THERMODYNAMICAL PROPERTIES OF ROTATING DISK ELECTRODES FOR SECOND ORDER ECE REACTIONS

by

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The thermodynamical model for rotating disk electrodes for second order ECE (electrochemical-chemical-electrochemical) reactions is considered, and the effect of concentrations of three species on the current for ECE reaction is theoretically analyzed, and the optimal current value is obtained. The Taylor series method is used, the derivation is simple and the accuracy can be improved if higher order Taylor series is considered. A fractal modification is also suggested for future research.

Key words: *Taylor series, rotating disk electrode, non-linear diffusion equation*

Introduction

The so-called ECE reaction implies a series of reactions in a diffusion layer between two electrodes as illustrated in fig. 1. A reactant, A, absorbs or loses an electron to produce an intermediate product, B, which will be reacted with a reactant, C, to produce D, which absorbs or loses an electron to produce E.

The ECE reaction can be expressed:

$$A \pm e^- \rightleftarrows B$$

$$B \pm C \xrightarrow{k} D$$

$$D \pm e^- \rightleftarrows E$$

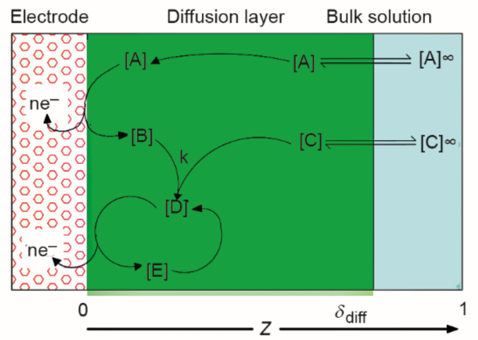

Figure 1. The ECE reaction system

In this paper we will study a non-linear system arising in rotating disk electrodes for second order ECE reactions [1, 2]:

$$\frac{d^2u}{dx^2} - kuv = 0, \quad u'(0) = -1, \quad u(1) = 0 \tag{1}$$

$$\frac{d^2v}{dx^2} - k\gamma uv = 0, \quad v'(0) = 0, \quad v(1) = 1 \tag{2}$$

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$$\frac{\mathrm{d}^2 w}{\mathrm{d}x^2} + kuv = 0, \quad w(0) = 0, \quad w(1) = 0 \tag{3}$$

where x is the dimensionless distance from the electrode surface, u, v, and w – the dimensionless concentrations of three species, respectively, γ reflects the balance between the original solution species, k is the second order homogeneous rate constant. The detailed derivation process is available in [1].

The dimensionless current for ECE reaction is:

$$\psi = \frac{1}{\delta_{\mathrm{diff}}}\left(1 + \left.\frac{\partial w}{\partial x}\right|_{x=0}\right) \tag{4}$$

where δ_{diff} is the thickness of the diffusion convection layer.

Analytical solution

The system of eqs. (1)-(3) is strongly non-linear, though various analytical methods can solve it, for examples, the variational method [3], the perturbation method [4-7], the variational iteration method [8-10], Chun-Hui He's iteration method [11-13], and Tian-Liu's direct algebraic method [14]. In this paper, we will solve the system by a simple but effective method, that is the Taylor series method [15, 16], which is accessible to all non-mathematicians.

We assume that:

$$u(0) = a, \quad v(0) = b, \quad w'(0) = c \tag{5}$$

where a, b, and c are unknowns to be determined later.

Differentiating eqs. (1)-(3) with respect to x n times, and setting $x = 0$, we can obtain $u^{(n)}(0)$, $v^{(n)}(0)$, and $w^{(n)}(0)$, $n = 2, 3, 4,\ldots$ We write down the derivatives up to the third order:

$$u''(0) = kab, \quad v''(0) = k\gamma ab, \quad w''(0) = -kab \tag{6}$$

$$u'''(0) = -kb, \quad v'''(0) = -k\gamma b, \quad w'''(0) = kb \tag{7}$$

The Taylor series solution is:

$$u(x) = u(0) + u'(0)x + \frac{1}{2}u''(0)x^2 + \frac{1}{6}u'''(0)x^3 = a - x + \frac{1}{2}kabx^2 - \frac{1}{6}kbx^3 \tag{8}$$

$$v(x) = v(0) + v'(0)x + \frac{1}{2}v''(0)x^2 + \frac{1}{6}v'''(0)x^3 = b + \frac{1}{2}k\gamma abx^2 - \frac{1}{6}k\gamma bx^3 \tag{9}$$

$$w(x) = w(0) + w'(0)x + \frac{1}{2}w''(0)x^2 + \frac{1}{6}w'''(0)x^3 = cx - \frac{1}{2}kabx^2 + \frac{1}{6}kbx^3 \tag{10}$$

By the boundary conditions, $u(0) = 0$, $v(0) = 1$, and $w(0) = 0$, we have:

$$a - 1 + \frac{1}{2}kab - \frac{1}{6}kb = 0 \tag{11}$$

$$b+\frac{1}{2}k\gamma ab-\frac{1}{6}k\gamma b=1 \tag{12}$$

$$c-\frac{1}{2}kab+\frac{1}{6}kb=0 \tag{13}$$

Solving the system of eqs. (11)-(13), we have:

$$a=1-c \tag{14}$$

$$b=1-\gamma c \tag{15}$$

$$c=\frac{k-\left(1+\frac{1}{3}k\gamma-\frac{1}{2}k\right)+\sqrt{\left(1+\frac{1}{3}k\gamma-\frac{1}{2}k\right)^2+2k}}{k\gamma} \tag{16}$$

Now the current is obtained, which reads:

$$\psi=\frac{1}{\delta_{\text{diff}}}\left(1+\left.\frac{\partial w}{\partial x}\right|_{x=0}\right)=\frac{1}{\delta_{\text{diff}}}(1+c)=$$

$$=\frac{1}{\delta_{\text{diff}}}\left[1+\frac{k-\left(1+\frac{1}{3}k\gamma-\frac{1}{2}k\right)+\sqrt{\left(1+\frac{1}{3}k\gamma-\frac{1}{2}k\right)^2+2k}}{k\gamma}\right] \tag{17}$$

The accuracy can be improved if a higher order series is used.

Conservation laws and variational principle

From eqs. (1)-(3), we can obtain the following conservation laws:

$$\frac{\mathrm{d}^2u}{\mathrm{d}x^2}-\frac{1}{\gamma}\frac{\mathrm{d}^2v}{\mathrm{d}x^2}=0 \tag{18}$$

$$\frac{\mathrm{d}^2u}{\mathrm{d}x^2}+\frac{\mathrm{d}^2w}{\mathrm{d}x^2}=0 \tag{19}$$

$$\frac{\mathrm{d}^2w}{\mathrm{d}x^2}-\frac{1}{\gamma}\frac{\mathrm{d}^2v}{\mathrm{d}x^2}=0 \tag{20}$$

Conservation laws [17, 18] are extremely important in mathematics and numerical analyses. The conservation laws lead to the following variational principle:

$$J(u,v,w)\int\left[-\frac{1}{2}\left(\frac{\mathrm{d}u}{\mathrm{d}x}\right)^2+u\frac{\mathrm{d}^2w}{\mathrm{d}x^2}-\frac{1}{\gamma}w\frac{\mathrm{d}^2v}{\mathrm{d}x^2}-\frac{1}{2\gamma^2}\left(\frac{\mathrm{d}v}{\mathrm{d}x}\right)^2\right]\mathrm{d}x \tag{21}$$

The Euler-Lagrange equations of eq. (21) are:

$$\frac{d^2u}{dx^2}+\frac{d^2w}{dx^2}=0 \tag{22}$$

$$-\frac{1}{\gamma}\frac{d^2w}{dx^2}+\frac{1}{\gamma^2}\frac{d^2v}{dx^2}=0 \tag{23}$$

$$\frac{d^2u}{dx^2}-\frac{1}{\gamma}\frac{d^2v}{dx^2}=0 \tag{24}$$

Equations (22)-(24) are the conservation laws given in eqs. (18)-(20). The variational principle is also a useful tool for both analytical and numerical solutions [19-24].

Generally the diffusion layer can be considered as a fractal space, and the porous structure has to be considered, so eqs. (1)-(3) can be modified:

$$\frac{d^2u}{dx^{2\alpha}}-kuv=0, \quad \frac{du}{dx^{\alpha}}(0^{\alpha})=-1^{\alpha}, \quad u(1^{\alpha})=0^{\alpha} \tag{25}$$

$$\frac{d^2v}{dx^{2\alpha}}-k\gamma uv=0, \quad \frac{dv}{dx^{\alpha}}(0^{\alpha})=0^{\alpha}, \quad u(1^{\alpha})=1^{\alpha} \tag{26}$$

$$\frac{d^2w}{dx^{2\alpha}}+kuv=0, \quad \frac{dw}{dx^{\alpha}}(0^{\alpha})=0^{\alpha}, \quad w(1^{\alpha})=0^{\alpha} \tag{27}$$

where d/dx^{α} is the fractal derivative [25-29] and α – the fractal dimensions of the porous layer. We will discusss eqs. (25)-(27) in a separate paper.

Conclusion

This paper suggests a universal approach to solving approximately non-linear equations arising in electrochemistry, it is simple but effective, and the accuracy can be greatly improved if higher order Taylor series is used.

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