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Influence of methylcellulose-coated paper separators on the corrosion, polarization and impedance characteristics of zinc in concentrated ammonium chloride solution. II. Comparison of data obtained in flooded electrolyte and battery environments

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An attempt has been made to determine *in situ* the corrosion rate of the zinc anode in Leclanché batteries devoid of $ZnCl_2$ in the electrolyte using steady-state polarization and a.c. impedance techniques. Previously obtained corrosion data for zinc immersed in flooded NH_4Cl electrolyte has been used as a point of reference with which to compare the *in situ* data and hence gauge its legitimacy. It is shown that in the case of cells containing *uncoated* paper separators, good agreement between the two sets of data is obtained, thus demonstrating that *in situ* corrosion rate measurements can be made. This allows the effects of ionic composition, zinc alloying constituents, amalgamation level, electrolyte impurities, and the role of oxygen, etc, to be determined in the battery environment. However, the anode polarization and impedance characteristics of $ZnCl_2$-free cells containing methylcellulose-*coated* paper separators do not reflect corrosion processes. In fact the electrochemical data is almost indistinguishable from that obtained in $ZnCl_2$-containing cells. It is postulated that the presence of the methylcellulose layer permits the zinc ion concentration to build up adjacent to the anode causing the cathodic hydrogen evolution process to be electrochemically masked by zinc deposition. The electrochemical characteristics therefore reflect zinc *exchange* processes only. Neither the presence of the separator coating itself nor the restricted volume of electrolyte appear to be unilaterally responsible for the anomalous behaviour of $ZnCl_2$-free cells, but rather a combination of these two conditions is necessary. Thus considerably restricted diffusion and the near absence of convection would appear to be the important factors which dictate the observations.

1. Introduction

In two earlier papers it was shown that the presence of methylcellulose-coated paper separators adjacent to planar zinc electrodes in flooded Leclanché and related electrolytes has a profound effect upon the rates of the zinc exchange reaction [1] and corrosion processes [2]. It was also demonstrated that the influence of the separator is quite specific, being dependent upon the particular reaction pertaining and the nature of the electroactive species present. A comparison of data obtained for the zinc exchange reaction in flooded Leclanché electrolyte with that in the battery environment revealed good agreement if the effects of surface roughness differences between the model zinc electrode and real battery anode were taken into account [1]. However, no attempt was made to establish whether a similar meaningful comparison of *corrosion* data could be made [2]. The present communication therefore seeks to redress the balance.

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The corrosion processes, and in particular the hydrogen evolution reaction, can only be characterized electrochemically using simple polarization techniques when the concentration of zinc ions in solution is very low [3, 4]. As a result of this, polarization and impedance measurements have been performed on R20 size Leclanché cells containing an electrolyte of concentrated NH_4Cl in place of the NH_4Cl–$ZnCl_2$ mixture normally present. The data from these experiments have been compared and contrasted with those obtained previously [1, 2]. Although the majority of the experiments have been performed with sealed cells or deoxygenated flooded electrolytes, a small number have also been performed with unsealed cells to reveal the effect of oxygen.

2. Experimental details

Materials, electrode preparation, cell, electrode assemblies, solution purification and general procedure have been described in Part I [2]. Experiments in flooded electrolyte were conducted with deaerated solutions.

Reference electrodes for studies in complete cells consisted of amalgamated zinc wires. These proved to form highly stable metal/metal-ion electrodes in the battery electrolytes. Other reference electrode types were examined, but were unsuccessful. The reference electrodes were constructed as follows. Disposable plastic pipette tips having a maximum diameter (at the pipette end) of 5 mm were first plugged with clean cotton wool and then filled with gelled electrolyte. The pipette tips were removed to yield an orifice of about 1 mm diameter. Zinc wires of diameter 1 mm were amalgamated using the technique described in Part I [2], inserted into the pipette assemblies and then sealed with hot-melt adhesive. Reference electrodes were inserted through a pre-drilled hole approximately mid-way down the cell such that they rested either just inside the can wall (anode impedance or polarization studies) or in the cathode mix (cathode impedance studies). Complete cells were either sealed or unsealed using a bitumen layer between the zinc can and the cathode current collector (carbon rod).

3. Results and discussion

3.1. *Experiments with uncoated paper separators*

Fig. 1 compares the complex plane impedance spectrum for a complete $ZnCl_2$-free Leclanché cell made with an uncoated paper separator with that obtained for a model zinc–flooded electrolyte system. It can be seen that the agreement between the two spectra is very good. This is an important result because it demonstrates that in the case of cells made with uncoated paper separators and elecrolyte devoid of $ZnCl_2$ the cell impedance reflects only corrosion processes at the zinc anode. Thus the impedance of the manganese dioxide cathode must be negligible in comparison with that of the anode as in the case of cells made with the complete Leclanché electrolyte formulation [1, 5]. The impedance spectrum consists of a large semicircle of diameter 135–160 Ωcm^2 followed by a much smaller semicircle, which is very difficult to resolve, and finally a shape which is consistent with a Warburg impedance. This is the straight line portion of the spectrum which collapses to the real axis as $\omega \rightarrow 0$. The corrosion rate is inversely proportional to the intercept $Z_{\omega \rightarrow 0}$ as discussed in Part I [2] and the process is diffusion controlled. This was confirmed by rotating the zinc electrode at 1000 r.p.m. in flooded electrolyte. Fig. 2 compares the impedance spectra obtained for the stationary and rotating situations. The change in the polarization resistance $R_p = (dE/di)_{i \rightarrow 0}$ is also inset. Clearly the corrosion rate increases significantly and this can be attributed either to stimulation of the anodic zinc dissolution component of the corrosion couple or increase in the rate of cathodic H_3O^+ reduction, which may become rate determining in place of NH_4^+ reduction on rotating electrodes [4]. Bearing in mind the results obtained in Part I, which showed the zinc dissolution process to be quasi-reversible [2], a rotation speed dependence would be predicted on the basis of this reaction alone. Hence a rotation speed dependence of the impedance diagram would also be expected and this has been demonstrated by Armstrong and Bell [6] for the case of zinc dissolution in alkaline solution which is also a quasi-reversible process.

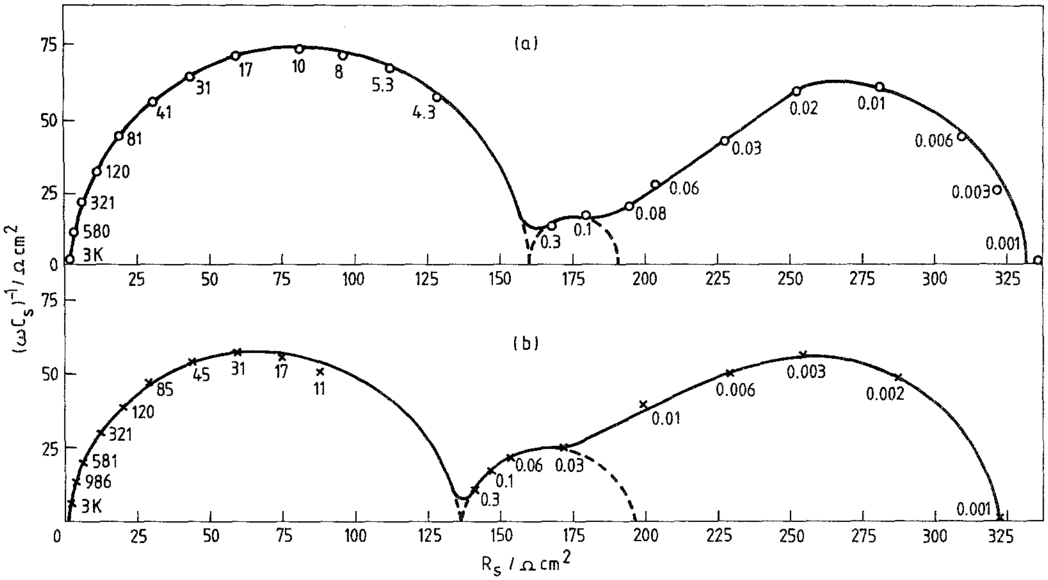

Fig. 1. Comparison of impedance spectra in flooded electrolyte and battery environments (frequency range 50 kHz–1 mHz). (a) Spectrum for a $ZnCl_2$-free, R20 size Leclanché cell containing an uncoated paper separator and no calomel; (b) spectrum for stationary pure zinc in flooded 6 M NH_4Cl.

Cachet and Wiart [7] have investigated the zinc dissolution reaction in Leclanché and related electrolytes using the impedance technique. In 2.67 M NH_4Cl at current densities in the range 4 to 40 mA cm^{-2} a low frequency capacitive loop was revealed between 12 and 0.3 Hz. The presence of this feature in the impedance spectrum appears to be in qualitative agreement with the low-frequency semicircles in Fig. 1. Although it is likely that this characteristic reflects the

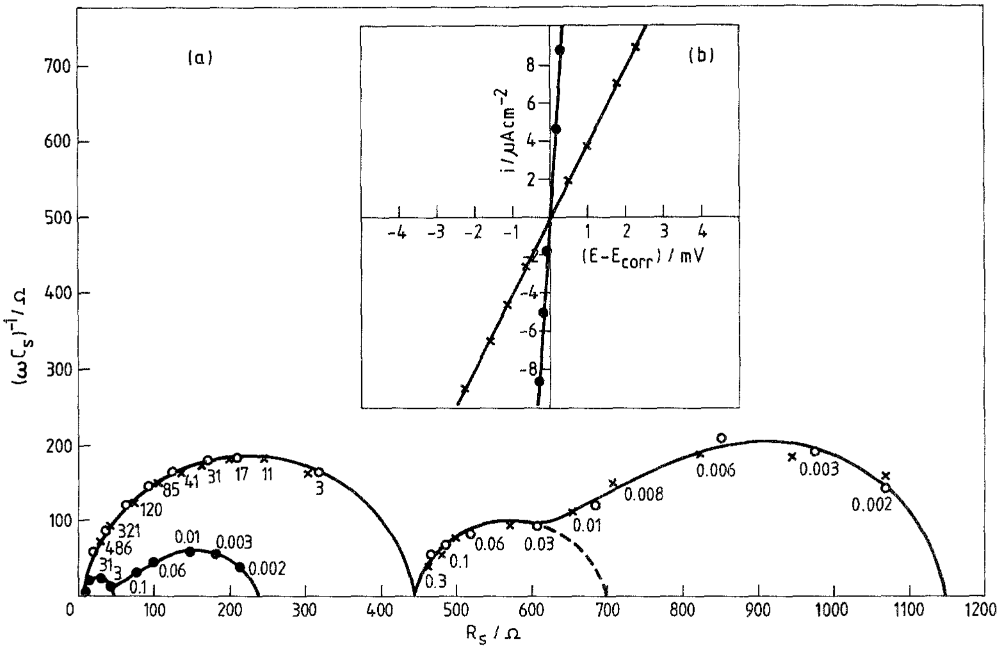

Fig. 2. (a) Impedance spectra (frequency range 50 kHz–2 mHz) and (b) polarization data at the rest potential for pure zinc in flooded 6 M NH_4Cl as a function of electrode rotation speed: ○×, stationary electrode; ●, electrode rotating at 1000 r.p.m.

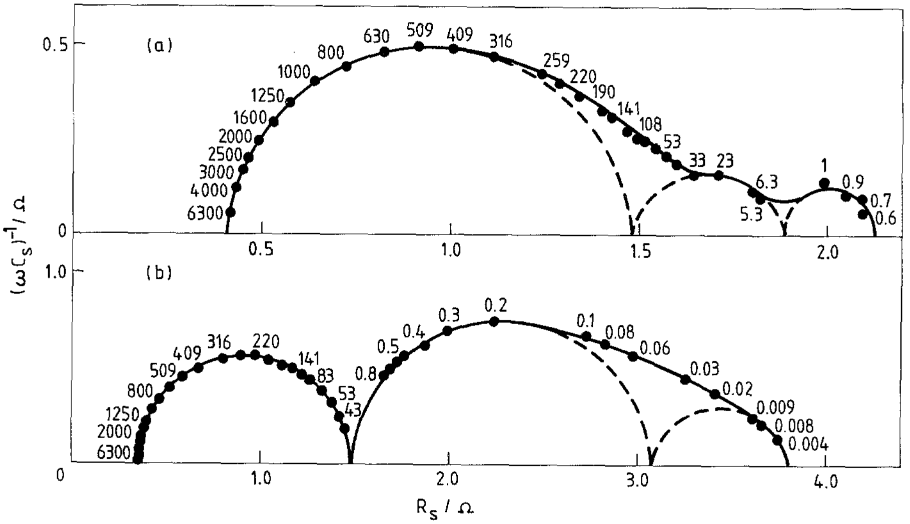

Fig. 3. Comparison of impedance spectra (frequency range 100 kHz–4 mHz) for a pure zinc rotating disc electrode (3000 r.p.m.) in flooded electrolytes at pH 2: (a) 2.67 M NH_4Cl; (b) 2.67 M NH_4Cl + 0.24 M $ZnCl_2$.

relaxation of an intermediate species in the dissolution reaction, which is probably adsorbed, the chemical nature of the species is not certain. In general it has been shown that *three* low-frequency relaxation processes can be revealed in Leclanché electrolyte: two inductive and one capacitive. It is usual to associate one of the inductive loops with relaxation of the adsorbed species Zn(I). In order to establish whether a low-frequency capacitive impedance could be obtained at the corrosion potential under similar conditions to those pertaining in the work of Cachet and Wiart [7], impedance measurements were performed on zinc electrodes rotating at 3000 r.p.m. either in 2.67 M NH_4Cl or 2.67 M NH_4Cl + 0.24 M $ZnCl_2$ at pH 2. At this speed of rotation any influence of diffusion is largely eliminated and the low pH value prevents interference from the formation of oxide films on the electrode [8, 10]. Fig. 3 shows the results. Although difficulty was experienced in determining the very low-frequency spectra, it is clear that the low-frequency capacitive loop persists even in strongly acid solutions. Interestingly, the size of the capacitive loop increases with $ZnCl_2$ concentration. It can also be seen from Fig. 3 that a *second* low frequency capacitive loop may exist, although it is very difficult to distinguish from a rapidly collapsing Warburg impedance.

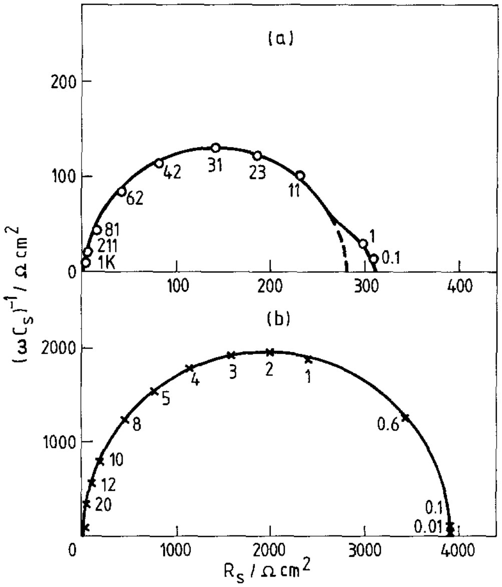

Fig. 4. Comparison of impedance spectra in flooded electrolyte and battery environments (frequency range 50 kHz–1 mHz). (a) Spectrum for a $ZnCl_2$-free, R20 size Leclanché cell containing the complete methylcellulose-coated calomel impregnated paper separator; (b) spectrum for amalgamated zinc (130 $\mu g\,cm^{-2}$) in flooded 6 M NH_4Cl in the presence of the complete methylcellulose coated paper separator.

3.2. *Experiments with coated paper separators*

3.2.1. Sealed cell construction. Fig. 4 compares the complex plane impedance spectrum for a complete $ZnCl_2$-free Leclanché cell made with a calomel impregnated methylcellulose-coated paper separator with that obtained for a model Zn(Hg)–methylcellulose–paper–flooded NH_4Cl

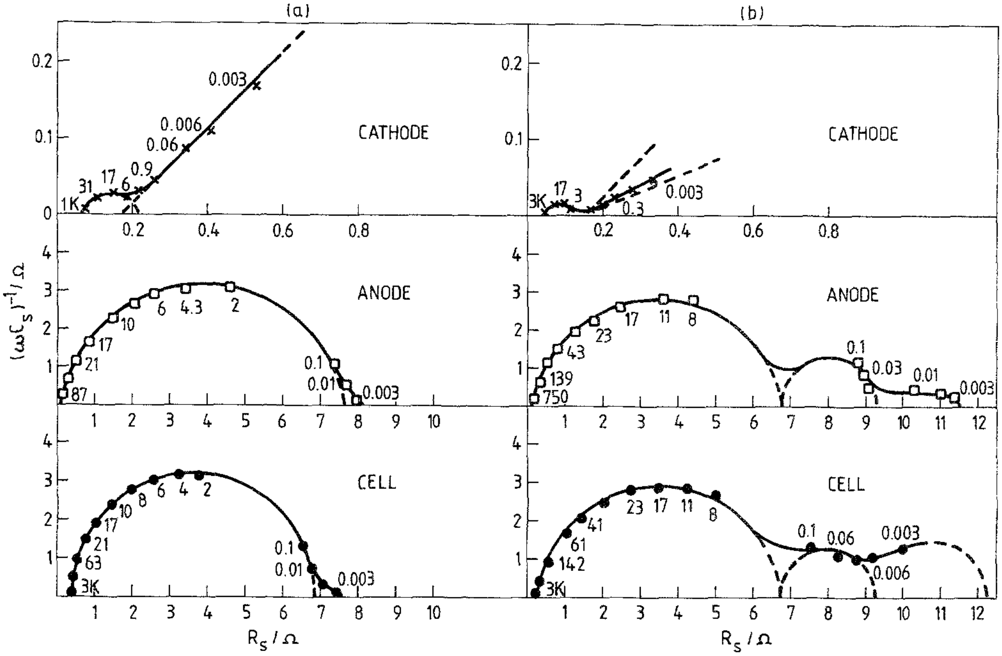

Fig. 5. Decomposition of impedance characteristics (frequency range 50 kHz–3 mHz) for R20 size Leclanché cells incorporating methylcellulose-coated calomel impregnated paper separators. (a) $ZnCl_2$-free cells; (b) standard $ZnCl_2$-containing cells; ×, cathode impedance; □, anode impedance, ●, complete cell impedance.

system. It can be seen that unlike the situation depicted in Fig. 1 for the uncoated paper, no agreement in the magnitude of the impedance is obtained. In fact the charge transfer resistance values differ by well over an order of magnitude. In order to explore further the problem and establish any influence from the MnO_2 cathode, measurements were made on the anode and cathode in turn and the results are depicted in Fig. 5a*. It is clear from this figure that the impedance of the MnO_2 is negligible and hence the cell impedance is dominated by that of the anode as in the case of $ZnCl_2$-free cells containing uncoated paper and Leclanché cells containing the complete electrolyte and separator formulations. Fig. 5b shows a breakdown of the impedance in the case of the latter. The similarity between Fig. 5a and 5b is striking. Whilst the low frequency spectra in the presence of $ZnCl_2$ show evidence of a capacitive loop and probably some diffusion effects as $\omega \longrightarrow 0$, any other differences appear to be negligible. In particular, the value of the charge-transfer resistance is very nearly independent of the presence of $ZnCl_2$. It can therefore be concluded from these results that the impedance spectrum shown in Fig. 4a is anomalous. The anomaly can be ascribed to the methylcellulose *coating* on the paper separator which apparently allows the $ZnCl_2$ concentration to build up close to the zinc surface to such an extent that the impedance characteristics become those of the Zn/Zn(II) exchange reaction rather than the corrosion process. This does not happen in flooded electrolyte (Fig. 4). Fig. 6 indicates the *expected* response in the polarization and impedance characteristics to the presence or absence of $ZnCl_2$ in the bulk electrolyte which is not apparently observed in the battery environment. The data refer to amalgamated zinc in flooded electrolyte. Here it is clear that the influence of $ZnCl_2$ in the electrolyte is appreciable. The charge-transfer resistance is greatly reduced from 14 to 2.2 kΩ and the polarization curves are significantly affected, in par-

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* In the diagrams for the anode and cell there is no data between 2 Hz and 0.1 Hz due to difficulties in determining the impedance at the bottom of the range for the lock-in amplifier method and the top of the range for the Lissajous figures method, respectively. This defect, however, does not influence the precision of the final diagrams.

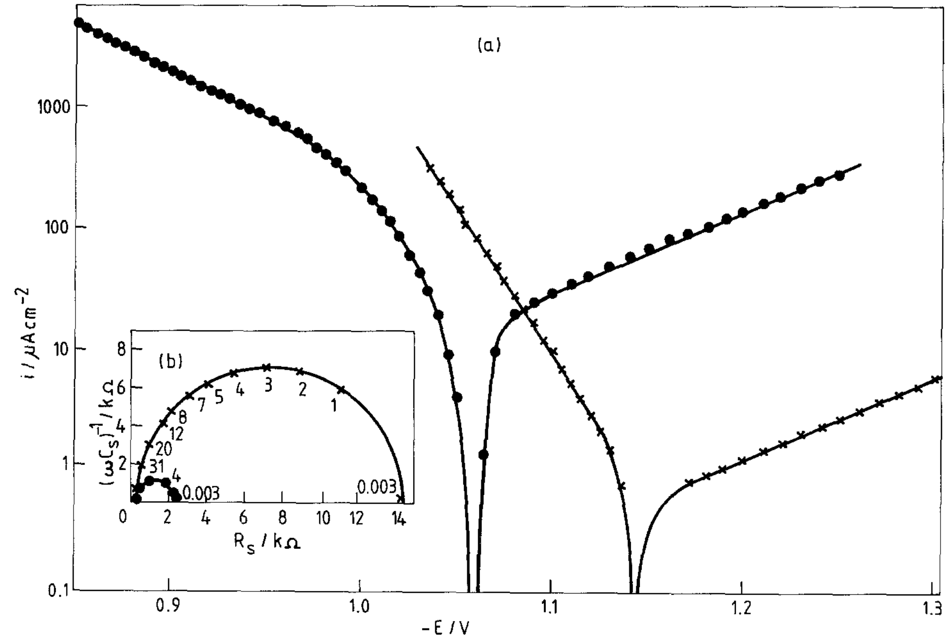

Fig. 6. (a) Polarization characteristics and (b) impedance spectra at the rest potential (frequency range 50 kHz–3 mHz) for the electrode–separator system Zn(Hg)–methylcellulose–paper in flooded electrolytes; ●, 6 M NH_4Cl + 2 M $ZnCl_2$; ×, 6 M NH_4Cl.

ticular, during cathodic polarization, where zinc deposition rather than hydrogen evolution is observed. Essentially, it is this change in the nature of the predominant cathodic process which allows the zinc exchange characteristics to be revealed at the open-circuit potential [1] rather than corrosion characteristics [2].

In an attempt to obtain more information about the anomalous behaviour of $ZnCl_2$-free Leclanché cells, anode polarization and impedance measurements were performed at various amalgamation levels. The results are shown in Fig. 7. Again, these results are both qualitatively and quantitatively very similar to those obtained for cells containing the complete Leclanché electrolyte formulation depicted in Fig. 8 which have been discussed previously [1]. Whilst the anodic polarization curves show evidence of mass transfer the cathodic curves conform very closely with charge transfer-controlled zinc deposition processes with Tafel slopes of approximately 120 mV per decade [1]. This is particularly true of the cathodic process in the pure NH_4Cl electrolyte where the slope is exactly 120 mV at the 1 mg Hg cm^{-2} level over a fair range of potentials (Fig. 7). For other mercury levels deviations from this slope occur at higher potentials. This is most severe at the 10 μg level at potentials < -110 mV. These results could be explained by assuming that excessive deposition of zinc, perhaps in the form of localized centres, results in significant area increases at the *higher* cathodic potentials. This could be more severe in the case where the surface concentration of mercury is low, since it would be expected that the higher the mercury concentration the more homogeneous the nature of the deposit. This represents a reversal of behaviour at lower potentials. However, further experimental proof of this hypothesis is required.

Although many features of Figs 7 and 8 compare very favourably, one difference is worthy of consideration. The very low-frequency impedance for the $ZnCl_2$-free cell (Fig. 7c) shows the influence of mass-transfer effects to a greater extent than that for the $ZnCl_2$-containing cell. Thus a complete Warburg impedance appears, of slope 45°, which shows no sign of collapse even at the lowest frequency studied (3 mHz). This can occur if the rate of the interfacial exchange reaction is *higher* in the case of the $ZnCl_2$-free cell due to either to an increase in the

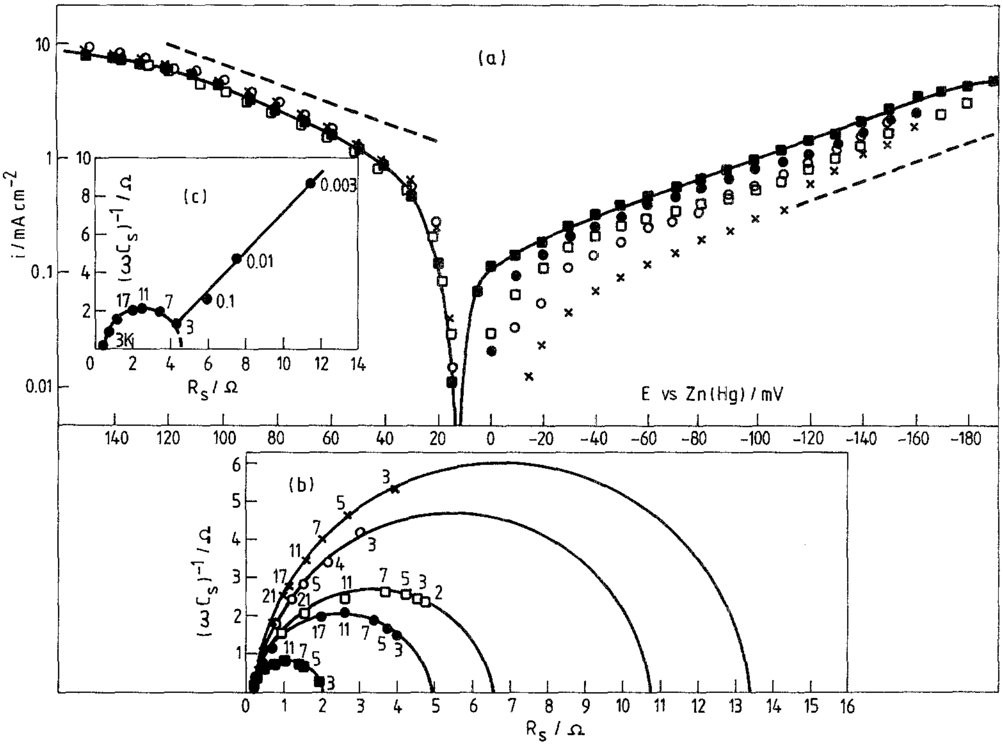

Fig. 7. Effect of amalgamation level on the polarization and impedance characteristics of the anode in $ZnCl_2$-free, R20 size Leclanché cells containing the complete methylcellulose-coated paper separator formulation. (a) Polarization curves at an amalgamation level of: ■—■, 1 mg cm^{-2}; ●, 100 μg cm^{-2}; □, 50 μg cm^{-2}; ○, 20 μg cm^{-2}; ×, 10 μg cm^{-2}; and (– – – –) Tafel lines of slope 120 mV per decade. (b) High-frequency impedance spectra (frequency range 50 kHz–3 Hz) at the equilibrium potential (symbols as above). (c) Impedance spectrum over the complete frequency range (50 kHz–3 mHz) at an amalgamation level of 100 μg cm^{-2}.

effective surface concentration of Zn(II) species or an increase in the effective amalgamation level. Table 1 summarizes cell internal resistance, R_Ω, charge-transfer resistance, R_{ct}, and charge transfer-derived exchange current values, i_0, obtained in the two types of cell over the complete range of mercury concentrations. The procedure for determining these parameters has been discussed previously [1]. It is clear that the exchange current is only higher in the $ZnCl_2$-free cells at amalgamation levels $> 50\,\mu g\,cm^{-2}$. At lower levels, the exchange current shows no systematic trend with mercury level. Fig. 9 shows an attempt at an empirical fit of the i_0 versus amalgamation level data. The mercury concentration must be raised to the power 0.4 in order to achieve approximate linearity. However, it is clear that the plots are divergent and

Table 1. Comparison of impedance-derived parameters for standard and $ZnCl_2$-free Leclanché cells as a function of anode amalgamation level

[Hg] ($\mu g\,cm^{-2}$)	$R_\Omega^{Zn^{2+}}$ ($\Omega\,cm^2$)	$R_\Omega^{NH_4^+}$ ($\Omega\,cm^2$)	$R_{ct}^{Zn^{2+}}$ ($\Omega\,cm^2$)	$R_{ct}^{NH_4^+}$ ($\Omega\,cm^2$)	$i_0^{Zn^{2+}}$ ($\mu A\,cm^{-2}$)	$i_0^{NH_4^+}$ ($\mu A\,cm^{-2}$)
10	7.2	7.2	478	446	27.2	29.2
25	7.1	7.1	360	403	36.1	32.3
50	7.0	7.0	288	216	45.3	60.3
100	7.2	7.1	216	176	60.3	74.1
1000	7.3	7.0	108	72	121.0	181.0

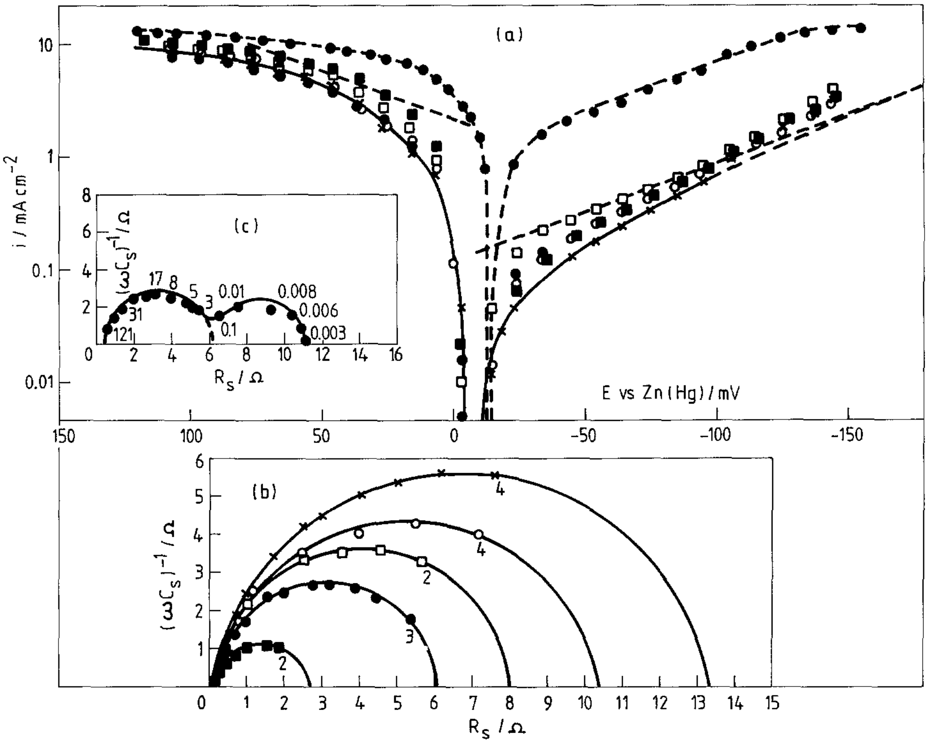

Fig. 8. Effect of amalgamation level on the polarization and impedance characteristics of the anode in $ZnCl_2$-containing R20 size Leclanché cells incorporating the complete methylcellulose-coated paper separator formulation. (a) Polarization curves at an amalgamation level of: x——x, $10\,\mu g\,cm^{-2}$; ○, $20\,\mu g\,cm^{-2}$; □ $50\,\mu g\,cm^{-2}$; ●, $100\,\mu g\,cm^{-2}$; ■, $1\,mg\,cm^{-2}$; and (– – – – – –) Tafel lines of slope 120 mV per decade. (b) High-frequency impedance spectra (frequency range 50 kHz–3 Hz) at the equilibrium potential (symbols as above). (c) Impedance spectrum over the complete frequency range (50 kHz–3 mHz) at an amalgamation level of $100\,\mu g\,cm^{-2}$.

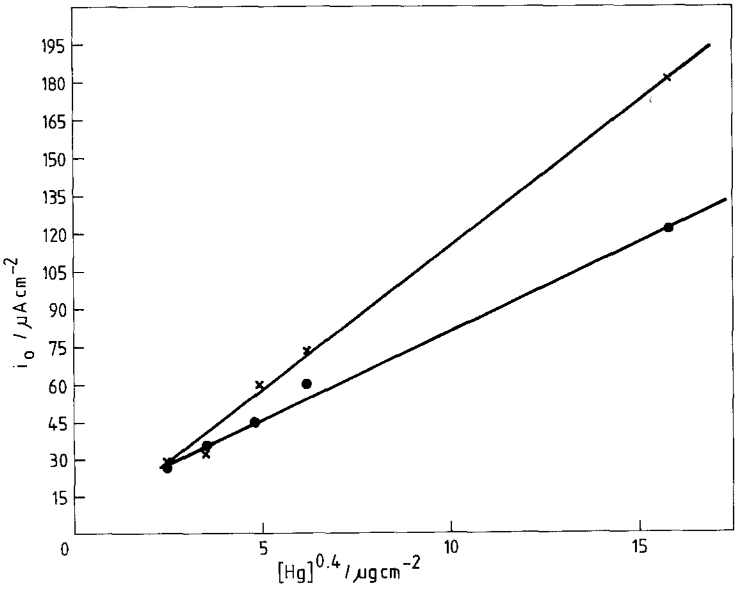

Fig. 9. Empirical relationship between the exchange current on the zinc anode and amalgamation level for R20 size Leclanché cells containing the complete methylcellulose-coated paper separator; x, $ZnCl_2$-free cells; ●, $ZnCl_2$-containing cells.

not parallel as would be required, for example, if the effective Zn(II) concentration at the anode surface were higher in the $ZnCl_2$-free electrolyte and the effective mercury concentration was independent of the electrolyte composition. Conversely, a theory which assumes an approximately constant surface concentration of Zn(II) but a higher effective mercury concentration in the $ZnCl_2$-free electrolyte also fails to explain the data, since this also would be expected to produce parallel plots. Nevertheless, further resolution of this problem is beyond the scope of the present investigation.

It it interesting to note from Table 1 that the internal resistance of the cells, R_Ω, is apparently independent of the presence of $ZnCl_2$ in the bulk electrolyte. This is unexpected in view of the fact that the conductivity ratio is about 1.5 : 1 in favour of the mixed electrolyte. This anomaly can be explained, however, if it is assumed that the contribution from the electrolyte resistance to the total internal resistance of the cell is determined principally by the electrolyte resistance *within* the separator, and in the case of cells originally devoid of $ZnCl_2$, the concentration of $ZnCl_2$ within the separator is significantly higher than that in the bulk. This result therefore provides further evidence that in the case of $ZnCl_2$-free cells, the $ZnCl_2$ concentration within the separator builds up fairly rapidly in the early stages of storage.

Two major conclusions can be drawn from the results obtained with $ZnCl_2$-free Leclanché cells containing the complete separator formulation. Firstly, as a result of their anomalous electrochemical behaviour, anode corrosion data cannot be determined by simple polarization techniques, and therefore in order to obtain such information measurements must be made with flooded electrolyte. This result contrasts with that obtained for $ZnCl_2$-free cells constructed with *uncoated* separators, discussed previously, where corrosion measurements are possible. Thus, neither the presence of a coated paper nor a restricted volume of electrolyte are unilaterally sufficient conditions to cause the anomalous behaviour of $ZnCl_2$-free cells, but rather a *combination* of these two conditions is necessary. The second conclusion concerns the fact that the electrochemical characteristics of $ZnCl_2$-free and standard $ZnCl_2$-containing cells are almost *identical*. This suggests that in the undischarged state a maximum equilibrium zinc ion composition and concentration is achieved within the methylcellulose coating irrespective of the bulk electrolyte composition. The fact that this

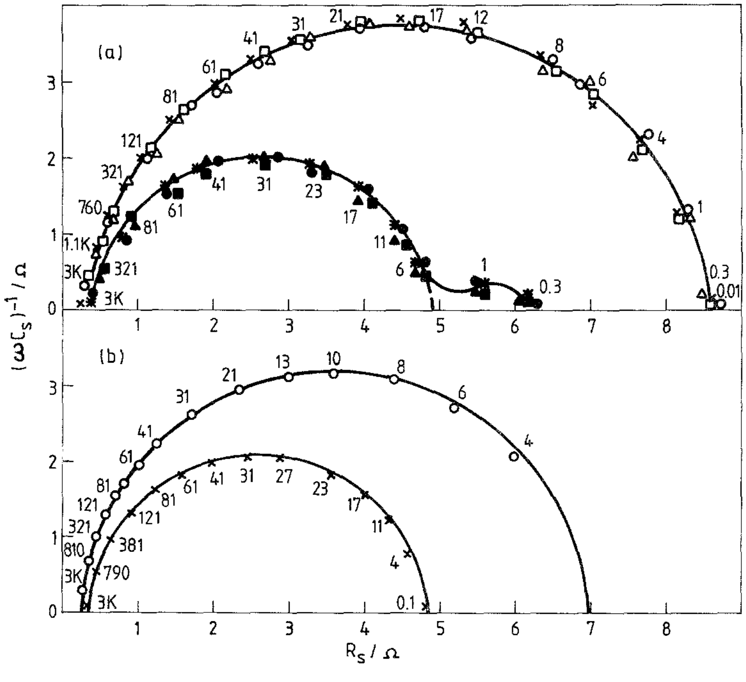

Fig. 10. Effect of oxygen on the impedance spectra of $ZnCl_2$-free Leclanché cells containing the complete methylcellulose-coated calomel impregnated paper separator formulation. (a) Impedance spectra for: □△×○, sealed cells; ■▲*●, unsealed cells (frequency range 50 kHz–1 mHz). (b) Impedance spectra for: ×, an unsealed cell in an air enclosure; ○, the same unsealed cell after flushing the enclosure with pure nitrogen for 5 h.

does not occur in flooded electrolyte proves that the near absence of convective effects and more restricted diffusion in the battery environment contributes significantly to the observation. What is by no means clear, however, is why a *critical* composition should be achieved as if the separator possessed some 'threshold capacity' for zinc ions. This points to a quite specific effect of the methylcellulose coating layer which requires further investigation.

3.2.2. Unsealed cell construction. Fig. 10a compares the impedance spectrum for unsealed $ZnCl_2$-free cells with that for sealed cells. It is clear that good reproducibility of experimental data is obtained. The effect of oxygen is to decrease the magnitude of the charge-transfer resistance by $\sim 50\%$ and hence increase the exchange current by a factor of two. This is accompanied by the appearance of some low-frequency detail which is consistent with mass transfer (collapsing Warburg impedance) resulting from the increased interfacial reaction rate. The influence of oxygen was also studied in another way. An unsealed cell was placed in a small plastic sealed box filled with air and its impedance spectrum determined. The box was then flooded with oxygen-free nitrogen for 5 h and the impedance remeasured. The results are shown in Fig. 10b. It can be seen that on flooding the enclosure with nitrogen the charge-transfer resistance increased from 4.5 to 6.2 Ω.

Table 2 compares values for the charge-transfer resistance, double-layer capacity and open-circuit voltage (OCV) obtained from the data of Fig. 10a. It can be seen that in addition to a lower charge-transfer resistance, the unsealed cells have a higher double-layer capacity and a lower OCV. Therefore, the change in double-layer capacity and charge-transfer resistance can be reconciled purely in terms of the change in the *potential* of the zinc anode. This in turn is caused by the depolarizing effect of oxygen which shifts the zinc potential by 20 mV in the positive (anodic) direction. (An increase in the double-layer capacity signifies that the zinc potential in both the sealed and unsealed cases is *positive* of the minimum in the capacity–potential profile. The more anodic potential will therefore be associated with the higher capacity.) These results provide further evidence that corrosion processes cannot be investigated in $ZnCl_2$-free cells containing the complete separator formulation, even in the presence of oxygen.

Table 2. Comparison of impedance parameters and open-circuit voltage for sealed and unsealed $ZnCl_2$-free Leclanché cells

Cell		R_{ct} (Ω)	R_{dc} (Ω)	C_{dl} ($\mu F cm^{-2}$)	*OCV* (*V*)
Sealed	1	8.15	8.45	31	1.592
	2	8.15	8.45	31	1.566
	3	8.25	8.55	31	1.583
	4	8.15	8.45	31	1.576
Mean		8.17	8.48	31	1.580
Unsealed	1	4.65	6.00	39	1.550
	2	4.65	6.00	36	1.552
	3	4.65	6.00	39	1.556
	4	4.65	6.00	38	1.582
Mean		4.65	6.00	38	1.560

4. Conclusions

1. In $ZnCl_2$-free Leclanché cells containing *uncoated* paper separators the impedance characteristics reflect corrosion processes at the zinc anode. This result permits corrosion data to be obtained in a complete battery environment and, in particular, the influence of ionic composition, zinc alloying components, amalgamation level, electrolyte impurities, the role of oxygen, etc.

2. In $ZnCl_2$-free cells containing uncoated paper separators and unamalgamated zinc the corrosion process is diffusion controlled. This confirms earlier studies conducted in flooded electrolyte. The detailed impedance spectrum provides evidence for an intermediate species in the zinc dissolution reaction which is probably adsorbed.

3. The anode polarization and cell impedance characteristics of $ZnCl_2$-free cells containing methylcellulose-*coated* paper separators do not reflect corrosion processes. In fact the electrochemical characteristics are almost indistinguishable from those of $ZnCl_2$-containing cells. It is assumed that the presence of the methylcellulose layer permits the zinc ion concentration to build

up adjacent to the anode causing the cathodic hydrogen evolution process to be electrochemically masked by zinc deposition. The electrochemical characteristics therefore reflect zinc exchange processes only and, hence, the influence of coated separators on corrosion processes can only be determined by simple electrochemical techniques in flooded electrolyte.

4. Neither the presence of the separator coating layer nor a restricted volume of electrolyte are unilaterally sufficient conditions to cause the anomalous behaviour of $ZnCl_2$-free Leclanché cells, but rather a *combination* of these two conditions is necessary. Thus considerably restricted diffusion and a near absence of convection seem to be the important factors which dictate the observations.

5. In unsealed $ZnCl_2$-free cells containing the complete coated separator formulation a slight depolarizing effect of the order of 20 mV due to oxygen accessibility is observed. However, the cell impedance characteristics continue to reflect zinc exchange processes only and cannot reveal quantitative information concerning the zinc corrosion rate.

6. It is concluded that a knowledge of the above restrictions is essential for the future successful electrochemical screening of potential separator materials with respect to their corrosion inhibiting/accelerating properties.

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