MASS TRANSFER AT GAS EVOLVING MERCURY ELECTRODE①

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ABSTRACT

Mass transfer at hydrogen evolving mercury electrode has been studied by determining mass transfer coefficients of indicator ions as the function of current density of hydrogen evolution for various kinds of indicator ions in sulphuric acid solution. Mercury adhering to metal substrates of Ni, Cu or Ag is used as mercury electrode to overcome its trembling during the electrolysis. The effect of different indicator ions, electrode characteristic, substrate material, diameter of electrode and temperature is examined. It is found that the mass transfer coefficient is proportional to the square root of current density of hydrogen evolution.

Key words: mercury electrode gas bubble mass transfer

1 INTRODUCTION

Gas evolving is an important phenomenon in electrolysis process in the field of electrochemistry. Mass transfer at gas evolving electrodes has been investigated by many authors [1-3]. All their work has been done on the mass transfer mechanism at gas evolving electrodes of solid, while little attention has been paid on mass transfer processes at gas evolving liquid-liquid interface . Ibl et al[4] studied the mass transfer of indicator ions of Cu^{2+} and Cd^{2+} at various metal electrodes evolving hydrogen, and found that indicator ions of Cu^{2+} and Cd^{2+} were easily deposited as metal powders on the surface of mercury electrode, which made the surface of the electrode unstable. Janssen[5]got the result that the mass transfer coefficient of indicator ion of Ce^{4+} was proportional to 0.36 power of current density of hydrogen evolution, when using mercury electrode consisting of a glass tube filled with mercury. he also found that the error of the experimental result was large for the mercury trembling in the tube during the elctrolysis.

Here the mass tranfer of indicator ions of Fe^{3+}, Ce^{4+} and Hg_2^{2+} at hydrogen evolving mercury electrodes are investigated in acid solution using mercury electrodes consisting of mercury contained in a glass cup and mercury adhering to metal substrates of Cu, Ni and Ag.

2 EXPERIMENTAL DETAILS

A normal H-type elctrolytic cell was used as shown in Fig.1. The horizontal test-electrode prepared with the method of Yoshida [6] was mercury contained in a glass cup or adhering to metal substrates of Cu, Ni or Ag. The vertical counter-electrode is a platinum foil 2×10^{-4} m^2 in surface area. 1 mol / L H_2SO_4

① Project supported by the Foundation of the State Education Commission for doctoral students; manuscript received July 30, 1991.

solution is used as supporting electrolyte. For different indicator ion the solution is made with 0.035 mol / L Fe^{3+} in $Fe_2(SO_4)_3$ or 0.035 mol / L Ce^{4+} in $Ce(SO_4)_2$ or 8.0×10^{-4} mol / L Hg_2^{2+} in $Hg_2(NO_3)_2$. Before each experiment the mercury electrode is polarized in the supporting electrolyte for 5 to 15 min at a current density equal to that of the experiment. The constant current electrolysis is processed in thermostated electrolytic cell usually with the temperature of 25 ℃. The electrolysis time is controlled according to the current density to maintain that the decrease in concentration of indicator ion determined by chemical analysis is about 2%, so that no correction for the diminishing concentration is needed. To test whether Fe^{3+} is reduced by H_2 in solution, Fe^{3+} is added into 100 mL supporting solution in which H_2 has been produced by electrolysis with 1A current for 30 min. No Fe^{2+} in the solution after the addition of Fe^{3+} for 5 to 10 min shows that Fe^{3+} could not be reduced by H_2 in solution.

3 EXPERIMENTAL RESULTS

For suitable indicator ion, of which the reduction reaction at electrode is controlled by mass transfer, its concentration at electrode is zero during the electrolysis with constant current density. The mass transfer coefficient K of the indicator ion can be determined with the following equation by analying the quantity M of indicator ion reduced in a specified period of time t:

$$K = M / (C_0 A\, t) \qquad (1)$$

where A is the surface area of the electrode and C_0 the concentration of the indicator ion in the solution.

The current density I of the electrode which is in the circuit of the electrolytic cell consists of two parts. The first part is the current density I_{ind} to reduce the indicator ion at electrode and the second part of the current density I_{H_2} to evolve hydrogen. From the Faraday's law it gives that

$$I_{ind} = ZFM / (t\, A) \qquad (2)$$

where Z is the number of electrons involved in the electrode reaction and F the constant of Faraday. From the equation, the current density I_{H_2} of hydrogen evolution is

$$I_{H_2} = I - I_{ind} \qquad (3)$$

With equation (1), (2) and (3) experimental data can be dealt to get the relation between mass transfer coefficients K (m / sec) and current density I_{H_2} (A / m^2) of hydrogen evolution.

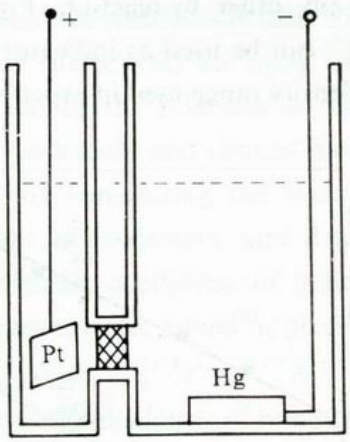

Fig. 1 Experimental apparatus

3.1 *Nature of the Indicator Ion and the Electrode Material*

The nature of various indicator ions is compared experimentally. The results show that the mercury loses its light and becomes rough after the mercury electrode immersed in electrolyte with Ce^{4+} as indicator ion because of its strong oxidation. The rough surface will resume its light by polarizing the mercury electrode cathodically. The standard electrical potential of the redox couple Ce^{4+} / Ce^{3+} is 1.61

V which is much larger than that of the redox couple Hg_2^{2+} / Hg in acid solution, so the mercury is easily oxidized by Ce^{4+} and it will not be used as indicator ion any more.

The standard potential of the redox couple Fe^{3+} / Fe^{2+} is close to that of Hg_2^{2+} / Hg. The results in Fig. 2 show that Fe^{3+} can be used as indicator ion to determine the mass transfer coefficients at hydrogen evolving mercury electrode. But Fe^{3+} may deposite on mercury and form iron amalgam that exists in the form of paste on the adhering mercury electrode when the current is too large and the electrical potential at the electrode is much negative. As indicator ion, Hg_2^{2+} can be reduced and enter into the mercury elctrode without any other by-reaction. Fig. 2 shows that Hg_2^{2+} can be used as indicator ion in the current density range used in experiment.

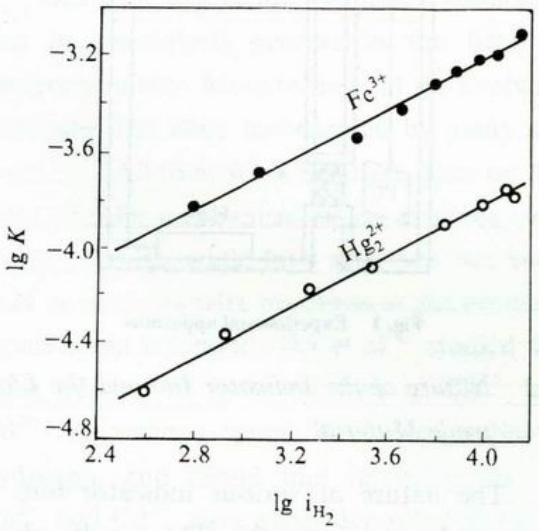

Fig. 2 Effect of indicator ions on mass transfer

It is found that the mercury electrode in glass cup trembles sometimes during the experiment of electrolysis, which may affect the mass transfer and make the results unreliable. Fig.3 shows the results selected from experimental without mercury trembling. Experimental data correlate well in Fig. 3, which have the same relation as those with other electrode materials. The adhering mercury electrode can overcome the tremble however is limited by substrate, Its experimental data can correlate and repeat well. As verified by Sibata[7], of the three kinds of adhering mercury electrodes, the electrode of Ni substrate is most stable, which can be used repeatedly without obvious change in its nature. Electrodes of Cu and Ag substrates will somewhat form pasted amalgam easily, so the electrode of Cu or Ag substrate needs to be reprepared after each experiment. Their results are identical with those of Ni substrate as shown in Fig. 3. Results in Fig. 3 also show that the mass transfer coefficients determined by the mercury electrode in glass cup are larger than those of adhering mercury electrodes. This may be caused by the trembling of mercury.

3.2 *Effect of Current Density*

Mass transfer coefficient K of indicator ion varies with the current density I_{H_2} of hydrogen evolution. The experimental results in

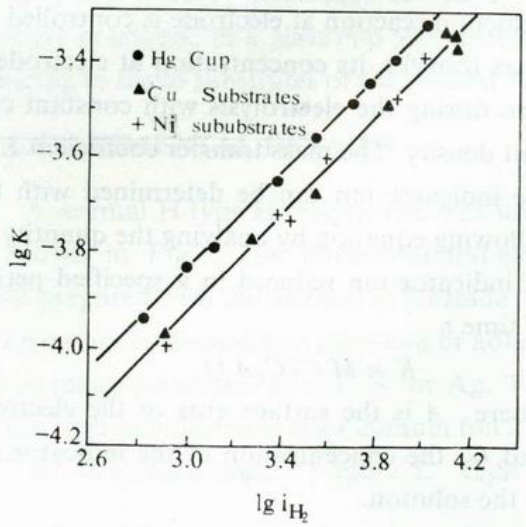

Fig. 3 Effect of different electrodes on mass transfer

Fig. 2 and 3 show that lg$K$ and lgI_{H_2} have linear relation. All slopes of the lines are about 0. 5 obtained by linear regression.

3. 3 *Effect of Electrode Size*

Experimental results of mercury electrode with different diameters and in glass cup are given in Fig. 4. It shows that the electrode size has no obvious effect on the linear relation between lg$K$ and lg I_{H_2}. In fact the diameters of the Cu and Ni substrates have a little difference but the relation between the mass transfer coefficient and current density is the same.

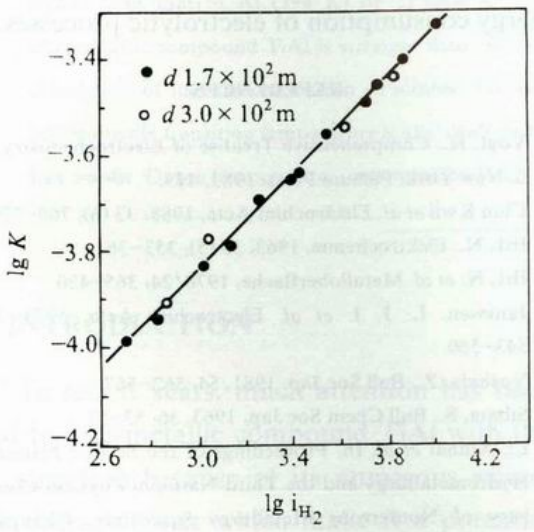

Fig. 4 Effect of electrode size on mass transfer

3. 4 *Effect of Temperature*

The results of mass transfer coefficients at temperatures of 5, 15 and 25 ℃ are given in Fig.5. It shows that the mass transfer coefficient increases with temperature slightly.

The effect of temperature on mass transfer at gas evolving electrode is complex. The mass transfer can be enhanced by the increase of diffusion coefficient of indicator ion in solution with temperature and by gas bubble evolution. The volumetric rate of gas bubble evolution increases with the temperature for the expansion of its volume by themselves and by water vapour entering into gas bubble. It is supposed that the effect of temperature on mass transfer is mainly due to the increase of the diffusion coeffcitent for very small water vapour at stabllizely normal temperature (<40 ℃).

4 DISCUSSION

Experimental results in Fig. 2–5 show that lg$K$ and lgI_{H_2} have linear relation with a slope of about 0. 5 under the experimental condition of current density. The hydrogen evolution rate at this condition lies in the region that gas bubbles coalesce and detach from the interface without slip after nucleation on electrode surface. So the mass transfer of indicatior ion to the interface is mainly enhanced by coalesence and detach- ment of gas bubbles. Only considering the mass transfer enhancement of coalesence and detachment, the mass transfer coefficient of indicator ion from the mass transfer model[8] is given by

$$K=3^{1/2}\delta_N D^{1/2} n_c^{2/3} n^{1/2} q^{1/2} R_d^{-1/2} \qquad (4)$$

where δ_N is the thickness of boundary layer, D the diffussion coefficient of indicator ion, n_c bubble number in each coalescence, n the number of detached bubbles per unit surface area at any moment, q the volumetric rate of gas evolution per unit surface area. It is assumed that the efficiency of hydrogen bubble evolution during the electrolysis is constant or 100% . Consequently the rate q of hydrogen evolution is proportional to the current density I_{H_2} of hydrogen electrolysis. It follows that

$$q=p\ I_{H_2} \qquad (5)$$

of which p is proportionality factor. From equations (4) and (5), it can be deduced that

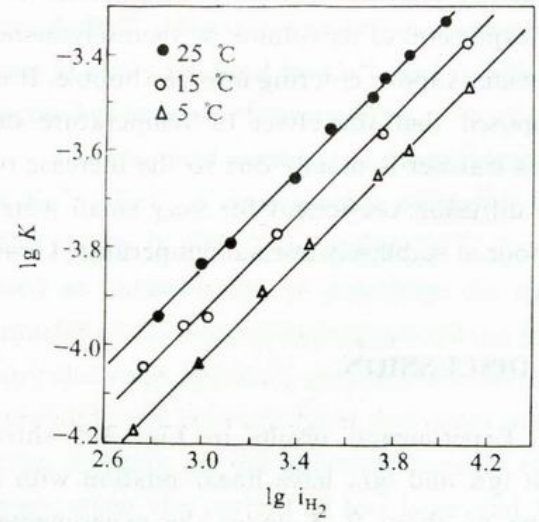

Fig. 5 Effect of temperature on mass transfer

$$K = 3^{1/2}\delta_N D^{1/2} n_c^{2/3} n^{1/2} p^{1/2} I_{H_2}^{1/2} R_d^{-1/2} \quad (6)$$

It is assumed that δ_N and D are constant under certain experimental conditions: n_c and R_d are constant at large current den- sity[8,9]. So equation (6) can be rewritten as

$$K = [3^{1/2}\delta_N D^{1/2} n_c^{2/3} n^{1/2} p^{1/2} R_d^{-1/2}] I_H^{1/2} \quad (7)$$

Each term in the bracket of equation (7) is constant at the experimental condition based on the above discussion. This means that K is proportional to I_{H_2}, i. e., lg$k$ and lgI_{H_2} have their linear relation with a slope of 0.5. So the theoretical model of equation (4) can well describe the mass transfer of indicator ion at gas evolving mercury electrode, which shows that the model is correct.

5 CONCLUSIONS

From the proceeding discussion, it can be concluded that the mass transfer of indicator ion of gas evolving electrode can be enhanced by the evolution of gas bubbles from the electrode. The mass transfer can be described well by the theoretical model derived previously. The resolution can be used to direct the electrolytic cell design of new type in electro-chemical engineering of metallurgical and chemical industry to increase the yield and minimize the energy consumption of electrolytic processes.

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