

ELECTROCHEMICAL MEASUREMENT OF FLOW PARAMETERS IN DILUTE SOLUTION*

Wang Degeng(王德耕)** and Zhu Shiliang(朱士亮)

Department of Chemical Engineering, Zhengzhou Institute of Technology, Zhengzhou 450002, China

Abstract A new theoretical method is proposed in the electrochemical measurement to obtain the relationship between flow parameter and the electrode current under the existence of ion migration effect. In this way the measurement of local mass transfer coefficient, wall shear stress and liquid velocity are presented and the experiment results are also described.

Keywords electrochemical measurement, ionic migration, mass transfer

1 INTRODUCTION

Electrochemical measurement of flow parameters based on the theory of limiting current has been widely used for many years and there is an increasing interest to use this technique in two-phase flow (TPF)^[1,2]. Conventionally for such electrochemical measuring purposes, a large amounts of supporting electrolyte were to be added to eliminate ionic migration effect. This may cause such as corrosion and crystallization problems because of the high concentration of supporting electrolyte. When the solution under measurement condition no or very little supporting electrolyte, it may be more handy for the measuring process. But under such conditions, the contribution of ionic migration to limiting current have to be taken into considered and this would lead to a very complicated mathematical problem even for a simple mass transfer system. Eucken, Okade^[4] and Gordon^[5] have studied this problem. The most important contribution in this field should be credited to Newman^[6,7] who has calculated the influences of ionic migration on limiting current by means of numerical method for four cases, namely the rotating disk, the growing mercury drop, penetration into a semiinfinite medium and stagnant Nernst diffusion layer. But the numerical method is not a good way to obtain a simple mathematical equation describing the relationship between measured parameter and flow variables. In this paper a new approach to solve the problem is presented and a measuring system with dilute electrolyte solution is proposed.

2 THEORETICAL

It is well-known that the fundamental equations to describe mass transfer in dilute solutions of electrolytes within which no reaction occurs can be represented by the two

Received 1996-05-20, accepted 1996-08-10.

* Supported by the National Natural Science Foundation of China.

** To whom correspondence should be addressed.

equations described bellows.

The flux of a solute species caused by migration in an electrical field, its diffusion in a concentration gradient and convection with the fluid velocity is

$$N_i = -D_i \nabla c_i - c_i U_i \nabla \phi + c_i \mathbf{u} \quad (1)$$

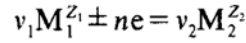
And the differential mass conservation equation for a small volume element is

$$\begin{aligned} \frac{\partial c_i}{\partial t} &= -\nabla \cdot N_i \\ &= D_i \nabla^2 c_i + \nabla \cdot (c_i U_i \nabla \phi) - \mathbf{u} \cdot \nabla c_i \end{aligned} \quad (2)$$

In most cases, the electroneutrality condition in electrolytic mass transport can be safely used as a good approximation^[8]

$$\sum Z_i c_i = 0 \quad (3)$$

Expressing a electrode reaction in dilute solution as a symbolic form



In the immediate vicinity of the electrode Eq.(1) can be represented by

$$\left\{ \begin{array}{l} -D_1 \nabla c_1 - c_1 U_1 \nabla \phi + c_1 \mathbf{u} = N \\ -D_2 \nabla c_2 - c_2 U_2 \nabla \phi + c_2 \mathbf{u} = -\frac{v_2}{v_1} N \\ -D_j \nabla c_j - c_j U_j \nabla \phi + c_j \mathbf{u} = 0 \quad j=3,4,\dots,m \\ \sum c_i Z_i = 0 \quad i=1,2,\dots,m \end{array} \right.$$

Considering the Einstein-Stokes relationship which is valid for dilute solutions

$$U_i = \frac{Z_i F}{RT} D_i$$

The potential gradient term can be deduced from the ion flux equation group as

$$\nabla \phi = \frac{RT}{F} \left[\frac{\frac{v_2 Z_2}{v_1 D_2} - \frac{Z_1}{D_1}}{\sum c_i Z_i^2} N + \frac{\sum \frac{Z_i c_i}{D_i}}{\sum c_i Z_i^2} \mathbf{u} \right] \quad (4)$$

Eliminating potential gradient and ionic mobility from the ion flux equation group using Eq.(4) and Einstein-stokes relationship, the following form will be obtained

$$N = -\xi D_1 \nabla c_1 + \eta c_1 \mathbf{u} \quad (5)$$

where

$$\xi = \frac{I}{I + \frac{1}{2} c_1 Z_1^2 \left(\frac{v_2 D_1 Z_2}{v_1 D_2 Z_1} - 1 \right)} \quad (6)$$

$$\eta = \frac{I - \frac{1}{2} D_1 Z_1 \sum \frac{Z_i}{D_i} c_i}{I + \frac{1}{2} c_1 Z_1^2 \left(\frac{\nu_2 D_1 Z_2}{\nu_1 D_2 Z_1} - 1 \right)} \quad (7)$$

$$I = \frac{1}{2} \sum c_i Z_i^2 \quad (8)$$

For binary ionic solutions such as CuSO_4 solution, the flux of a solute species is as follows

$$\begin{cases} -D_1 \nabla c_1 - c_1 U_1 \nabla \phi + c_1 \mathbf{u} = N \\ -D_2 \nabla c_2 - c_2 U_2 \nabla \phi + c_2 \mathbf{u} = 0 \end{cases}$$

and the following simplified expressions can be obtained

$$\xi = 1 + \left| \frac{Z_1}{Z_2} \right| \quad \eta = 1 + \frac{D_1}{D_2} \left| \frac{Z_1}{Z_2} \right|$$

In the above equations the effects of ionic migration are included in the factors ξ and η which can be defined respectively as the coefficient of migration effect on diffusion and on convection.

Substituting Eq.(5) into Eq.(2), and combining with the total mass conservation equation, yield

$$\frac{\partial c_1}{\partial t} = D_1 \nabla \cdot (\xi \nabla c_1) - \mathbf{u} \cdot \nabla (\eta c_1) \quad (9)$$

For time-smooth stationary flow, the equation is

$$\mathbf{u} \cdot \nabla (\eta c_1) = D_1 \nabla \cdot (\xi \nabla c_1) \quad (10)$$

Eqs.(9) and (10) are basic equations for solving the ionic mass transfer problems under the existence of ionic migration effect. The mass transfer flux to electrode is related to flow field near the electrode and then the flow parameter can be obtained by the electric current from the electrode.

In many cases, even if the supporting electrolyte in solution is not in a large excess, the variation in ξ and η is small in the concentration boundary layer. So, ξ and η can be taken as constants and the integration of the mass transfer equations will be greatly simplified.

A two-electrode system, consisted by a measuring electrode and an auxiliary electrode, is used for flow parameter measurement. The area of the auxiliary electrode is much greater than the area of the measuring electrode in order to eliminate concentration polarization of the auxiliary electrode.

3 MEASUREMENT OF FLOW CHARACTERISTICS NEAR THE WALL

Wall electrode mounted flush to the wall is used as a sensor for local flow parameter measurements (Fig.1). With the wall electrode the mass transfer coefficient, wall shear stress and even heat transfer coefficient can be measured in accordance with the

analogy of momentum, mass and heat transfer.

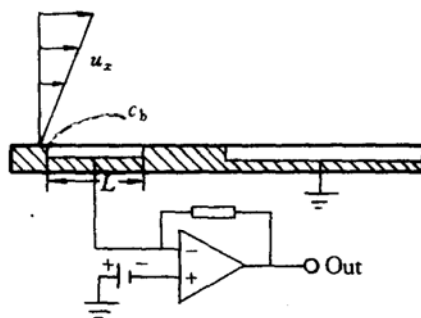


Figure 1 Working principle of wall probe

For a small wall probe in time-smooth stationary flow, neglecting the effect of the diffusion in the direction of flow and the velocity in the direction of perpendicular to the wall probe, Eq.(10) can be simplified as

$$u_x \frac{\partial(\eta c_1)}{\partial x} = D_1 \frac{\partial}{\partial y} \left(\xi \frac{\partial c_1}{\partial y} \right) \quad (11)$$

At the stage of limiting current, the boundary condition is

$$c_1|_{x=0} = c_1|_{y=\infty} = c_b, \quad c_1|_{y=0} = 0$$

Since the Schmidt number of the aqueous solution is very large ($>10^3$), the concentration boundary layer is much thinner compared with the viscous sublayer and then the flow velocity within the concentration boundary will be a linear function of y

$$u_x = \left. \frac{du_x}{dy} \right|_{y=0} \cdot y = sy$$

Combining the above equation and taking ξ and η as constants, Eq.(10) can be solved

$$c_1 = \frac{c_b}{\Gamma\left(\frac{4}{3}\right)} \int_0^\lambda e^{-\lambda^3} d\lambda \quad \text{where, } \lambda = y \left(\frac{\eta s}{9\xi D_1 x} \right)^{1/3}$$

Since the mean rate of mass transfer over the overall length of electrode is

$$\bar{N}_y = -\xi D_1 \left[\frac{1}{L} \int_0^L \left(\frac{\partial c_1}{\partial y} \right)_{y=0} \cdot dx \right] \quad (12)$$

the following expression can be obtained

$$\bar{N}_y = \frac{\xi c_b}{\Gamma\left(\frac{4}{3}\right)} \left(\frac{3\eta s D_1^2}{8\xi L} \right)^{1/3}$$

As the current is

$$I_e = \frac{n}{v_1} A_0 F \bar{N}_y \quad (13)$$

the wall shear stress will be

$$\tau_w = \mu s = \frac{8L\mu}{3\xi^2\eta D_1^2} \left[\frac{\Gamma(\frac{4}{3})v_1 I_e}{nFA_0c_b} \right]^3 \quad (14)$$

Since a constant temperature is being maintained during the measurement, the above equation can be rewritten in the form of calibration relationship

$$\tau_w = AI_e^3, \text{ where } A = \frac{8L\mu}{3\xi^2\eta D_1^2} \left[\frac{v_1\Gamma(\frac{4}{3})}{nFA_0c_b} \right]^3 \quad (15)$$

Where A is a constant.

The relationship between total mass transfer rate to the surface of the electrode and mass transfer rate contributed solely by diffusion is^[9]

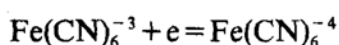
$$N_y = (\xi^2\eta)^{1/3} N_D \quad (16)$$

$$N_D = k_D c_b \quad (17)$$

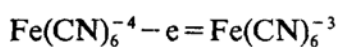
Most cases, the purpose of modular experiment is to obtain the mass transfer coefficient caused solely by molecular diffusion within the boundary layer. Since, the coefficient of mass transfer caused only by molecular diffusion within the boundary layer under similar flow conditions can be deduced as

$$k_D = \frac{v_1 I_e}{(\xi^2\eta)^{1/3} n A_0 F} \quad (18)$$

Experiments for testing theoretical equation were conducted proceeded in a flow loop within a 20mm I. D. duct. The recycled solution consists of $0.011 \text{ kmol} \cdot \text{m}^{-3} \text{ K}_3\text{Fe}(\text{CN})_6$ and $0.0105 \text{ kmol} \cdot \text{m}^{-3} \text{ K}_4\text{Fe}(\text{CN})_6$. The wall electrodes both measuring electrode and auxiliary electrode are with Pt films. The reaction of the cathode is



and the reaction of the anode is



The measuring electrode can be taken as the cathode or the anode because the reactions at the electrode are reversible. For the purpose of changing the effect of ionic migration, the various amount of NaOH is added in the solution. The concentrations of NaOH vary from $0.01 \text{ kmol} \cdot \text{m}^{-3}$ to $0.16 \text{ kmol} \cdot \text{m}^{-3}$. The respective ranges of ξ and η are 0.85–0.91 and 0.51–0.99 for the cathode reaction, 1.23–1.11 and 0.70–1.20 for the anode reaction.

Fig.2 shows the results of the experiment. The experimental data agree well with the theoretical calculations, indicating the validity of the equations presented in this paper.

In the study of turbulent flow conditions, the measurement of turbulent intensity at the wall is important for it is believed that the turbulence is initiated at the wall area.

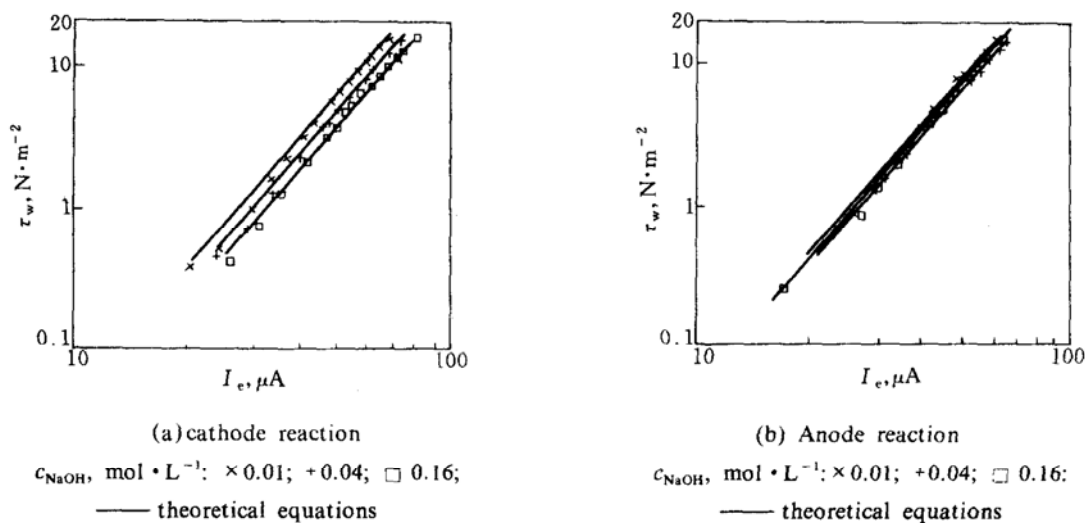


Figure 2 Results of wall probe experiments

Using a wall electrode to measure wall turbulent intensity proves to be more ascendant than other methods of measurement such as hot-wire anemometer and laser velocimeter. With the wall electrode, it is found

$$\frac{\sqrt{u_{x,0}^{\prime 2}}}{u_{x,0}} = \lim_{y \rightarrow 0} \frac{\sqrt{(\Delta u_x' / \Delta y)^2}}{\Delta u_x / \Delta y} = \frac{\sqrt{s'^2}}{s} \quad (19)$$

According to Eq.(14) the turbulence intensity at the wall can be easily obtained. Fig.3 shows the results of the measurement in a rectangular tube with cross section of 20mm×18mm. The solution is by 0.008 kmol · m⁻³ K₃Fe(CN)₆ with equiconcentration of K₄Fe(CN)₆ and 0.091 kmol · m⁻³ KCl. It is noticed from the measurement that the turbulence intensity at the wall is not a constant as the experimental results in circular tube flow provided by other authors but a variable decreasing with the increases in flow rate in the rectangular tube. Only at heigher Reynolds number, the turbulence intensity approaches a constant.

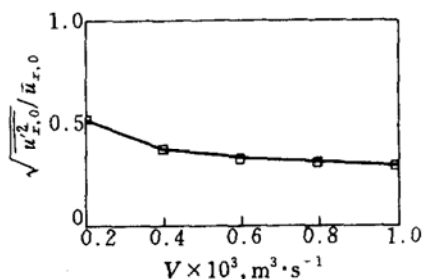


Figure 3 Turbulent intensity at the wall of rectangular tube

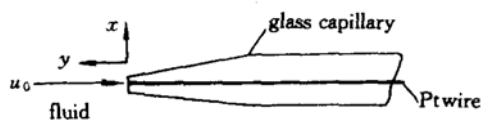


Figure 4 Blunt nose probe (head)

4 MEASUREMENT OF LIQUID VELOCITY

A blunt nose electrode is used for measuring liquid velocity and the local void fraction in two-phase flow. In the case of blunt nose electrode, what happened is much similar with the mass transfer to a stagnant point and can be described as follows^[10]

$$\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} = 0 \quad (20)$$

$$u_x \frac{\partial u_x}{\partial x} + u_y \frac{\partial u_x}{\partial y} = l^2 x + \frac{\mu}{\rho} \left(\frac{\partial^2 u_x}{\partial x^2} + \frac{\partial^2 u_x}{\partial y^2} \right) \quad (21)$$

$$u_x \eta \frac{\partial c_1}{\partial y} = D_1 \frac{\partial}{\partial y} \left(\xi \frac{\partial c_1}{\partial y} \right) \quad (22)$$

The relevant boundary conditions are

$$y=0: u_x = u_y = 0, c_1 = c_w$$

$$y = \infty, u_x \rightarrow lx, u_y \rightarrow ly, c_1 = c_b$$

Transforming, we get

$$y = \sqrt{\frac{\mu}{l\rho}} t \quad u_y = \sqrt{\frac{l\mu}{\rho}} \psi \quad \Omega = \frac{c - c_w}{c_b - c_w}$$

And Eqs.(20), (21) and (22) can be resulted as

$$u_x = lx\psi' \quad (23)$$

$$\begin{cases} \psi'''' + \psi\psi'' + \psi'^2 + 1 = 0 \\ \psi|_{t=0} = \psi'|_{t=0} = 0 \\ \psi'|_{t=\infty} = 1 \end{cases} \quad (24)$$

$$\begin{cases} (\xi\Omega')' + Sc\eta\psi\Omega' = 0 \\ \Omega|_{t=0} = 0 \quad \Omega|_{t \rightarrow \infty} = 1 \end{cases} \quad (25)$$

Solving above equations and according to

$$N_y = \xi(0)D_1 \frac{\partial c_1}{\partial y} \Big|_{y=0} = \xi(0)\Omega(0)D_1(c_b - c_w) \sqrt{\frac{l\rho}{\mu}}$$

several results can be obtained^[10]. The rate of mass transfer is given by

$$N_y = \frac{\sqrt{\lambda Re} \xi D_1 (c_b - c_w)}{L_r [1.513(\xi/\eta Sc)^{1/3} + 0.201(\xi/\eta Sc)^{2/3}]} \quad (26)$$

and the Sherwood number is given by

$$Sh = \frac{\sqrt{\lambda} \xi Re^{1/2} Sc^{1/3}}{1.513(\xi/\eta Sc)^{1/3} + 0.201(\xi/\eta Sc)^{2/3}} \quad (27)$$

where

$$N_y = k_c(c_b - c_w) \quad Sh = \frac{k_c L_f}{D} \quad Re = \frac{\rho u_0 L_f}{\mu}$$

Since velocity measuring probe is microelectrode, the edge effect of mass transfer can not be neglected. The mass transfer to the edge of the electrode will behave much similar to that in solely ionic diffusion^[5]. Hence

$$N_e = \frac{2d\xi D_1(c_b - c_w)}{A_0} \quad (28)$$

The final forms of the equations for the microelectrode are

$$N_y = \left[\frac{2d}{A_0} + \frac{\sqrt{\lambda} Re^{1/2} Sc^{1/3}}{L_f [1.513(\xi/Sc\eta)^{1/3} + 0.201(\xi/Sc\eta)^{2/3}]} \right] D_1 \xi (c_b - c_w) \quad (29)$$

$$Sh = \frac{2dL_f\xi}{A_0} + \frac{\sqrt{\lambda} \xi Re^{1/2} Sc^{1/3}}{1.513(\xi/Sc\eta)^{1/3} + 0.201(\xi/Sc\eta)^{2/3}} \quad (30)$$

So, the limiting current can be represented as

$$I_e = a + b\sqrt{u_0} \quad (31)$$

where

$$a = \frac{2dnFD_1\xi c_b}{v_1} \quad (32)$$

$$b = \frac{nFA_0\xi D_1 c_b (\lambda\rho/L_f\mu)^{1/2} (Sc)^{1/3}}{v_1 [1.513(\xi/\eta Sc)^{1/3} + 0.201(\xi/\eta Sc)^{2/3}]} \quad (33)$$

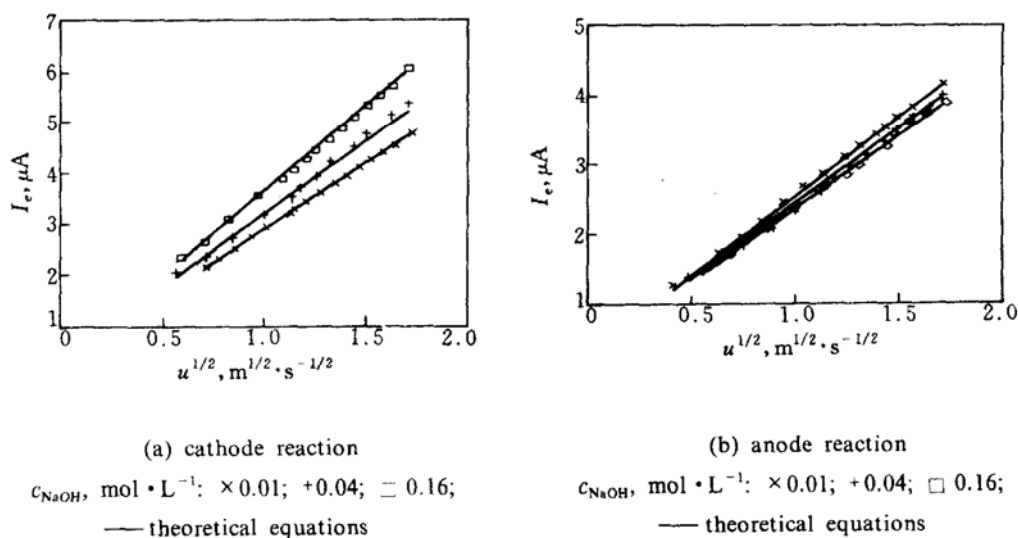


Figure 5 Experimental results of blunt probe

Where a and b are constants when the temperature in the operation system is kept invariable and Eq.(31) can also be taken as a calibration relationship of the velocity probe.

Fig.5 presents the experimental results of the velocity measuring probe. The experiments are carried out under the same conditions as those described in Section 2 of this paper.

5 CONCLUSIONS AND DISCUSSION

The results of theoretical analyses agree well with that of the experiments and the calibration relationships of the wall probe and the blunt nose probe exhibit same forms as those when large supporting electrolyte are added, but different values for the constants are being retread.

The theoretical analyses and experimental results show that it is appropriate to use this electrochemical methods for measuring flow parameters under ionic migration. This method not only minimizes the unexpected effects caused by higher concentration electrolyte and simplifies the experimental process but also brings about improvements in the frequency response of the probe. It can also be seen that when the direction of the ionic migration is coherent with the direction of the diffusion, the frequency response of the probe will be speeded up^[3]. It is expected that the application area of the method will be extended in the future.

NOMENCLATURE

A	defined by Eq.(15)
A_0	area of electrode surface, m^2
c	concentration, $kmol \cdot m^{-3}$
D	diffusion coefficient, $m^2 \cdot s^{-1}$
d	diameter of electrode, m
F	Faraday Constant, $A \cdot s \cdot mol^{-1}$
I	ionic strength, $mol \cdot m^{-3}$
I_c	current, A
k	coefficient of mass transfer, $m \cdot s^{-1}$
L_f	characteristic width, m
l	constant, s^{-1}
M	chemical composition
m	number of species
N	mass transfer rate, $mol \cdot s^{-1} \cdot m^{-2}$
n	charge number of the cell reaction
Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number
s	velocity gradient, s^{-1}
T	temperature, K
t	time, s
U	ionic mobility, $m^2 \cdot s^{-1} \cdot V^{-1}$
u	liquid velocity, $m \cdot s^{-1}$
V	volum flow, $m^3 \cdot s$
Z	charge number of ion
λ	constant

- μ viscosity, Pa \cdot s
 ρ density, kg \cdot m⁻³
 τ_w wall shear stress, N \cdot m⁻²
 ν stoichiometric coefficient of electrode reaction
 ϕ electrical potential, V

Superscripts

- ' turbulence
- average

Subscripts

- b bulk of solution
c total
D diffusion
e edge
i ith species
j jth species without reaction
x direction parallel to electrode
y direction perpendicular to electrode

REFERENCES

- 1 Nakoryakov, V. E., Kashinsky, O. N. and Kozuenko, B. K., IUTAM Symposium, Nancy/France; Springer Verlag, 695(1984).
- 2 Souhar, M. and Cognet, G., IUTAM Symposium, Nancy/France, Springer Verlag, 723(1984).
- 3 Wang, D.G. and Zhu, S. L., Symposium on 1991's Annual meeting of Chinese Society of Chemical Engineering, Press of Chengdu University of Science and Technology, Chengdu, 635(1991).
- 4 Okada, S. and Yoshizawa, S., *et al.*, *J. Electrochem. Soc., Japan*, **27**, E51 (1959).
- 5 Gordon, S. L., Newman, J. S. and Tobias, C. W., *Berichte der Bunsengesellschaft fur Physikalische: Chemie*, **70**, 414(1966).
- 6 Newman, J., *Ind. Eng. Chem. Fund.*, **5**, 525(1966).
- 7 Newman, J., *Electrochemical Systems*, Prentice-Hall Englewood Cliffs, NJ (1973).
- 8 Yeager, E. and Bockris, J. O'M, *et al.*, *Comprehensive Treatise of Electrochemistry*, Vol.6, Plenum Press, New York (1983).
- 9 Wang, D. G., Lian, C. G. and Zhu, S. L., *J. Chem. Ind. & Eng. (China)*, **43**(6), 765(1992).
- 10 Wang, D. G., Symposium on 2th youth's meeting of Chinese Society of chemical Engineering, Press of South China University of Technology, Guangdong, 135(1993).