SHORT COMMUNICATION

Numerical calculation of secondary current distribution in a two-dimensional electrochemical cell with a resistive electrode

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Nomenclature

- F Faraday's constant (96 487 C mol^{-1})
- i_{ave} averaged current density at interface between cathode and electrolyte (A m^{-2})
- i_0 exchange current density (A m^{-2})
- i_n current density to electrode (A m^{-2})
- L characteristic length, minimum gap between anode and cathode (m)
- l distance from terminal along electrode (m)
- $\boldsymbol{n}$ unit normal vector perpendicular to boundaries
- R universal gas constant (8.3143 J mol^{-1} K^{-1})
- T absolute temperature (K)
- t_e thickness of thin electrode (m)
- Wa_L Wagner number for linear kinetics
- Wa_T Wagner number for Tafel kinetics
- α_a, α_c anodic and cathodic transfer coefficients
- η_s surface overpotential ($= \phi_e - \phi_y$) (V)
- σ conductivity of electrolyte (Ω^{-1} m^{-1})
- σ_e conductivity of electrode (Ω^{-1} m^{-1})
- ϕ potential (V)
- ϕ_0 potential difference between anode and cathode terminals (V)

Subscripts

- a anode
- c cathode
- e electrode
- y electrolyte

1. Introduction

It is essential, in the design of electrochemical systems, to accurately calculate the distribution of current density in the electrolyte and over electrode surfaces without any geometrical or kinetic simplification [1, 2]. There is substantial literature on numerical methods to calculate secondary current distributions [2], but these methods require simplifications with regard to conductive features of electrodes. In some work [3–10] it is assumed that the electrode conductivity is infinite to avoid the difficulty of calculating large changes in the potential from the electrolyte to the electrode region. This assumption is unrealistic when electrodes are thin or highly resistive, as in the case of electrodeposition on microelectronic devices, such as plating onto through-holes of printed circuit boards, semiconducting compounds, printing heads of printers, and so on. Though several reseachers have reported investigations of current distribution with resistive electrodes [11–15], they are restricted to idealized cell configurations and not applicable for complex shapes.

The purpose of the present work is to establish a method of numerical analysis for calculating the secondary current distribution, which is applicable for arbitrary two-dimensional electrochemical cells having electrodes of uniform, but finite, conductivities with nonlinear Butler–Volmer polarization kinetics.

2. Modelling

2.1. *Basic equations*

It is assumed that the system consists of well stirred electrolyte with no concentration gradients, and electrodes, anode and cathode, whose conductivities are uniform and finite. The Laplace equation applies in both electrolyte and electrode regions [16].

$$\nabla^2 \phi_y = 0, \quad \nabla^2 \phi_e = 0. \tag{1}$$

By conservation of current,

$$\boldsymbol{n} \cdot \sigma \nabla \phi_y = \boldsymbol{n} \cdot \sigma_e \nabla \phi_e, \tag{2}$$

at the electrolyte–electrode interfaces. The Butler–Volmer equation describes the relationship between the surface overpotential and the current density at the electrodes.

$$i_n = -\sigma \boldsymbol{n} \cdot \nabla \phi_y = i_0 \left[\exp\left(\frac{\alpha_a F \eta_s}{RT} \right) - \exp\left(\frac{-\alpha_c F \eta_s}{RT} \right) \right], \tag{3}$$

where $\eta_s = \phi_e - \phi_y$. The applied voltage is constant at the terminals, if the electrochemical cell is operated under constant voltage, ϕ_0.

$$\phi_a = \phi_0, \quad \phi_c = 0 \tag{4}$$

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The natural boundary condition applies on insulated boundaries or planes of symmetry.

$$\boldsymbol{n} \cdot \nabla \phi_{y,e} = 0. \tag{5}$$

To calculate the secondary current distribution in the cell, the Laplace Equations 1 may be solved subject to the boundary conditions 4 and 5 satisfying the conservation of current (Equation 2) and the internal boundary condition (Equation 3). The nonlinear boundary condition (Equation 3) and the difference in conductivity between the electrolyte and electrode complicate the numerical calculation.

2.2. *Thin electrode*

If the electrode is thin, it is not necessary to solve the two-dimensional Laplace equation with respect to the electrode and the potential along the electrode is determined by the following integral equation [17].

$$\sigma_e \frac{d\phi_e}{dl} = \int_0^l \left(\frac{1}{t_e}\right) \sigma \boldsymbol{n} \cdot \nabla \phi_y \, dl \tag{6}$$

2.3. *Numerical method*

A double iterative numerical method was used to solve the system of equations. A flowchart of the numerical method is shown in Fig. 1. The Laplace equation, $\nabla^2 \phi_y = 0$, was solved by the boundary element method (BEM) under initial boundary conditions, $\phi_a = \phi_0$ at the anode and $\phi_c = 0$ at the cathode (Step 2 in Fig. 1). The surface overpotential, η_s, was explicitly determined by Equation 3, and the boundary values, $\phi_a = \phi_0 - \eta_{sa}$, $\phi_c = \eta_{sc}$, were replaced by those of the previous step (Step 3). Calculation of the Laplace equation was repeated with the new boundary values (Step 2) until converged values of ϕ_y and $\nabla \phi_y$ were obtained. Once converged values of ϕ_y and $\nabla \phi_y$ had been obtained (Step 4), another Laplace equation, $\nabla^2 \phi_e = 0$, was solved (Step 6) by the BEM under the boundary condition of the second kind determined by Equation 2 at the interface between electrolyte and electrode (Step 5). For a thin electrode, assumed as one-dimensional, Equation 6 was solved instead of the Laplace equation and ϕ_e along the electrode was determined. The calculated potential at the interface was added to η_s (Step 7) and the procedure was again repeated until converged values of both ϕ_y and ϕ_e, potential difference less than $10^{-4}\,\phi_0$ at the edge of the cathode, were obtained (Step 8). The over-relaxation method was employed for the iterative procedure.

Although the finite element method (FEM) or the finite difference method (FDM) are also useful for numerical calculations of the Laplace equation, the boundary element method [19, 20] was used in the present study, because (i) it is not necessary to input coordinates of internal nodal points, (ii) the method is suitable for the calculation on a microcomputer with relatively simple programming (in the present study, an NEC Model PC-9801UV personal computer was used with BASIC programming), and (iii) the potential gradient, necessary for calculations of Equations 2, 3, 5 and 6, is directly determined.

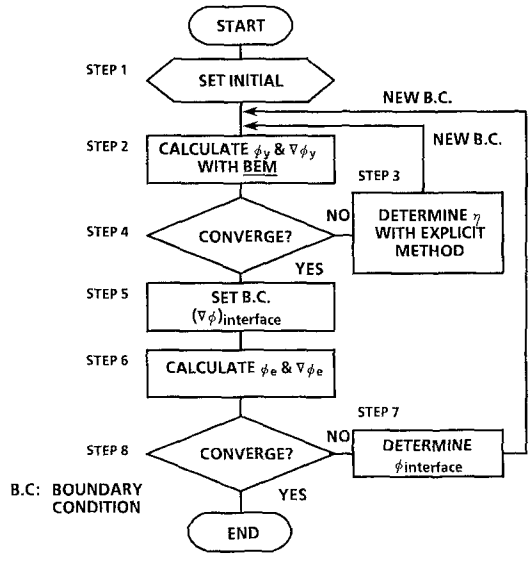

Fig. 1. Flowchart of numerical calculation based on a double iterative boundary element method.

3. Results and discussion

3.1. *Calculation conditions*

Parametric calculations for cells consisting of flat anodes and corner cathodes were performed to demonstrate the present method. Calculation parameters are listed in Table 1 and cell geometries are shown in Fig. 2. The anode was assumed to be infinitely conductive, but conductive properties of the cathode, as well as the Wagner number, were selected as calculation parameters. Linear basis functions were employed between nodal points.

3.2. *Potential and current density distributions*

Figure 3 shows the result of calculations on potential distributions in the cells, and Fig. 4 the normal current

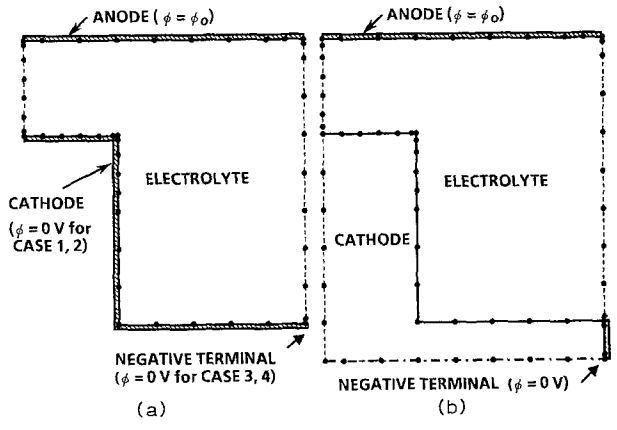

Fig. 2. Cell geometries for calculations. (●) Nodal point, (- - -) insulated boundaries, (– – –) planes of symmetry. (a) Infinitely conductive or thin cathode (45 nodal points); (b) resistive cathode (45 nodal points on electrolyte; 37 nodal points on cathode).

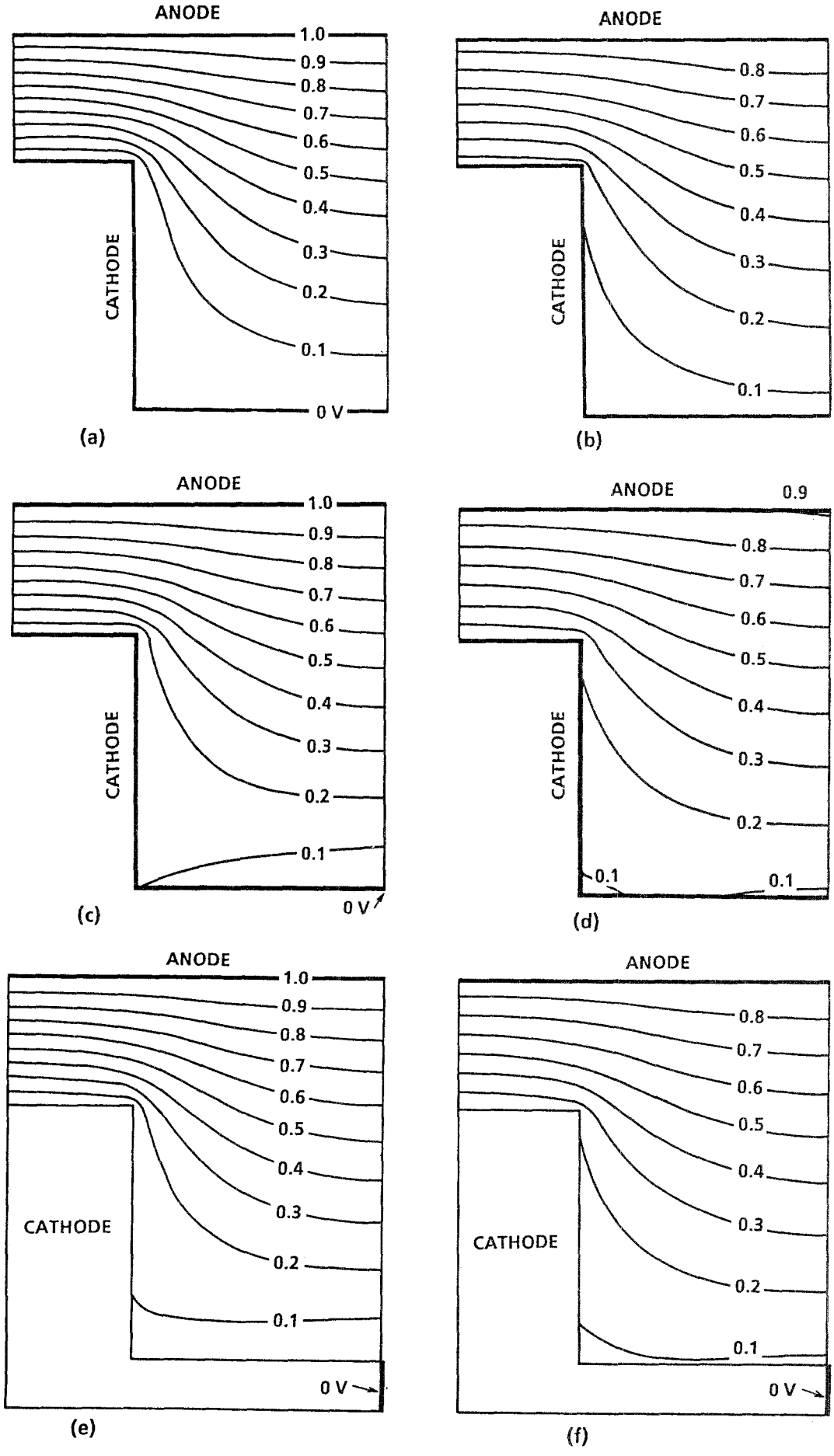

Fig. 3. Potential distribution. Curves in the figures designate 10% pitch equipotential surfaces. (a) CASE 1: $Wa_T = 0.12$; (b) CASE 2: $Wa_T = 0.16$; (c) CASE 3; $Wa_T = 0.14$; (d) CASE 4: $Wa_T = 0.18$; (e) CASE 5: $Wa_T = 0.14$; and (f) CASE 6: $Wa_T = 0.17$.

*Table 1. Calculation conditions**

Cathode	$Wa_L = 0$ *(Primary current distribution)*	$Wa_L = 0.5$	*Cell geometry*	*Remarks*
Infinitely conductive	CASE 1	CASE 2	Fig. 3a	
Thin	CASE 3	CASE 4	Fig. 3a	$t_e/L = 2 \times 10^{-3}$ $\sigma_e/\sigma = 10^6$
Resistive	CASE 5	CASE 6	Fig. 3b	$\sigma_e/\sigma = 10^2$

* According to Dukovic's definition [2], three dimensionless parameters which characterize the nonlinear polarization system are used. $Wa_L \equiv RT\sigma/[(\alpha_a + \alpha_c)FLi_o]$, $Wa_T \equiv RT\sigma/(\alpha_c FLi_{ave})$, and $\alpha_a/\alpha_c = 1$.

density along the cathodes. The number of iterations was around 15 for CASEs 2–6 to obtain a potential difference less than 10^{-4} ϕ_0 at the edge of the cathode.

The following observations can be made from the figures:

(i) In CASE 1 the current density is concentrated at the edge of cathode. (The edge corresponds to a singular point. The current density at the edge is theoretically infinite [18].) On the other hand, the current density is zero in this case at the corner of the cathode [18].

(ii) In accordance with the increase in polarization (CASEs 2, 4, 6), a potential drop (or surface overpotential) appears at the electrode–electrolyte interfaces and the current distribution becomes more uniform. The singularity at the edge is nonexistent in polarized cases, and the current density is finite both at the edge and the corner of the polarized cathode.

(iii) The non-polarized thin or resistive electrode (CASEs 3, 5) also eliminates the singularity. Although a surface overpotential does not exist at interfaces in these cases, a potential drop due to ohmic resistance arises in the cathode.

(iv) The polarized thin or resistive electrode (CASEs 4, 6) further reduces the rise in current density at the edge because of the polarization at the interfaces and the ohmic potential drop in the cathode.

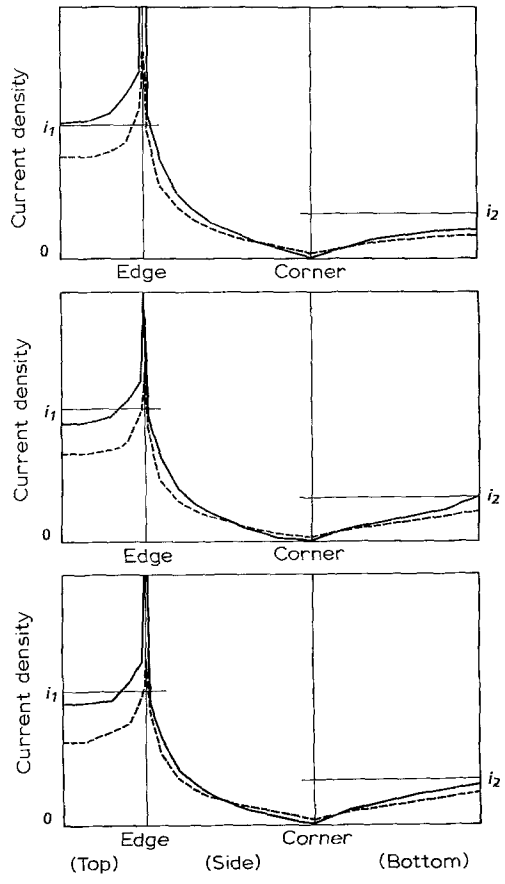

Fig. 4. Current density distributions along cathodes. The abscissa is a distance along the cathode and the ordinate is the normalized current density, where $i_1 = \sigma\phi_0/L$ (current density in case of infinite parallel plate separated at the distance of L) and $i_2 = \sigma\phi_0/L_2$ (current density in case of infinite parallel plate separated at the distance of L_2, where L_2 is the distance between the anode and the bottom plate of the cathode.) (a) Infinitely conductive cathode: CASE 1 (——) $Wa_L = 0$; CASE 2 (– – – –) $Wa_L = 0.5$. (b) Thin cathode: CASE 3 (——) $Wa_L = 0$; CASE 4 (– – – –) $Wa_L = 0.5$. (c) Resistive cathode: CASE 5 (——) $Wa_L = 0$; CASE 6 (– – – –) $Wa_L = 0.5$.

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