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APPENDIX C

A MATHEMATICAL MODEL FOR PREDICTING CYCLIC VOLTAMMOGRAMS OF ELECTRONICALLY CONDUCTIVE POLYPYRROLE

A MATHEMATICAL MODEL FOR PREDICTING CYCLIC VOLTAMMOGRAMS OF ELECTRONICALLY CONDUCTIVE POLYPYRROLE

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Abstract

Polypyrrole is an attractive polymer for use as a high-energy-density secondary battery because of its potential as an inexpensive, lightweight, and noncorrosive electrode material. A mathematical model to simulate cyclic voltammograms for polypyrrole is presented here. The model is for a conductive porous electrode film on a rotating disk electrode (RDE) and is used to predict the spatial and time dependence of concentration, overpotential, and stored charge profiles within a polypyrrole film. The model includes both faradaic and capacitive charge components in the total current density expression.

Introduction

Electrochemically synthesized conducting polypyrrole has received much attention as a secondary battery electrode because it has high conductivity, high specific charge capacity, and stable and reversible electrochemical redox behavior (1-4). Polypyrrole, in its conducting polycationic form (PPy^+), is readily obtained by a simple one-step electrochemical oxidation of the pyrrole monomer. This reaction is electronically irreversible and fairly complex. A detailed discussion of the mechanism of synthesis is beyond the scope of this study.

Electronically conductive polypyrrole has a number of potential technological applications. It is used 1) as a battery electrode, 2) in display devices, 3) in electronic devices, and 4) as a component of new high-energy-density secondary batteries. All of these applications rely on the ability of the polypyrrole to switch between the conductive and nonconductive states. Polypyrrole in its conducting polycationic form can be transformed by cathodic reduction into the neutral insulating state (PPy°) with conductivity less than 10^{-5} $ohm^{-1}cm^{-1}$. This film is extremely unstable and easily reoxidized to yield PPy^+. In contrast, oxidized polypyrrole film is stable in a wide range of solvents.

An experimental cyclic voltammogram of polypyrrole approximates the behavior of a quasi-reversible couple with the distinct characteristic of a large capacitive background current (5). Some authors (6-8) have tried to analyze the capacitance effect in order to separate the faradaic current from the capacitive current. In spite of this, the capacitance effect is still not fully understood. Feldberg (6) suggested a mathematical model of the capacitive current with the electrochemical switching polymer films, but failed to include transport effects (diffusion and migration) of the counter-ions. Pickup and Osteryoung (7) developed a mathematical model for potential step chronoamperometry and concluded that a polymer film could be modeled as a porous electrode. The porous electrode model they used is not satisfactory because it is based on the assumption that faradaic reactions are negligible.

The model presented here is used to simulate potentiostatic cyclic voltammograms for a polypyrrole film on a RDE. The rotating disk electrode was chosen because of its well-defined hydrodynamics. The model consists of a combination of the models presented by Feldberg (6) for the capacitance effect on the current density and by Ryan *et al.* (9) for a conductive porous layer on a rotating disk electrode. The polypyrrole film is treated as a porous electrode with a high surface-to-volume ratio and a large double layer capacitance, which is proportional to the amount of oxidized polypyrrole film (4-7). These model conditions were chosen so that the simulated predictions could be compared to experimental results available in the literature. The faradaic and capacitive current components associated with the electrochemical switching of a film between the insulating and electronically conducting states are included in the model.

The transport equations of the model are based on the conservation of mass and charged species. The equations include migration of charged species in an electric field, diffusion of charged and uncharged species, and the electrochemical reaction that occurs within the porous polypyrrole film. Since the surface of a solid electrode is composed of active (oxidized) and inactive (reduced) sites during charge and discharge processes, averaged values are used to describe local variables within a volume element throughout the porous layer to account for the effect of nonhomogeneity of the electrode surface (9).

The model is used to predict concentration, overpotential, and stored charge profiles within the polypyrrole film as a function of position and time. The model is also used to predict the dependence of the faradaic, capacitive, and total current density on applied overpotential.

Model Development

The model presented here is for predicting potentiostatically controlled cyclic voltammograms for a porous polypyrrole film on a RDE in a one-compartment cell. The one-compartment electrochemical cell contains a platinum RDE coated with polypyrrole film, a platinum counter electrode, and a saturated calomel reference electrode (SCE). A schematic diagram of a typical experimental system is shown in Fig. 1. The Luggin capillary tip of the reference electrode is placed as close as possible to the center of the disk. This enables one to use the reference electrode to detect the solution potential near the working electrode. The electrolyte consists of 0.1 M $LiClO_4$ in acetonitrile. In the solution, $LiClO_4$ dissociates into charged Li^+ and ClO_4^-.

During a potential sweep, a polypyrrole film can be cycled repetitively between its oxidized and reduced forms in the absence of oxygen with no evidence of polypyrrole decomposition (4). The reaction occurring during the potential sweep is assumed to be described as follows:

$$PPy^{\circ} + ClO_4^- \rightleftharpoons PPy^+ClO_4^- + e^- \qquad [1]$$

The rate of this reaction is controlled primarily by the available electroactive area and the transport rate (diffusion and migration) of ClO_4^-.

Figure 2 is a schematic representation of the regions close to the RDE surface that are relevant to the development of the model equations. As shown in Fig. 2, there are two separate regions: the porous electrode region of width δ_{PE} and the solution diffusion region of width δ_{RE}.

The dependent variables in the diffusion layer are: the concentration of Li^+ (c_+), the concentration of ClO_4^- (c_-), and the potential of the solution phase (Φ_2). In the porous polypyrrole region, the dependent variables include the ones in the diffusion layer, the local faradaic charge per unit volume (Q_F), and the potential of the solid polymer phase (Φ_1). Values for these unknowns depend on the perpendicular distance from the electrode surface (y) and time (t), and they are obtained by solving the governing equations with associated boundary conditions.

Assumptions

The assumptions used in developing the governing equations for the model are as follows:

1) no homogeneous reactions occur in the bulk solution.
2) the solution is Newtonian and isothermal.
3) transport occurs only in the axial direction (i.e., y direction).
4) the platinum current collector is solid and inert.
5) the differential capacitance of the platinum is negligible.
6) the differential capacitance of the double layer is proportional to the amount of oxidized polypyrrole.

7) the differential capacitance of polypyrrole is independent of potential.
8) the electrochemical reaction occuring within the porous electrode is a pseudo-homogeneous reaction whose rate is based on the Butler-Volmer equation, as presented below.

Governing Equations – Solution Diffusion Layer

Mass transfer in the diffusion layer is governed by the following material balance equation for species i:

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \mathbf{N}_i \qquad \text{where} \quad i = +, - \tag{2}$$

Eq. [2] depends on the flux, $\mathbf{N}_i$, of species i which is due to migration in the electric field, diffusion in the concentration gradient, and convection in the flow field

$$\mathbf{N}_i = -z_i u_i F c_i \nabla \Phi_2 - D_i \nabla c_i + c_i \mathbf{v} \qquad \text{where} \quad i = +, - \tag{3}$$

The ionic mobility, u_i, is assumed to be described by the Nernst-Einstein equation (10)

$$u_i = \frac{D_i}{RT} \qquad \text{where} \quad i = +, - \tag{4}$$

Only the axial component of Eq. [3] is considered in the model and the velocity component in that direction depends only on the normal distance from the electrode surface according to the no-slip condition (9)

$$v_y = -a'\Omega\sqrt{\frac{\Omega}{\nu}}(y - y_{PE})^2 \tag{5}$$

Combining Eq. [2], [3], [4], and [5] yields the governing equation for species i within the solution diffusion layer on the RDE:

$$\frac{\partial c_i}{\partial t} = \frac{z_i D_i F}{RT}\left(c_i \frac{\partial^2 \Phi_2}{\partial y^2} + \frac{\partial c_i}{\partial y}\frac{\partial \Phi_2}{\partial y}\right) + D_i \frac{\partial^2 c_i}{\partial y^2} + a'\Omega\sqrt{\frac{\Omega}{\nu}}(y - y_{PE})^2 \quad \text{where} \quad i = +, - \tag{6}$$

The electroneutrality condition provides the additional governing equation needed to solve for Φ_2 within the diffusion layer

$$\sum_i z_i c_i = z_+ c_+ + z_- c_- = 0 \tag{7}$$

Governing Equations – Porous Electrode Layer

To account for the nonhomogeneous structure of the polymer film, macroscopic properties are used to describe the porous electrode layer in terms of measurable parameters without regard for the actual geometric detail of the pore structure. Two of these properties are the porosity (ϵ) and the MacMullin number ($N_{\mathrm{M,PE}}$). The porosity represents the void volume occupied by the electrolyte per unit volume of porous region. The MacMullin number (11) is defined as the ratio of the tortuosity to the porosity:

$$N_{\mathrm{M,PE}} = \tau/\epsilon \tag{8}$$

The porosity and MacMullin number are assumed to be constant.

Within the porous electrode layer, the material balance equation is formulated in terms of average quantities that include the reaction rate term for the electrochemical reaction

$$\frac{\partial \epsilon c_{\mathrm{i}}}{\partial t} = -\nabla \cdot \mathbf{N}_{\mathrm{i}} + R_{\mathrm{i}}' \qquad \text{where} \quad \mathrm{i} = +, - \tag{9}$$

and R_{i}' is the production rate of species i due to a pseudo-homogeneous reaction (electrochemical reaction) within the porous electrode.

The flux expression, Eq. [3], is modified to account for the porous and tortuous structure of the polypyrrole film. This is accomplished by replacing the diffusion coefficient in Eq. [3] by an effective diffusion coefficient within the porous layer

$$D_{\mathrm{i,e}} = \frac{D_{\mathrm{i}}}{N_{\mathrm{M,PE}}} \qquad \text{where} \quad \mathrm{i} = +, - \tag{10}$$

Thus, the flux of species i within the solution phase of the porous layer becomes

$$\mathbf{N}_{\mathrm{i}} = -\frac{z_{\mathrm{i}} D_{\mathrm{i}} F}{N_{\mathrm{M,PE}} RT} c_{\mathrm{i}} \nabla \Phi_2 - \frac{D_{\mathrm{i}}}{N_{\mathrm{M,PE}}} \nabla c_{\mathrm{i}} \qquad \text{where} \quad \mathrm{i} = +, - \tag{11}$$

and where it has been assumed that there is no convective flow within the porous layer. Combining Eq. [11] with the material balance expression, Eq. [9], subject to the assumptions mentioned above, yields the governing equation for species i within the porous electrode layer:

$$\frac{\partial \epsilon c_{\mathrm{i}}}{\partial t} = \frac{z_{\mathrm{i}} D_{\mathrm{i}} F}{N_{\mathrm{M,PE}} RT}\left(c_{\mathrm{i}}\frac{\partial^2 \Phi_2}{\partial y^2} + \frac{\partial c_{\mathrm{i}}}{\partial y}\frac{\partial \Phi_2}{\partial y}\right) + \frac{D_{\mathrm{i}}}{N_{\mathrm{M,PE}}}\frac{\partial^2 c_{\mathrm{i}}}{\partial y^2} + R'_{\mathrm{i}} \qquad \text{where} \quad \mathrm{i} = +,- \qquad [12]$$

The production rate of species i due to an electrochemical reaction is given by (12):

$$R'_{\mathrm{i}} = -\frac{s_{\mathrm{i}}}{nF} j_{\mathrm{F}} \qquad \text{where} \quad \mathrm{i} = +,- \qquad [13]$$

and j_{F} is the faradaic transfer current per unit volume (A/cm^3) of the porous region and is disscussed later.

It is a consequence of the assumption of electroneutrality that the charge which leaves the solid phase must enter the solution phase. This is expressed as (12)

$$\nabla \cdot i_1 + \nabla \cdot i_2 = 0 \qquad [14]$$

where i_1 is the superficial current density (current per projected area of the electrode) in the solid electrode phase, and i_2 is the superficial current density in the solution phase. In the solid phase, the movement of electrons is governed by Ohm's law

$$i_1 = -\sigma(1-\epsilon)\frac{\partial \Phi_1}{\partial y} \qquad [15]$$

where σ is the conductivity of polypyrrole, and $\sigma(1-\epsilon)$ is equivalent to the effective solid conductivity. It is assumed that the conductivity of polypyrrole is proportional to the degree of the oxidation of polypyrrole as follows:

$$\sigma = \frac{\sigma_{\mathrm{MIN}} - \sigma_{\mathrm{MAX}}}{Q_{\mathrm{F,MIN}} - Q_{\mathrm{F,MAX}}}\left(Q_{\mathrm{F}} - Q_{\mathrm{F,MAX}}\right) + \sigma_{\mathrm{MAX}} \qquad [16]$$

where σ_{MIN} represents the conductivity of the polypyrrole film at minimal charge state ($Q_{\mathrm{F,MIN}}$), and σ_{MAX} represents the conductivity of the film at its maximal charge state ($Q_{\mathrm{F,MAX}}$). The current density in the solution phase is given by

$$i_2 = -\frac{\kappa}{N_{\mathrm{M,PE}}}\frac{\partial \Phi_2}{\partial y} \qquad [17]$$

where κ is the specific conductivity of electrolyte and is assumed to be constant. The term $\kappa/N_{\mathrm{M,PE}}$ is the effective solution conductivity. Substitution of Eq. [15] and [17] into the conservation of charge equation, Eq. [14], yields

$$\nabla \cdot \left(-\sigma(1-\epsilon)\frac{\partial \Phi_1}{\partial y}\right) + \nabla \cdot \left(-\frac{\kappa}{N_{\mathrm{M,PE}}}\frac{\partial \Phi_2}{\partial y}\right) = 0 \qquad [18]$$

Electroneutrality, Eq. [7], is also used as the governing equation for Φ_2 in the porous region.

The rate of accumulation of the faradaic charge contained in the oxidized polypyrrole per unit volume, Q_{F}, is assumed to be related to the faradaic transfer current, j_{F}, as follows:

$$\frac{\partial Q_{\mathrm{F}}}{\partial t} = j_{\mathrm{F}} \qquad [19]$$

Current Density

The faradaic transfer current per unit volume, j_{F}, is assumed to be given by the Butler-Volmer equation (13):

$$j_{\mathrm{F}} = a i_{\mathrm{O,REF}} \left\{ \left(\frac{Q_{\mathrm{F,MAX}} - Q_{\mathrm{F}}}{Q_{\mathrm{F,MAX}}}\right)\left(\frac{c_-}{c_{-,\mathrm{REF}}}\right)\exp\left(\frac{\alpha_a F}{RT}\eta\right) - \left(\frac{Q_{\mathrm{F}}}{Q_{\mathrm{F,MAX}}}\right)\exp\left(\frac{-\alpha_c F}{RT}\eta\right)\right\} \qquad [20]$$

where a is the electroactive surface area per unit volume, $i_{\mathrm{O,REF}}$ is the exchange current density at a given reference concentration ($c_{\mathrm{i,REF}}$), and η is the overpotential. The overpotential is defined as:

$$\eta = (\Phi_1 - \Phi_{\mathrm{RE}}) - (\Phi_2 - \Phi_{\mathrm{RE}}) - U_{\mathrm{REF}} \qquad [21]$$

where Φ_{RE} is the solution potential at the Luggin tip, and U_{REF} is the open circuit potential at a given reference concentration ($c_{\mathrm{i,REF}}$) and is relative to SCE. Anodic and cathodic current densities are taken to be positive and negative, respectively. Note also that $\alpha_a + \alpha_c = n$. It can be seen that the local transfer current predicted by the Butler-Volmer kinetic expression, Eq. [20], depends upon the difference between the potential of the solid phase and that of the adjacent solution within the porous electrode.

The anodic faradaic current in the porous polymer film leads to charging of the double layer within the pores of the polymer film in a manner consistent with that proposed by Feldberg (6). That is, the amount of capacitive charge that goes to charging the double layers within the pores of the porous film, Q_C, is related to the amount of the faradaic charge added to the polymer film by the faradaic reaction:

$$Q_C = a^{\star}(\eta - \eta_{PZC})Q_F \tag{22}$$

where $a^{\star}$ is a proportional constant which is assumed to be independent of potential, and η_{PZC} is the total overpotential across the double layer at the point of zero charge (PZC) which is given by

$$\eta_{PZC} = \left\{(\Phi_1 - \Phi_{RE}) - (\Phi_2 - \Phi_{RE}) - U_{REF}\right\}_{PZC} \tag{23}$$

The capacitive transfer current per unit volume, j_C, associated with charging of the double layer is defined as follows:

$$j_C = \frac{\partial Q_C}{\partial t} \tag{24}$$

Substituting Eq. [19] and [22] into Eq. [24] shows that

$$j_C = a^{\star}\left(Q_F \frac{\partial \eta}{\partial t} + (\eta - \eta_{PZC})j_F\right) \tag{25}$$

with the assumption that $\Phi_{RE} = (\Phi_{RE})_{PZC}$. The total transfer current per unit volume, j_T, is defined as the sum of the faradaic and capacitive transfer currents per unit volume:

$$j_T = j_F + j_C \tag{26}$$

Eq. [26] can be used to predict the total current density, i_{T} (current per projected area), by integrating j_{T} over the porous layer:

$$i_{\mathrm{T}} = \int_{y=0}^{y=y_{\mathrm{PE}}} j_{\mathrm{T}} dy \qquad [27]$$

Note that the faradaic current density, i_{F}, and the capacitive current density, i_{C}, can be obtained in a similar manner from j_{F} and j_{C}, respectively.

Boundary Conditions

The boundary conditions at the polymer film/substrate interface ($y = 0$) are

$$-\frac{z_{\mathrm{i}} D_{\mathrm{i}} F}{RT} c_{\mathrm{i}} \frac{\partial \Phi_2}{\partial y} - D_{\mathrm{i}} \frac{\partial c_{\mathrm{i}}}{\partial y} = 0 \qquad \text{where} \quad \mathrm{i} = +, - \qquad [28]$$

$$\Phi_1 = E_{\mathrm{APP}} + \Phi_{\mathrm{RE}} \qquad [29]$$

$$\sum_{\mathrm{i}} z_{\mathrm{i}} c_{\mathrm{i}} = z_+ c_+ + z_- c_- = 0 \qquad [30]$$

where E_{APP} and Φ_{RE} are constants. The boundary conditions at the polymer film/diffusion layer interface ($y = y_{\mathrm{PE}}$) are

$$\mathbf{N}_{\mathrm{i,y}}|_{\text{porous layer}} = \mathbf{N}_{\mathrm{i,y}}|_{\text{diffusion layer}} \qquad \text{where} \quad \mathrm{i} = +, - \qquad [31]$$

$$\frac{\partial \Phi_1}{\partial y} = 0 \qquad [32]$$

$$\sum_{\mathrm{i}} z_{\mathrm{i}} c_{\mathrm{i}} = z_+ c_+ + z_- c_- = 0 \qquad [33]$$

The boundary conditions in the bulk solution ($y = y_{\mathrm{RE}}$) are

$$c_{\mathrm{i}} = c_{\mathrm{i,REF}} \qquad \text{where} \quad \mathrm{i} = +, - \qquad [34]$$

$$\Phi_2 = \Phi_{\mathrm{RE}} \qquad [35]$$

Initial Conditions

The initial concentration of each species i is set equal to its bulk concentration:

$$c_i = c_{i,\mathrm{REF}} \qquad \text{where} \quad i = +, - \tag{36}$$

For convenience, it is assumed that the polypyrrole film is initially fully reduced and is ready to be oxidized. Consequently, the faradaic charge per unit volume in the porous region is initially equal to $Q_{\mathrm{F,MIN}}$, a minimal charge state:

$$Q_{\mathrm{F}} = Q_{\mathrm{F,MIN}} \tag{37}$$

Solution Method

The governing equations and boundary conditions can be written in finite difference form and solved by using Newman's pentadiagonal block matrix equation solver (14). Implicit stepping can be used for the time derivatives (15). In the diffusion layer, Q_{F} and Φ_2 are dummy variables treated as constants and are set arbitrarily equal to zero. During the potential sweep, the applied potential (E_{APP}), which is the difference between Φ_1 at y=0 and Φ_2 at y=y_{RE} (Φ_{RE}=0), is changed linearly between E_{INI} and E_{FIN} according to a specified scan rate (v_{S}).

Results and Discussion

Cyclic voltammograms of polypyrrole can be predicted using the model described above. The values used for the fixed parameter are given in Table I. Figure 3 shows predicted cyclic voltammograms for the polypyrrole film at various scan rates. Comparison of these predictions with those obtained experimentally for a similar system, as shown in Fig. 4, shows qualitative agreement.

Figure 5 shows the total current density and its components at a 100 mV/sec scan rate. Note that when the maximal quantity of oxidized polypyrrole is formed, no further oxidation of the film occurs and the current is entirely dominated by capacitive charge.

Figure 6 shows the dynamic profile of the concentration of ClO_4^- in the porous electrode region at an 100 mV/sec scan rate. For convenience, the concentration of ClO_4^- was made dimensionless relative to its reference concentrations ($c_{-,\mathrm{REF}}$). The position coordinate was made dimensionless by using the thickness of the film (δ_{PE}) so that $\xi = 1$ represents the interface between the diffusion layer and the polymer film. Time was made dimensionless by using the time required to scan the applied potential from E_{INI} to E_{FIN} (τ°) so that $\zeta = 1$ represents the intermediate point where the polypyrrole film is totally oxidized.

During the oxidation process, the reacting species (ClO_4^-) is transported from the bulk to the porous electrode layer where it diffuses and migrates to reactive sites within the porous layer. During reduction, the opposite is true. Since the effective diffusivities of Li^+ and ClO_4^- within the porous layer are smaller than the free stream diffusivity of these species, then concentration gradients within the porous region must be larger to make up for the slower movement of the ions. The concentration profiles of both species are the same because of the electroneutrality condition.

Figure 7 shows the faradaic charge per unit volume due to the electrochemical reaction within the film at a sweep rate of 100 mV/sec. The faradaic charge per unit volume was made dimensionless by using the maximum faradaic charge value ($Q_{\mathrm{F,MAX}}$) as the reference point. The rate of charge accumulation is faster in the outer layer of the film during oxidation because of diffusion and migration effects. Note that charge accumulates rapidly throughout the entire film.

Summary

Theoretical calculations were carried out that describe quantitatively the current responses of the quasi-reversible behavior of electronically conductive polypyrrole. Porous electrode theory was applied to the conductive polymer to provide the basis for understanding the transport behavior of the switching process within the polymer film. The effects of diffusion and migration were included because it is likely that counter-ion movement limits the oxidation and reduction rates. The net cyclic voltammetric current was decomposed into two components: a capacitive current due to the double layer charging and the faradaic current due to an electrochemical reaction. It may be possible to use this model together with experimental data and parameter estimation techniques to determine the transport and kinetic parameters of the model.

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NOTATION

a	specific surface area of the porous material, cm^{-1}
a'	0.51023
$a^\star$	double layer constant, V^{-1}
c_+	concentration of Li^+, $\mathrm{mol/cm^3}$
c_-	concentration of $\mathrm{ClO_4^-}$, $\mathrm{mol/cm^3}$
c_i	concentration of species i, $\mathrm{mol/cm^3}$
c_i^*	dimensionless concentration of species i, $(c_\mathrm{i}/c_{\mathrm{i,REF}})$
$c_{\mathrm{i,REF}}$	initial concentration of species i in the porous region, $\mathrm{mol/cm^3}$
D_i	diffusion coefficient of species i, $\mathrm{cm^2/sec}$
$D_{\mathrm{i,e}}$	effective diffusion coefficient of species i in a porous layer, $\mathrm{cm^2/sec}$
E_{APP}	applied potential (potential difference between the current collector and Φ_{RE}), V
E_{FIN}	final applied potential, V
E_{INI}	initial applied potential, V
F	Faraday's constant, 96487 C/mol
i_{C}	capacitive current density, $\mathrm{A/cm^2}$
i_{F}	faradaic current density, $\mathrm{A/cm^2}$
$i_{\mathrm{O,REF}}$	exchange current density at reference concentrations, $\mathrm{A/cm^2}$
i_{T}	total current density, $\mathrm{A/cm^2}$
i_1	superficial current density in the porous electrode phase, $\mathrm{A/cm^2}$
i_2	superficial current density in the solution phase, $\mathrm{A/cm^2}$
j_{C}	capacitive transfer current per unit volume, $\mathrm{A/cm^3}$
j_{F}	faradaic transfer current per unit volume, $\mathrm{A/cm^3}$
j_{T}	total transfer current per unit volume, $\mathrm{A/cm^3}$

NOTATION (Continued)

n	number of electrons transferred
$\mathbf{N}_\mathrm{i}$	flux vector of species i, mol/cm^2-sec
$\mathbf{N}_\mathrm{i,y}$	y component of flux vector of species i, mol/cm^2-sec
$N_\mathrm{M,PE}$	MacMullin number for the porous electrode layer
Q_C	capacitive charge of double layer per unit volume, C/cm^3
Q_F	faradaic charge of polymer film per unit volume, C/cm^3
Q_F^*	dimensionless faradaic charge of polymer film, $(Q_\mathrm{F}/Q_\mathrm{F,MAX})$
$Q_\mathrm{F,MAX}$	maximum faradaic charge of polymer film per unit volume, C/cm^3
$Q_\mathrm{F,MIN}$	minimum faradaic charge of polymer film per unit volume, C/cm^3
R	universal gas constant, 8.3143 J/mol-K
R_i'	pseudohomogenous reaction rate of species i, mol/cm^3-sec
s_i	stoichiometric coefficient of species i
t	time, sec
T	absolute temperature, K
u_i	mobility of species i, mol-cm^2/J-sec
U_REF	theoretical open-circuit potential at reference concentration, V
v	electrolyte velocity vector, cm/sec
v_S	scan rate, V/sec
v_y	electrolyte velocity in the normal direction, cm/sec
y	perpendicular distance from a porous electrode/substrate interface, cm
y_PE	position of a porous region/diffusion layer interface in y coordinate, cm
y_RE	position of a bulk solution in y coordinate, cm
z_i	proton charge number of species i

NOTATION (Continued)

Greek Symbols

α_a	anodic transfer coefficient
α_c	cathodic transfer coefficient
δ_{PE}	thickness of polypyrrole film, cm
δ_{RE}	thickness of diffusion layer, cm
ϵ	porosity or void volume fraction
ζ	dimensionless time, (t/τ°)
η	overpotential, V
η_{PZC}	overpotential at point of zero charge, V
κ	solution conductivity, $\Omega^{-1}\text{cm}^{-1}$
ν	kinematic viscosity, cm^2/sec
ξ	dimensionless distance, $(1 - y/\delta_{PE})$
ρ_o	pure solvent density, kg/cm^3
σ	conductivity of polypyrrole film, $\Omega^{-1}\text{cm}^{-1}$
σ_{MAX}	conductivity of totally oxidized polypyrrole film, $\Omega^{-1}\text{cm}^{-1}$
σ_{MIN}	conductivity of totally reduced polypyrrole film, $\Omega^{-1}\text{cm}^{-1}$
τ	tortuosity of porous material
τ°	time required to scan the potential from E_{INI} to E_{FIN}, sec
Φ_1	potential in solid phase, V
Φ_2	potential in solution phase, V
Φ_{RE}	potential in the solution at $y = y_{RE}$, V
Ω	disk rotation velocity, rad/sec

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Table I. Fixed parameter values used for cyclic voltammograms.

Operating Variables	T	298.15 K
	Ω	377 rad/sec
	y_{RE}	0.01 cm [a]
	Φ_{RE}	0.0 V
	E_{INI}	−0.8 V (vs. SCE) [b]
	E_{FIN}	0.4 V (vs. SCE) [b]
Electrolyte Properties	D_+	1.03×10^{-5} cm^2/sec [c]
	D_-	1.81×10^{-5} cm^2/sec [c]
	$c_{+,\mathrm{REF}}$	1.547×10^{-4} mol/cm^3 [c]
	$c_{-,\mathrm{REF}}$	1.547×10^{-4} mol/cm^3 [c]
	κ	0.0165 Ω^{-1}cm^{-1} [c]
	ν	6.6×10^{-3} cm^2/sec [d]
	ρ	0.777×10^{-3} kg/cm^3 [d]
Electrode Properties	δ_{PE}	20 nm
	ϵ	0.1
	$N_{\mathrm{M,PE}}$	1.0×10^6
	$Q_{\mathrm{F,MAX}}$	344.65 C/cm^3 [b]
	$Q_{\mathrm{F,MIN}}$	1.0×10^{-14} C/cm^3
	σ_{MAX}	100.0 Ω^{-1}cm^{-1} [b]
	σ_{MIN}	1.0×10^{-14} Ω^{-1}cm^{-1}
Kinetic Parameters	$\mathrm{a} \cdot i_{\mathrm{o,REF}}$	1.0×10^3 A/cm^3
	α_a	0.5
	α_c	0.5
	n	1
	U_{REF}	−0.2 V (vs. SCE) [b]
	$a^\star$	1.076 V^{-1} [e]
	η_{PZC}	−0.1056 V (vs. SCE) [e]

[a] chosen arbitrarily

[b] obtained from Ref. (4)

[c] calculated from Ref. (16)

[d] obtained from Ref. (17)

[e] calculated from Ref. (6)

LIST OF FIGURE CAPTIONS

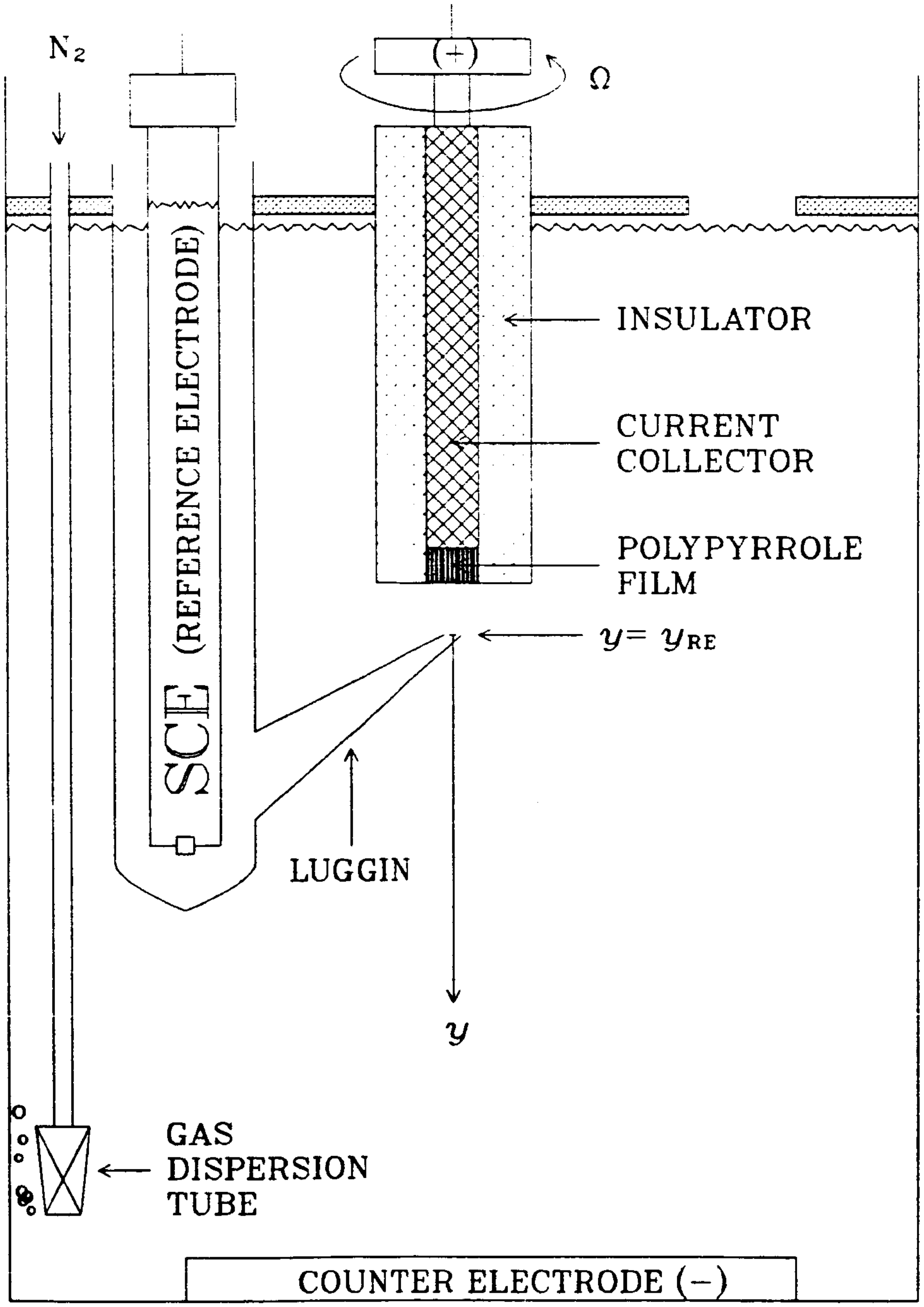

Fig. 1. T. Yeu *et al.*

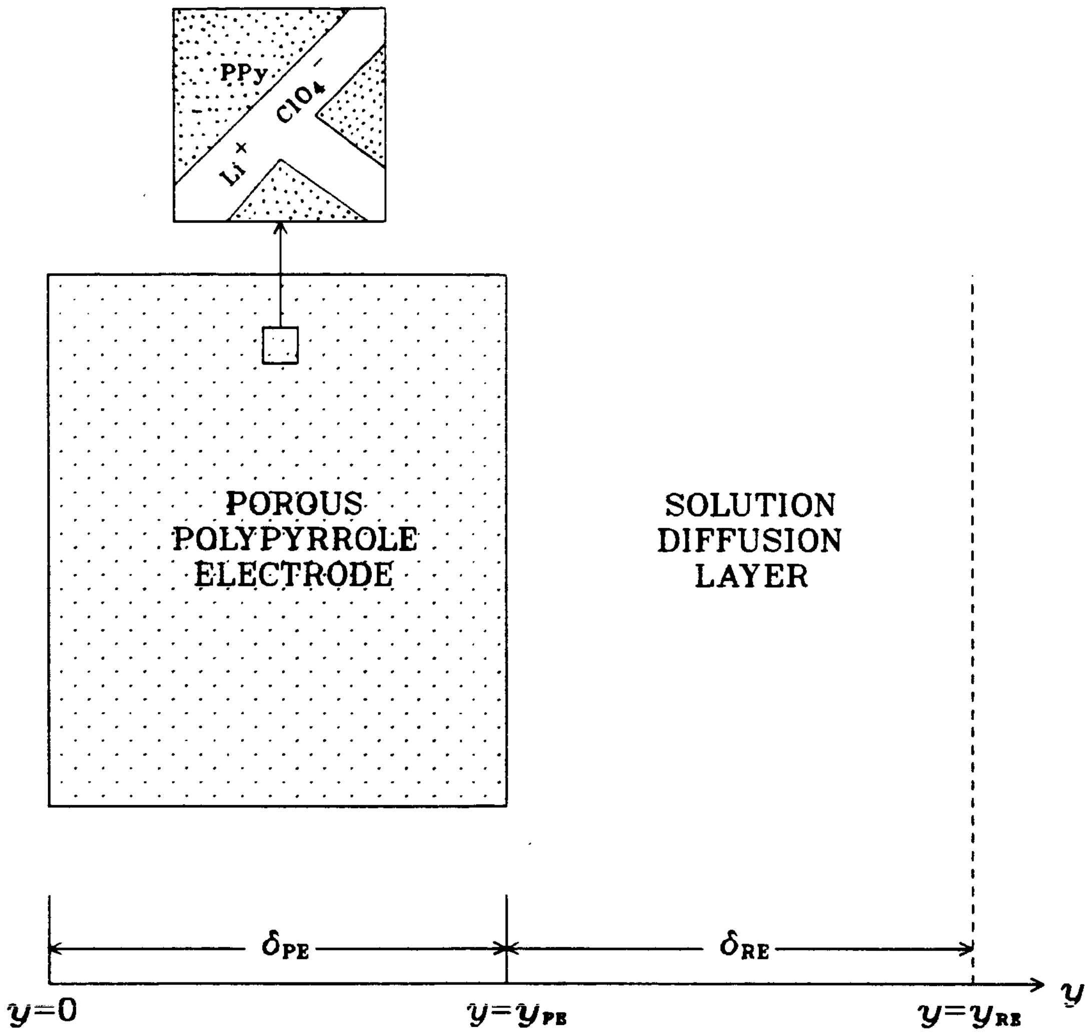

Fig. 2. T. Yeu *et al.*

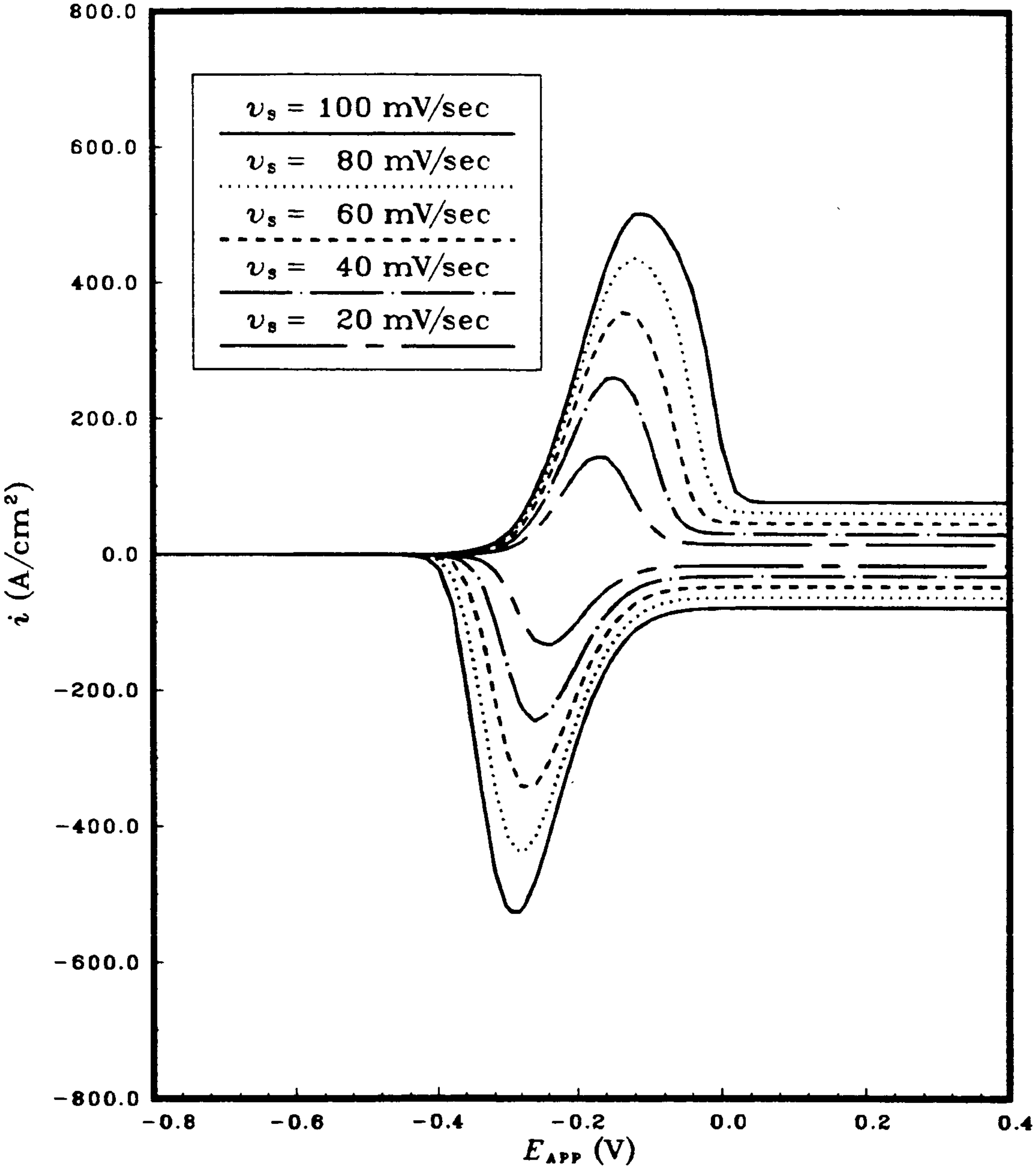

Fig. 3. T. Yeu *et al.*

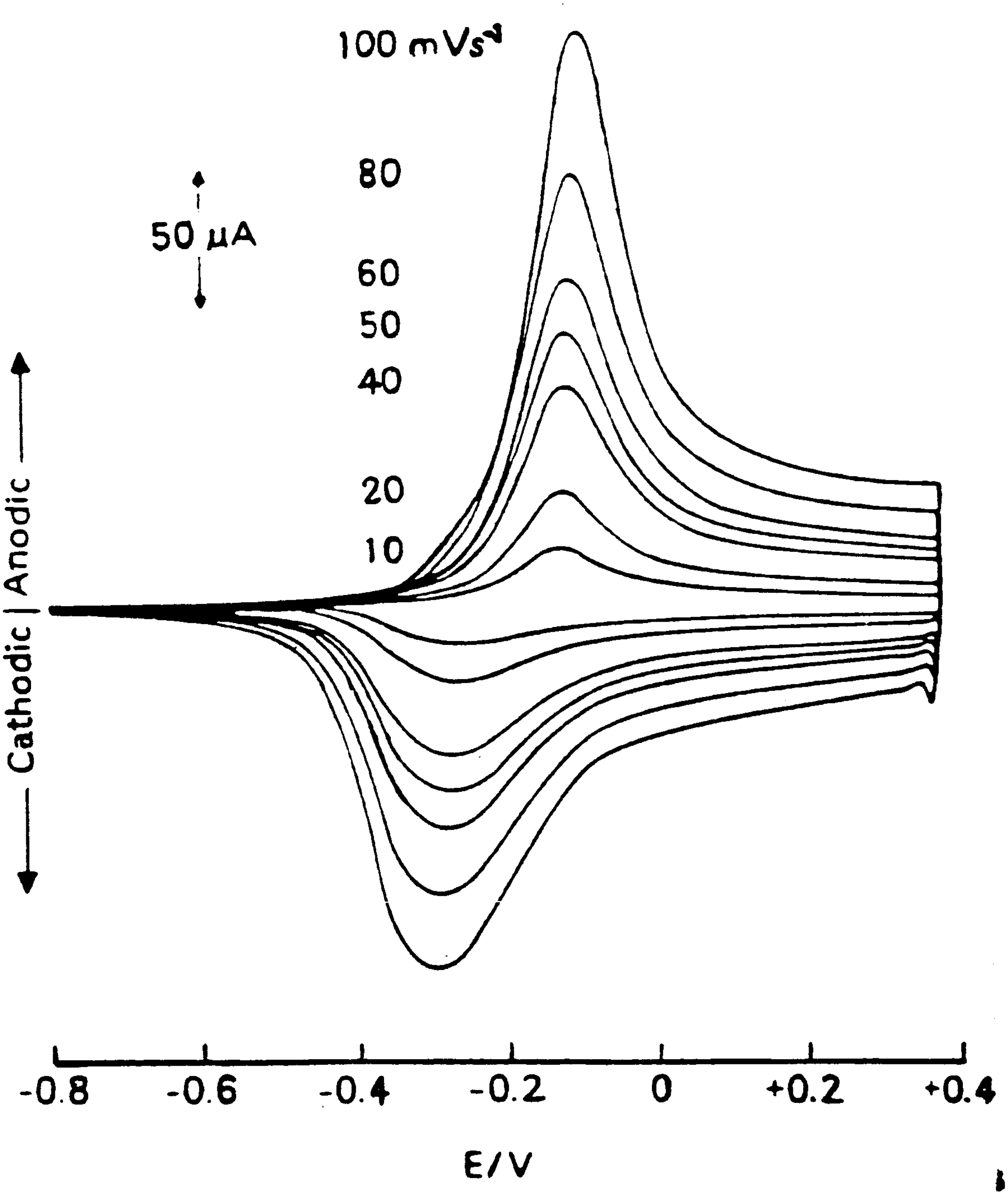

Fig.4. T. Yeu *et al.*

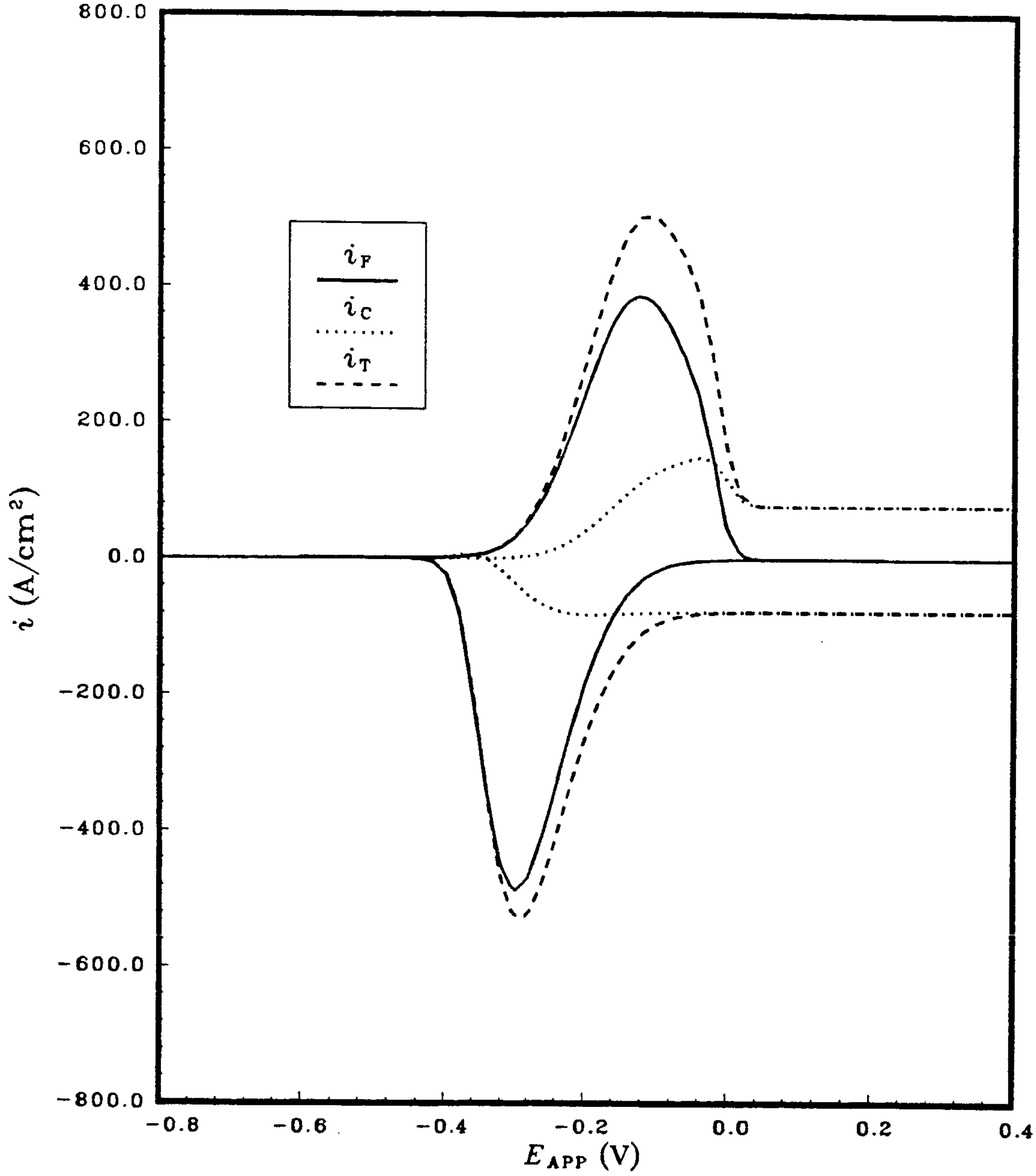

Fig. 5. T. Yeu *et al.*

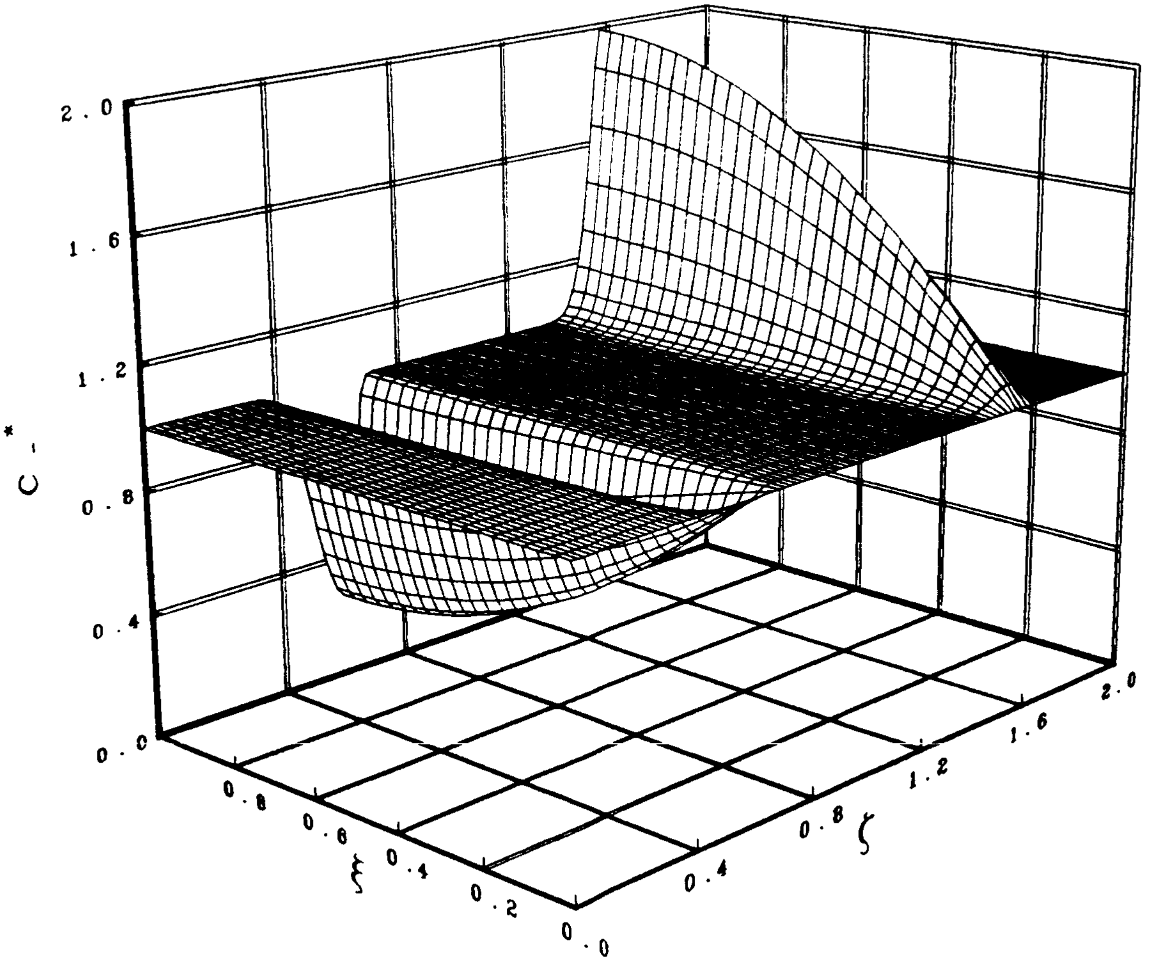

Fig. 6. T. Yeu *et al.*

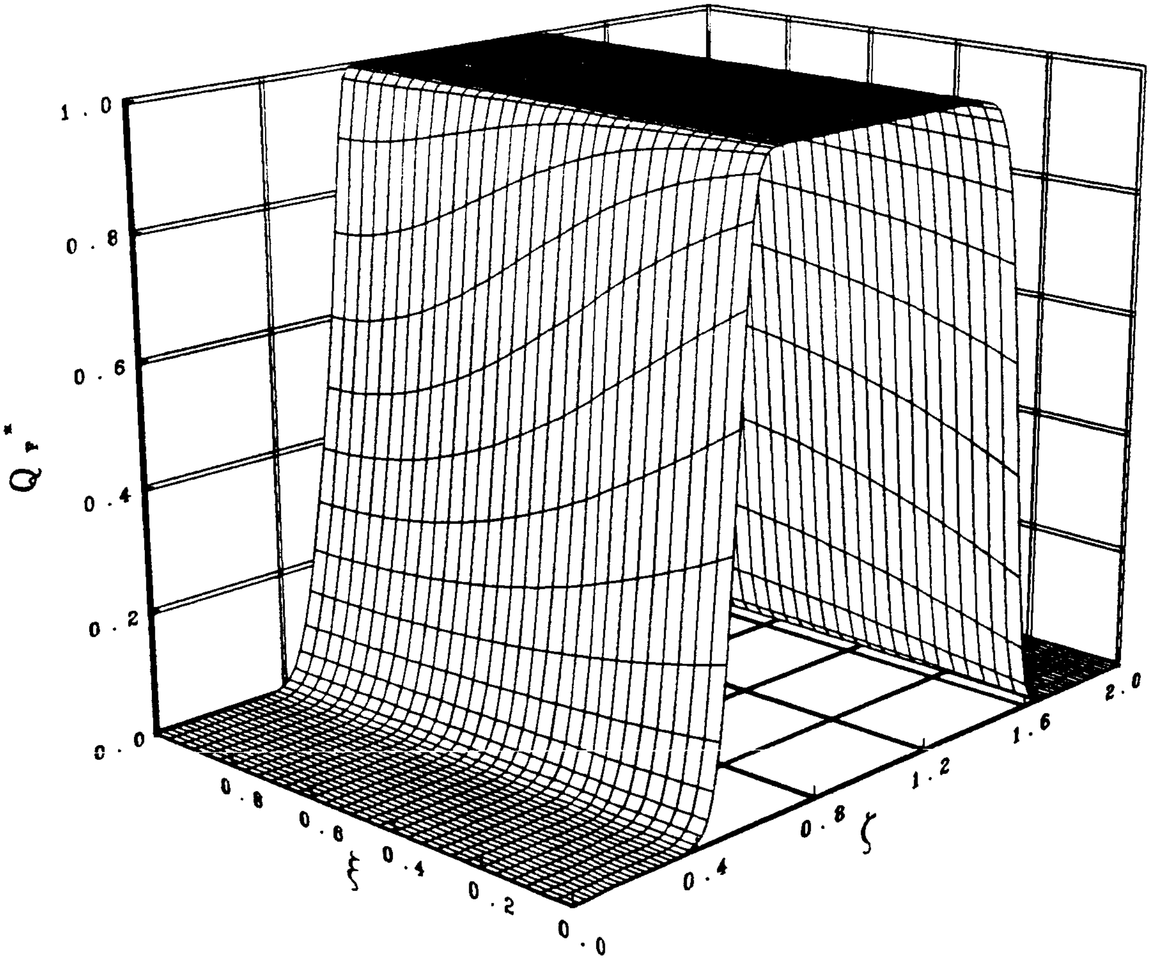

Fig. 7. T. Yeu *et al*.