oxygen source, as discussed above. The potential of the air cathode will then again become more positive. Which of the two effects will dominate thereafter, depends on the condition of the anode surface. A blockage of the anode surface by an oxide layer is indicated by the shift in curvature of curve 2 in Fig. 1 A–C.

When the anode is completely discharged, its potential will shift to the region for oxygen evolution and the HO_2^--ions will easily be oxidized. Having regard to the small distance between the electrodes, the oxygen evolution will to some extent affect the potential measurements with the Luggin capillary. The air cathode will therefore not attain its initial value until the nickel counter electrode is used. In this case, the electrodes are situated 30 mm from each other, which means that the gas evolution will then not interfere with the potential measurements.

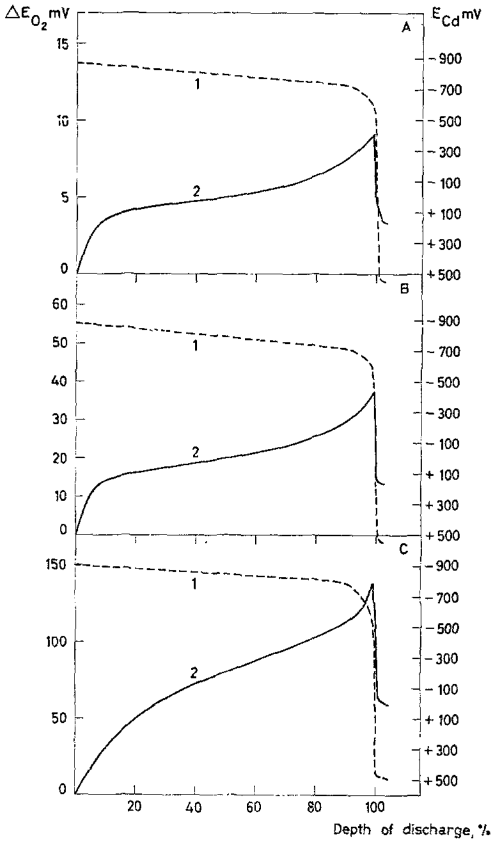

Fig. 4. The change in potential of the air cathode (curve 1) and the cadmium anode potential (curve 2) during discharge with a 30 mA/cm^2 constant cathodic current density. (The cell volume was reduced step-wise.) Electrolyte volume: A, 25 ml; B, 12·2 ml; C, 5·3 ml.

Effects similar to those discussed above are also seen in Fig. 2. When the electrolyte volume is decreased, not only the concentration of HO_2^--ions in the solution but also the fraction of the anode surface covered with oxide will increase. The cathode potential becomes more negative as the HO_2^--ions concentration increases.

In Fig. 2C the 'oxygen effect' becomes visible again.

All the effects described above are less pronounced at lower current densities (Fig. 3) as lower concentrations of HO_2^--ions are produced.

When a cadmium anode (about 1·5 Ah) is used instead of zinc we could not observe the 'oxygen effect' even when a limited electrolyte volume was used. The results are shown in Figs. 4 and 5. In comparison with the zinc anode, the 'oxide-free' anode surface available for electrochemical

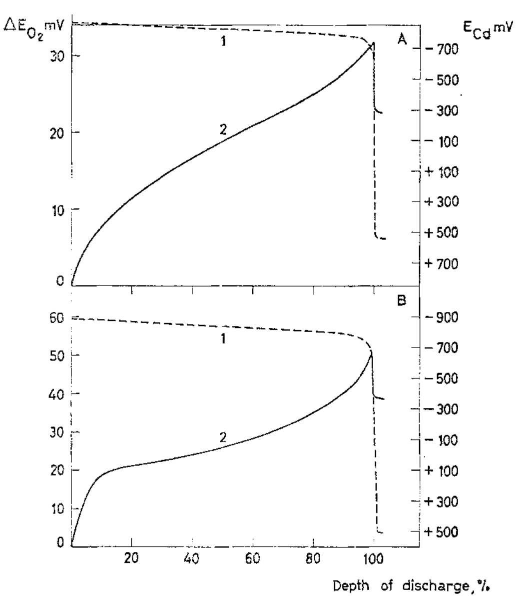

Fig. 5. The change in potential of the air cathode (curve 1) and the cadmium anode potential (curve 2) during discharge with a 15 mA/cm^2 constant cathodic current density. (The cell volume was changed step-wise.) Electrolyte volume: A, 10·7 ml; B, 5·2 ml.

reaction of HO_2^--ions was much larger at the highly porous cadmium electrode. Possibly the mechanism for HO_2^- reduction was also promoted by the nickel-sinter structure.

The picture of the HO_2^- reactions at the metal anode discussed above and the influence of these reactions on the air cathode was supported by a final experiment with the air–cadmium cell.

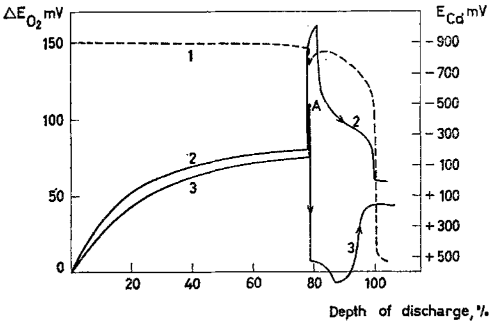

Fig. 6. The change in potential of the cathode when supplied with air (curve 3) or pure oxygen (curve 2), and the cadmium anode potential (curve 1) during discharge with a 30 mA/cm^2 constant cathodic current density. At point A a few drops of hydrogen peroxide were added to the electrolyte.

The cell was discharged to 78% of its actual capacity at which point a few drops of hydrogen peroxide were added to the electrolyte.

As seen in Fig. 6, curve 3, the cathode potential was at first shifted towards more negative values but then (at point A) there was a strong shift to more positive values as a result of the 'oxygen effect'. Also, the cadmium electrode was slightly affected and a mixed potential was established (curve 1). When the added HO_2^--ions were consumed electrochemically, the conditions became normal again. If, instead of air, pure oxygen (overpressure about 15 cm of water) was used, only the negative potential shift could be observed, because in this case there was no lack of oxygen at the cathode (curve 2).

Summing up, we can say that our experiments in 6 N KOH at room temperature with different air–zinc or air–cadmium cell arrangements have shown that the anode has a clear influence on the overpotential of the porous air cathode. The electrolyte volume was also found to have an effect.

At a constant load of 30 mA/cm^2, the polarization curve for the oxygen reduction at the air cathode was, depending on the cell arrangement, shifted by up to about 150 mV in the direction of more negative values compared to that measured in the half-cell. Moreover, in some cases, this negative shift was followed by a smaller positive one. The experimental curves showing changes in cathodic polarization have the same general form for zinc and cadmium anodes.

The picture of these effects put forward makes it appear plausible that they are controlled by the concentration of HO_2^--ions which in turn is controlled by the potential and the surface state of the anode.

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