

SHORT COMMUNICATION

Simulation of a packed bipolar cell involving cathodic limiting current and anodic Tafel behaviourYOSHINORI MIYAZAKI¹, AKIRA KATAGIRI², SHIRO YOSHIZAWA¹¹Department of Industrial Chemistry, Faculty of Engineering, and ²Department of Chemistry, College of Liberal Arts and Sciences, Kyoto University, Sakyo-ku, Kyoto 606, Japan

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Nomenclature

a	length of unit cell (cm)		tion (V)
b	anodic Tafel b-factor (V)	V_{cell}	voltage applied to unit cell (V)
E	average electric field in solution (V cm^{-1})	x, y	Cartesian coordinates defined in Fig. 1 (cm)
I_F	faradaic current in unit cell (A)	η_p	power efficiency (dimensionless)
I_S	bypass current through solution in unit cell (A)	κ	specific conductivity of solution or conducting paper (Ω^{-1})*
I_T	total current in unit cell (A)	ϕ_{ma}	inner potential of electrode in anodic region (V)
i	current density (A cm^{-1})*	ϕ_{mc}	inner potential of electrode in cathodic region (V)
i_d	cathodic limiting current density (A cm^{-1})*	ϕ_{sa}	inner potential of solution in anodic region (V)
R	apparent resistance of solution in unit cell (Ω)	ϕ_{sc}	inner potential of solution in cathodic region (V)
r	radius of cylindrical electrode (cm)		
V_0	threshold voltage (V)		
V_{0a}	characteristic voltage for anodic reaction (V)		
V_{0c}	characteristic voltage for cathodic reac-		

* These units correspond to the two-dimensional model.

1. Introduction

The packed bipolar cell is a type of electrolytic cell in which a large number of conducting particles are placed between the main electrodes and a sufficiently high field is applied so that each particle behaves as a bipolar electrode [1]. This type of cell has been investigated by several workers [1–7]. In order to understand cell characteristics such as the effective electrode area and the energy efficiency it is necessary to study the potential and current distributions in the system. Although the primary and secondary current-potential distributions have been obtained for some geometries of cells by analytical and numerical methods [8–11], it has been difficult to solve the problem in packed bipolar cells since the boundary condition at the surface of bipolar electrodes cannot be given either by the electrode potential or by the current density.

In a previous paper we have proposed a new method of simulating a packed bipolar cell by using a combination of conducting paper and an electric model circuit [12]. The principle of the method has been shown in a very simplified case in which both anodic and cathodic reactions occur at a limiting current of the same magnitude, although this condition is not realistic. In the present communication we describe the method in a more general case in which the cathodic reaction occurs at a limiting current while the anodic reaction is characterized by a Tafel behaviour.

2. Technique

The technique used is similar to that used previously [12]. Thus, a packed bipolar cell is simulated by a combination of conducting paper and electric model circuits, the former

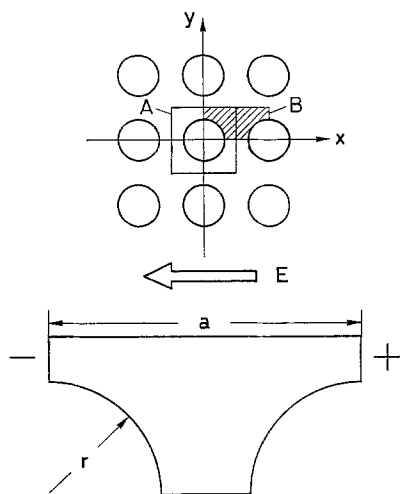


Fig. 1. Arrangement of cylindrical electrodes and the pattern of conducting paper.

representing the electrolyte solution and the latter representing the current-potential dependencies, i.e. a limiting current behaviour at the cathode and a Tafel behaviour at the anode. It is assumed that cylindrical electrodes are arranged parallel to each other with the square lattice configuration as shown in Fig. 1. The x - and y -axes are chosen as indicated, and the z -axis (not shown) is taken in the direction of the cylinder axes. Electric field is assumed to be applied in the direction of $-x$. When a sufficiently high field is applied, a part of the right hand side of each cylinder becomes the cathode and a part of the left hand side of each cylinder becomes the anode. The square region indicated A is considered as a unit cell. The potential and current distributions in the unit cell are symmetric with respect to the plane $y = 0$. When the applied field is not too high, the current lines at the position $x = 0$ should be approximately parallel to the x -axis, and therefore the plane perpendicular to the x -axis at $x = 0$ should be approximately an equipotential surface. Based on the above considerations it is more convenient to look at the potential and current distributions in the hatched region (B), which is enlarged at the bottom of the figure, since the side ends of the region are regarded as equipotential surfaces.

Fig. 2a shows the basic concept of the simulation. A piece of conducting paper was cut to the pattern and conducting paste was put on the side

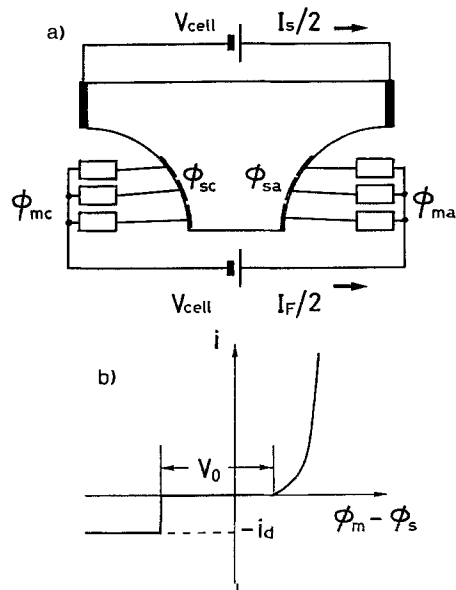


Fig. 2. (a) Schematic diagram of the simulation system. (b) Current-potential relationship for a bipolar electrode.

ends. (The two-dimensional 'specific conductivity' of the paper was $\kappa = 2.2 \times 10^{-3} \Omega^{-1}$.) The circular ends of the paper, which correspond to the anode (right) and cathode (left) surfaces, were divided into nine sections, each of which was connected to a current-controlling unit. Fig. 3a and 3b show the current-potential characteristics of the units used for the anode and cathode, respectively. Fig. 2b is the current-potential relationship which is expected when there is no ohmic potential drop in the electrolyte.

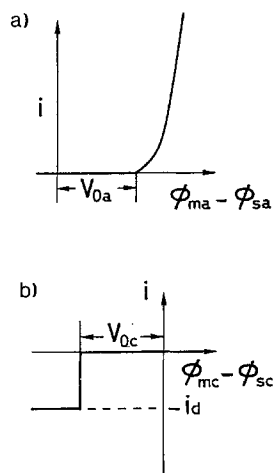


Fig. 3. (a) Current-potential relationship for the anode. (b) Current-potential relationship for the cathode.

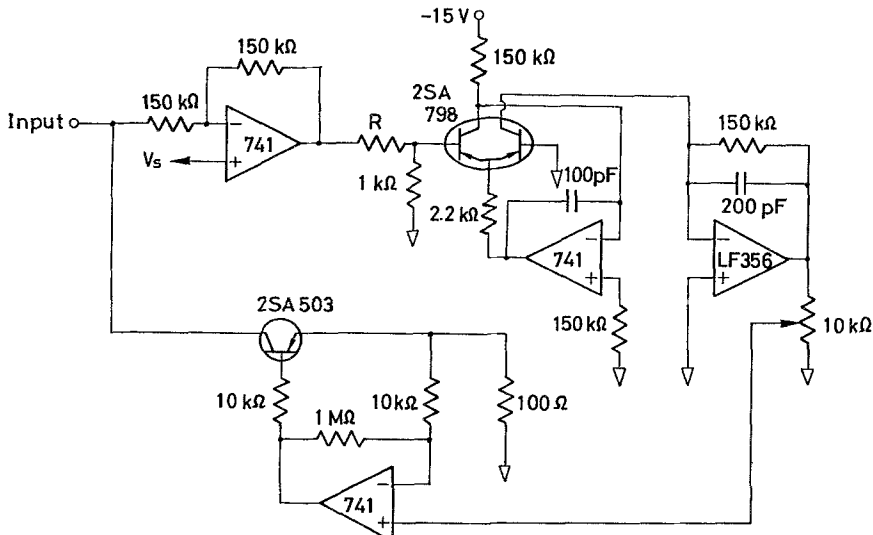


Fig. 4. Electric circuit simulating the Tafel relationship.

Fig. 4 shows the electric circuit of the anode units, which was composed of an exponential amplifier and a current-regulating circuit. It supplied a constant current, i , according to the Tafel equation:

$$\phi_{ma} - \phi_{sa} = V_{0a} + b \log i \quad (1)$$

The cathode units, which regulated the current according to the current-potential relationship of Fig. 3b, was the same as described in the previous paper [12]. The voltage $V_0 = V_{0a} + V_{0c}$ is regarded as a parameter and is compared to the 'threshold voltage' in the previous simple model.

An equal voltage, V_{cell} , was applied from two identical but independent d.c. sources as shown in Fig. 2a. Thus, the anodic and cathodic currents were balanced and the potentials ϕ_{ma} and ϕ_{mc} at the lower terminals (electrodes) were automatically adjusted at certain values which were different from the potentials at the side ends of the conducting paper (electrolyte). Half the faradaic current in the unit cell (I_F) and half the solution current in the unit cell (I_S) were recorded. The potential distribution on the conducting paper was measured by using an electrometer and a probe. The power efficiency was calculated by the equation

$$\eta_P = V_0 I_F / V_{cell} I_T \quad (2)$$

where I_T is the total current in the unit cell, i.e. $I_T = I_F + I_S$.

3. Results and discussion

The solution current (bypass current) was measured at different cell voltages. Fig. 5 shows $I_S/2$ and $2R$ plotted against V_{cell} . When V_{cell} is larger than a certain value, each electrode begins to function as a bipolar electrode and $I_S/2$ and $2R$ begin to deviate from straight lines. An

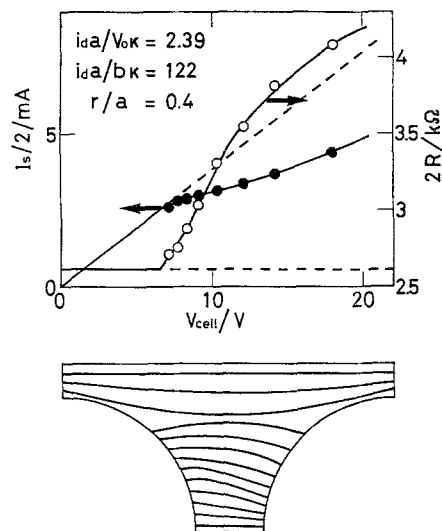


Fig. 5. Current in the solution and the apparent resistance of the solution as functions of cell voltage.

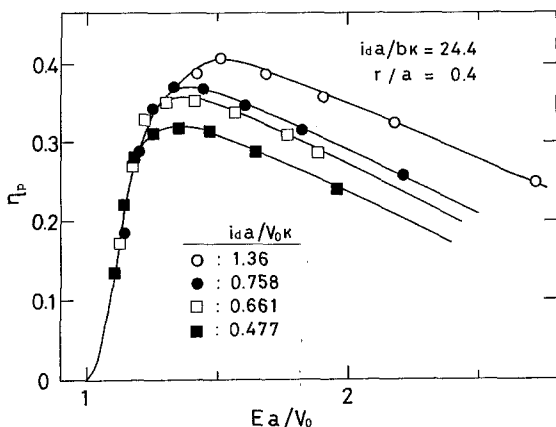


Fig. 6. Power efficiency as a function of Ea/V_0 for different values of $i_d a/V_0 \kappa$.

example of the current distribution is shown at the bottom of Fig. 5. Apparently, the passage of the solution current is constricted by the faradaic current; this is the reason for the increase in the apparent solution resistance.

Previously, it has been reported that the cell characteristics are expressed in terms of the dimensionless parameters, r/a , $i_d a/V_0 \kappa$ and Ea/V_0 for the limiting current condition [12]. For the present model an additional dimensionless parameter containing the Tafel b -factor, $i_d a/b \kappa$, is considered. Fig. 6 shows η_p , as a function of

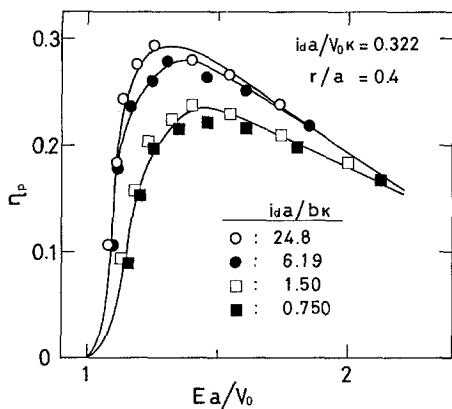


Fig. 7. Power efficiency as a function of Ea/V_0 for different values of $i_d a/b \kappa$.

Ea/V_0 , obtained at different values of V_0 and E under otherwise identical conditions. The result is depicted in terms of the dimensionless parameters of r/a , $i_d a/V_0 \kappa$ and $i_d a/b \kappa$. The maximum value of η_p increases with increasing value of $i_d a/V_0 \kappa$, indicating that the packed bipolar cell is advantageous when the solution resistance is large in comparison to the limitation of reaction at the electrode (cathode). Fig. 7 shows η_p obtained at different values of b and E as a function of Ea/V_0 . The maximum value of η_p is large when the b -factor is small ($i_d a/b \kappa$ is large), i.e. when the current-potential curve in Fig. 3a rises sharply.

The method described here may be applicable to other types of electrolyzers.

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