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DYNAMIC SIMULATION OF CYCLIC VOLTAMMOGRAM ON THE ELECTROCHEMICAL REDUCTION OF VO^{2+} IONS

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Abstract – An electrochemical reduction of VO^{2+} ions in a formic acid electrolyte was analyzed by cyclic voltammetry. A new four step reaction mechanism, EECE, was proposed to derive the mass transfer equation, and then it was solved by numerical method, which enabled us to obtain theoretical cyclic voltammograms. Kinetic parameters such as diffusion coefficients, rate constants and transfer coefficients, describing the VO^{2+} ion reduction system, were estimated by fitting the theoretical curve with the experimental data. The parameters obtained were then evaluated on their extended applicability in various concentrations and scan rates. It was shown that the theoretical voltammograms obtained using the above parameters fitted well with the experimental curves for the scan rate variation from 2 to 20 V/sec, while the deviation increased in proportion to the VO^{2+} ion concentration.

Key words: *Cyclic Voltammogram, Electrochemical Reduction, Decontamination, Dynamic Simulation, Vanadous Picolinate*

INTRODUCTION

Vanadous picolinate, V(II)(Pic)$_n$ ($1 \leq n \leq 3$) has been developed as a decontaminating agent to dissolve the corrosion oxides containing Fe(III) in nuclear facilities [Wood, 1991; Bradbury, 1983]. The vanadous ion is prepared by electrochemical reduction of vanadyl ions in formic acid.

Cyclic voltammetry has been widely used for kinetic studies of electrode reactions [Bard and Faulk, 1980]. Cyclic voltammetry makes it possible to investigate the electrode reaction products and to detect electroactive intermediates, especially for simple reaction mechanisms such as EC and ECE. In an electrochemical system, an electron transfer reaction on the electrode surface and a chemical reaction in the bulk phase can occur in sequence. When the electron transfer reaction is followed by a chemical reaction, the mechanism is referred to as EC (Electron transfer-Chemical reaction), and that of the opposite sequence is defined as CE (Chemical reaction-Electron transfer). In this way, the ECE mechanism is defined as the electrochemical reaction in which a chemical reaction is coupled between two electron transfer reactions. Nicholson [1964; 1965] reported the extended use of the basic theory of cyclic voltammetry for analysis of electrochemical reactions with ECE mechanisms. He also suggested an experimental diagnosis method to evaluate kinetic parameters directly from the cyclic voltammograms. And Polcyn [1966] illustrated the general method to derive kinetic parameters such as rate constants and diffusivities for simple electrochemical reaction mechanisms such as EC and ECE.

The reduction mechanisms for the vanadium systems, however, can be different from the experimental conditions such as supporting electrolyte, accompanied anions, solution pH, etc. In acid media, the electrochemical standard reactions for vanadium system proceeded with the two step electron transfer (EE) reactions as follows.

$$VO^{2+} + 2H^{+} + e^{-} = V^{3+} + H_2O \qquad E^{o} = 0.337\ V \tag{1}$$

$$V^{3+} + e^{-} = V^{2+} \qquad E^{o} = -0.225\ V \tag{2}$$

However, DeSesa et al. [1953] reported the direct reduction combined the chemical reaction referred to as EC mechanism for the reduction of VO^{2+} ion in the acetic acid electrolyte as follows.

$$VO^{2+} + H^{+} + 2e^{-} = VOH^{+} \tag{3}$$

$$VOH^{+} + H^{+} = V^{2+} + H_2O \tag{4}$$

And Jung [1989] reported another mechanism of ECE in his study on the reduction of VO^{2+} ions chelated with EDTA and DTPA.

Recently, we also found that the electrochemical reduction of VO^{2+} ion in the formic acid supporting electrolyte could be explained by the four step electrochemical reaction mechanism of EECE (Electron transfer-Electron transfer-Chemical reaction-Electron transfer), which is rather new and somewhat complicated [Oh et al., 1993]. The complication of the mechanism made it difficult to obtain the kinetic parameters directly from the experimental cyclic voltammograms.

In this study, we conducted computer simulation to obtain the kinetic parameters for the VO^{2+} ion reduction system. In the diffusion controlled region, the mass transfer equations for electrode reaction of VO^{2+} ions were derived based on the EECE mechanism and solved by a numerical method, which can give us the theoretical cyclic voltammograms. The kinetic parameters were then evaluated by fitting the theoretical voltammograms with the experimental curves.

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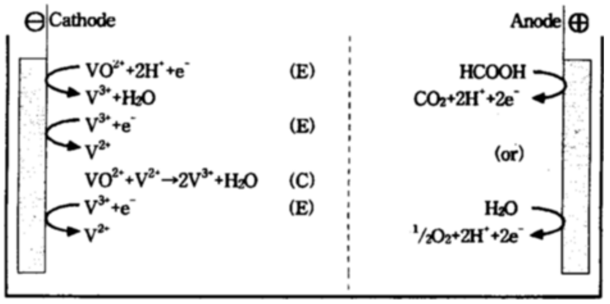

Fig. 1. Schematic diagram for the electrochemical reduction of VO^{2+} ion in the formic acid supporting electrolyte.

THEORY

1. Reduction Mechanism

The electrochemical reduction of VO^{2+} ion in the formic acid supporting electrolyte includes two electron transfer reactions and a chemical reaction. These reaction steps are represented in Fig. 1 and described in the following:

$$VO^{2+}+2H^{+}+e^{-} \underset{k_{4b}}{\overset{k_{4f}}{\rightleftarrows}} V^{3+}+H_2O \qquad \text{(electron transfer)} \qquad (5)$$

$$V^{3+}+e^{-} \underset{k_{3b}}{\overset{k_{3f}}{\rightleftarrows}} V^{2+} \qquad \text{(electron transfer)} \qquad (6)$$

$$VO^{2+}+V^{2+}+2H^{+} \xrightarrow{k_{42}} 2V^{3+}+H_2O \qquad \text{(chemical)} \qquad (7)$$

$$V^{3+}+e^{-} \underset{k_{3b}}{\overset{k_{3f}}{\rightleftarrows}} V^{2+} \qquad \text{(electron transfer)} \qquad (8)$$

The reaction starts with VO^{2+} ion reduction to V^{3+} ion by an electron transfer reaction as in Eq. (5) which is known as a very slow reaction with high activation energy [Lingane, 1945]. The high activation energy of the reaction causes the reduction potential on a cyclic voltammogram to shift more cathodically than its standard potential which is reportedly 0.337 V [Bard and Faulkner, 1980]. The VO^{2+} ion reduction is then followed by V^{3+} ion reduction by another electron transfer reaction as in Eq. (6). This reaction is reportedly very fast with a standard potential of -0.225 V [Lingane and Meites, 1948]. The V^{2+} ion generated from the V^{3+} ion reduction reacts chemically with the VO^{2+} ion in the bulk solution to form V^{3+} ion again. Finally, V^{3+} ion is then reduced by electron transfer reaction to form V^{2+} ion as in Eq. (8). This set of reactions, electron transfer-electron transfer-chemical-electron transfer, is referred to as the EECE mechanism.

The reactions of Eqs. (6)-(8) are very fast and occur simultaneously [Lingane and Meites, 1948; Oh et al., 1993]. Therefore the characteristic peak for each reduction step does not appear clearly on the cyclic voltammogram. This fact makes it very difficult to analyze cyclic voltammogram and to obtain the kinetic parameters experimentally.

2. Modeling

The mass transfer equations for the vanadium components are represented as follows. In the regions where the diffusional mass transfer dominates over the migrational effect,

$$\frac{\partial C_4}{\partial t} = D_4 \frac{\partial^2 C_4}{\partial x^2} - \frac{1}{2} k_{42} C_2 C_4 \qquad (9)$$

$$\frac{\partial C_3}{\partial t} = D_3 \frac{\partial^2 C_3}{\partial x^2} + k_{42} C_2 C_4 \qquad (10)$$

$$\frac{\partial C_2}{\partial t} = D_2 \frac{\partial^2 C_2}{\partial x^2} - \frac{1}{2} k_{42} C_2 C_4 \qquad (11)$$

where, C_2, C_3, C_4, are ion concentrations of V^{2+}, V^{3+} and VO^{2+}, respectively, and C_4^* is the VO^{2+} ion concentration in the bulk phase.

The initial and boundary conditions are:

$$\text{for } t=0,\ x \geq 0 \quad C_4(x, 0)=C_4^*,\ C_3(x, 0)=0,\ C_2(x, 0)=0 \qquad (12)$$

$$\text{for } t>0,\ x \rightarrow \infty \quad C_4(x, t)=C_4^*,\ C_3(x, t)=C_2(x, t)=0 \qquad (13)$$

for $t>0$, $x=0$

$$D_4 \frac{\partial C_4}{\partial x} \Big|_{x=0} + D_3 \frac{\partial C_3}{\partial x} \Big|_{x=0} + D_2 \frac{\partial C_2}{\partial x} \Big|_{x=0} = 0 \qquad (14)$$

$$D_4 \frac{\partial C_4}{\partial x} \Big|_{x=0} = k_{4f} C_4 - k_{4b} C_3 \qquad (15)$$

$$D_2 \frac{\partial C_2}{\partial x} \Big|_{x=0} = k_{3b} C_2 - k_{3f} C_3 \qquad (16)$$

If the charge transfer is irreversible, Eqs. (15)-(16) can be defined in terms of the Eyring equation [Nicholson and Shain, 1965] providing the relationship between the ion fluxes and the applying potentials as follows:

$$D_4 \frac{\partial C_4}{\partial x} \Big|_{x=0} = \left\{ k_{4s} \operatorname{Exp}\left[-\left(\frac{\alpha_4 F}{RT} \right)(E - E_4^o) \right] \right\} \cdot \left\{ C_4\big|_{x=0} - C_3\big|_{x=0} \operatorname{Exp}\left[\left(\frac{F}{RT} \right)(E - E_4^o) \right] \right\} \qquad (17)$$

$$D_2 \frac{\partial C_2}{\partial x} \Big|_{x=0} = - \left\{ k_{3s} \operatorname{Exp}\left[-\left(\frac{\alpha_3 F}{RT} \right)(E - E_3^o) \right] \right\} \left\{ C_3\big|_{x=0} - C_2\big|_{x=0} \operatorname{Exp}\left[\left(\frac{F}{RT} \right)(E - E_3^o) \right] \right\} \qquad (18)$$

where,

E=electrode potential,

E_3^o, E_4^o=standard reduction potentials for V^{3+} and VO^{2+} ions, respectively,

k_{3s}, k_{4s}=standard rate constants for V^{3+} and VO^{2+} ions, respectively,

F=Faraday constant,

α_3, α_4=charge transfer coefficients for V^{3+} and VO^{2+} ions.

The current flowing through the electrode can be expressed by

$$i = FA\left(D_4 \frac{\partial C_4}{\partial x} \Big|_{x=0} - D_2 \frac{\partial C_2}{\partial x} \Big|_{x=0} \right) + FAD_3 \frac{\partial C_3}{\partial x} \Big|_{x=0} \qquad (19)$$

where, A is electrode surface area.

For the case of cyclic voltammetry, the potential in Eqs. (17) and (18) is a function of time, given by the relations [Nicholson, 1964]

$$\text{for } 0 \le t \le \lambda \qquad E = E_i - vt \tag{20}$$

$$\text{for } \lambda < t \qquad E = E_i - 2v\lambda + vt \tag{21}$$

where, E_i is initial potential, v is the rate of potential scan, and λ is the time at which the scan is reversed. Eqs. (9)-(11) and their initial and boundary conditions can now be converted into dimensionless expressions, using the following dimensionless variables.

$$\mu = C_4/C_4^*,\ v = C_3/C_4^*,\ \omega = C_2/C_4^* \tag{22}$$

$$\tau = (Fv/RT)t,\ y = x/\delta \tag{23}$$

$$\gamma_1 = D_4/D_3,\ \gamma_2 = D_4/D_2 \tag{24}$$

$$k = (1/2)k_{42} \cdot C_4^*\ RT/Fv \tag{25}$$

$$D = (D_4\ RT)/(Fv\delta^2) \tag{26}$$

where, δ is the thickness of the diffusion-convection layer when the C_4 equals bulk phase concentration C_4^*.

Then,

$$\frac{\partial\mu}{\partial\tau} = D\frac{\partial^2\mu}{\partial y^2} - k\mu\omega \tag{27}$$

$$\frac{\partial\nu}{\partial\tau} = \frac{D}{\gamma_1}\frac{\partial^2\nu}{\partial y^2} + 2k\mu\omega \tag{28}$$

$$\frac{\partial\omega}{\partial\tau} = \frac{D}{\gamma_2}\frac{\partial^2\omega}{\partial y^2} - k\mu\omega \tag{29}$$

The initial condition is given by

$$\text{for } t = 0,\ 0 \le y \le 1, \qquad \mu = 1,\ v = \omega = 0 \tag{30}$$

And the boundary conditions are given by

$$\text{for } y = 1,\ t \ge 1, \qquad \mu = 1,\ v = \omega = 0 \tag{31}$$

for y = 0, t > 1,

$$\left.\frac{\partial\mu}{\partial y}\right|_{y=0} = \phi_1\xi_1^{-\alpha_1} \cdot \mu|_{y=0} - \phi_1\xi_1^{(1-\alpha_1)} \cdot \nu|_{y=0} \tag{32}$$

$$\left.\frac{\partial\omega}{\partial y}\right|_{y=0} = \phi_2\xi_1^{1-\alpha_2} \cdot \omega|_{y=0} - \phi_2\xi_2^{\alpha_2} \cdot \nu|_{y=0} \tag{33}$$

$$\frac{\partial\mu}{\partial y} + \frac{1}{\gamma_1}\frac{\partial\nu}{\partial y} + \frac{1}{\gamma_2}\frac{\partial\omega}{\partial y} = 0 \tag{34}$$

where,

$$\xi_1 = \exp\left[\left(\frac{F}{RT}\right)\left(E - E_4^0\right)\right] \tag{35}$$

$$\xi_2 = \exp\left[\left(\frac{F}{RT}\right)\left(E - E_3^0\right)\right] \tag{36}$$

$$\phi_1 = k_{4s}\,RT/DFv\delta \tag{37}$$

$$\phi_2 = k_{3s}\,RT/DFv\delta \tag{38}$$

To simplify the notations

$$R_1 \equiv \frac{\partial\mu}{\partial y}|_{y=0},\ R_2 \equiv \frac{\partial\nu}{\partial y}|_{y=0},\ R_3 \equiv \frac{\partial\omega}{\partial y}|_{y=0} \tag{39}$$

Then the Eq. (19) can be rearranged to

$$i = \frac{F^2AC_4^*Dv\delta}{RT}\left(R_1 - \frac{R_2}{\gamma_2}\right) \tag{40}$$

These boundary value problems make it possible to evaluate the dynamic potential-current response resulting from the electrochemical reduction of vanadium ions.

3. Numerical Analysis

An orthogonal collocation method [Finlayson, 1980] was used to solve the transient problem composed of parabolic partial differential equations. As the solution has no symmetry property, it can be given by a polynomial expression.

$$C(x, t) = a(t) + b(t)x + x(1-x)\sum_{i=0}^{N} a_i(t)\,P_{i-1}(x) \tag{41}$$

This expression can be rearranged to

$$C(x,t) = \sum_{i=1}^{N+2} d_i(t)x^{i-1} \tag{42}$$

For every collocation point,

$$C(x_j, t) = \sum_{i=1}^{N+2} d_i(t)x_j^{i-1} \qquad \text{or} \qquad \underline{C}(t) = \underline{Q}\,\underline{d}(t) \tag{43}$$

The first order space derivative at each collocation point is given by

$$\left.\frac{\partial C}{\partial x}\right]_{x_j} = \sum_{i=1}^{N+2} d_i(t)\,(i-1)x_j^{i-2} \qquad \text{or} \qquad \frac{\partial \underline{C}}{\partial x} = \underline{C}\,\underline{d}(t) \tag{44}$$

where, $Q_{ji} = X_j^{i-1}$ which is independent of time, and Eq. (44) can be expressed by

$$\frac{\partial \underline{C}}{\partial x} = \underline{C}\,\underline{Q^{-1}}\,\underline{C} \equiv \underline{A}\,\underline{C} \tag{45}$$

The second order space derivative is also given by

$$\frac{\partial^2 \underline{C}}{\partial x^2} = \underline{D}\,\underline{Q^{-1}}\,\underline{C} \equiv \underline{B}\,\underline{C} \tag{46}$$

The time derivative expression is given by

$$\left.\frac{\partial C}{\partial t}\right]_{x_j} = \frac{d}{dt}C(x_j, t) = \frac{dC_j}{dt} \tag{47}$$

In this way, the collocation method transforms the partial differential equations to ordinary differential equations. Using the collocation method, the differential equation describing electrochemical reduction of vanadium ions can be represented by the following equations.

$$\frac{\partial\mu_j}{\partial t} = D\sum_{i=1}^{N+2} B_{ji}\,\mu_i - k\mu_j\,\omega_j \tag{48}$$

$$\frac{\partial\nu_j}{\partial t} = \frac{D}{\gamma_1}\sum_{i=1}^{N+2} B_{ji}\,\nu_i + 2k\mu_j\,\omega_j \tag{49}$$

$$\frac{\partial\omega_j}{\partial t} = \frac{D}{\gamma_2}\sum_{i=1}^{N+2} B_{ji}\,\omega_i - k\mu_j\,\omega_j \tag{50}$$

Initial and boundary conditions are

$$\mu_j=1 \qquad (j=1,\ 2,\ 3,\ \ldots\ldots\ldots\ldots,\ N+2) \tag{51}$$

$$\nu_j=\omega_j=0 \qquad (j=1,\ 2,\ 3,\ \ldots\ldots\ldots\ldots,\ N+2) \tag{52}$$

$$\mu_{N+2}=1, \qquad \nu_{N+2}=\omega_{N+2}=0 \tag{53}$$

$$\sum_{i=1}^{N+2} A_{1j}\ \mu_j=\phi_1\,\xi_1^{-\alpha_1}\,\mu_1-\phi_1\,\xi_1^{(1-\alpha_1)}\,\nu_1 \tag{54}$$

$$\sum_{i=1}^{N+2} A_{1j}\ \omega_j=\phi_2\,\xi_2^{(1-\alpha_2)}\,\omega_1-\phi_2\,\xi_2^{-\alpha_2}\,\nu_1 \tag{55}$$

$$\sum_{i=1}^{N+2} A_{1j}\ \mu_j+\frac{1}{\gamma_1}\sum_{i=1}^{N+2} A_{1j}\ \nu_j+\frac{1}{\gamma_2}\sum_{i=1}^{N+2} A_{1j}\ \omega_j=0 \tag{56}$$

The parameters, μ, ν, and ω can be calculated by using Eqs. (54)-(56) and then there are 3 N unknown variables of μ_j, ν_j, and ω_j (j=2, 3, 4,..., N+1). The gear method in IMSL (international mathematics and statistics library) was used to solve the ordinary differential Eqs. (48)-(50), and to calculate the unknown variables.

EXPERIMENTS

The cyclic voltammograms were obtained using the potentiostat (EG&G PAR model 273) in which HMDE (hanging mercury drop electrode), Pt and Ag/AgCl were attached as the working electrode, the counter electrode and the reference electrode, respectively. $VOSO_4 \cdot 3H_2O$ (99.99 %) was used for the vanadyl ion (VO^{2+}) source and GR grade formic acid (99.0 %) for the supporting electrolyte, respectively. The concentration of supporting electrolyte was adjusted using ultra pure water purified through the three step purifying processes. Experiments were performed for the various VO^{2+} ion concentrations in the range of 2.7 mM to 25 mM and for the scan rate variations from 2 to 20 V/sec under nitrogen atmosphere. The scan rate and the potential were controlled precisely by PC with M270 software.

RESULTS AND DISCUSSION

1. Kinetic Parameter Evaluation

For theoretical estimation of the kinetic parameters, a computer simulation was conducted using the following experimental and well-known values.

$C^*=5\times10^{-6}$ mol/L

$F=9.64846\times10^{4}$ C/equiv.

$A=0.02\ cm^2$

R=8.31441 J/mole·K

v=2 V/sec

T=293 K

$E_3^0=-0.4962$ V vs SCE (saturated calomel electrode)

$E_4^0=-0.0958$ V vs SCE

$\alpha_3=0.5$

$k_{3s}=1.0\times10^{-3}$ cm/sec

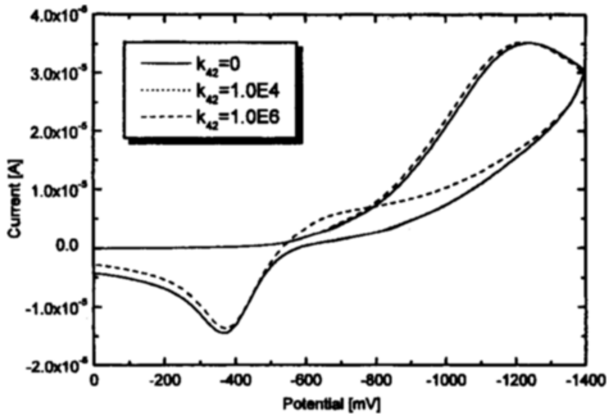

Fig. 2. Effect of k_{42} on cyclic voltammogram.

Then there are four variables, k_{42}, k_{4s}, α_4 and D_4, to be determined.

To check the effects of parameters on the shape of cyclic voltammograms, the simulations were performed with varying parameter values.

Fig. 2 shows the effect of k_{42} on the curves. No significant effect was found when the k_{42} was less than 10^4. When k_{42} became larger than 10^6, however, the curve of the reverse scan was crossing the forward scanning line, which might be due to the increase in V^{3+} ions by the chemical reaction.

The effect of D_4 on the cyclic voltammograms is shown in Fig. 3. The peak current increased in proportion to $D^{1/2}$ as expected.

Fig. 4 shows the effect of k_{4s} on the cyclic voltammograms. The cathodic peaks are displaced anodically along the potential axis when k_{4s} becomes large without a change in peak current intensity. Whereas, the increase in k_{4s} caused the current to increase without any anodic peak displacement.

The dependence on α_4 is shown in Fig. 5 where the curves for the three values of α_4 are compared. The peak current increased and shifted anodically as the α_4 increased. For the irreversible reaction, it is well known that peak current is proportional to $\alpha^{1/2}$ and peak potential shifts anodically according to the equation, $|E_p-E_{p/2}|=1.857RT/\alpha n_a F$ [Bard and Faulkner, 1980].

From the above results, it was found that the simulation

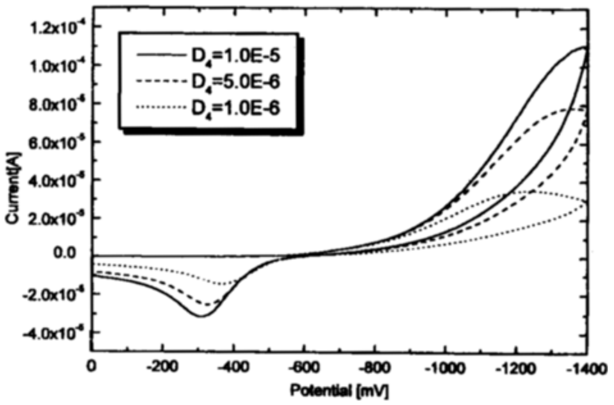

Fig. 3. Effect of D_4 on cyclic voltammogram.

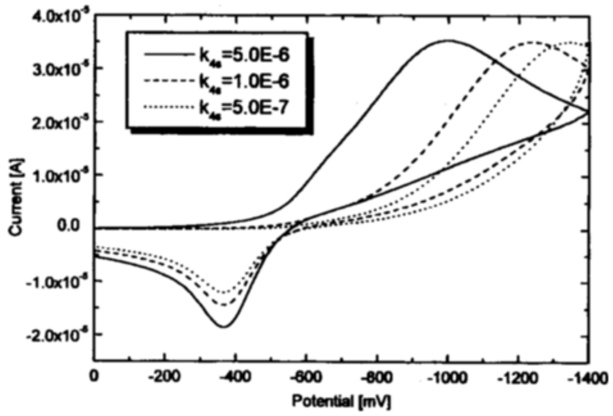

Fig. 4. Effect of k_{4s} on cyclic voltammogram.

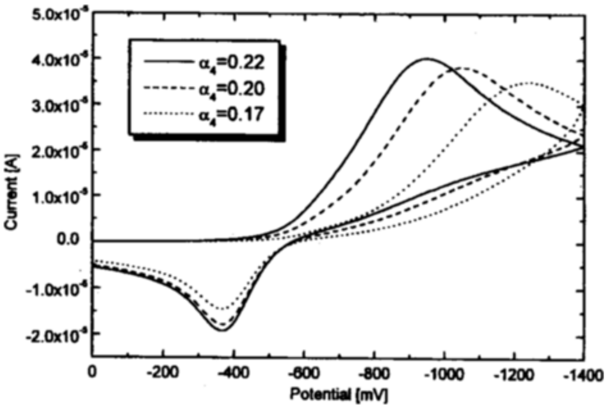

Fig. 5. Effect of α_4 on cyclic voltammogram.

was conducted well and described the parameter effects correctly, and each parameter had characteristic effects on the shape of the cyclic voltammogram, which can be used for selection of experimental data points for simulation. The Marquette Parameter Estimation Method was used to find the optimum values of k_{4s}, k_{42}, D_4 and α_4. Nine data points, which characterize the experimental cyclic voltammogram, were selected to estimate the parameters. The best fitted curve, taking into account the spherical correction factor (SCF), is shown in Fig. 6, and the optimum parameters were obtained as follows.

SCF=1.51

D_4=5.81 × 10^{-6}

k_{4s}=5.31 × 10^{-6}

k_{42}=1.00 × 10^4

α_4=0.23

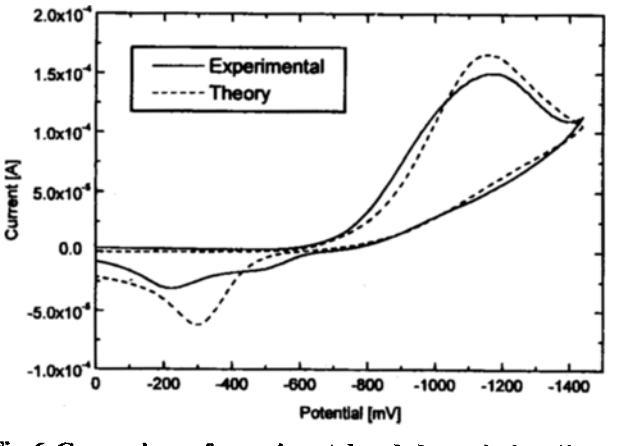

Fig. 6. Comparison of experimental and theoretical cyclic voltammogram for the VO^{2+}-formate system; [VO^{2+}]=5.2 mM, [HCOOH]=1 M, scan rate=5 V/sec.

From the simulation results, the theoretical cyclic voltammogram was found to be fited well with the experimental curve, except the slight deviation in the anodic scanning curve, which requires further study to explain the reasons.

2. Effect of VO^{2+} Ion Concentration on the Simulation

Using the simulated parameters, a simulation was conducted to demonstrate the extended applicability of the parameters for the wide experimental ranges. The VO^{2+} ion concentrations were varied from 2.7 mM to 25 mM, with the scan rate fixed at 2 V/sec as represented in Fig. 7.

This showed that the simulation could predict approximately the electrochemical reduction of the VO^{2+} ion. However, the deviation increased in proportion to the VO^{2+} ion concentrations. This might be due to the increase in migrational

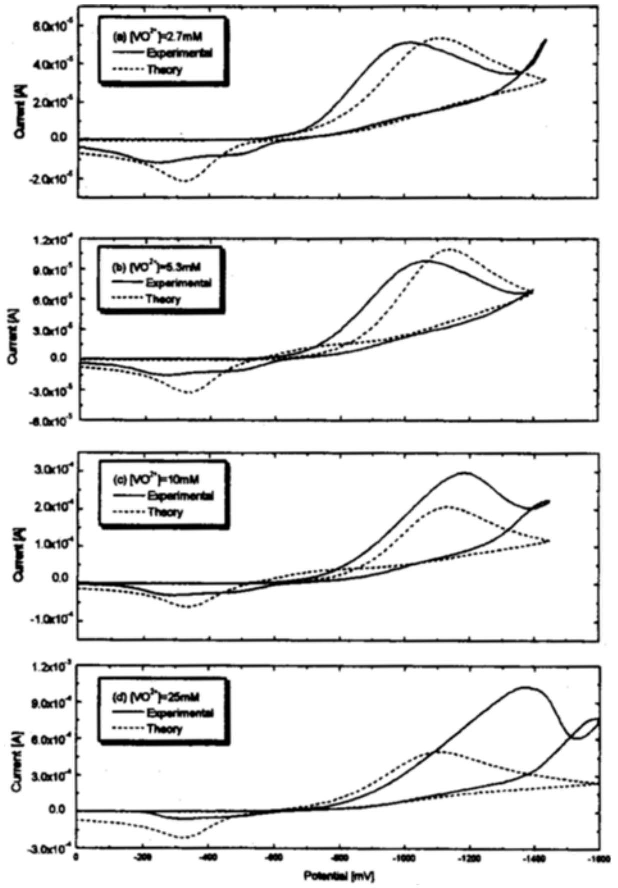

Fig. 7. Comparison of experimental and theoretical cyclic voltammograms for various VO^{2+} ion concentration in the VO^{2+}-formate system; [HCOOH]=1 M, scan rate=2 V/sec.

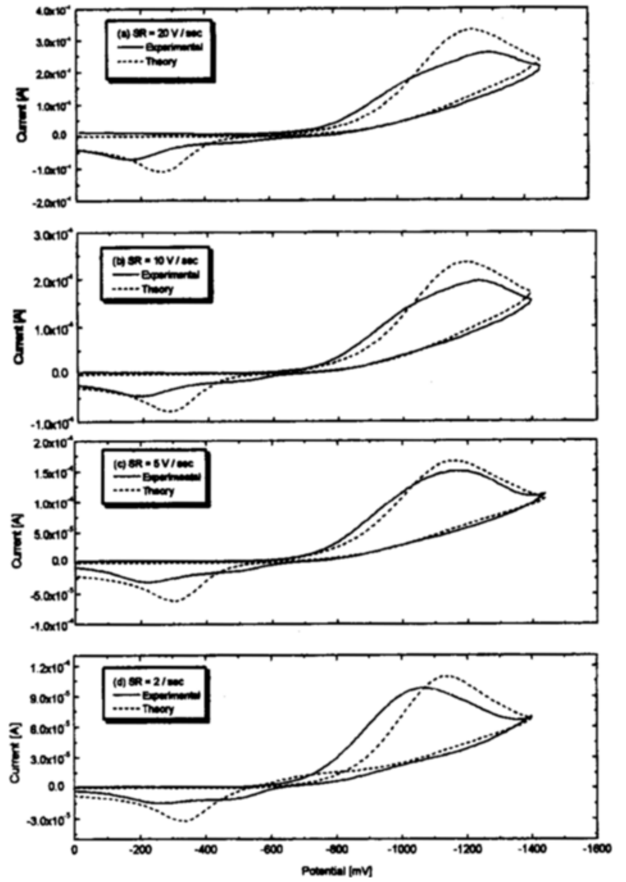

Fig. 8. Comparison of experimental and theoretical cyclic voltammograms for various scan rate of the VO^{2+}-formate system; $[VO^{2+}]=5.3$ mM, [HCOOH]=1 M.

mass transfer effects of the bulk solution, which were not considered in this study.

3. Effect of Scan Rate on the Simulation

The scan rates were varied from 2 V/sec to 20 V/sec to check the applicability of the estimated parameters for the extended scan rate conditions. The results in Fig. 8 reveal similar trends between the theoretical and the experimental results in spite of slight deviation.

CONCLUSIONS

Electrochemical reduction of VO^{2+} ion in the formic acid electrolyte could be explained by dynamic simulation of cyclic voltammetry based on the EECE reaction mechanism.

The optimum kinetic parameters were obtained by fitting the experimental and the theoretical cyclic voltammograms. The simulation using these parameters could be extended for a scan rate from 2 V/sec to 20 V/sec, while the deviation increased in proportion to the VO^{2+} ion concentration.

In spite of the fact that the suggested dynamic simulation could be used to analyse approximately the electrochemical reduction of VO^{2+}, it was also shown that further study to reduce the deviations for the anodic reaction and for the concentrated solutions was also required.

NOMENCLATURE

A : electrode surface area [cm^2]
C_2, C_3, C_4 : concentrations for V^{2+}, V^{3+}, VO^{2+}, ions, respectively [mol/cm^3]
C_2^*, C_3^*, C_4^* : bulk phase concentrations for V^{2+}, V^{3+}, VO^{2+}, ions, respectively [mol/cm^3]
C(x,t) : concentration at distance x at time t [mol/cm^3]
D_2, D_3, D_4 : diffusion coefficients for V^{2+}, V^{3+}, VO^{2+}, ions, respectively [cm^2/sec]
E : electrode potential vs. reference [V]
E^o : standard electrode potential [V]
E_3^o, E_4^o : standard reduction potentials for V^{3+} and VO^{2+} ions, respectively [V]
E_i : initial electrode potential [V]
E_p : peak potential [V]
$E_{p/2}$: potential where $i=i_p/2$ [V]
F : Faraday constant [C/equiv.]
i : current [A]
k_{3f}, k_{3b} : reduction and oxidation rate constants for V^{3+} ions, respectively [cm/sec]
k_{4f}, k_{4b} : reduction and oxidation rate constants for VO^{2+} ions, respectively [cm/sec]
k_{3s}, k_{4s} : standard rate constants for V^{3+} and VO^{2+} ions, respectively [cm/sec]
k_{42} : rate constant for chemical reaction between VO^{2+} and V^{2+}
n_α : number of electrons involved in the rate determining step [-]
R : gas constant [J/mol·K]
T : absolute temperature [K]
t : time [sec]
v : rate of potential scan [V/sec]
x : distance from an electrode [cm]

Greek Letters

α_3, α_4 : transfer coefficients for V^{3+} and VO^{2+} ions [-]
δ : thickness of the diffusion-convection layer when the C_4 equals C_4^* [cm]
λ : time at which the scan is reversed [sec]

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