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The impedance of the Leclanché cell.
II. The impedance of the individual cell components

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The impedances of the various component parts of the Leclanché cell have been measured in experiments in which the complete cell is progressively built up. The results confirm previous conclusions that the zinc 'can' provides the impedance characteristic of the assembled cell. The contributions of the other parts of the cell are discussed.

1. Introduction

In a recent review [1] we discussed the feasibility of using the impedance of electrical storage cells as the basis for the development of a nondestructive, *in situ*, state-of-charge indicator. It was concluded that the impedance did indeed offer such a facility and consequently measurements were commenced on the Leclanché cells in order to establish the experimental foundation for the construction of such an instrument.

The results of a study of the impedance of an 'undischarged' Leclanché cell were presented in a later paper [2]. Both Sluyters (complex plane) and Randles (separate resistive and capacitive) representations were used to decompose the cell impedances with the aid of a computer. We were able to suggest that the electrical impedance behaviour of the cell was largely controlled by the zinc 'can', while the 'manganese dioxide' electrode acted as a counter electrode of large area and the manganese/carbon interface produced a combined resistive/capacitive effect. It is known from preliminary experiments on these cells that the impedance frequency response changes markedly on discharging [3]; however, before we can properly ascribe the change in frequency response to any particular element, it is crucial to know the impedance behaviour of each element. It was of interest therefore to examine the behaviour of each elemental component in the cell and this paper describes the results of our investigation.

2. Experimental

The experimental test circuit has already been described [2]. Cell components used were those of the Ever Ready Leclanché-type SP11.* These cells are 26 mm in diameter x 50 mm in height. At 25 mA per cell, these would nominally discharge for 100 h at room temperature [4]. The cells and components were used immediately on receipt from the manufacturer so that no deterioration of the components due to the development of oxide films could take place. The SP11 cell consists essentially of a zinc 'can' containing a paste composed mainly of MnO_2 (53%) with the following additions:

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* We gratefully acknowledge a gift of cell components from the BEREC Group by courtesy of Mr B. Golightly.

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C	7%
ZnO	0.6%
NH_4Cl	16.8%
$ZnCl_2$	7.8%
H_2O	14.8%.

These are separated from the metal by a porous separator of parchment material. At the centre of the paste is a carbon rod with a metal cap to form the current take-off terminal.

In order to facilitate the interpretation of our experimental results, the bottom and the top 1 cm depth of the can were 'stopped-off' with Lacomit. In this way we carried out measurements on a cell with electrodes of cylindrical geometry. In the first group of experiments, the 'can' was filled with an electrolyte solution of 5 M NH_4Cl containing 42.5% $ZnCl_2$. This solution avoided the development of a film of ZnO which would have choked-off the zinc. Raising the carbon contact rod rod ($\phi = 6$ mm) had the effect of reducing the electrode area. In subsequent groups of experiments the effect of each component (MnO_2, carbon, electrolyte) was examined by omitting each component in turn. In some experiments the effect on the impedance of the carbon rod was investigated by replacing it with a cylinder of platinum gauze. This was considered satisfactory for the relatively low acid-strength system in which platinum is not particularly soluble. However, prolonged contact with platinum was avoided for fear of local action due to the hydrogen evolution reaction from platinum centres possibly introduced on to the zinc.

The experimental set-up [2] consisted of a Solatron 1170 frequency response analyser driven by a Kemitron PS40 potential controller. The procedure was to measure the impedance of the various systems at the equilibrium potential, i.e. under conditions of no d.c. at the electrodes. This was achieved by first measuing the open-circuit voltage of the cell, setting this value on the potential controller and carrying out the impedance measurements at this potential. We observed with all the systems investigated that a well-defined open-circuit voltage was rapidly established. At the end of the electrical measurements this voltage was found to be unaltered and furthermore remained unaltered (to within 1 mV) whilst standing on open-circuit for long periods. This was considered a satisfactory criterion that the impedance measurement did not disturb the electrochemistry of the systems.

3. Results and discussion

3.1. *Experiments with a zinc 'can'/42.5% $ZnCl_2$ in aqueous 5 M NH_4Cl/carbon rod cell*

When cells of this type were assembled, the voltages observed between the carbon rod and the zinc electrode 'can' were found to be quite different from experiment to experiment. This potential, when established, was in the range 0.98–1.58 V. For a zinc electrode combined with a carbon electrode in acid solution (pH = 4.2) where hydrogen is evolved, the cell potential would be ~ 0.76 V [5] and hence some considerable degree of depolarisation must be occurring at the carbon electrode. The reduction of oxygen ($4H^+ + O_2 + 4e \rightleftharpoons 2H_2O$ or $2H_2O + O_2 + 4e \rightleftharpoons 4OH^-$) must be the other reaction, its importance depending on pH, mass transport, accessibility of oxygen and other factors. The voltage of the completely air-depolarised cell corresponding to the second equation is ~ 1.5 V, which is in the same region as the highest experimental potentials and confirms the argument that oxygen is the depolarizer involved. The cell potentials were well defined, unaffected by the impedance measurement and stable over a sufficiently long period. It should be noted that our reason for not excluding oxygen was to approach as near as possible to commercial conditions of Leclanché cell manufacture and operation.

Fig. 1 shows the Sluyters plots for two cells with different rest potentials. The numbers shown on the plots are the frequencies in hertz corresponding to the impedance measurements. At both of the rest potentials the carbon electrode was raised and the resulting impedance spectra are shown in Fig. 2. Table 1 gives the salient features of the Sluyters plots. It is clear from the increase of the impedance on reducing the area of the carbon/electrolyte interface that the impedances observed are mainly those of the carbon electrode. The shape of the Sluyters plot for the 0.98 V cell suggests a reaction controlled by charge transfer. From the argument given above concerning the open-circuit potential, we can conclude that the

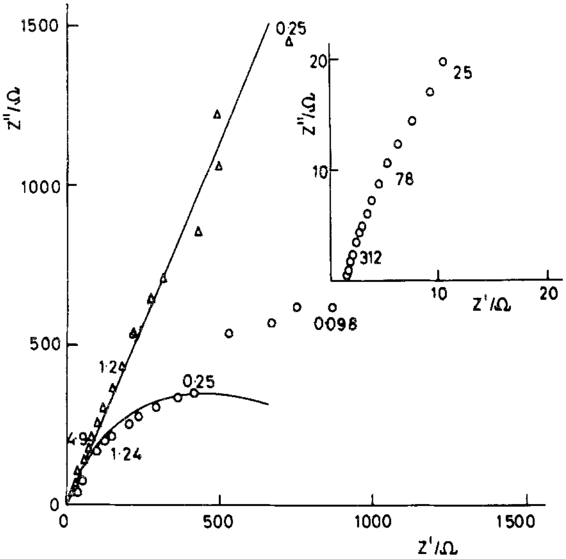

Fig. 1. The complex-plane plot for a carbon rod–electrolyte–zinc system at 23° C. Electrolyte 42% $ZnCl_2$ in 5 M NH_4Cl. ○ 0.98 V, △ 1.58 V.

reaction concerned is the partly-oxygen-depolarized, hydrogen evolution reaction.

The shape of the lower-frequency part of the Sluyters plot for the 1.58 V cell is difficult to interpret and the slope, well in excess of $\frac{1}{4}\pi$, indicates that the electrode is rapidly polarized by the electrode reaction products. At the high-frequency end there is some evidence for the presence of a semicircle, especially for the system with an open-circuit voltage of 0.98 V. An expanded plot of the high-frequency region is also shown in Fig. 1 and the diameter of 17.3 Ω agrees with the high-frequency semicircle for the undischarged commercial cell, suggesting that under these conditions the impedance is due to the zinc electrode. When the carbon electrode area is decreased, the semicircular shapes disappear (Fig. 2) as the impedance of the carbon rod tends to dominate over the full frequency range.

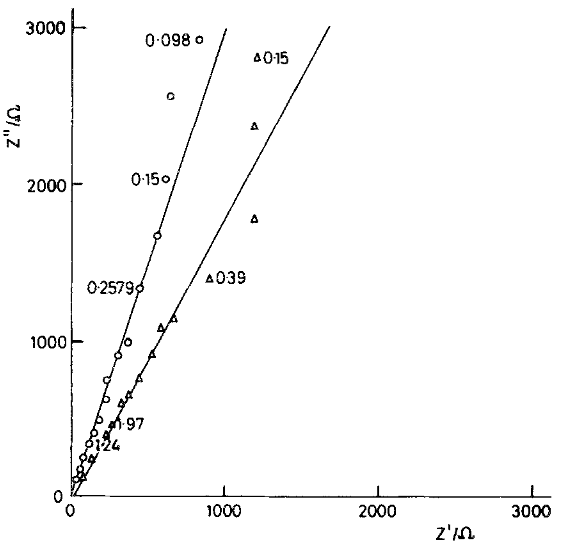

Fig. 2. As Fig. 1. Carbon rod raised by 1 cm. ○ 0.98 V, △ 1.58 V.

3.2. *Experiments with a zinc/42.5% $ZnCl_2$ in aqueous 5 M NH_4Cl/platinum gauze cell*

This system again showed rest potentials which were considerably variable from cell to cell but the range of values observed (0.7–1.1 V) was of smaller magnitude than with the carbon electrode. A similar argument applies to these potentials as we used for the carbon experiments, i.e. that the potential of the platinum is a mixed rest potential of that of the hydrogen evolution reaction and the reaction of hydrogen ions with molecular oxygen to form water. A further feature of these experiments was that the shape of the impedance loci was independent of the length of the gauze used. A series of loci is shown in Fig. 3 corresponding to typical open-circuit potentials in the observed range. In principle, the shapes of the loci are all similar with a small high-frequency semicircle which in some cases is quite well defined. This is followed by a $\frac{1}{4}\pi$ slope which becomes steeper at lower frequency. The Randles plots of R and $1/\omega C$ versus $\omega^{-1/2}$ shown in Fig. 4 indicate quite clearly that, at the higher frequencies, we are dealing with a charge transfer reaction but, at lower frequencies, the parallel lines diverge. Such behaviour would result if the products of electron transfer intruded into the electrode reaction at the zinc and rendered the electrode unreactive. In the simplest case this would be due to a covering of gaseous hydrogen on the zinc electrode. This seems to be the most sensible interpretation and confirms the above observation that changing the platinum electrode area between wide limits does not affect the cell impedance since the hydrogen evolution reaction at a platinum electrode is relatively reversible.

Table 1 gives the salient details of the results. As in the previous case, it is clear that the diameter

Table 1. Summary of results of the Sluyters plots. The dimensions of the zinc cylinder exposed to the electrolyte are $r = 11$ mm, $h = 32$ mm; those of the carbon rod are $r = 3$ mm, $h = 32$ mm. f_0 is the frequency at the top of the semicircle

System	*Open-circuit voltage* (V)	*Low-frequency semicircle*		*High-frequency semicircle*		*Slope of low-frequency line* (degree)
		Radius (Ω)	f_0(Hz)	*Radius* (Ω)	f_0(Hz)	
Zn/electrolyte/carbon rod	0.98	492	0.25	17.3	19.7	–
As above, carbon rod raised by 1 cm	0.98	–	–	–	–	71.5
Zn/electrolyte/carbon rod	1.58	–	–	–	–	66.5
As above, carbon rod raised by 1 cm	1.58	–	–	–	–	66
Zn/electrolyte/Pt gauze (Zn 'can', $h = 1$ cm)	1.12	–	–	1.73	1241	45; 81
As above	1.16	–	–	17.2	39.3	81.5
Zn/electrolyte + carbon/carbon rod	1.04	–	–	4.64	62.4	90
As above	1.23	–	–	3.25	78.5	135
Zn/electrolyte + carbon + MnO_2/carbon rod	1.65	–	–	8.64	12.4	~ 45
As above	1.64	–	–	3.41	78.5	~ 45

of the small semicircle, when corrected for area, coincides with that observed for the undischarged cell and is due to the zinc 'can'.

3.3. *Experiments with a zinc–separator/42.5% $ZnCl_2$ in aqueous 5 M NH_4Cl/carbon–carbon rod cell*

The filling between the carbon rod and the zinc 'can' was identical with the conventional cell-filling mixture except that the manganese dioxide was omitted. (For these experiments it was necessary to include a separator to keep the carbon from contact with the zinc.) This had the immediate effect of narrowing the band of rest potentials observed and the system appeared to be much less polarisable.

The impedance locus of this combination is shown in Fig. 5. It can be seen that the effect of incorporating carbon powder is to considerably reduce the impedance of the system. This may well be the effect of the increased carbon electrode area, for provided that the carbon particles are in good contact, the positive electrode is now formally equivalent to a solution-filled porous electrode of very large area compared to the zinc 'can'. Impedance loci in Fig. 5 show distorted semicircles coming off the real axis at an angle of less than $\frac{1}{2}\pi$ and their diameters are in the same order as those obtained for commercial cells. Furthermore the values of the double layer capacitance estimated from the frequency at the top of the semicircle indicate that the impedance loci correspond to a charge transfer reaction on solid metal, i.e. on the zinc electrode. But the low-frequency data do not correspond to a well-defined line, either at $\frac{1}{4}\pi$ to the real axis for a plane electrode or $\frac{1}{8}\pi$ as for a porous electrode; rather the plot appears more or less as a vertical line which would be characteristic of a polarisable system. We can interpret this using the reactions:

$$Zn^{2+} + 2e \rightleftharpoons Zn \tag{1}$$

at the negative electrode and

$$\begin{aligned} &2H^+ + 2e \rightleftharpoons H_2 \\ \text{and}\quad &2H_2O + O_2 + 4e \rightleftharpoons 4OH^- \end{aligned} \tag{2}$$

at the positive electrode. (Reaction 1 is quite complex and the oxidised species has been represented by such species as $ZnCl_2 \cdot 4ZnO \cdot H_2O$ and $Zn(NH_3)_2Cl_2$ depending on the amount of NH_4Cl present in the system.)

At the lower frequencies, in the absence of MnO_2 as a depolariser for the carbon electrode, the quantity of H_2 or O_2 (from the atmosphere)

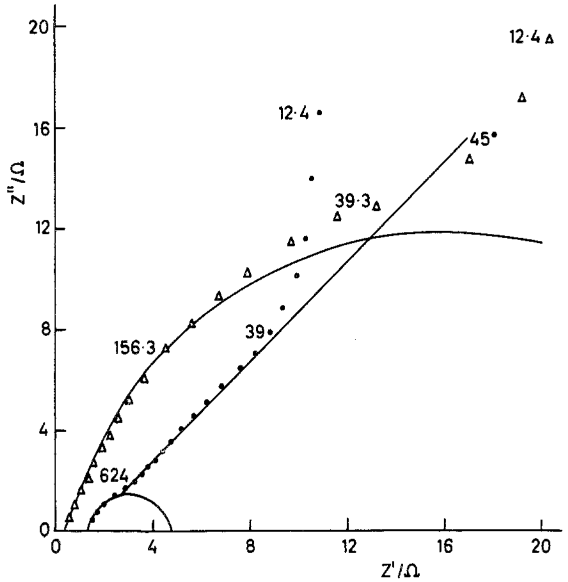

Fig. 3. The complex-plane plot for a platinum gauze–electrolyte–zinc system at 23° C. Electrolyte as Fig. 1. ○ 1.12 V, △ 1.16 V.

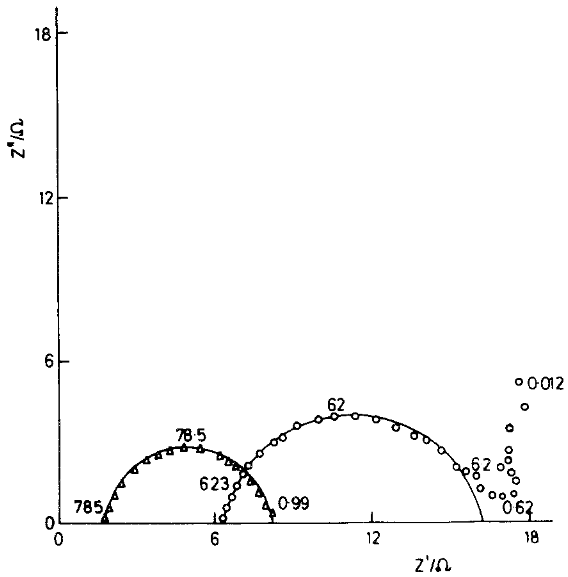

Fig. 5. The complex-plane plot for a carbon/carbon powder/electrolyte/zinc system at 23° C. Electrolyte as Fig. 1. ○ 1.04 V, △ 1.23 V.

that has to be adsorbed and subsequently reconverted on the carbon is high, and any inadequacy in either sorption properties or the electrocatalytic properties of the carbon will be evident as a rapidly increasing impedance. A vertical impedance loci at the low-frequency end of Fig. 5 confirms this deduction. In the intermediate and high-frequency regions, however, the effects of polarisation of the carbon electrode are small and hence the measured impedance values are those due to the charge transfer reaction at the zinc 'can'.

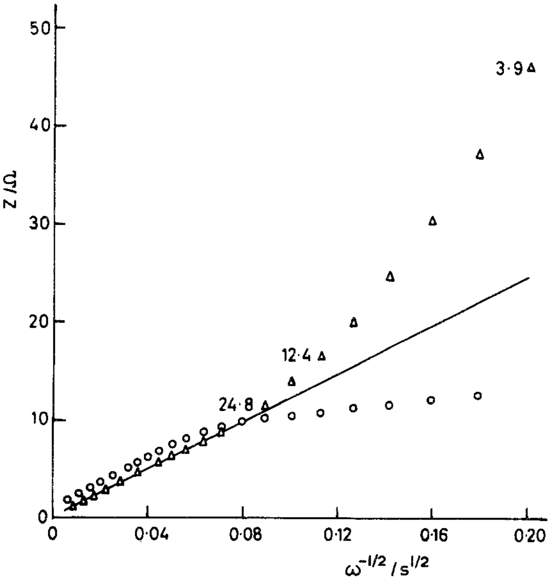

Fig. 4. The Randles plot corresponding to the system of Fig. 3 at 1.12 V. ○ R, △ $1/\omega C$.

According to the theory of porous electrodes [6], the Sluyters plot should be a distorted semicircle coming off the real axis at an angle less than $\frac{1}{2}\pi$. For the case of the semi-infinite pore this angle should in the limit be $\frac{1}{4}\pi$. It is clear that this type of behaviour is observed in Fig. 5, but the initial angle is somewhat greater than $\frac{1}{4}\pi$, probably because the porosity associated with the electrode controlling the impedance in this range cannot be considered as semi-infinite.

The distortion of the semicircle was tested by the process of 'squaring' outlined by de Levie [6] and this produced the curves shown in Fig. 6. The plots are much more closely semicircular in shape throughout the range of rest potential observed. By comparing Figs. 5 and 6, it is seen that the centre of the high-frequency semicircular shape falls on the real axis. The semicircles are, however, overcompensated at the high-frequency side. This may be due to either one or two reasons. First we may have incorrectly assessed the 'solution resistance' of the system. This is found from our maximum available frequency and since 10 kHz is the top limit it may not be the best choice. Alterna-

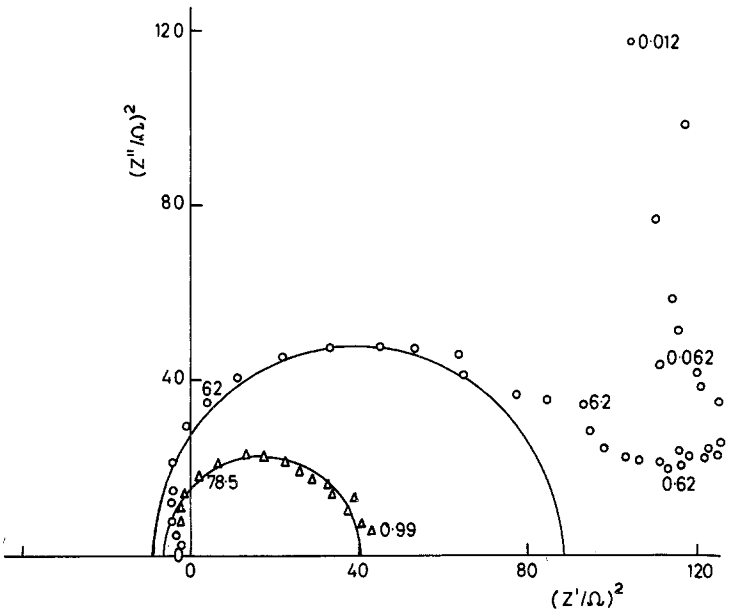

Fig. 6. The results of the process of 'squaring' the data of Fig. 5.

tively it is much more likely that the pore length of the structure of the Zn 'can'/electrolyte side cannot be considered 'infinite' as required by theory [6]. A more closely semicircular shape appears only after squaring because the mercury in the separator causes the zinc electrode to become porous as in the previous combinations. The mercury attacks the zinc giving rise to an initial porosity effect with grain boundaries being preferentially attacked by the mercury as amalgamation proceeds. This apparently engenders a degree of porosity which is progressively removed on standing when the surface structure becomes more uniform as a consequence of more complete overall amalgamation.

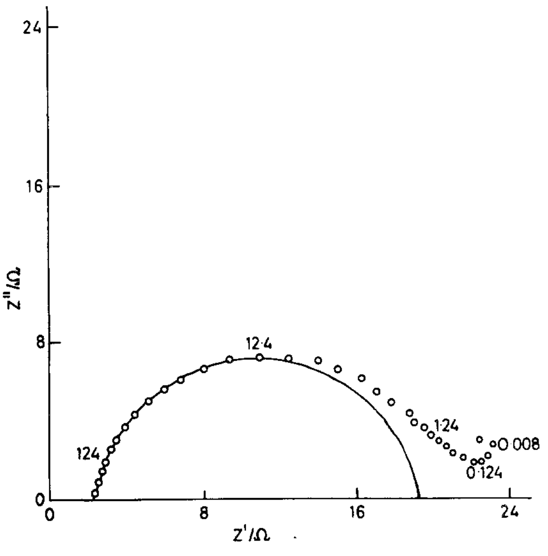

Fig. 7. The complex-plane plot for a carbon/carbon–MnO_2/electrolyte/zinc system at 23° C and 1.65 V. Electrolyte as Fig. 1.

3.4. *Experiments with a zinc–separator–electrolyte/carbon/manganese dioxide–carbon cell*

The filling between the carbon rod and the zinc 'can' was identical in every respect with the conventional mixture for the cell including the separator. The rest potential (1.65 V) was now formally that of the undischarged new cell and was constant from cell to cell to within 10 mV. In comparison with commercially available units the potentials of our assemblies were about 10 mV higher; we were unable to ascribe this to any factor.

Fig. 7 shows the impedance locus of the assemblies. The curve is similar in shape to that of the 'carbon' cells at high frequency, i.e. a distorted semicircle, but at low frequencies the assembly is very polarisable. The Warburg component is not, however, the normal $\frac{1}{4}\pi$ slope for the plane electrode (or $\frac{1}{8}\pi$ for the porous electrode) characteristic of diffusional control, but degenerates to a point. This is characteristic of a reactive but relatively unpolarisable system. As before we have tested the porosity effect by the 'squaring' pro-

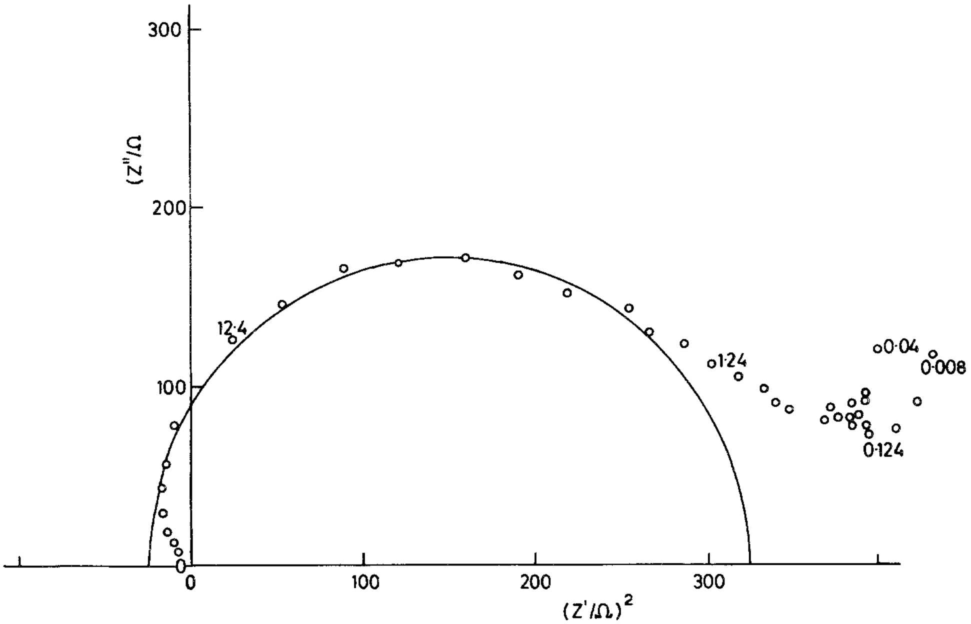

Fig. 8. The results of 'squaring' the data of Fig. 7.

cedure and Fig. 8 shows the results. A somewhat over-compensated semicircle is observed at higher frequencies with a Warburg-type impedance part coming off at low frequency. These plots agree in magnitude and position of the semicircle with our previous work on commercially produced Leclanché cells. The explanation offered in the previous section, based on considerations of porosity, seems to hold equally well here, for when the cell assembly was stored, the locus of the impedance agreed with that of the undischarged SP11 cell.

4. Conclusions

(a) The carbon rod in ammonium chloride electrolyte is a fairly polarisable electrode.

(b) The effect of the addition of powdered carbon to the electrolyte phase with separation of the electrodes by a parchment separator is to form a fairly polarisable, highly porous electrode with a large surface area.

(c) The effect of manganese dioxide is to depolarise the carbon electrode and the cell impedance becomes that associated with the zinc 'can'.

(d) The impedance in the frequency range (10 kHz to 0.001 Hz) of the undischarged Leclanché cell is that of the zinc 'can'.

Acknowledgement

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References

[1] N. A. Hampson, S. A. G. R. Karunathilaka and R. Leek, *J. Appl. Electrochem.* **10** (1980) 3.
[2] S. A. G. R. Karunathilaka, N. A. Hampson, R. Leek and T. J. Sinclair, *ibid* **10** (1980) 357.
[3] *Idem*, *ibid* in press.
[4] 'Modern Portable Electricity', Ever Ready Company, London (1976). Interpolated value.
[5] R. Huber, 'Trockenbatterien und Luftsauerstoffelemente', Varta Aktiengesellshaft, Hanover (1972) p. 80.
[6] R. de Levie in 'Advances in Electrochemistry and Electrochemical Engineering', Vol. 6 (edited by P. Delahay) John Wiley Interscience, New York (1967) p. 329.