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The distribution of potential and electrochemical reaction rate in molten polysulphide electrodes

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A simple mathematical derivation is given of the distribution of potential in a porous carbon electrode saturated with molten sulphur/sodium polysulphide. The equations show how the spatial distribution of reaction products in the sodium/sulphur cell depends on the relative electrical resistivities of the melt and the carbon matrix and, also, the electrode thickness. This distribution is shown to be of particular significance, as far as polarization and utilization are concerned, if the formation of passive films occurs.

1. Introduction

There is considerable interest, at present, in making a practical electrochemical energy storage device based on sodium and sulphur. In essence this system consists of reservoirs of sodium metal and sulphur separated by a solid ceramic electrolyte, β-alumina, which is a good conductor of sodium ions ($\rho = ca.\ 5\ \Omega$ cm; $t_{\mathrm{Na}^+} = 1{\cdot}0$) at 350°C. On discharge, sodium ions migrate through the solid electrolyte and form a series of polysulphides. At 350°C discharge must be terminated when the ratio Na:S corresponds to an overall composition $Na_2S_{2{\cdot}7}$ otherwise precipitation of insoluble Na_2S_2 and Na_2S occurs. The possibility that electrode inhibition (passivity) may be due to these precipitated compounds has been mentioned in a previous publication by South *et al.* [1]. The anodic production of sulphur during charge may result in passivity also. Since passivity is frequently caused by kinetic factors, which can produce considerable localized displacement from the overall equilibrium state, it is of interest to know which of the parameters involved in the design of the electrode most influence the kinetics. The simple treatment given here is similar to that used by Edeleanu and Gibson [2] in a previous investigation of anodic protection.

2. Model and mathematical treatment

2.1. *General treatment*

Consider a flat cylindrical electrode bounded at one circular face by a solid ceramic electrolyte capable of conducting sodium ions but electronically insulating. The other circular face is a charge-injecting pole piece regarded, in the first instance, as electrochemically inert. The space between contains porous carbon felt saturated with the melt and the carbon felt forms an electrochemically active extension to the pole piece throughout the whole volume up to the ceramic. The cylindrical boundary wall is some inert, non-conducting, material which closes the system. On the far side of the ceramic electrolyte is a reservoir of molten metallic sodium which forms the opposite electrode.

It is assumed that on applying a voltage across the system the pole presents an equipotential surface and, because of the radial symmetry, the only gradients of potential are parallel to the principal axis of the cylinder. Therefore the system can be simplified for the purpose of analysis to that shown in Fig. 1. In this figure the charge injecting pole is situated at the voltage ordinate and the ceramic electrolyte boundary is at a distance, L cm, from it.

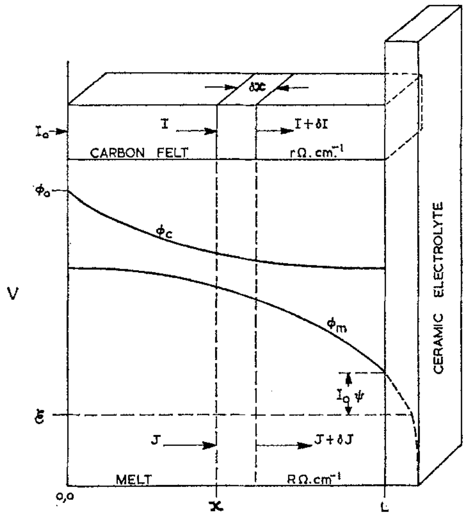


Fig. 1.

Consider a piece of carbon felt of unit cross-sectional area into which a positive (charging) current, I_0 amp, is injected at the pole. This electronic current will be dissipated by electrochemical reaction at the carbon/melt interface, finally attenuating to zero at the ceramic boundary ($x = L$). If the resistance per unit length of the carbon felt is r Ωcm^{-1} then, at any instant, there will be a voltage distribution in the carbon given by

$$-\frac{1}{r}\frac{d^2\phi_C}{dx^2} = \frac{\delta I}{\delta x} \tag{1}$$

Similarly, for the melt of resistance R Ωcm^{-1}

$$-\frac{1}{R}\frac{d^2\phi_m}{dx^2} = \frac{\delta J}{\delta x} \tag{2}$$

where δI is the increment of change in electronic flux over an increment of length δx of the carbon felt. I, J are the current fluxes through the carbon and melt respectively so that, at any arbitrary point x.

$$I + J = I_0; \quad \delta I = -\delta J$$

ϕ_C and ϕ_m are the electrostatic inner potentials in the carbon and melt respectively.

Unit area of carbon felt refers to the bulk material. If the felt is, say, 95% porous then the cross-sectional area of melt associated with this amount of felt will be 0·95 cm^2. Hence, for very porous matrices, R, the resistance per unit length of melt, will be approximately equal to the melt resistivity.

The electrochemical reaction rate, δI, associated with the small volume element, δx, of carbon felt can be expressed as

$$-\frac{\delta I}{\delta x} = \frac{\phi_C - \phi_m}{\rho} \tag{3}$$

where $\rho\Omega$ cm is the slope resistance (considered constant) of the current/voltage characteristic associated with unit volume of carbon felt in a melt of given composition.

From Equations 1 and 2 one obtains

$$-\frac{1}{r}\frac{d^2\phi_C}{dx^2} = \frac{1}{R}\frac{d^2\phi_m}{dx^2} \tag{4}$$

Integrating Equation 4 and noting that

$$\left.\begin{aligned} \frac{d\phi_m}{dx} &= 0 \\ \frac{d\phi_C}{dx} &= -rI_0 \end{aligned}\right| \quad \text{at } x = 0$$

$$\frac{1}{R}\frac{d\phi_m}{dx} = -\frac{1}{r}\frac{d\phi_C}{dx} - I_0 \tag{5}$$

Integrating Equation 5 and transferring the voltage origin so that

$$\left.\begin{aligned} \phi_C &= \phi_L \\ \phi_m &= 0 \end{aligned}\right| \quad \text{at } x = L$$

we get

$$\frac{\phi_m}{R} = -\frac{\phi_C}{r} - I_0x + I_0L + \frac{\phi_L}{r} \tag{6}$$

From Equations 1, 3 and 6 one obtains

$$\frac{d^2\phi_C}{dx^2} = \frac{r}{\rho}\left[\phi_C\left(1+\frac{R}{r}\right) + RI_0x - RI_0L - \frac{R}{r}\phi_L\right]$$

$$\text{i.e.}\left(D^2 - \frac{r+R}{\rho}\right)\phi_C = \frac{r}{\rho}\left(RI_0x - RI_0L - \frac{R}{r}\phi_L\right) \tag{7}$$

where D is the differential operator with respect to x.

Equation 7 can be integrated [3] in the usual manner to give a particular integral and a complementary function, the sum of which gives the complete integral

$$\phi_C = \alpha e^{k^{\frac{1}{2}}x} + \beta e^{-k^{\frac{1}{2}}x} - \frac{rRI_0x}{r+R} + \frac{rRI_0L + R\phi_L}{r+R} \tag{8}$$

where $k = \dfrac{r+R}{\rho}$

Equation 8 contains two arbitrary constants, α and β, and satisfies Equation 7. The constants α and β can be determined by noting that

$$\left.\begin{array}{l}\phi_C=\phi_L\\[4pt] \text{and}\quad \dfrac{d\phi_C}{dx}=0\end{array}\right|\ \text{at } x=L$$

Thus,

$$\phi_L=\alpha e^{k^{\frac{1}{2}}L}+\beta e^{-k^{\frac{1}{2}}L}+\frac{R\phi_L}{r+R} \tag{9}$$

$$0=k^{\frac{1}{2}}[\alpha e^{k^{\frac{1}{2}}L}-\beta e^{-k^{\frac{1}{2}}L}]-\frac{rRI_0}{r+R} \tag{10}$$

Hence,

$$\left.\begin{array}{l}\alpha=e^{-k^{\frac{1}{2}}L}\dfrac{r}{2(r+R)}\left[\phi_L+\dfrac{RI_0}{k^{\frac{1}{2}}}\right]\\[8pt] \beta=e^{k^{\frac{1}{2}}L}\ \dfrac{r}{2(r+R)}\left[\phi_L-\dfrac{RI_0}{k^{\frac{1}{2}}}\right]\end{array}\right\} \tag{11}$$

Substituting Equation 11 in Equation 8 and rearranging into the hyperbolic form gives

$$\phi_C=\frac{r}{r+R}\left[\phi_L\cosh k^{\frac{1}{2}}(L-x)-\frac{RI_0}{k^{\frac{1}{2}}}\sinh k^{\frac{1}{2}}(L-x)\right]-\frac{rRI_0x}{r+R}+\frac{rRI_0L+R\phi_L}{r+R} \tag{12}$$

Substituting Equation 12 in Equation 6 gives

$$\phi_m=\frac{-R}{r+R}\left[\phi_L\cosh k^{\frac{1}{2}}(L-x)-\frac{RI_0}{k^{\frac{1}{2}}}\sinh k^{\frac{1}{2}}(L-x)\right]-\frac{rRI_0x}{r+R}+\frac{rRI_0L+R\phi_L}{r+R} \tag{13}$$

Equations 12 and 13 are the general expressions for the potentials at any point, x, in the carbon and melt respectively. However, they cannot be evaluated because of the unknown term ϕ_L. This term can be eliminated by subtracting Equation 13 from Equation 12, substituting in Equation 3 and integrating, thus:

$$\frac{1}{\rho}\int_0^L(\phi_C-\phi_m)dx=-\int_0^L dI$$

$$=+I_0$$

$$=\frac{k}{r+R}\int_0^L\left[\phi_L\cosh k^{\frac{1}{2}}(L-x)-\frac{RI_0}{k^{\frac{1}{2}}}\sinh k^{\frac{1}{2}}(L-x)\right]dx$$

$$=\frac{k^{\frac{1}{2}}}{r+R}\left[-\phi_L\sinh k^{\frac{1}{2}}(L-x)+\frac{RI_0}{k^{\frac{1}{2}}}\cosh k^{\frac{1}{2}}(L-x)\right]_0^L$$

$$=\frac{k^{\frac{1}{2}}}{r+R}\left[\frac{RI_0}{k^{\frac{1}{2}}}+\phi_L\sinh k^{\frac{1}{2}}L-\frac{RI_0}{k^{\frac{1}{2}}}\cosh k^{\frac{1}{2}}L\right] \tag{14}$$

Rearranging Equation 14

$$\phi_L=\frac{rI_0+RI_0\cosh k^{\frac{1}{2}}L}{k^{\frac{1}{2}}\sinh k^{\frac{1}{2}}L} \tag{15}$$

Substituting Equation 15 in Equation 12 at $x=0$, we get

$$\phi_0=\frac{r}{r+R}\left\{\left[\frac{rI_0+RI_0\cosh k^{\frac{1}{2}}L}{k^{\frac{1}{2}}\sinh k^{\frac{1}{2}}L}\right]\cosh k^{\frac{1}{2}}L-\frac{RI_0}{k^{\frac{1}{2}}}\sinh k^{\frac{1}{2}}L\right\}+\frac{rRI_0L}{r+R}+\frac{R}{r+R}\left[\frac{rI_0+RI_0\cosh k^{\frac{1}{2}}L}{k^{\frac{1}{2}}\sinh k^{\frac{1}{2}}L}\right] \tag{16}$$

which simplifies to

$$\frac{\phi_0}{I_0}=\frac{1}{R+r}\left[\frac{(r^2+R^2)\coth k^{\frac{1}{2}}L}{k^{\frac{1}{2}}}+\frac{2rR+rRL}{k^{\frac{1}{2}}\sinh k^{\frac{1}{2}}L}\right] \tag{17}$$

The terminal voltage of the cell V_T is given by

$$V_T=\phi_0+\mathscr{E}+I_0\psi+P \tag{18}$$

where $\mathscr{E}$ = open circuit cell voltage
ψ = resistance of the ceramic electrolyte
P = any other voltages e.g. membrane voltages and polarization at the Na/ceramic interface

Equation 17 is a general expression for the resistance of the positive electrode as a function of r, R and ρ. There are two things to notice about this equation: firstly, it is independent of interchanging the values of r and R, i.e. it satisfies the necessary physical requirement that the resistance should be independent of the direction of current flow. Secondly, it asymptotes to infinity as $L \to 0$, i.e. when the carbon felt vanishes.

2.2. *Modification for an electrochemically active pole*

If the total current passing through the electrode is subdivided such that:

$$I_0 = I_p + I_c \tag{19}$$

where

I_p = current associated with electrochemical reaction at the pole

I_c = current associated with electrochemical reaction at the carbon matrix

then the equations remain unchanged up to, and including, Equation 13. However, when deriving the expression for ϕ_L, the integral of the current on the l.h.s of Equation 14 must now be put equal to I_c and a new value, ϕ'_L is obtained where

$$\phi'_\mathrm{L} = \phi_\mathrm{L} - \frac{I_\mathrm{p}(r+R)}{k^{\frac{1}{2}} \sinh k^{\frac{1}{2}} L} \tag{20}$$

Primed values apply when the pole is active ($I_\mathrm{p} \neq 0$) and unprimed values when the pole is inert ($I_\mathrm{p} = 0$).

Substituting Equation 20 in Equation 12 at $x = 0$ gives

$$\phi'_0 = \phi_0 - \frac{I_\mathrm{p}(R + r\cosh k^{\frac{1}{2}} L)}{k^{\frac{1}{2}} \sinh k^{\frac{1}{2}} L} \tag{21}$$

From Equation 21 it is seen that the previous expression for the overall resistance of the electrode will contain a correction term:

$$-\frac{I_\mathrm{p}}{I_0} \frac{(R + r\cosh k^{\frac{1}{2}} L)}{k^{\frac{1}{2}} \sinh k^{\frac{1}{2}} L}$$

Substituting Equation 20 in Equations 12 and 13 gives

$$\phi'_\mathrm{C} = \phi_\mathrm{C} - I_\mathrm{p} \frac{[R + r\cosh k^{\frac{1}{2}}(L-x)]}{k^{\frac{1}{2}} \sinh k^{\frac{1}{2}} L} \tag{22}$$

$$\phi'_m = \phi_m + I_\mathrm{p} \frac{[R\cosh k^{\frac{1}{2}}(L-x) - R]}{k^{\frac{1}{2}} \sinh k^{\frac{1}{2}} L} \tag{23}$$

The pole current, I_p, is defined by the current/voltage characteristic of the pole/electrolyte interface, thus

$$I_\mathrm{p} = \frac{\phi'_{\mathrm{C},0} - \phi'_{m,0}}{Z} \tag{24}$$

where Z is the slope resistance.

Substituting in Equation 24 from Equations 22, 23 gives

$$I_\mathrm{p} = \left[\phi_\mathrm{L} \cosh^{\frac{1}{2}} k\ L - \frac{RI_0}{k^{\frac{1}{2}}} \sinh \mathrm{k}^{\frac{1}{2}} L\right] \Big/ \left[Z + \frac{(r+R)\cosh k^{\frac{1}{2}} L}{k^{\frac{1}{2}} \sinh k^{\frac{1}{2}} L}\right] \tag{25}$$

Using this value of I_p in the correction term referred to above allows the overall resistance of the electrode to be calculated. This is shown in Fig. 8 for various values of the parameter Z. With $Z = 100\ \Omega$ the situation is almost exactly that for the inert pole. $Z = 0{\cdot}3\ \Omega$ is a value which might be expected in practice (see [1]). $Z = 0{\cdot}0\ \Omega$ is included for academic interest. The effect on the distribution of potential, as shown in Fig. 9, is obtained from Equations 22, 23 and 25.

In both figures the values of the other parameters have been fixed at $r = R = 1\ \Omega\ \mathrm{cm}^{-1}$; $\rho = 0{\cdot}02\ \Omega$ cm; $I_0 = 0{\cdot}1$ amp.

3. Disscussion

In the situation where the pole is electrochemically inert, the salient equations are 12, 13, 15 and 17. These equations were evaluated on a computer and some of the results are illustrated graphically in Figs. 2–7. In the evaluation $I_0 = 0{\cdot}1$ amp, R was set at $1{\cdot}0\ \Omega\ \mathrm{cm}^{-1}$ and the ratio $R{:}r$ was varied two orders of magnitude by setting $r = 0{\cdot}1$, $1{\cdot}0$ and $10{\cdot}0\ \Omega\ \mathrm{cm}^{-1}$. The condition $r = R = 1{\cdot}0\ \Omega\ \mathrm{cm}^{-1}$ is thought to approximate to the electrodes currently being investigated. It is not obvious what value should be assigned to ρ nor how this value can be determined by an independent experiment; a value of $0{\cdot}02\ \Omega$ cm. was finally chosen based on experimental observations.

Fig. 2 illustrates the resistance/electrode thickness characteristics given by Equation 17. The expected minimum is seen to be poorly defined because the resistance is not very sensitive to changes in electrode thickness for relatively thick electrodes. However, it is clear that trouble may arise with very thin electrodes. The distribution of potential according to Equations 12 and 13 is illustrated in Fig. 3 for the case where $r = R = 1{\cdot}0\ \Omega\ \mathrm{cm}^{-1}$; a, b, c, d correspond

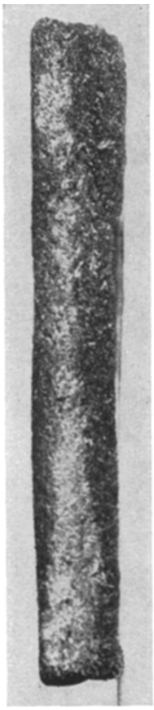


Fig. 4. Cross section of a carbon felt matrix after washing in water showing a zone of unreduced sulphur in the interior.

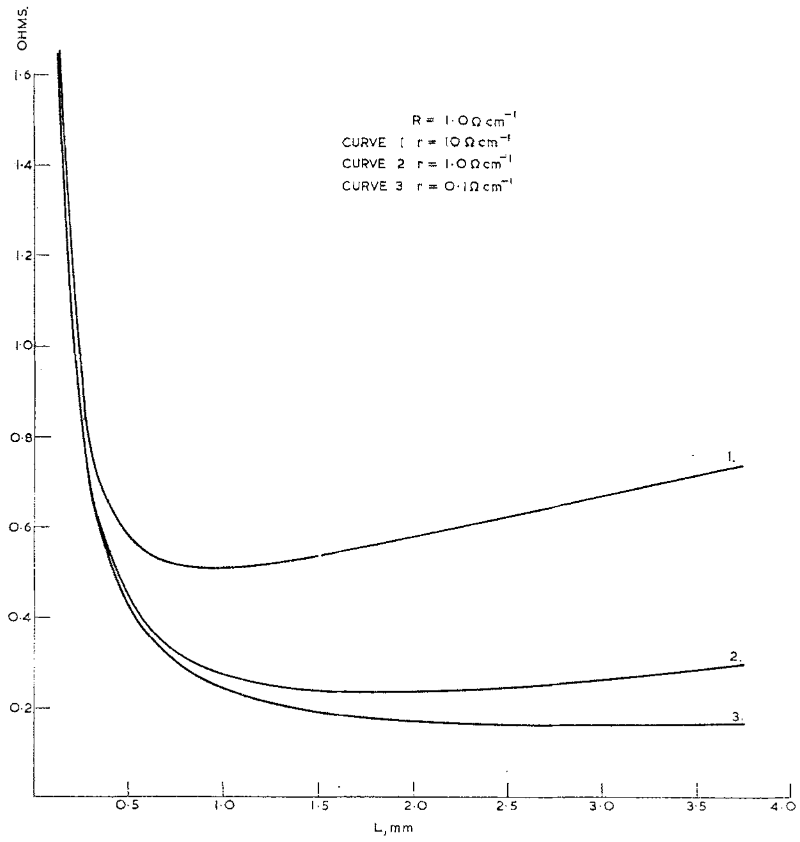


Fig. 2.

to 1, 2, 3, 4 mm thick electrodes respectively. In this symmetrical case it can be seen that there is a minimum in the electrochemical reaction rate, which always appears in the centre of the electrode. In Fig. 3a the minimum is quite shallow and the electrode reaction should proceed fairly homogeneously throughout the whole matrix. As the electrode thickness increases, however, the minimum sharpens and reaction is expected to be concentrated at the surfaces of the pole and the β-alumina. Since the formation of passive films depends on both the rate and extent of reaction it is clear that in this case such films are more likely to be formed at these two surfaces. One practical result which seems to substantiate the situation shown in Fig. 3d is the formation of a 'woolly-faced electrode'. This electrode was a carbon felt matrix 46 mm diameter × 5 mm thick that had been taken from a cell which had polarized badly on discharge. After thoroughly washing the felt in water the two end faces were found to have been completely leached and showed the characteristic soft woolly texture of carbon felt. However, a cross section of the felt revealed the presence of a zone of unreduced sulphur in the interior, as shown in Fig. 4.

The effect that changing the ratio R:r has on the distribution of potential is shown in Figs. 5 and 6. Both figures refer to electrodes 2 mm thick. The variation of these characteristics with thickness is similar to that shown in Fig. 3. For example, Fig. 7 illustrates the case of a 4 mm electrode with R:r = 10·0 from which it is predicted that the production of sulphur during the charging cycle would occur predominantly at the β-alumina interface. A very poor practical performance might be expected for such an electrode.

The occurrence of electrochemical reaction at the surface of the pole does nothing to alleviate the heterogeneous distribution of reaction rate; on the contrary, the situation seems to be made worse. Fig. 9 shows that approximately 38%

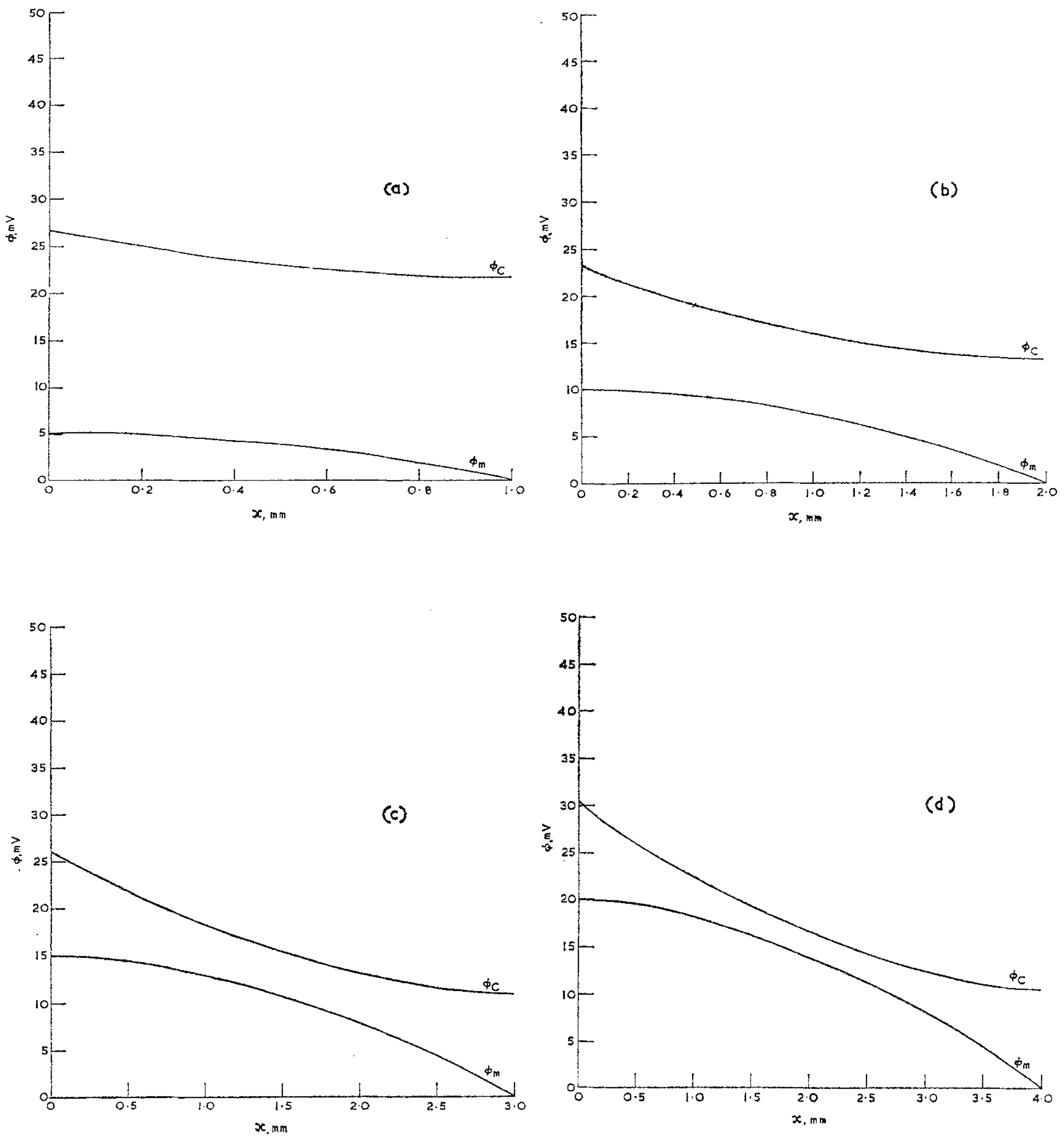


Fig. 3. $r = R = 1{\cdot}0\ \Omega\ \text{cm}^{-1}$; a, b, c, d, L = 1, 2, 3 and 4 mm respectively.

and 21% of the current in the 1 mm and 4 mm thick electrodes, respectively, is consumed at the pole ($Z = 0{\cdot}3\ \Omega$). The reaction products corresponding to this current are produced in the very limited volume in the vicinity of the pole surface and constitute a gross heterogeneity. In the charging mode such an excessive reaction rate at the pole is likely to produce a film of sulphur which could interfere with and possibly destroy the electronic contact to the carbon felt. If this happened the situation would be further aggravated until, finally, the entire current would be consumed at the pole. Such a situation would probably result in premature polarization and, effectively, loss of capacity. In the discharge mode the excessive current at the pole would be expected to facilitate the formation and precipitation of insoluble Na_2S_2 which, again, would constitute a loss of capacity.

The situation is summarized more generally

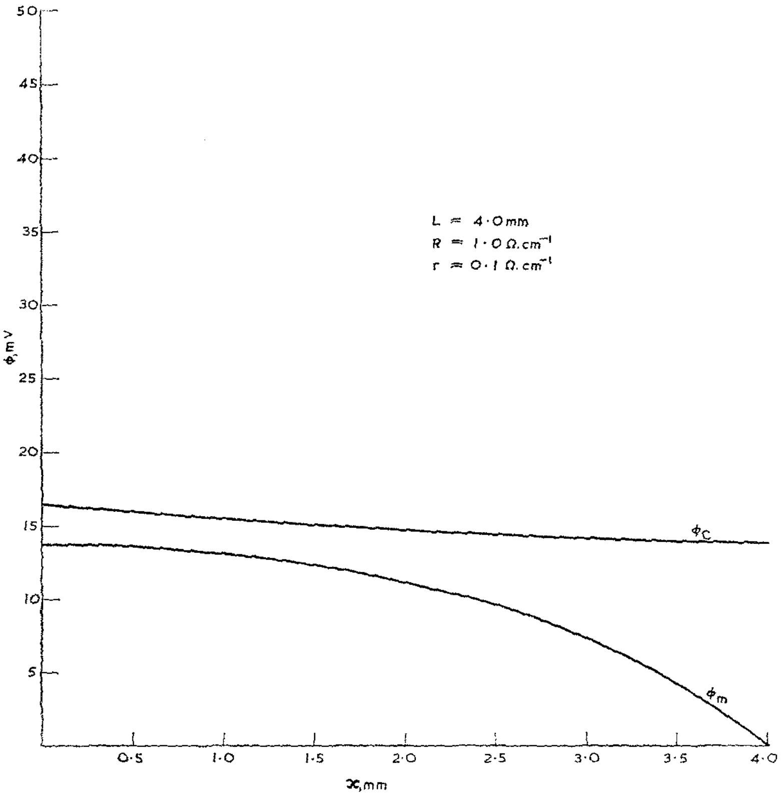

L = 4·0mm
R = 1·0 Ω.cm⁻¹
r = 0·1 Ω.cm⁻¹
φ, mV
50
45
40
35
30
25
20
15
10
5
φc
φm
0·5
1·0
1·5
2·0
2·5
3·0
3·5
4·0
x, mm

Fig. 5.

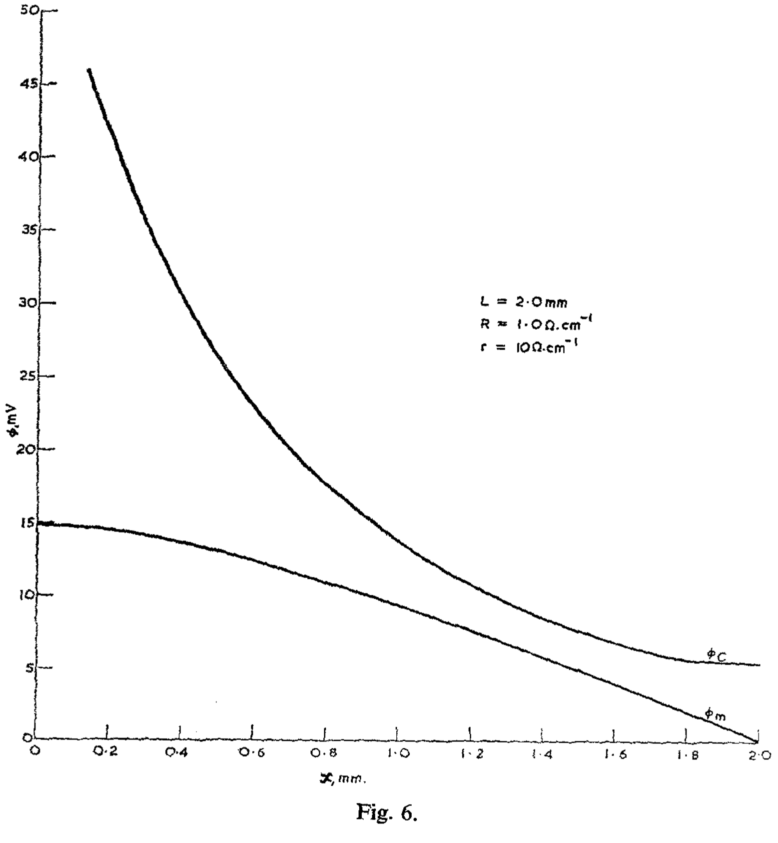
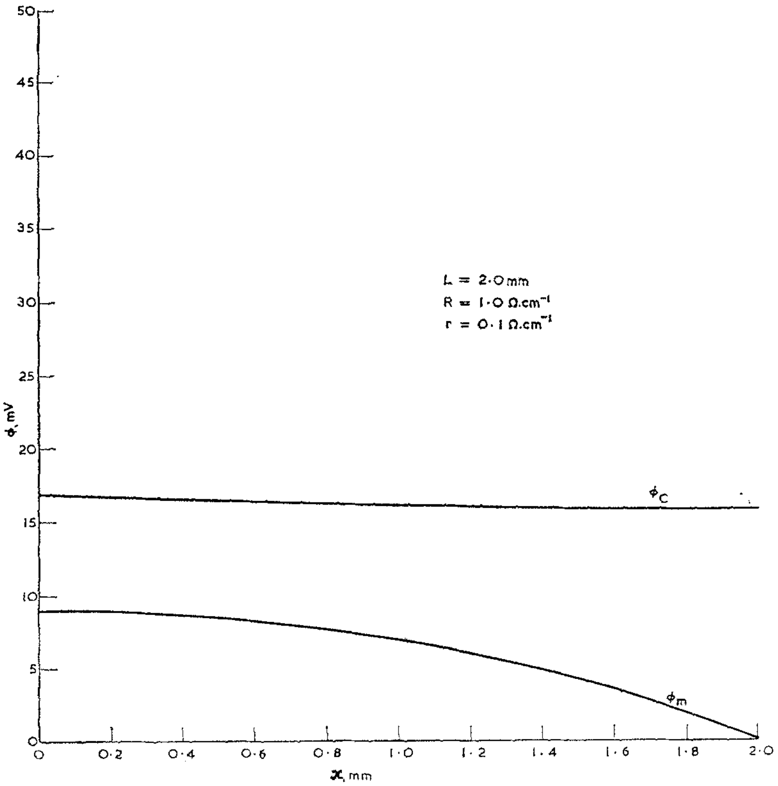

L = 2·0mm
R = 1·0Ω.cm⁻¹
r = 10Ω.cm⁻¹
φ, mV
50
45
40
35
30
25
20
15
10
5
0
φc
φm
0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
2·0
x, mm.

Fig. 6.


50
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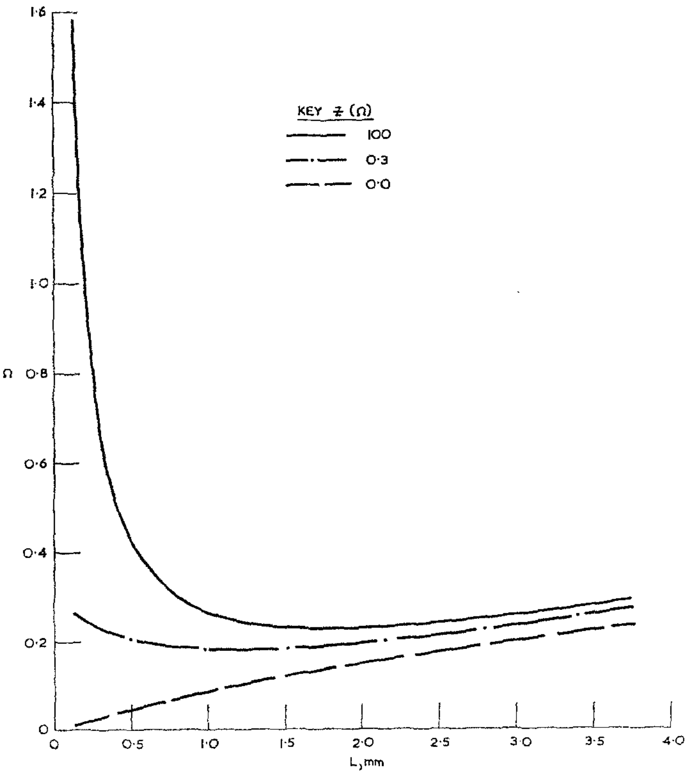
15
10
5
0
ϕ, mV
L = 2·0 mm
R = 1·0 Ω.cm^{-1}
r = 0·1 Ω.cm^{-1}
ϕ_c
ϕ_m
0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
2·0
x, mm

Fig. 7.


1·6
1·4
1·2
1·0
Ω
0·8
0·6
0·4
0·2
0
KEY z (Ω)
100
0·3
0·0
0
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1·5
2·0
2·5
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4·0
L, mm

Fig. 8.

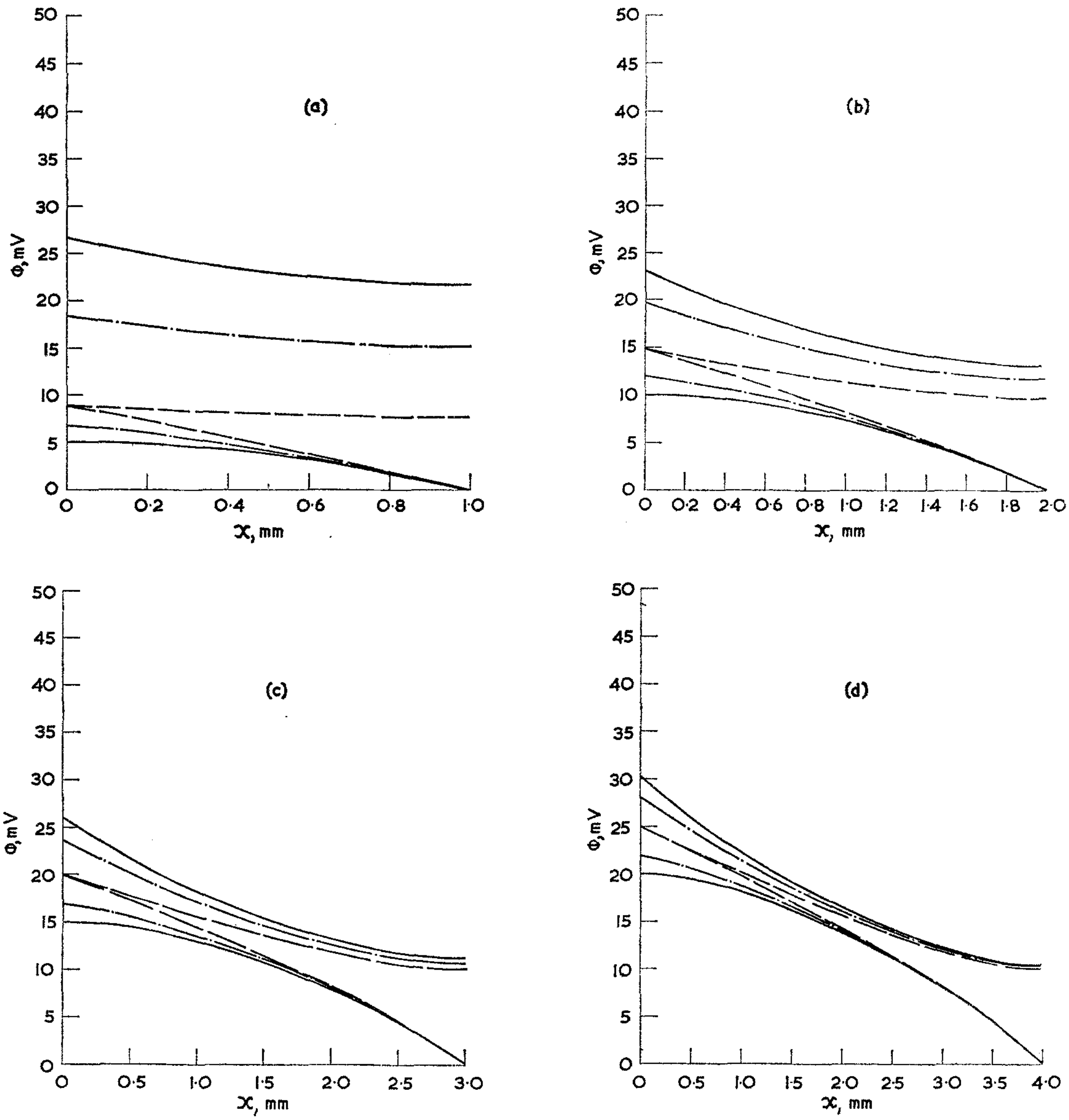

Fig. 9. $r = R = 1{\cdot}0\ \Omega\ \text{cm}^{-1}$; a, b, c, d, $L = 1$, 2, 3 and 4 mm respectively. Values of Z (Ω): —— 100; —·— 0·3; — — 0·0.

in Table 1 from which it can be seen that the current at the pole is reduced by using a matrix of relatively low resistance. But a low resistance matrix gives the potential distribution shown in Fig. 7, a condition leading towards electrode blocking due to the formation of passive layers at the β-alumina surface.

It will be appreciated that by keeping the various parameters constant the validity of the treatment is limited to instantaneous or short-term behaviour. The parameters ρ, R will vary

Table 1. Values of I_p (mA)

	L			
r	1 mm	2 mm	3 mm	4 mm
$0{\cdot}1\ \Omega\ \text{cm}^{-1}$	35	17	9·6	6·1
$1{\cdot}0\ \Omega\ \text{cm}^{-1}$	38	26	22	21
$10\ \Omega\ \text{cm}^{-1}$	57	56	55	55

$Z = 0{\cdot}3\ \Omega$; $I_0 = 100$ mA

as polarization and composition gradients develop in the melt. Any changes in the physical structure of the carbon felt or changes in the inter-fibre contact resistance due to wetting, adsorption etc. will affect the value of *r*. The parameter *Z* will probably be altered by corrosion processes occurring at the pole as will the contact resistance between the pole and the carbon matrix. Even the seemingly constant parameter *L* will alter if, under some conditions, the formation of insoluble Na_2S_2 at the pole were a progressive process from cycle to cycle. This might cause an attenuation of the effective working length of the electrode to a steady-state thickness, at which the electrode capacity is only a fraction of its theoretical capacity.

4. Conclusions

The model electrodes considered can display gross heterogeneity in the distribution of reaction products in both the charging and discharging modes. In view of the fundamental behaviour associated with the sulphur/sodium polysulphide redox system, namely the formation of electronically insulating sulphur in the charge mode and solid sulphides in the discharge mode, the suitability of this electrode design for high rate applications is questionable. Careful experimental work would be needed to resolve this problem.

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