

The impedance of the alkaline zinc-manganese dioxide cell.

I. Variation with state of charge

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The impedance spectra of undischarged commercial alkaline zinc-manganese dioxide cells (Mallory, type MN 1500) have been measured. Newly produced cells have different impedance characteristics from ones stored for periods of time (up to one year). The difference introduced by the ageing process is interpreted as the effect of Hg on the zinc particle electrode. The impedance behaviour of the cells is dominated by the zinc negative electrode which behaves as a relatively simple charge transfer and diffusion process. The porous nature of the particulate electrode has relatively little effect on the behaviour of the zinc which behaves as quasiplanar.

On discharging, the frequency spectrum changes as does the open-circuit potential, the latter due to the progressive change in composition of the positive electrode. The former changes as a consequence of the negative electrode reaction.

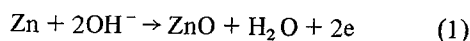
1. Introduction

We have reviewed the published work relating to the impedance of electrical storage cells [1] and demonstrated that the conventional Leclanché dry cell can be treated satisfactorily using conventional a.c. theory [2]. For the Leclanché cell in an undischarged state the behaviour was interpreted in terms of rate control by charge transfer and diffusion at a rough zinc electrode. The carbon/manganese dioxide electrode behaved as a counter electrode of large surface area which contributed a small effect, represented in the cell analogue by a combined parallel resistance and capacitance. This picture of the cell was confirmed later [3] when the impedance of the separate cell components was measured.

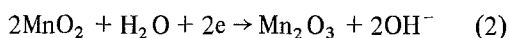
The effect of discharging the Leclanché cell on the impedance spectrum was considered in a further paper [4] and it was reported that dis-

charging down to the nominal fully discharged state did not change the rate-controlling mechanism, although the magnitudes of the impedances were progressively changed. In fact, in the range from fully charged down to 90% fully charged, the change in the in-phase component of the electrode impedance at a frequency of 31 Hz was proportional to the amount of charge delivered by the cell and this was associated with a very satisfactory statistical correlation (correlation coefficient 98.9%). This was considered to be a fortuitous relationship for the Leclanché cell which might not be expected to hold generally.

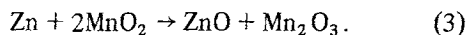
The so-called alkaline manganese cell is related to the Leclanché cell, the only difference being in the electrolyte, which is alkaline (KOH). The generally accepted mechanism for the alkaline manganese cell is



and



giving the overall cell reaction



In the whole-cell reaction there is no change in the concentration of the electrolyte solution and the equilibrium potential might be expected to be independent of the state-of-charge since the activity of the solid species is to be considered constant and equal to unity. This is not observed in practice: the on-load cell voltage falls fairly linearly with time and even the open-circuited stabilized potential does not produce a constant cell potential. This behaviour follows from the electrochemical behaviour of the MnO_2 electrode. For this system, Tye [5] reported that the activity of the Mn(III) and Mn(IV) species changes with the mole fraction conversion and that the behaviour can be quantitatively understood on this basis (a difference in behaviour exists between $\gamma\text{-MnO}_2$ and $\beta\text{-MnO}_2$, however, although this does not alter our present argument).

We should expect therefore a change in impedance spectrum as the cell is discharged due both to the accumulation of ZnO in the vicinity of the negative electrode and to activity changes in the manganese dioxide. Part I of this paper records the results of experiments made with 'alkaline zinc-manganese' cells at various stages of charge: the electrochemical interpretation will be given in Part II.

Two groups of cells have been investigated; the first group was examined immediately after manufacture, the second group was stored at 5°C for 12 months and then examined. This paper records the results.

2. Experimental

The cells investigated were the Duracell MN 1500 type (Mallory Batteries Ltd) which are capable of delivering 1800 mA h at 20°C . The dimensions are $\phi = 14.5$ mm, height = 50.5 mm, volume = 7.4 cm^3 , weight = 23 g. The nominal voltage was 1.5 V.

The experimental apparatus and procedure by which the impedance of the cell was measured when poised at the equilibrium potential have

already been described. Cells were tested in quadruplicate, undischarged (stored and immediately after manufacture) and after discharging galvanostatically at 25 mA (72 h rate).

After the impedance data had been obtained as a Sluyters plot on an X - Y recorder, they were fed into the computer via the punched tape from the frequency response analyser [3].

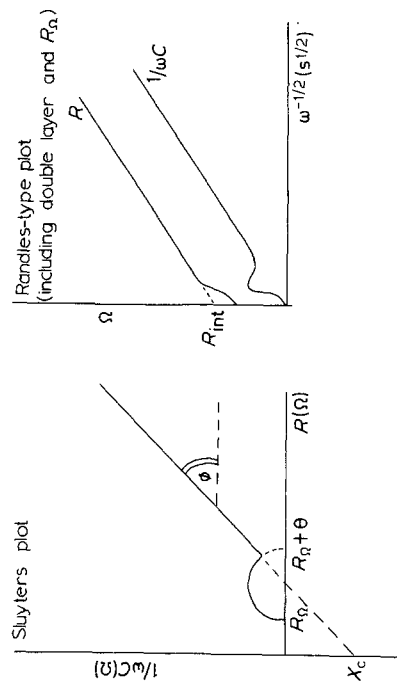
3. Results and discussion

Fig. 1 shows a Sluyters plot corresponding to a cell immediately after manufacture. It consists simply of a small semicircular shape at high frequency giving way to an approximately $\pi/4$ slope at low frequency. The slopes of the low-frequency lines are given in Table 1 and from these data values of 40° are typical. This is somewhat surprising since the cells incorporate negative electrodes made from zinc powder and it would be expected that a 22.5° slope, characteristic of an electrode with semi-infinite pores, would be observed. The previously investigated planar zinc electrode gave an ideal slope of 45° [2] for the dissolution process in acid solution; however, there was no doubt that this slope became much less, tending towards 22.5° , as discharging roughened the electrode [4]. In this present case there is no doubt that the electrode is porous in the physical sense. However, there is sufficient data to indicate that it is not particularly porous in the electrochemical sense. This is confirmed by the results of impedance measurements on cells which have been stored for 12 months at 5°C . A typical impedance locus is shown in Fig. 2. Here the high-frequency circular shape is now very much enlarged and quite well defined. In fact, that of Fig. 2 is much better defined than that of Fig. 1, which is rather elongated. The slope of the low-frequency portion of Fig. 2 is 40° , confirming the data of Fig. 1.

The interpretation of these curves is that the current-controlling reactions are charge transfer and diffusion at the zinc electrode and that the zinc electrode, although porous, physically behaves as if it were electrochemically planar. The reason for this possibly lies in the amalgamation process by which a small quantity of Hg ($\sim 7\%$) is introduced into the porous electrode in order to improve discharge behaviour and limit gassing from the negative electrode due to the hydrogen

Table 1. Data from Sluymers and Randles plots for four different cells. The diagrams illustrate the two types of plot

Discharge (%)	0	1	2	3	4	5	6	7	8	9	10	20	30	40	50	60	70	80	90	100
θ (deg)	35.4	35.7	33.9	42.2	33.9	32.3	28.0	32.5	28.7	31.7	33.7	37.3	38.1	36.9	33.4	36.6	36.8	38.9		
$R_{\Omega} + \theta$ (Ω)	33.1	36.1	34.7	34.0	35.5	35.7	36.1	36.0	35.2	35.7	35.7	35.9	29.6	33.6	26.1	33.4	33.2	12.8		12.2
	36.3	33.3	37.6	36.4	33.4	33.8	36.2	38.2	36.6	36.4	36.6	35.5	34.6	42.4	35.3	29.9	34.1	30.9	20.9	
	35.0	34.2	34.4	33.8	33.6	34.6	32.8	35.8	36.3	35.1	35.2	36.2	34.4	30.5	2.80	30.7	35.5	12.5	20.5	
R_{Ω} (Ω)	0.306	0.307	0.324	0.358	0.331	0.336	0.459	0.382	0.380	0.354	0.365	0.443	0.449	0.530	0.549	0.672	0.814	1.16		
	0.273	0.285	0.289	0.294	0.300	0.307	0.312	0.328	0.326	0.312	0.393	0.345	0.388	0.445	0.493	0.590	0.629	0.532	0.319	
	0.276	0.275	0.287	0.289	0.282	0.288	0.301	0.303	0.299	0.300	0.303	0.324	0.363	0.430	0.460	0.493	0.609	0.822	1.10	
	0.278	0.280	0.287	0.292	0.298	0.297	0.298	0.313	0.312	0.310	0.313	0.333	0.373	0.411	0.456	0.505	0.622	0.461	1.29	
$-x_c$ (Ω)	0.218	0.188	0.218	0.324	0.223	0.212	0.243	0.243	0.209	0.218	0.244	0.337	0.352	0.398	0.361	0.499	0.610	0.941		
	0.178	0.207	0.200	0.198	0.214	0.221	0.227	0.239	0.230	0.224	0.283	0.249	0.220	0.296	0.241	0.389	0.411	0.125	0.473	
	0.202	0.181	0.222	0.213	0.187	0.193	0.221	0.239	0.222	0.221	0.225	0.231	0.250	0.392	0.326	0.283	0.412	0.491	0.420	
	0.195	0.190	0.196	0.196	0.198	0.205	0.192	0.226	0.230	0.218	0.221	0.243	0.255	0.242	0.242	0.300	0.444	0.102	0.481	
R_{int} (Ω)	0.317	0.320	0.335	0.365	0.343	0.347	0.473	0.395	0.393	0.366	0.378	0.453	0.470	0.562	0.595	0.708	0.872	1.23		
	0.277	0.290	0.297	0.300	0.308	0.316	0.321	0.339	0.334	0.319	0.405	0.359	0.410	0.484	0.533	0.636	0.686	1.01	1.46	
	0.282	0.286	0.294	0.295	0.295	0.296	0.308	0.311	0.308	0.308	0.312	0.337	0.387	0.462	0.497	0.537	0.662	0.941	1.47	
	0.294	0.288	0.295	0.308	0.314	0.311	0.306	0.323	0.318	0.319	0.323	0.346	0.394	0.442	0.499	0.547	0.668	1.00	1.67	



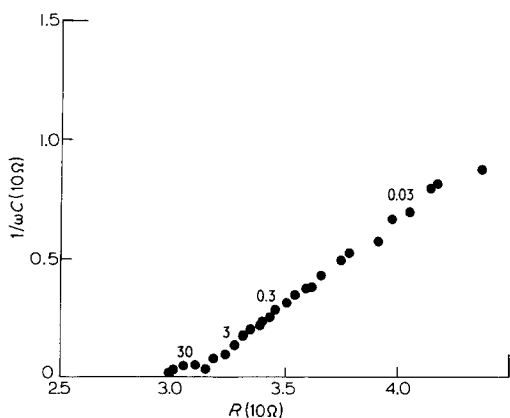


Fig. 1. Impedance locus for newly produced MN 1500 cell, frequencies marked on curve (Hz).

evolution reaction. If we assume that the outside surfaces of the zinc particles have the highest concentration of mercury then the reaction can be visualized as occurring at the outer face of the nominally porous electrode on a surface which is a highly concentrated amalgam. There are indications of some porosity; the lines of Figs. 1 and 2 come off the abscissa at an angle of less than 45° yet the behaviour is redolent of a planar surface. This must imply that to some extent the zinc particles sinter together at points of contact and that the voids between the outer particles are removed. A contributory factor to this is that carboxymethyl cellulose is added to the amalgam which acts as an expander. The application of internal pressure during manufacture, when the

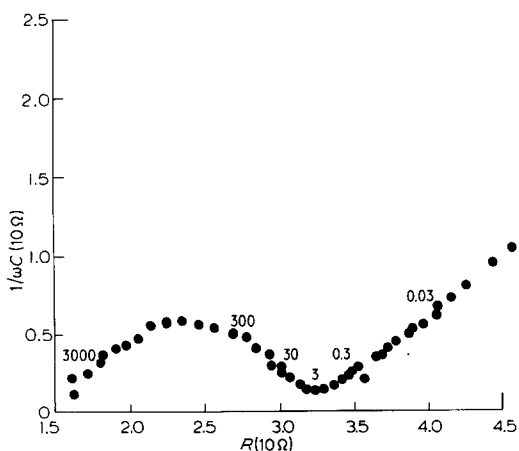


Fig. 2. Impedance locus for stored (12 months, 5°C), fully charged MN 1500 cell.

current collector (central post) is fitted, coupled with this and the mercury-rich, semi-fluid outer surface of the particles accounts for the generation of a quasiplanar amalgam surface.

With ageing, the surface concentration of mercury falls as the liquid metal diffuses into the centre of the zinc particles. The effect of zinc concentration on the charge-transfer resistance θ (the diameter of the high-frequency semicircle) of Zn (Hg) in alkali has been investigated by Gerischer [6] who confirms that θ decreases as C_{Zn} increases in accord with

$$\theta = \frac{RT}{ZFk_s C_{\text{ZnHg}}^{0.5} C_{\text{Zn}^{2+}}^{0.5}} \quad (4)$$

where k_s is the specific rate constant and the concentrations are those at the interface. If the geometry of the reactive interface is similar in new ($\theta \approx 0.25 \Omega$) and aged ($\theta \approx 1.5 \Omega$) cells, then storage for one year at 5°C implies a concentration change of 36:1 taking place during this time.

Fig. 3 shows the resistance and reactance presented in the form of a Randles plot. The expected shapes are observed: the curvature at high frequency represents the double-layer capacitance, the separation between the lines is $(\theta + R_\Omega)$ where the electrode resistance R_Ω (the intercept on the $1/\omega C$ axis) is enough to be insignificant and the lines at frequencies greater than 50 Hz are only approximately rectilinear. This is the effect

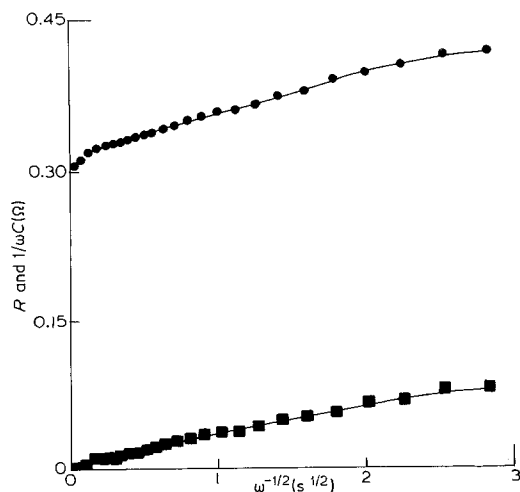


Fig. 3. Randles representation (R and $1/\omega C$ versus $\omega^{-1/2}$) of impedance data corresponding to Fig. 1.

of the limited porosity which is better considered as a roughness. At high frequency the diffusion layer is thin compared with the roughness and the electrode behaves as a flat one while at low frequency the diffusion layer is thick and the electrode structure becomes more important; in other words the higher the frequency the more the phase angle approaches that for the planar electrode (45°). This can also be seen from Fig. 1 where initially the line comes off the semicircle at $\sim 45^\circ$; at the lower frequencies this becomes 40° . The curvature of the line at lower frequencies probably indicates the tendency to the limit of 22.5° (unobtainable in these experiments due to the time needed to obtain data at ultra-low frequencies).

For the aged cells, the initial slopes at 45° are missing, which implies that the structure of these is rather more porous (rough), i.e. the pores are deeper.

Fig. 4 shows the impedance locus of a new cell which has been discharged for 5% of its rated capacity. The shape is approximately the same as in Figs. 1 and 2, i.e. a high-frequency semicircle followed by a line which goes off at something less than 45° , although the first few data points appear to be at 45° . This region is much less well defined than in Fig. 1 and it can be argued that the (new) cells with the highest surface concentration of Hg provide the system most likely to produce a quasiplanar surface. The diameter of the high-frequency semicircle is increased by the removal of the available charge; however, the slope of the low-frequency tail is largely unchanged. Progression to around 10% discharged (Fig. 5) increases the

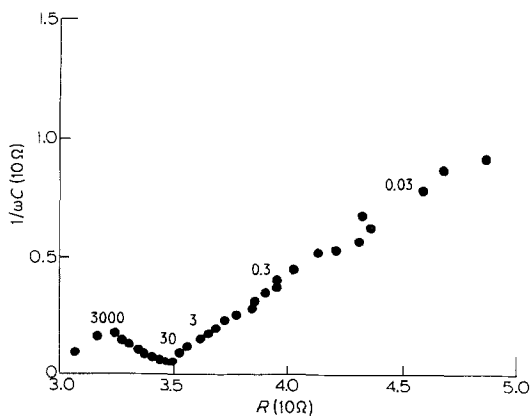


Fig. 4. As Fig. 1, 5% discharged.

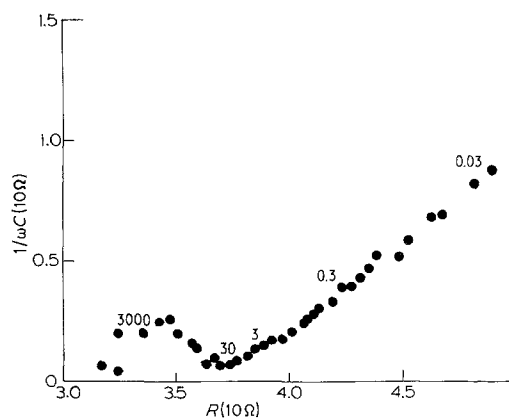


Fig. 5. As Fig. 1, 10% discharged.

diameter of the semicircle but leaves the angle the low-frequency line makes with the abscissa almost unaltered.

The same type of behaviour occurs with cells which have been stored; the general shape of the impedance locus remains the same but the position on the real axis is changed to higher values which indicate an increased resistance. This can be seen when Fig. 6 is compared with Fig. 2; the whole shape is displaced along the resistance axis by the discharging process. If the discharge simply produced zinc oxide at the zinc electrode and Mn(III) at the manganese dioxide electrode so that somewhat more resistive phases were produced, then this behaviour is readily understood. When Figs. 1 and 4 are compared, it is evident that this simple process of cause and effect does not occur with the newly produced cells.

It is only when the newly produced cell is discharged to a value in excess of 15% that the shape of the impedance locus begins to change. Fig. 7, corresponding to 15% discharge, is considerably altered by a further 5% charge removal, as shown

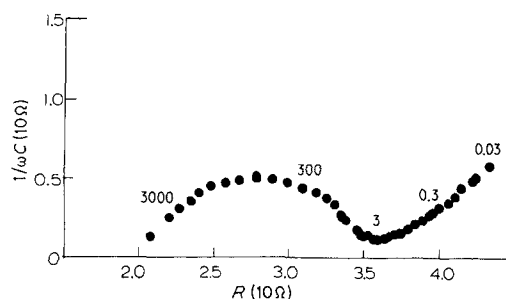


Fig. 6. As Fig. 2, 10% discharged.

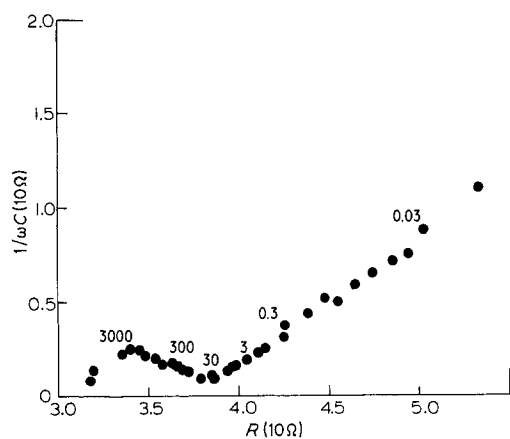


Fig. 7. As Fig. 1, 15% discharged.

by Fig. 8, corresponding to 20%. Here the high-frequency semicircle has been flattened and a much more complex shape is apparent which ultimately goes off to the Warburg line. As the discharging continues the high-frequency part becomes more and more elongated as shown in Fig. 9, corresponding to 50%.

The form of the Randles representations was altered in magnitude by the discharging process. Fig. 10 shows the changed form from the undischarged cell represented by Fig. 3. The very slight 'relaxation' in the in-phase curves observable in the new cell is much better defined in the discharged cell but the general shape remains the same.

Fig. 11 shows the impedance spectrum corresponding to 100% discharge. This plot is extremely complex and appears to consist of a high-frequency semicircle followed by another elongated circular

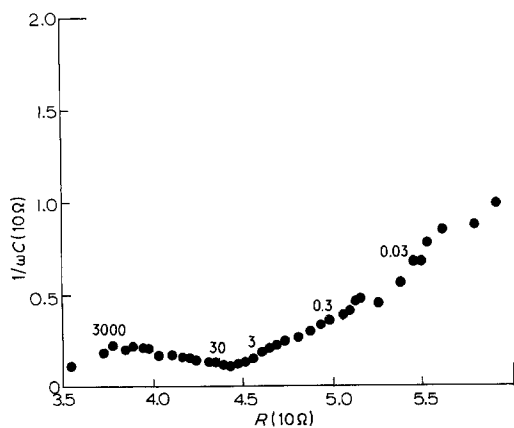


Fig. 8. As Fig. 1, 20% discharged.

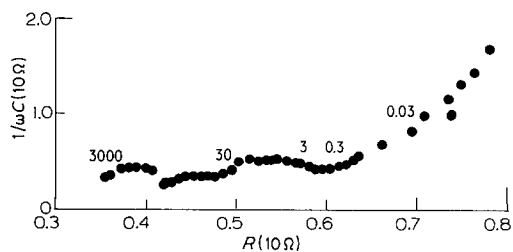


Fig. 9. As Fig. 1, 50% discharged.

shape coming off in a part which resembles a Warburg line. The final part of the shape was at a frequency too low for clear definition even using our techniques. It is difficult to see how the components of the cell impedance may be recovered with confidence at frequencies below 0.01 Hz in view of the time required and the difficulties with cells containing porous commercial electrodes.

The method of manufacture of these cells is to pour the amalgamated zinc powder into the cavity between the positive electrode and the electrode outer container which acts as the current collector. The positive and negative electrodes are separated by two thicknesses of separator material which is based on a nylon polyester. These poured electrodes and separators introduce a certain amount of non-conformity between the cells which is observed in a certain amount of variability from cell to cell. It also has the effect of producing a total cell behaviour which is in essence the envelope of a number of behaviours. The construction, moreover, precludes the possibility of testing each

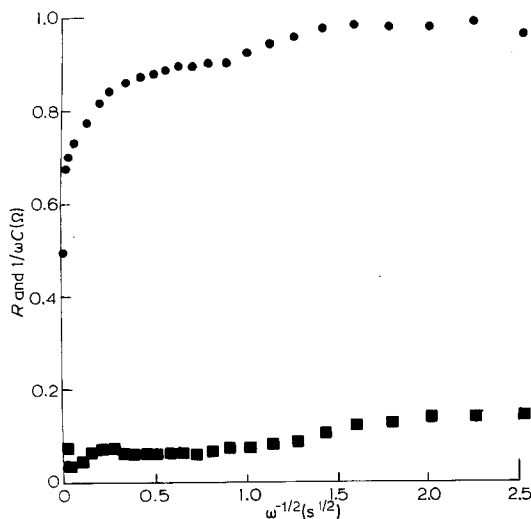


Fig. 10. As Fig. 3, 70% discharged.

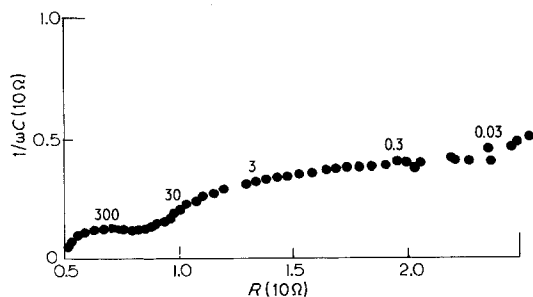


Fig. 11. As Fig. 1, 100% discharged.

electrode separately as we did for the Leclanché cell [3]; we must therefore infer what we can from the behaviour of the assembled cell.

The composition changes in the cell which occur during the discharging process are reflected in the variation of the open-circuit potential V throughout the process (Fig. 12). The curve has the expected sigmoidal shape and ranges from 1.58 V (V_{init}) to 1.09 V after the nominal capacity has been delivered. This curve is generally as expected. There is a considerable range of discharge levels where a rectilinear relationship exists of the form:

$$V = V_{\text{init}} - B \log(P/100 - P) \quad (5)$$

where P is the percentage discharge. The constant B is not, however, even approximately the Nernstian value of 60 mV over the central section

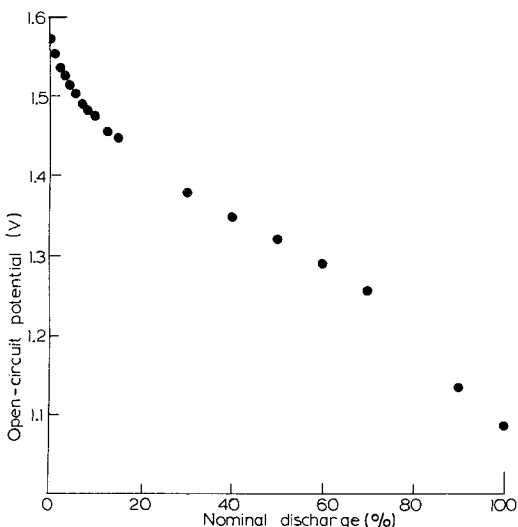
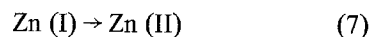


Fig. 12. Open-circuit potential (stabilized) against discharge (%) for MN 1500 cell.

of the curve, which is not surprising in view of the concentration changes in the cell, which are not as simple as those of Equation 2 for the MnO_2 electrode.

The discharge of the zinc negative in alkali has been the subject of a great many investigations. In the main, systems have been chosen to yield model situations and there does not seem to be any record of investigations of exchange processes at very highly concentrated amalgams. Gerischer [6] has considered dilute amalgams and finds that the simple processes of charge transfer and diffusion account for his impedance data. Other workers have considered the solid metal [8–10]. It is generally considered that the process of zinc dissolution consists of 2 one-electron steps:



the second of which is the rate-determining step. If this is so and provided that the rates of Reactions 6 and 7 are very different, then the impedance spectrum should consist of a high-frequency semi-circle followed by the Warburg shape for mass transport. Armstrong [9] has shown that under conditions where the Zn(I) intermediate is adsorbed at the electrode an inductive loop might be expected: this was never observed in any of our experiments but this might be due to the presence of ill-defined diffusion in the cell and also to the potential of the electrode being outside the region at which inductive loops might have been observed.

An interesting feature of the cell results is the Warburg slope which is nearer 45° for the plane electrode than $22\frac{1}{2}^\circ$ for the porous electrode (see Table 1) and, moreover, this slope is observed virtually throughout all the states of charge. It is clear that the quasiplanar nature of the porous zinc electrode is maintained throughout all the states of charge. The interpretation of this effect is that a quasiplanar reaction zone occurs at the front of the electrode and progresses into the porous mass as the reaction proceeds. The product of the process is ZnO which remains as a porous structure overlaying the unreacted zinc. We are concerned therefore with a 'porous electrolyte' and a quasiplanar electrode rather than a porous electrode reacting in depth. This type of

behaviour has actually been observed visually with the porous zinc electrode [11] and inferred in the case of the PbO_2 electrode [12].

The salient data from all the cell tests are given in Table 1. Discharging the cell generally increases the ohmic resistance, increases the charge transfer resistance and elongates the high-frequency semi-circular shape; finally this elongation is gross and may be considered the envelope of a whole series of semicircles centred on the real axis.

The Warburg part of the impedance loci is approximately equiangular at all states of charge but begins to come off at lower frequencies as the degree of discharge is increased, indicating a less reactive system. The 'electrolyte' resistance of the cell generally increases with discharging as ZnO replaces the electrolyte. The fully discharged cell marks the ultimate end to this process and the very complex picture is difficult to interpret.

3.1. State-of-charge test

Attempts to correlate the impedance data with state-of-charge were not really successful, as judged by the correlation coefficients. The best parameter in the range 1–10% discharged was the in-phase impedance component for which a correlation coefficient of ~ 0.85 was found to apply at 0.5 Hz with a gradient of $0.005 \Omega/\text{percentage discharge}$. This is too insensitive for a viable instrument and it was considered that the best procedure would be to recommend that a

'go/no go' test for a satisfactory MN 1500 cell would constitute having a resistance of 0.30Ω at a frequency of 0.5 Hz coupled with an open-circuit voltage of 1.48 V.

Acknowledgement

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