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

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ABSTRACT

A new numerical method has been developed to calculate secondary current distribution in electrochemical cells. The method is applicable in arbitrary two-dimensional systems which include thin, non-uniform, and/or anisotropical resistive electrodes with nonlinear polarization kinetics such as the Butler-Volmer polarization at electrolyte-electrode interfaces. The calculation uses a double iterative method employing the boundary element method in the electrolyte region and the uniform resistive electrode region and the finite element method in the non-uniform and/or anisotropical resistive electrode region. Parametric calculations for a corner electrode were performed to demonstrate the present method. The present simulation method is expected to be utilized in the design of micro-electrochemical cells with resistive electrodes.

INTRODUCTION

It is essential in the design of electrochemical systems to accurately calculate the distribution of current density over electrode surfaces without any geometrical or kinetic simplification. There is substantial literature on numerical methods to calculate secondary current distributions, but these methods require simplifications with regard to conductive features of electrodes. In some works it is assumed that the electrode conductivity is infinite to avoid the difficulty of calculating large changes in the potential from electrolyte to 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, printheads of printers, and so on. Though several researchers have reported investigations of current distribution with resistive electrodes, they are restricted to idealized cell configurations and not applicable for complex shapes. In addition to the resistance, non-uniformity of the electrode conductivity should be considered when the electrode is made of layered films or impurity doped materials. If the electrode is made of compounds containing fibers, anisotropic features should also be taken into consideration. For example, microelectronic circuits or resistors by means of the thick film technology are sometimes highly non-uniform due to non-uniform spatial distribution of metal particles and glass. Since the conduction mechanism in thick films is point-to-
point contact of metal particles, small non-uniformity of the particle distribution causes large non-uniformity of the resistivity. A non-magnetic contact development roller, a biased transfer roller, and a charger roller of the xerographic engine are other examples of the non-uniform resistive electrode. The roller consists of a metal shaft and conductive elastic layer(s). Since the layer is made of resin or rubber containing carbon particles, these resistivity are non-uniform even in the single layer roller due to the same reason of the thick film circuit. Resistive fibers are sometimes mixed in the resin to control the resistivity. Radial resistivity is high compared with axial resistivity in this case, if the roller is made by the injection molding method.

The purpose of the present work is to establish a numerical method to calculate secondary current distribution, which is applicable to arbitrary two-dimensional electrochemical cells having electrodes of thin, resistive, non-uniform and/or anisotropic conductivities with nonlinear Butler-Volmer polarization kinetics.

MODELING

Basic Equations

It is assumed that an electrochemical cell (see Figure 2) consists of well stirred electrolyte with no concentration gradients, and electrodes, anode and cathode, whose conductivities are non-uniform and/or anisotropic. The following two Equations (1) and (2) apply in the electrolyte region and the electrode region, respectively.

\[ \nabla^2 \phi_y = 0 \quad (1) \]
\[ \nabla \cdot (\sigma_e \nabla \phi_e) = 0 \quad (2) \]

where \( \phi \) is electric potential, \( \sigma \) is conductivity, and the subscripts \( y \) and \( e \) denote electrolyte and electrode, respectively. It should be emphasized that the conductivity of the electrode, \( \sigma_e \), is generally a tensor. From the conservation law of current, the current that flows into the electrode is equal to that from the electrolyte.

\[ \sigma_y \mathbf{n} \cdot \nabla \phi_y = \sigma_e \mathbf{n} \cdot \nabla \phi_e \quad (3) \]

where \( \mathbf{n} \) is a unit normal vector perpendicular to the electrode. On the other hand, the potential at the interfaces between the electrolyte and electrodes is not continuous, but the surface overpotential, \( \eta_s \), exists.

\[ \eta_s = \phi_e - \phi_y \quad (4) \]

The Butler-Volmer equation describes the relationship between the surface overpotential and the current density at the electrodes.

\[ i_n = -\sigma_y \mathbf{n} \cdot \nabla \phi_y - i_o \left[ \exp \left( \frac{\alpha_a F \eta_s}{RT} \right) - \exp \left( -\frac{\alpha_c F \eta_s}{RT} \right) \right] \quad (5) \]

Here \( i_n \) is the current density to the electrode, \( i_o \) is the exchange current density, \( \alpha_a \) and \( \alpha_c \) are anodic and cathodic transfer coefficients, \( F \) is Faraday’s constant, \( R \) is the universal gas constant, and \( T \) is absolute temperature. The applied voltage is constant at the terminals if the electrochemical cell is operated under constant voltage, \( \phi_o \).

\[ \phi_o = \phi_a , \quad \phi_c = 0 \quad (6) \]

Subscripts \( a \) and \( c \) denote the anode and the cathode, respectively. The natural boundary condition applies on insulated boundaries or planes of symmetry.

\[ \mathbf{n} \cdot \nabla \phi_{y,e} = 0 \quad (7) \]
To calculate the secondary current distribution in the cell, Laplace equation (1) and Equation (2) may be solved subject to the boundary conditions (6) and (7) satisfying the conservation law of current (3) and the internal boundary condition (5). Equation (2) is reduced to the Laplace equation, if electrodes are uniform resistive.

The nonlinear boundary condition (5), the difference in conductivity between the electrolyte and the electrode, and the non-uniform and/or anisotropic conductivity of the electrode complicate the numerical calculation.

**Thin Electrode**

If the electrode is thin, it is not necessary to solve the two-dimensional equation (2) and the potential along the electrode is determined by the following integral equation:

\[ \frac{d\phi_e}{dl} = \int_0^l \left( \frac{1}{t_e} \right) \sigma_y \mathbf{n} \cdot \nabla \phi_y \, dl \]  

(8)

where \( l \) is a distance from the terminal along the electrode, \( t_e \) is the thickness of the thin electrode.

**Numerical method**

A double iterative numerical method was used to solve the system of equations. A flowchart of the numerical method is shown in Figure 1. Laplace equation (1) was solved by the boundary element method (BEM)\(^{23, 24}\) under initial boundary conditions, \( \phi_a = \phi_o \) at the anode and \( \phi_e = 0 \) at the cathode (STEP 2 in Figure 1). The surface overpotential, \( \eta_{s_e} \), was explicitly determined by Equation (4), and the boundary values, \( \phi_a = \phi_o \cdot \eta_{s_e}, \phi_e = \eta_{s_c} \), 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 \( \phi_e \) and \( \eta_{s_e} \) were obtained. Once converged values of \( \phi_y \) and \( \nabla \phi_y \) had been obtained (STEP 4), Equation (2) was solved (STEP 6) by the finite element method (FEM)\(^{25}\) in case of non-uniform electrodes or the BEM in case of uniform electrodes under the boundary condition of the second kind determined by Equation (3) at the interface between electrolyte and electrode (STEP 5). For a thin electrode assumed as one-dimensional, Equation (8) was solved instead of the Equation (2) and \( \phi_e \) along the electrode was determined. The calculated potential at the interface was added to \( \eta_{s_e} \) (STEP 7) and the procedure was again repeated until converged values of both \( \phi_y \) and \( \phi_e \), potential difference less than \( 10^{-4} \phi_o \) at the edge of the cathode, were obtained (STEP 8). The over-relaxation method was employed for the iterative procedure.

Although the FEM or the finite difference method (FDM) are also useful for numerical calculations of the Laplace equation, the BEM 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, and (iii) the potential gradient, necessary for calculations of Equations (3), (5), (7) and (8), is directly determined.

However, the FEM was used to calculate the potential distribution in the electrode with non-uniform and/or anisotropic resistance, because the FEM is suitable for the calculation of non-uniform and anisotropic fields.

An EPSON Model PC-386G personal computer (33 MHz 80386 CPU with the Intel® mathematical coprocessor 387™DX-33) was used with a BASIC program for numerical calculations.
RESULTS AND DISCUSSION

Calculation conditions

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

Table 1 Calculation conditions

<table>
<thead>
<tr>
<th>Cathode</th>
<th>$Wa_L = 0$ (Primary)</th>
<th>$Wa_L = 0.5$ (Secondary)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infinitely conductive</td>
<td>CASE 1</td>
<td>CASE 2</td>
</tr>
<tr>
<td>Thin</td>
<td>CASE 3</td>
<td>CASE 4</td>
</tr>
<tr>
<td>Uniform resistive</td>
<td>CASE 5</td>
<td>CASE 6</td>
</tr>
<tr>
<td>Non-uniform but isotropic</td>
<td>CASE 7</td>
<td>CASE 8</td>
</tr>
<tr>
<td>Non-uniform and anisotropic</td>
<td>CASE 9</td>
<td>CASE 10</td>
</tr>
</tbody>
</table>

According to Dukovic's definition, three dimensionless parameters which characterize the nonlinear polarization system were used in this report. $Wa_L = RT \sigma_y [(a_a + a_c)FLi_a]$; Wagner number for linear kinetics,$Wa_T = RT \sigma_y (a_cFLi_{ave})$; Wagner number for Tafel kinetics, $a_a/a_c = 1$, where $L$ is characteristic length (a gap
between the anode and the cathode land) and $i_{ave}$ is an average current density at the interface between the cathode and the electrolyte. In the present calculation, $W_{aiL}$ was given as the calculation condition but $W_{aiT}$ was derived from the calculated current density at the interface between the cathode and the anode.

**Potential and current density distributions**

Figure 3 shows the result of calculations on potential distribution in the cells of CASEs 1 and 10, and Figure 4 is the normal current density along the cathodes. Calculation results of the other cases were shown in the references 27, 28 and 29. The number of iterations was around 50, and the calculation time was about 2 hours with the compiled BASIC program for CASEs 6, 8 and 10 till convergence error, defined by max[(φ$_{i+1}$ - φ$_i$)/φ$_i$], becomes less than 0.01%.

The following can be made from the results of calculations.

1. 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.) On the other hand, the current density is zero in this case at the corner of the cathode. These are the typical characteristics of the primary current distribution.

2. The non-polarized resistive electrode (CASEs 3, 5, 7 and 9) reduced current concentration at the edges. The surface overpotential did not exist at interfaces in the non-polarized cases but a potential drop due to ohmic resistance arose in the cathodes.

3. In accordance with the increase in polarization (CASEs 2, 4, 6, 8 and 10), a potential drop (or surface overpotential) appeared at the electrode-electrolyte interfaces and the current distribution became more uniform. The singularity at the edges was nonexistent in the polarized cases, and the current density was finite both at the edge and corner of the polarized cathodes. These are typical characteristics of secondary current distribution.

4. The polarized thin (CASE 4) or resistive electrode (CASEs 6, 8 and 10) further reduced current concentration at the edge because of polarization at the interfaces and the ohmic potential drop in the cathodes depending on resistive properties of the electrode.

**SUMMARY AND CONCLUSIONS**

A numerical method has been developed to calculate secondary current distribution in electrochemical cells. The method is applicable in arbitrary two-dimensional systems which include a uniform concentration electrolyte and thin, non-
uniform and/or anisotropical resistive electrodes with Butler-Volmer nonlinear polarization kinetics at electrolyte-electrode interfaces. The calculation uses a double iterative method employing the BEM in the electrolyte and uniform electrode region and the FEM in the non-uniform resistive electrode region coded in BASIC to obtain secondary current distribution with nonlinear polarization and resistive electrodes. The present simulation method is expected to be utilized in the design of micro-electrochemical cells with resistive electrodes.

A part of this work was published in the references 27, 28 and 29.
LIST OF SYMBOLS

\( F \) Faraday's constant \((96,487 \text{ C equiv}^{-1})\)

\( i_{\text{ave}} \) averaged current density at interface between cathode and electrolyte \((\text{A m}^{-2})\)

\( i_o \) exchange current density \((\text{A m}^{-2})\)

\( i_n \) current density to electrode \((\text{A m}^{-2})\)

\( L \) characteristic length, minimum gap between anode and cathode \((\text{m})\)

\( \ell \) distance from terminal along electrode \((\text{m})\)

\( n \) unit normal vector perpendicular to boundaries \((-)\)

\( R \) universal gas constant \((8.3143 \text{ J mol}^{-1} \text{ K}^{-1})\)

\( T \) absolute temperature \((\text{K})\)

\( t_e \) thickness of thin electrode \((\text{m})\)

\( W_{AL} \) Wagner number for linear kinetics \(\equiv RT\sigma_f/[(a_a + a_c)FLi_o]\) \((-)\)

\( W_{AT} \) Wagner number for Tafel kinetics \(\equiv RT\sigma_f/a_cFLi_{\text{ave}}\) \((-)\)

\( a_a, a_c \) anodic and cathodic transfer coefficients \((-)\)

\( \eta_s \) surface overpotential \(\equiv \phi_e - \phi_y\) \((\text{V})\)

\( \sigma \) conductivity \((\text{S m}^{-1})\)

\( \phi \) potential \((\phi_o: \text{potential difference between anode and cathode terminals})(\text{V})\)

Subscripts \( a \) anode, \( c \) cathode, \( e \) electrode, \( y \) electrolyte

REFERENCES


