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The effect of electrode material resistance on potential distribution in disc electrode cells

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A theoretical analysis of the effect of electrode material resistance on potential distribution in disc electrode cells is described. The results of the analysis are presented in terms of effectiveness or a utilisation factor and are compared to equivalent data for electrodes of rectangular geometry. The effect of various methods of current feed to the cells is also considered.

Nomenclature

B Breadth of electrode (m)
E Effectiveness factor
E_a Local potential in metal phase of anode (V)
E_c Local potential in metal phase of cathode (V)
i_y Local current density (Am^{-2})
h Electrode separation (m)
I_a Local current flowing along anode (A)
I_c Local current flowing along cathode (A)
I_t Total cell current (A)
I_m Theoretical total cell current (A)
l Thickness of electrode (m)
L Length of electrode (m)
m Dimensionless parameter
m_r Dimensionless parameter for disc electrode
r Radial distance in disc electrode (m)
r_f Radius of current feed point (m)
r_T Radius of disc (m)
R Dimensionless radial distance
V Cell voltage (V)
x Dimensionless distance along electrode length
y Distance along electrode in direction of current flow (m)
z Distance along electrode width (m)
σ Specific conductance of electrode ($\Omega^{-1} m^{-1}$)
σ_e Specific conductance of electrolyte ($\Omega^{-1} m^{-1}$)
ϕ Potential difference between cathode and anode (V)
ϕ_0 The potential at $r = r_f$ or r_T

1. Introduction

A traditional approach to the design of plate and frame cells is to use either rectangular or square electrodes and to feed current at one edge rather than at multiple points around the periphery so as to

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reduce cost and minimize complexity in design. This, in certain cases when thin, low electrically conductive electrodes are used and high current densities employed, may result in a maldistribution of electrode potential caused by ohmic potential drops in the electrode structure. A number of previous studies have been published on this effect, the majority of which are referred to by Robertson [1].

Disc electrodes have not until recently* been considered in the design of plate and frame cells (although they are used in disc stack cells) even though they are a viable alternative to rectangular electrodes as in most respects performance characteristics will be similar. They also have the advantage that frames etc., can be readily made from standard commercially available materials and fabrication time can be reduced. However, the method of electrical connection to disc cells may differ from their rectangular counterparts. Peripheral feed is a possibility although it may be expensive. The simplest connection is a single central contact to the disc which is often used in disc plate and frame cell design. This however may well produce poor electrode potential and current distribution as a result of potential drops in the disc material resulting in lower production capacity per unit electrode area. This method of electrical connection and the effect of ohmic potential drop in the disc material on electrode potential distribution is the subject of this communication. Potential and current distribution is assessed in terms of an effectiveness factor (effectiveness or utilisation efficiency) and compared to other current feed arrangements in disc and square and rectangular cells using a simple mathematical model.

The results may also be useful in assessing the effect of electrode resistance on potential distribution in disc stack cells, especially when electrode materials such as graphite are used.

2. Mathematical model

2.1. *Rectangular electrodes*

The electrolytic cell comprises two parallel rectangular electrodes of length, L, and width, B, separated by a distance, h, of electrolyte of specific conductance, σ_e. For simplicity it is assumed that cathode and anode are of equal thickness l and specific conductance σ. It is assumed that current flows parallel through the electrolyte perpendicular to the electrode surface. The electrochemical characteristics of the cell are assumed to be represented by pure resistance (or a linear approximation of the polarisation characteristics).

2.1.1 One dimensional model. Current is assumed to be evenly distributed over the width of the electrode and flows in a y-direction down the electrode length. The metal currents I_a (anode) and I_c (cathode) at a distance y from the top of the electrode are from Ohm's Law:

$$I_a = -Bl\sigma\frac{dE_a}{dy}; \qquad I_c = -Bl\sigma\frac{dE_c}{dy} \tag{1a, b}$$

where E_a and E_c are the local anode and cathode potentials respectively measured versus the cathode current feeder.

The change in metal current for an element of electrode of length dy is:

$$-dI_a = i_y B dy = dI_c \tag{2}$$

where i_y is the current density over the element dy. Differentiating (1) and substituting (2) gives:

$$\frac{d^2E_a}{dy^2} = \frac{i_y}{l\sigma} \qquad \frac{d^2E_c}{dy^2} = -\frac{i_y}{l\sigma} \tag{3}$$

The current flowing between the electrodes is given by:

$$i_y = (E_a - E_c)\frac{\sigma_e}{h} \tag{4}$$

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which on substituting in (3) gives:

$$\frac{d^2E_a}{dy^2} = \frac{\sigma_e}{hl\sigma}(E_a - E_c); \qquad \frac{d^2E_c}{dy^2} = -\frac{\sigma_e}{hl\sigma}(E_a - E_c) \tag{5a, b}$$

Subtracting these equations and introducing the dimensionless terms, $x = y/L$ and $m = \sigma_e L^2/hl\sigma$, gives:

$$\frac{d^2\phi}{dx^2} = 2m\phi \tag{6}$$

where $\phi = E_a - E_c$.

This second order differential equation governing potential distribution in the cell can be solved subject to suitable boundary conditions.

(a) Current feeders at the same ends of the electrodes. The general solution of Equation 6 is:

$$\phi = a_1 \exp[(2m)^{1/2}x] + a_2 \exp[-(2m)^{1/2}x] \tag{7}$$

The boundary conditions in this case are:

$$x = 0 \qquad \phi = V \text{ (cell voltage)} \qquad x = 1 \qquad \frac{d\phi}{dx} = 0$$

giving the following expressions for the coefficients

$$a_1 = \frac{V}{\{\exp[2(2m)^{1/2}] - 1\}} \qquad a_2 = \frac{V\exp[2(2m)^{1/2}]}{\{\exp[2(2m)^{1/2}] - 1\}}$$

Effectiveness E is defined by:

$$E = \frac{I_t}{I_m} \tag{8}$$

where I_t is the total current fed to the cell and I_m the total current that would flow if the current density was uniform and equal to the maximum observed. The effectiveness of this electrode arrangement is:

$$E = \frac{\tanh(2m)^{1/2}}{(2m)^{1/2}} \tag{9}$$

(b) Current feeders at opposite ends of the electrodes. Boundary conditions in this case are:

$$x = 0, \qquad E_a = V \quad \text{and} \quad \frac{dE_c}{dx} = 0$$

$$x = 1, \qquad E_c = 0 \quad \text{and} \quad \frac{dE_a}{dx} = 0$$

Substituting 7 into 5 gives:

$$\frac{d^2E_a}{dx^2} = m\{a_1 \exp[(2m)^{1/2}x] + a_2 \exp[-(2m)^{1/2}x]\} \tag{10}$$

$$\frac{d^2E_c}{dx} = -m\{a_1 \exp[(2m)^{1/2}x] + a_2 \exp[-(2m)^{1/2}x]\} \tag{11}$$

the solution of which are

$$E_a = \{a_1 \exp[(2m)^{1/2}x] + a_2 \exp[-(2m)^{1/2}x]\} + a_3x + a_4 \tag{12}$$

$$E_c = -\{a_1 \exp[(2m)^{1/2}x] + a_2 \exp[-(2m)^{1/2}x]\} + a_3x + a_4 \tag{13}$$

where:

$$a_1 = \frac{V}{[1 + \exp(2m)^{1/2}]}; \qquad a_2 = \frac{V}{\{1 + \exp[-(2m)^{1/2}]\}}$$

$$a_3 = \left(\frac{m}{2}\right)^{1/2} (a_1 - a_2);$$

$$a_4 = \tfrac{1}{2}\{a_1 \exp (2m)^{1/2} + a_2 \exp [-(2m)^{1/2}]\}$$

The effectiveness of this arrangement is given by:

$$E = \left(\frac{2}{m}\right)^{1/2} \tanh\left(\frac{m}{2}\right)^{1/2} \tag{14}$$

2.1.2. Two dimensional model. The problem of two dimensional current distribution in a parallel plate electrode can be generalised as:

$$\frac{\partial^2\phi}{\partial y^2} + \frac{\partial^2\phi}{\partial z^2} = \frac{2\sigma_e}{hl\sigma}\phi \tag{15}$$

where z is the distance measured along the width of the electrode.

The solution to this equation [2] gives an expression for effectiveness of a square electrode as:

$$E = \left(\frac{2}{m}\right)^{1/2} \tanh\left(\frac{m}{2}\right)^{1/2} + \frac{2}{\pi}\sum_{n=0}^{\infty}\left[\frac{1}{n+\frac{1}{2}} - \frac{4(n+\frac{1}{2})^2\pi^2}{2m+4(n+\frac{1}{2})^2\pi^2}\right]\left[\frac{\tanh(2m+4(n+\frac{1}{2})^2\pi^2)^{1/2}\frac{1}{2}}{(n+\frac{1}{2})\pi(2m+4(n+\frac{1}{2})^2\pi^2)^{1/2}\frac{1}{2}}\right] \tag{16}$$

2.2. *Circular electrodes*

The mathematical formulation of the problem for circular electrodes is similar to that for square electrodes. In this case current flows in the electrode structure in a radial direction r and the disc electrode is of radius r_T. The governing differential equation describing the potential distribution in the cell is:

$$\frac{d^2\phi}{dR^2} + \frac{1}{R}\frac{d\phi}{dR} = 2m_r\phi \tag{17}$$

where: $R = r/r_T$ and $m_r = \sigma_e r_T^2/hl\sigma$.

Electrical connection to disc electrodes considered here are either to the periphery or to the centre.

2.2.1. Central feed. The solution to Equation 17 can be written in terms of Bessel functions as:

$$\phi = AI_0[(2m_r)^{1/2}R] + BK_0[(2m_r)^{1/2}R] \tag{18}$$

Boundary conditions in this case are:

$$R = 1, \qquad \frac{d\phi}{dR} = 0$$

$$r = r_f, \qquad (R = r_f/r_T), \qquad \phi = \phi_0$$

(i.e. current is fed evenly over an area described by r_f at the centre of the electrode).

Which give values of the coefficients A and B as:

$$A = \frac{\phi_0}{I_0[(2m_r)^{1/2}r_f/r_T]\left\{1 + \dfrac{I_1(2m_r)^{1/2}K_0(2m_r)^{1/2}r_f/r_T}{I_0[(2m_r)^{1/2}r_f/r_T]K_1(2m_r)^{1/2}}\right\}}$$

$$B = A\frac{I_1(2m_r)^{1/2}}{K_1(2m_r)^{1/2}}$$

where I_0, I_1, K_0 and K_1 are Bessel functions values of which are tabulated in [3].

The effectiveness is given by:

$$E = \frac{2}{(2m_r)^{1/2}} \frac{r_f r_T}{(r_T^2 - r_f^2)} \cdot \frac{AI_1[(2m_r)^{1/2} r_f/r_T)] - BK_1[(2m_r)^{1/2} r_f/r_T]}{AI_0[(2m_r)^{1/2} r_f/r_T)] + BK_0[(2m_r)^{1/2} r_f/r_T]} + \frac{r_f^2}{r_T^2} \tag{19}$$

the last term in Equation 19 takes account of the central feed point being at constant potential.

2.2.2. Peripheral feed. The boundary conditions in this instance are:

$$R = 1, \qquad \phi = \phi_0, \qquad r = 0, \qquad \frac{d\phi}{dR} = 0$$

where ϕ_0 is the potential when $R = 1$.

The effectiveness is given by:

$$E = \frac{2}{(2m)^{1/2}} \frac{I_1(2m)^{1/2}}{I_0(2m)^{1/2}} \tag{20}$$

3. Results and discussion

The variation of effectiveness, E, with parameter, m, for rectangular electrodes with various current feed arrangements is shown in Fig. 1. In all cases E decreases as m increases, with the same end feed giving the inferior performance of all three. The application of an opposite end feed is seen to greatly increase effectiveness in comparison to the same end feed and values are close to the peripheral feed case. The use of peripheral feed electrodes would require relatively complex and expensive electrical connections to the cell and therefore an opposite end feed arrangement is more likely to be adopted. An exception to this would be when bipolar connection of parallel plate cells is anticipated where it has been shown [4] that the opposite end feed is not always the most effective method of current supply.

For the disc electrodes the variation of effectiveness as a function of m, shown in Fig. 2, is similar to the rectangular electrodes. As expected the peripheral feed case gives a superior performance especially at values of $m > 1$, where for the centrally fed cases E values drop rapidly. This is a result

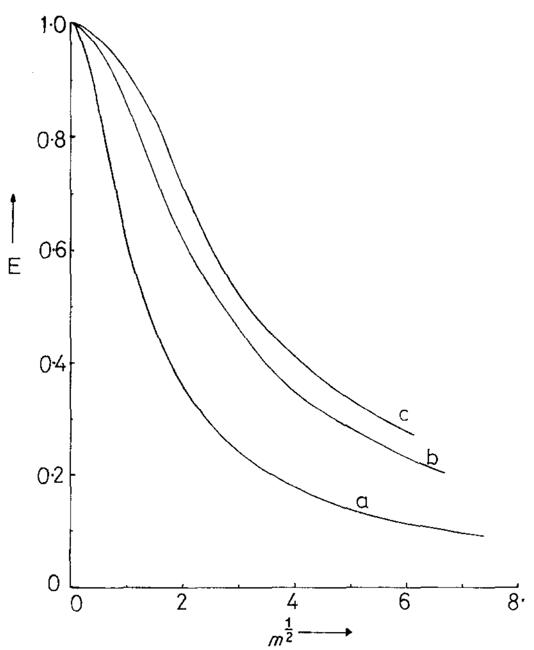

Fig. 1. Comparison of the effectiveness of square electrodes. a, same end feed; b, opposite end feed; c, peripheral feed.

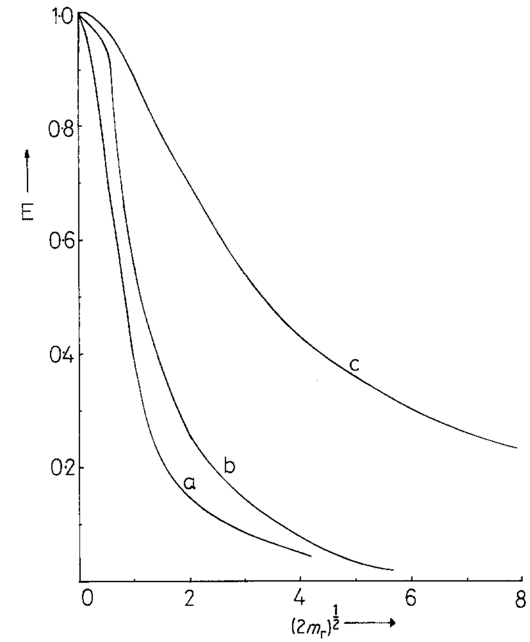

Fig. 2. Comparison of the effectiveness of disc electrodes. a, central feed $r_T/r_f = 50$; b, central feed $r_T/r_f = 10$; c, peripheral feed.

of the ever increasing distance over which current must be distributed as the relative size of the electrode increases.

The size of the electrical connection for the centrally fed electrode is seen in Fig. 2 to have a significant effect on effectiveness. By decreasing the value of r_T/r_f from 50 to 10, E values are considerably improved at values of $m \leqslant 1$. A value of r_T/r_f of 10 is probably the lower practical limit for this type of electrical connection.

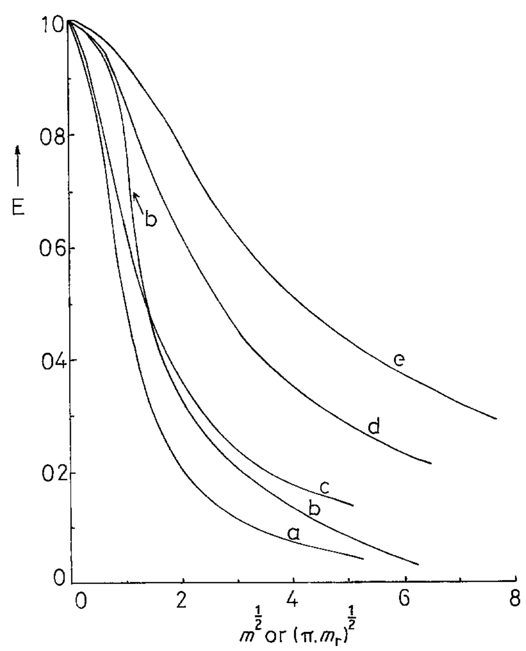

Fig. 3. Comparison of the effectiveness of disc and square electrodes. a, disc, central feed $r_T/r_f = 50$; b, disc, central feed $r_T/r_f = 10$; c, square, same end feed; d, square, opposite end feed; e, disc, peripheral feed.

4. Comparison of square and disc electrodes

A quick comparison of disc and square electrodes indicates that overall, square electrodes tend to be more effective at equivalent m (or m_r) values. However, a more accurate comparison of electrode types should be based on equal electrode areas (implying a ratio of $m/m_r = \pi$ as a comparative base) and Fig. 3 gives such a comparison for various feed arrangements.

The disc electrode with peripheral feed is seen to give the best performance of all. For the centrally fed disc, effectiveness values are comparable to the same end feed square electrode at values of $m^{1/2}(m_r\pi)^{1/2}$ approximately $\leqslant 1$. In fact for the disc with $r_T/r_f = 10$ the performance is superior but at values of $m > 2$ the square electrode becomes more effective.

In conclusion, in the operation of discs with a central current feed a uniform current density distribution will be obtained at values of $(m_r)^{1/2} < 0.5$. Hence in designing disc electrode cells a central feed should not prove too detrimental to performance except in cases when small inter-electrode gaps are used such as in disc stack cells.

References

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