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Zinc-air cell with neutral electrolyte

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The zinc-air electrochemical system in 5M NH_4Cl was studied. The optimum electrolyte-zinc ratio was found to be 50 ml g^{-1} Zn and the optimum electrolyte-cathode ratio, 15 ml cm^{-2} of carbon cathode. The air cathode polarization is not increased by intermittent usage of the cell. Electrodes made from zinc sponge with addition of lead show the smallest corrosion in the given electrolyte. The cell voltage is about 0·9–0·95 V at a load of 10 mA cm^{-2} of carbon cathode at ambient temperature.

1. Introduction

Porous carbon electrodes for the reduction of oxygen from the air are commonly used as cathodes in air-depolarized primary [1–5, 7], mechanically rechargeable [5, 6] and secondary [5, 8–10] cells. Their development was stimulated by the need for carbon cathodes for fuel cells with strongly acidic or strongly alkaline electrolytes, where in general the three-phase boundary in the porous cathode had to be fixed. The successful solution of this problem makes this sort of cathode very suitable for primary electrochemical power sources, especially in combination with a metal anode. However, both extreme pH ranges present difficulties which must be considered in the construction of electrochemical metal-air power sources. In strongly alkaline media, the main difficulty is the formation of carbonate in the pores of the cathode when the latter is in direct contact with air. This causes blocking of the porous system almost exclusively during the time when no current is being withdrawn from the cell. In such a case no mass transfer due to the reactions

$$O_2 + H_2O + 2e^- \rightleftarrows OH^- + HO_2^-$$

and

$$HO_2^- \longrightarrow 1/2\ O_2 + OH_2^-$$

takes place between the pore electrolyte and the bulk electrolyte. Blocking of the porous system of the cathode by alkali carbonate causes its gradual passivation, thus overloading those parts of the pores which remain non-passivated, and increasing the polarization of the cathode.

In acid media, on the other hand, the catalytic activity of the electrode and its life time are important problems. Transport phenomena do not play such an important role as in the case of alkaline electrolytes. In addition, the choice of a carbon support, which participates in the electrode's catalytic activity, is critical.

Electrodes for strongly alkaline media require, therefore, the elimination of access of air to the gas side when the cell is standing idle. Electrodes for strongly acid media require a suitable catalyst and support. At present, electrodes prepared from active carbon without additional catalyst and operating on air in alkaline media [11] can be loaded permanently with 50–100 mA cm^{-2}. In acid media [12] with pure oxygen the practical load is 10–20 mA cm^{-2}.

Between these extremes are the air-depolarized cells which employ a quasi-neutral electrolyte which is substantially an ammonium chloride solution. In these cells the load of the air-depolarized cathode does not exceed 1 mA cm^{-2} in most cases. This is, by one or two orders of

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magnitude, lower than that with acid or alkaline cell cathodes.

The purpose of the present work was to check the behaviour of the air cathode in quasi-neutral electrolytes and to find out why the current load cannot be substantially elevated. Since measurements were performed on half-cells as well as on complete cells, we paid attention also to the behaviour of the Zn anode. We were thus able to compare its corrosion rate and the influence of current collector material in these electrolytes with similar findings in strongly alkaline media.

Kächele [13] and co-workers studied the reduction of manganese dioxide in quasi-neutral electrolytes. They chose 5M solutions of ammonium chloride, sulphate and thiosulphate, magnesium and sodium chlorides, and confirmed that the most suitable one was 5M NH_4Cl.

Carbon cathodes operating on air in quasi-neutral electrolytes have been studied only recently. Kozawa [14–16] studied the reduction of oxygen on graphite catalysed with iron phthalocyanine (which had been employed mainly in acid media [12]) to develop an implantable electrochemical cell based on the electro-oxidation of glucose and capable of feeding a cardiostimulator.

2. Experimental

Carbon electrodes, 31 mm in diameter and 1 mm in thickness, were prepared by pressing active carbon bound with Teflon [11]. The gas side was provided with a porous Teflon layer which prevented the penetration of electrolyte [17]; a gold mesh current collector was pressed-in on the electrolyte side. In most cases, the electrodes were 'self-breathing', either with a nickel counter electrode, or in a complete cell with a zinc anode. The contact area between the electrode and electrolyte or air was 5 cm^2, from which the current densities given below were calculated. The electrolyte vessel had a variable volume which allowed the volume of electrolyte to be changed whilst all other conditions were kept constant. Electrolytes were 6M KOH, 5M NH_4Cl, saturated KCl, 5M NH_4NO_3, 1M $(NH_4)_2SO_4$, 2M KNO_3, and 0·6M K_2SO_4. Potentials are referred to the SCE. The distance between the tip of the Luggin capillary and the measured electrode was kept constant so that all measurements include the same ohmic resistance.

The anodes were zinc electrodes of dimensions $3 \times 3 \times 0{\cdot}25$ cm prepared by two methods: (1) Cathodic reduction of ZnO powder (reagent grade) containing 5% Teflon and 0·5% HgO, or of a mixture of 20% Zn+80% ZnO, on an iron mesh or on a silver wire in 5M KOH with a Ni counter-electrode. The electrode was then washed till the resulting solution was neutral and dried for several hours at 60°C. (2) Pressing a zinc sponge, prepared electrolytically [18], onto a brass grid and washing and drying at 60°C.

All measurements were made at ambient temperature. Corrosion tests on the zinc electrodes were based on measuring the volume of hydrogen evolved during corrosion in 5M NH_4Cl.

3. Results and discussion

The relationship between potential and time for the air and zinc electrodes at a load of 50 mA (10 mA cm^{-2} of cathode) are shown in Fig. 1. The electrolyte volume was 150 ml. The theoretical discharge time corresponding to the amount of zinc present was 34 h. It is seen that the air electrode maintains a nearly constant potential during the test. Except in the case of 5M NH_4Cl, the cathode potential tends to come close to the value in 6M KOH as a result of the alkalinity of the electrolyte arising from the OH^- ions formed by reduction of oxygen. Obviously the buffering capacity of the electrolytes used influences the stationary potential of the air electrode.

Two groups of electrolytes can be distinguished according to their pH: Neutral solutions such as KCl, KNO_3, or K_2SO_4 ($pH \approx 7$), and solutions of ammonium salts, which are slightly acidic owing to hydrolysis ($pH \approx 5$). These can be considered as quasi-neutral in comparison with solutions of H_2SO_4 or KOH. During galvanostatic load, the buffering capacity of ammonium salts was manifested most distinctly in the case of ammonium chloride. The reason for the shift of the cathode potential in solutions of ammonium sulphate or nitrate to more negative values, remains unclear.

The zinc anode performs best in chloride

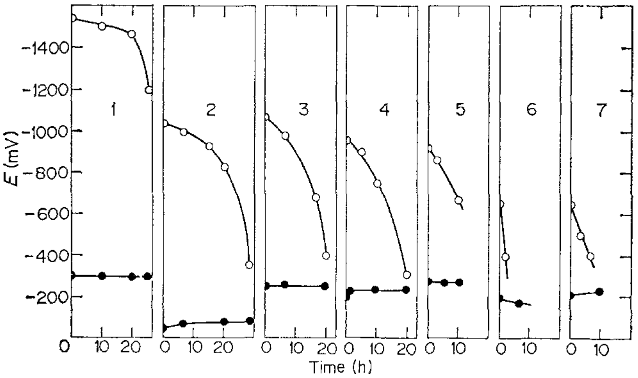

Fig. 1. The potential of the zinc electrode (upper curves) and the air electrode (lower curves) as a function of time in various electrolytes at 50 mA current load. 1, 6M KOH; 2, 5M NH_4Cl; 3, saturated KCl; 4, 1M $(NH_4)_2SO_4$ 5, 0·6M K_3SO_4; 6, 5M NH_4NO_3; 7, 2M KNO_3.

solutions, whereas it undergoes rapid corrosion in solutions of nitrates.

On this basis, further electrochemical tests were made only with 5M NH_4Cl. The influence of the electrolyte volume on the changes of potential of both electrodes with time and therefore the sensitivity of the air electrode towards the presence of anodic oxidation products of zinc in the electrolyte and the critical concentration of Zn(II) at which solid ZnO begins to precipitate from the solution, are points of interest. Formation of a solid layer on the zinc anode causes a diffusion hindrance and finally total passivation of the anode.

With the air electrode, blocking of the porous system was noticeable at an electrolyte volume of 75 ml (15 ml cm^{-2} of cathode). With the zinc electrode the elevated concentration of Zn(II) in the electrolyte had a deleterious effect at 130 ml (50 ml g^{-1} of Zn), as can be seen from Fig. 2. The geometry of both electrodes remained the same, only the volume of the test cell was gradually diminished. It follows from Fig. 2 that the minimum volume of electrolyte is 130 ml (26 ml cm^{-2} of cathode).

The electrolyte concentration is also of importance. A decrease of concentration results in a drop in conductivity and buffering capacity. This lower conductivity leads to a higher ohmic potential drop in the cathode pores and thus the utilization of the cathode's porous system drops. Therefore under a galvanostatic load the active centres which are situated near to the electrode surface are overloaded. The mass transport on the electrolyte and gas sides of the cathode is also vitiated. All these phenomena lead to an increase of the cathode polarization with time. On the other hand, with the zinc anode, an improvement of their performance can be expected as a result of a less-easy formation of a solid deposit of oxidation products.

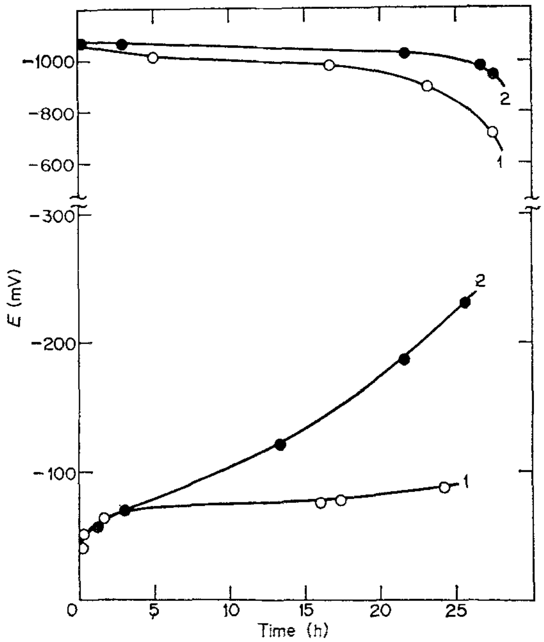

Fig. 2. Dependence of potential on time for zinc (above) and air (below) electrodes in cell under 50 mA load. 1, 375 ml; 2, 130 ml; 3, 75 ml 5M NH_4Cl.

The correctness of the above considerations

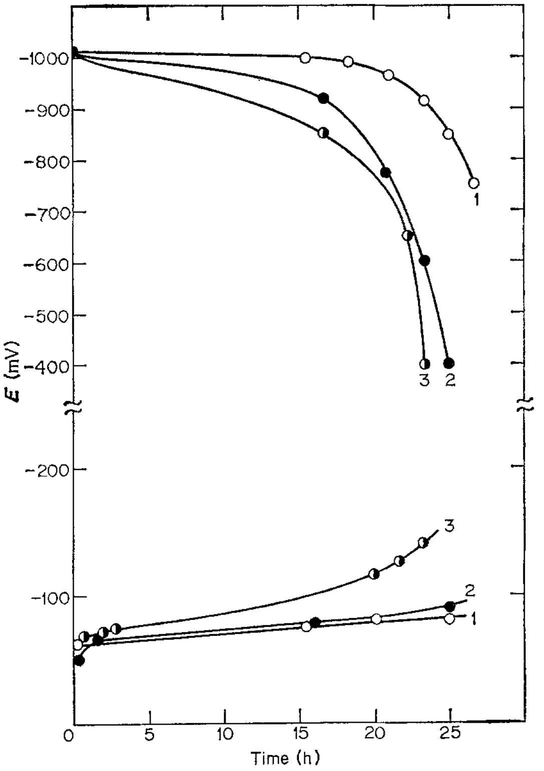

Fig. 3. Influence of electrolyte concentration on potential-time curves for electrodes of zinc (above), air (below). Cell under 50 mA load. Electrolyte volume 150 ml. 1, 5M NH_4Cl; 2, 2·5M NH_4Cl.

is confirmed by the curves in Fig. 3. The concentration of 5M NH_4Cl can thus be considered as an optimum one.

The formation of carbonate, observed in the cathode pores in alkaline electrolytes when standing idle, open to the atmosphere and which manifested itself most markedly during the first few minutes of load after idling [19], was not observed in the cells filled with 5M NH_4Cl. Fig. 4 shows that the period during which the cell stands idle has no influence on its performance; the air cathode attains, after a 1h load, a potential of -40 mV (versus SCE) and maintains this value for several tens of hours.

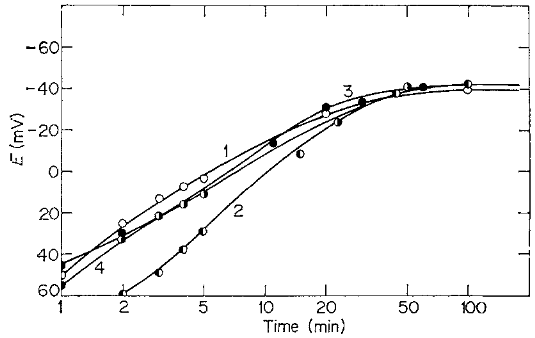

Fig. 4. Dependence of potential on time for air electrode in zinc-air cell under 50 mA load. 1, 1st start; 2, 2nd start after 92 h idleness; 3, 3rd start after 18 h idleness; 4, 4th start after 19 h idleness.

Table 1. Results of corrosion tests on zinc electrodes in 5M NH_4Cl

Starting material	*Collector*	*Volume of* H_2 *evolved* $\mathrm{ml\ h^{-1}\ g^{-1}}$
Zn+ZnO+CdO	Fe	4·1
Zn+ZnO+CdO	Ag	1·58
Zn+ZnO+CdO	none	1·25
Zn+HgO	Fe	2·54
Zn+HgO	Ag	0·66
Zn+HgO	none	0·70
ZnO	none	1·12
Zn+ZnO	none	0·92
Zn+ZnO+HgO	none	0·34
Zn sponge+Pb(II)acetate	brass	0·10
Zn sponge	brass	0·87

Since zinc corrodes strongly in ammonium chloride solutions [20], we considered it of importance to measure its corrosion rate. The results of measurements, based on the volumetric determination of the evolved hydrogen, are summarized in Table 1. (The term 'none' under 'collector' is used for a zinc sample from which the silver collector, used in the reduction of starting material, was removed.) The following results are to be noted.

(1) The maximum corrosion rate was found with zinc in contact with an iron collector, obviously owing to a low hydrogen overvoltage on iron.

(2) Electrodes with a silver collector, corrode much more slowly than those with iron collectors. The corrosion rates with and without silver collectors are practically the same.

(3) Addition of 2% HgO to the starting material lowers the rate of corrosion.

(4) The smallest corrosion rate was observed with electrodes made from a zinc sponge with addition of lead in combination with a brass current collector.

Analogous results were found in a parallel series of corrosion tests of zinc electrodes in alkaline electrolytes. However, in this case the corrosion rates were at least an order of magnitude lower [21].

4. Conclusions

The most suitable quasi-neutral electrolyte for zinc-air primary cells is 5M NH_4Cl. This has a sufficiently high buffering capacity and conductivity, and leads to the formation of oxidation products of the zinc anode which do not substantially hinder mass transport. The optimum amount of this electrolyte is 15 ml cm^{-2} of cathode and 50 ml g^{-1} of zinc. No formation of carbonate by absorption of CO_2 from the atmosphere was observed. Porous zinc electrodes from a zinc sponge with addition of lead on a brass collector show a sufficiently low corrosion rate in 5M NH_4Cl. Because of their advantages over alkaline cells (mainly because carbonate is not formed by reaction of the electrolyte with CO_2 from the air), the envisaged zinc-air cells appear to offer practical possibilities, especially for intermittent service. Its operating voltage is 0·90–0·95 V at 10 mA cm^{-2} of cathode, without added cathode catalyst.

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