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The anodic behaviour of porous zinc electrodes. II. The effects of specific surface area of the zinc compact material

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A study has been made of the galvanostatic polarization behaviour of porous zinc electrodes as a function of electrode surface area. Correlations have been established between the electrode polarization parameters and surface areas as measured by BET and methylene blue adsorption methods.

1. Introduction

Porous zinc electrodes are of interest because of their growing use in alkaline primary cells, e.g. zinc-air, alkaline manganese. Their use derives from the high surface areas of such electrodes which are able to tolerate high current densities without undue polarization. As emphasized by a number of workers [1], the reduced polarization conferred by high porosity is in theory best realized at low current densities where mass transport is insignificant. This is because the presence of fine pores does not necessarily improve mass transport; at very high rates of discharge the overpotential is likely to be controlled by mass transport in the bulk of the solution. In practice, the use of porous electrodes allows higher currents to be drawn, by virtue of their reduced susceptibility to passivation. Equations representing the behaviour of porous and rough electrodes have been summarized [1], however, the solutions even to simple situations are relatively difficult to obtain and for electrodes manufactured by compacting a metal powder of differently sized particles, no theoretical treatment has been attempted.

The experimental work reported with porous zinc electrodes confirms the conclusions obtained from analysis of simplified model porous electrode systems. Breiter [2] has found that only a small fraction of the inner surfaces of the electrodes participates in the electrochemical process. Elsdale *et al.* [3] found that the major source of passivation of a porous zinc electrode was the formation of insoluble ZnO within the electrode pores. This material was apparently the product of the decomposition of the concentrated zincate solution forming inside the electrode as the anodic process proceeded and gave rise to an increasing anode ohmic resistance. In the experiments described by Elsdale *et al.* [3] the transition from the active to the passive electrode condition was not abrupt as is well established for a planar zinc electrode in alkali [4], rather a gradual increase in electrode potential was observed, corresponding to the electrode reaction being driven deeper into the anode as discharging pores became blocked with oxide.

The effect of particle size and shape of the zinc powder used determines the porosity of the

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electrode and the discharge behaviour. No investigation of the interrelationship of these characteristics has been published: our purpose is to provide experimental data and establish the relationships between the surface areas and the discharge characteristics. Assuming that the behaviour of the electrode at relatively high rates is a realistic criterion of performance, the aim of the present work was to devise a production test for the quality control of porous zinc anodes for zinc/air primary cells.

2. Experimental

2.1. *Zinc powder*

Zinc powder was produced by electrodeposition from a suitable electrolyte solution [5]. The powder was washed, dried and divided into five separate fractions by sieve (range: B.S.S. +22 to −85). Electrodes corresponding to each of the five sieve fractions were made by die pressing at $7{\cdot}7\times10^4$ kNm^{-2}. The electrodes had a porosity of ~ 70% and a mean oxide content of ~4%.

2.2. *Surface area determinations*

The surface areas of each fraction of zinc powder were determined using the BET technique [6]. For each sample the nitrogen adsorption isotherm was measured using nitrogen as the adsorbate at 77·5 K. The experimental data were evaluated by a computer programme which gave the specific surface area and a plot of $p/(V_{\text{ads}}-(p_0-p))$ versus p/p_0 where:

p_0 = saturated vapour pressure,
p = pressure and
V_{ads} = volume adsorbed at STP.

The surface areas were also estimated (indexed) by methylene blue adsorption (MBI). The change in concentration of the dye produced by the addition of a weighed sample of zinc to a known volume of aqueous dye solution was measured using the adsorption maximum determined in the range 640–75 nm (SP 600 UV spectrometer). The area was calculated by assuming monolayer coverage by molecules occupying 8·4 nm^2.

2.3. *Electrometric measurements*

Galvanostatic measurements were made with the electrodes horizontal with the electrolyte vertically above as described by Elsdale *et al.* [3]; in this way convection was minimized.

3. Results

Fig. 1 shows a typical overpotential/time curve. The initial part of the curve rises linearly with time in agreement with the observation of Elsdale *et al.* [3]. During anodic polarization, also in agreement with these authors [3], hydrogen gas was seen leaving the electrode. It is not possible to determine any transition point between active and passive parts of the polarization; accordingly, as before, the useful discharge of the electrode was considered to end when (after $t_{0{\cdot}3}$) the overpotential had increased by 0·3 V from its initially established

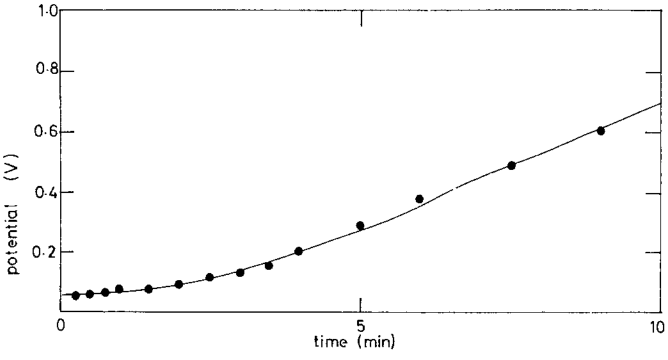

Fig. 1. Typical overpotential/time curves. Porous zinc anode. 7 M KOH, 23°C, ● 0·5 A.

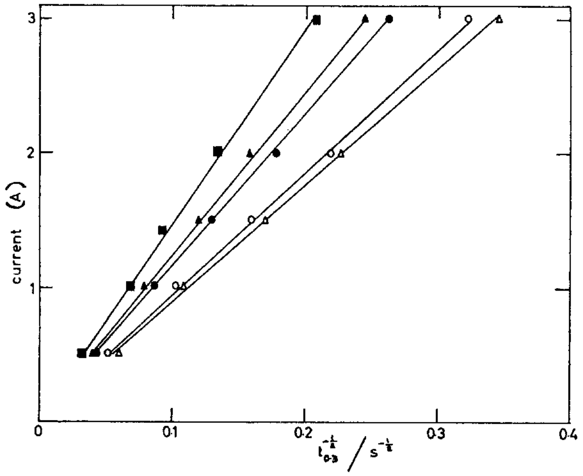

Fig. 2. i-$t_{0.3}^{-\frac{1}{2}}$ correlation ■ +22 B.S. mesh size, ▲ −22+44 B.S. mesh size, ● −44+60 B.S. mesh size, ○ −60+85 B.S. mesh size, △ −85 B.S. mesh size at 23°C.

value. The correlations of $t_{0.3}$ with current in the form current, I, versus $t_{0.3}^{-\frac{1}{2}}$ are shown in Fig. 2. It is desirable to use the current density; however in the present context, this has little meaning and the data presented refer to an electrode of nominal surface area 2·4 cm^2. Good straight lines were obtained from which the slopes k ($A{\cdot}s^{\frac{1}{2}}$) were calculated; the values of k are measures of the ability of the electrodes to withstand the process of passivation (attainment of $\Delta\eta = 0{\cdot}3$ V). The values of k for each sieve fraction are shown in Table 1 together with BET and MBI areas. Figs. 3 and 4 show the relationship between k and the surface areas obtained from BET (N_2) and MBI adsorption respectively. The gradient of the initial linear parts of the polarization curves were measured and the rate of polarization ($d\eta/dt$) plotted against the current. The relationship can be seen in Fig. 5. Good straight lines were obtained from these from which the slopes ϕ (V min^{-1} A^{-1}) were

Table 1

Anode type	*B.S. mesh size*	*Methylene blue surface area* (m^2 g^{-1})	*BET* (N_2) *surface area* (m^2 g^{-1})	*Gradient of* $i/t^{-\frac{1}{2}}$ (A s$^{-\frac{1}{2}}$)
C	+22	2·27	0·77	14·8
B	−22 +44	2·78	0·85	12·2
A	−44 +60	2·94	0·93	11·9
D	−60 +85	3·40	0·99	9·3
E	−85	4·46	1·80	9·1

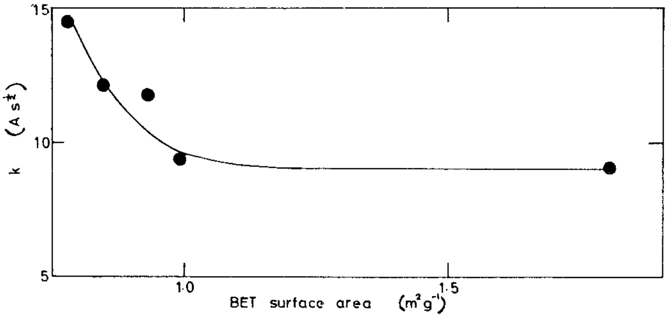

Fig. 3. Relationship between k (from $(I\text{-}I_c) = kt_{0.3}^{-\frac{1}{2}}$) and BET (N$_2$) surface area.

calculated; the values of ϕ are a measure of the specific rate of polarization. Figs. 6 and 7 show the relationship between ϕ, the specific rate of polarization, and the surface areas as determined by BET (N_2) and MBI adsorption respectively.

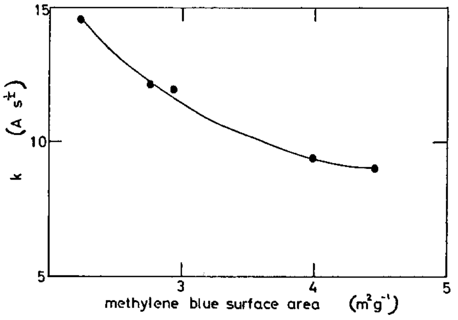

Fig. 4. Relationship between k and MBI surface area.

4. Discussion

The potential/time curve (Fig. 1) resembles those reported by Elsdale *et al.* [3] although our results were not so consistent. This could be due to the different method of electrode manufacture used by the former workers [3], namely, by reducing zinc oxide on silver wire mesh. This method of production has the advantage that electrical conductivity of the electrodes is very uniform whereas with the present electrodes oxide films between particles might not be

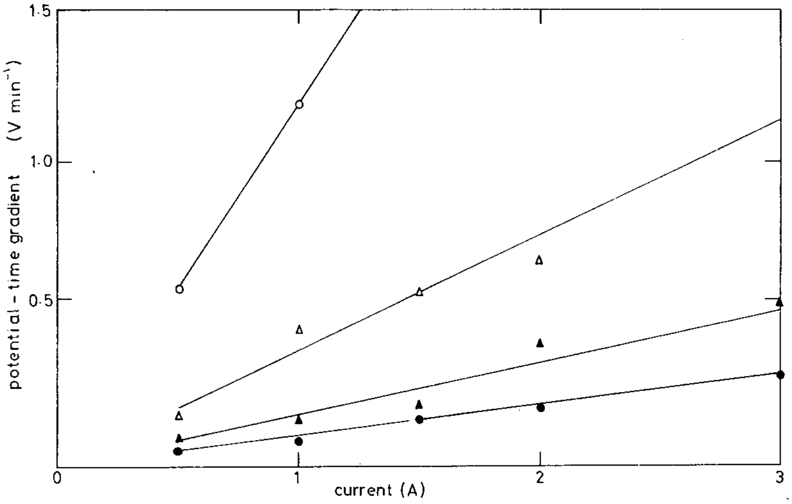

Fig. 5. Overpotential/time gradient–current correlation ● +22 B.S. mesh size, ▲ −22+44 B.S. mesh size, △ −60+85 B.S. mesh size, ○ −85 B.S. mesh size at 23°C.

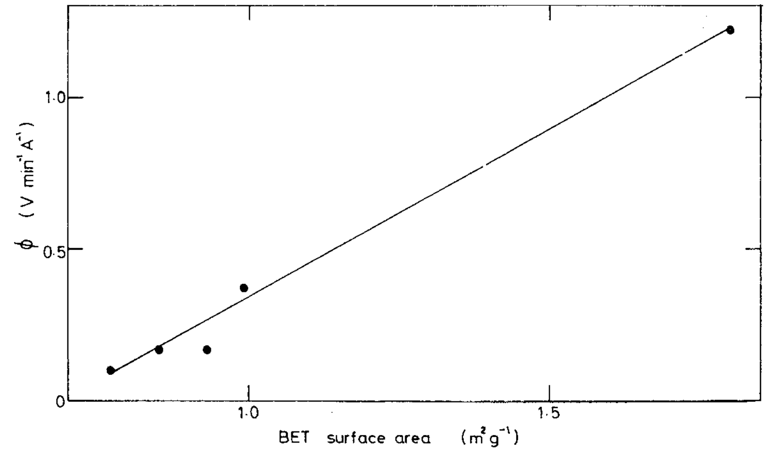

Fig. 6. Relationship between ϕ (specific rate of polarization) and BET (N_2) surface area.

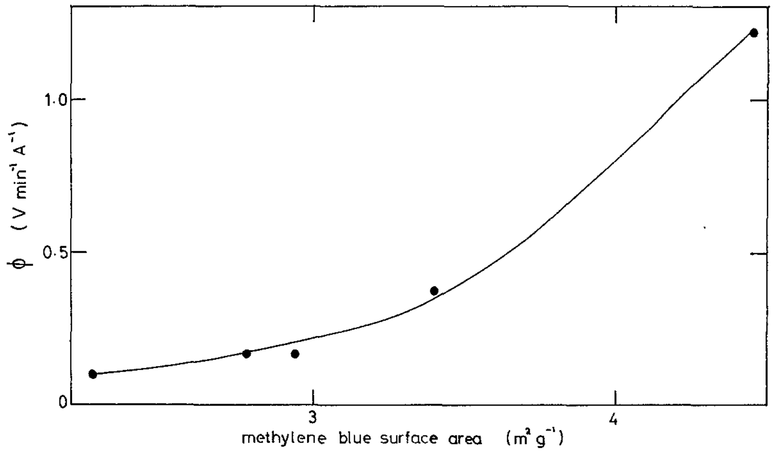

Fig. 7. Relationship between ϕ and MBI surface area.

sufficiently disrupted in the pressing process to achieve as good an electrical path from particle to particle as with plates reduced after compacting. That some variability existed initially between electrodes was confirmed by the relationship between the initial value of the overpotential and the current density. With the 'silver mesh' electrodes a well-defined linear relationship existed [3]; in the present experiments the relationship, although broadly similar, was not quite so consistent.

Figs. 3 and 4 show the relationships between k, surface area and MBI. Although a good correlation between MBI and k is obtained, the magnitude of the apparent surface areas indicates that the dye molecules are adsorbing as a multilayer. The relationship between BET (true) surface area and k shows that the sample with the largest surface area does not give a proportional improvement in performance over the other types of anode. This observation agrees with that of Breiter [2] and the theoretical predictions of De Levie [1] that, unless very low reaction rates are used, the inner regions of the porous electrode contribute little to the total current flowing from the electrode to the bulk electrolyte. It is known that a slightly higher zinc oxide content exists in the finer material (6% rather than 4% [5]) and it may be that this factor contributes to the fall-off with BET (true) area, however, the magnitude of the difference in oxide contents appears to be far too small to account for the observed behaviour.

The MBI gives a better measure of the performance of the electrode than the BET determination. This can be explained if the methylene blue molecules although giving multilayer adsorption (to be expected from a complex organic molecule with different types of reactive groups) are unable to enter the finer pores of the electrode. The presence of very fine pores (microporosity) was investigated by a De Boer t-plot [7]. The results were not conclusive and indicated that if any degree of microporosity was present, it was not great, nevertheless, relatively fine pores were clearly indicated.

A further method used to indicate the discharge behaviour of the electrodes was to measure the specific rate of polarization. This was calculated from the slopes of the straight-line relationship which was found empirically to relate the rate of polarization ($d\eta/dt$) with current density (Fig. 5). For a flat electrode from which the electrode products were unable to escape it might be expected that ($d\eta/dt$) would show a linear relationship to I^2 [4]. For porous electrodes of the type considered no relationship in general has yet been established between the potential and the time on load. Qualitatively, one may be justified if, as the potential required to support the current flow is increased due to the blocking of the more accessible areas of the electrode, the discharge is driven into the inner parts of the electrode. Once the whole of the electrode is involved in the discharge the rate of polarization would be expected to increase more rapidly with time as observed (Fig. 1). Whether or not the apparent relationship can be justified by our present knowledge of these porous electrodes does not really affect the point that the specific polarization rate, ϕ, is related to the true surface area as shown in the Figs. 6 and 7. It is interesting that ϕ, a parameter representing the early part of the discharge, correlates with the true surface area better than it does with the MBI which is more representative of the 'more accessible' surface. This is in agreement with the ideas of Karaoglanoff [8] and Lorenz [9] that when the diffusion layer is thin (early in the experiment) the true surface area determines the *I-E* relationships whereas at a later stage when the diffusion layer is thick the important area is the superficial area.

It is clear, therefore, that in order to relate the low-rate (conventional) performance of the porous zinc electrode to surface area factors an assessment of the 'more accessible' electrode area is of more use than a knowledge of the absolute area as revealed by BET measurements. The latter are useful only in revealing the likely 'initial' behaviour of the electrode.

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References

[1] For example, the review by R. De Levie in Tobias and Delahay, *Advances in Electrochemistry and Electrochemical Engineering*. Vol. 6, p. 329 *et seq*., Interscience, New York (1967).
[2] M. W. Breiter, *Electrochim. Acta*, **15** (1970) 1297.
[3] R. N. Elsdale, N. A. Hampson, P. C. Jones and A. N. Strachan, *J. Appl. Electrochem.*, **1** (1971) 213.
[4] N. A. Hampson and M. J. Tarbox, *J. Electrochem. Soc.*, **110** (1963) 95.
[5] Private communication, Energy Conversion Ltd., Basingstoke, Hants.
[6] S. Brunauer, P. H. Emmett and E. Teller, *J. Amer. Chem. Soc.*, **60** (1938) 309.
[7] J. H. De Boer, B. C. Lippens, B. G. Linsen, J. C. P. Broekhoff, A. van der Heuvel and Th. J. Osinga, *J. Coll. and Interfac. Sci.*, **21** (1966) 405.
[8] Z. Karaoglanoff, *Z. Elektrochem.*, **12** (1906) 5.
[9] W. Lorenz, *Z. Elektrochem.*, **58** (1954) 912.