JOURNAL OF APPLIED ELECTROCHEMISTRY **22** (1992) 1091-1094

Mass transfer at rotating ring-cone electrodes

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Received 30 March 1992; accepted 15 April 1992

The rotating ring-cone electrode (RRCE) is a useful electrode assembly to investigate electrochemical reactions when gas bubble evolution occurs. Theoretical relations describing the effect of the apex half-angle of an RRCE on the rate of mass transfer to a cone electrode of an RRCE and on the collection efficiency of an RRCE are given in literature. It has been found that the experimental results support the theoretical relation presented in literature.

Nomenclature

A	surface of working electrode (mm^2, m^2)
c	concentration ($mol\,m^{-3}$)
$c_{Fe(II)}$	concentration of ferrocyanide ($mol\,m^{-3}$)
$c_{Fe(III)}$	concentration of ferrocyanide ($mol\,m^{-3}$)
c_b	concentration in bulk of solution ($mol\,m^{-3}$)
D	diffusion coefficient ($m^2\,s^{-1}$)
E	electrode potential with respect to SCE (V)
F	Faraday constant. ($C\,mol^{-1}$)
h_c	inverse slope of $(I_{C,gd,Fe(III)})^{-1}/\omega^{-1/2}$ straight line (A $rad^{-1/2}\,s^{1/2}$
h_R^0	inverse slope of $(I_{R,gd,Fe(III)})^{-1}/\omega^{-1/2}$ straight line at $I_c = 0$ (A $rad^{-1/2}\,s^{1/2}$)
h_1	height of the cone of RRCE (mm)
h_2	distance from the top of the frustrum to base of the frustrum of RRCE (mm)
h_3	distance between the cone and frustrum of RRCE, gap width of RRCE (mm)
I	current (A)
I_c	cone current (A)
$I_{C,Fe(III)}$	I_C for reduction of ferricyanide (A)
I_R	ring current (A)
$I_{R,Fe(III)}$	I_R for reduction of ferricyanide (A)
$I_{R,Fe(II)}^0$	ring current at $I_C = 0$ for oxidation of ferrocyanide (A)
n	number of electrodes involved in oxidation or reduction of a species (–)
N_0	collection efficiency of RRCE (–)
r_1	radius of the base of cone of RRCE (mm)
r_2	radius of the base of the cone frustrum of RRCE (mm)
r_3	radius of the top of the cone frustrum of RRCE (mm)
θ	apex half-angle of cone of RRCE (degree)
ν	kinematic viscosity of solution ($m^2\,s^{-1}$)
ω	rotation speed of RRCE ($rad\,s^{-1}$)

Subscripts

C	cone of RRCE
D	disc of RRDE
g	limiting conditions
gd	limiting diffusion conditions
R	ring or frustrum of RRCE

1. Introduction

A rotating ring-cone electrode (RRCE) has similar possibilities for electrochemical research as a rotating ring-disc electrode. Investigating an electrode reaction with gas bubble evolution on an RRCE offers additional advantages in regard to a rotating ring-disc electrode (RRDE) [1]. Gas bubbles cannot be trapped at the tip of an RRCE and a smooth liquid flow past the RRCE surface is expected. An RRCE is schematically represented in Fig. 1. Mass transfer to a rotating cone electrode has been considered by several authors [2–6].

For laminar flow, Newman and Mohr [4, 5] derived a relation for the overall mass transfer rate for a rotating cone electrode of base radius r_1. From their relation it follows that the limiting diffusion current is given by

$$I_{gd,cone} = 0.62 n F c_b \pi r_1^2 \left(\frac{\nu\omega}{\sin\theta}\right)^{0.5} \left(\frac{D}{\nu}\right)^{0.67} \tag{1}$$

where θ is the apex half-angle of the cone and the other symbols have their usual meanings.

Usually, the limiting diffusion current for a rotating cone is related to that of a rotating disc [3] by

$$I_{gd,cone} = I_{gd,disc}(\sin\theta)^{-0.5} \tag{2}$$

a geometric parameter β for an RRDE has been introduced [7] to correlate the mass transfer rate to the ring electrode and that to the disc electrode of an RRDE.

The ratio between the limiting diffusion current for the ring electrode at $I_D = 0$ and that for the disc electrode of an RRDE [7] is given by

$$\frac{I_{R,gd}^0}{I_{D,gd}} = \beta^{2/3} \tag{3}$$

The parameter β for an RRDE depends only on the diameter of the disc and the inner and outer diameter of the ring. Because of the similarity between the RRCE and the RRDE it can be stated that, for an RRCE

$$\frac{I_{R,gd}^0}{I_{c,gd}} = \beta^{2/3} \tag{4}$$

where $I_{R,gd}^0$ is the limiting diffusion current for the ring

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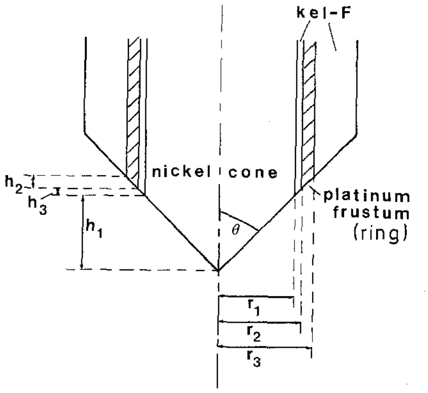

Fig. 1. Nomenclature and geometry of RRCE.

electrode at $I_c = 0$, and

$$\beta = \frac{r_3^3}{r_1^3} - \frac{r_2^3}{r_1^3} \tag{5}$$

and the radii r_1, r_2 and r_3 are indicated in Fig. 1.

The electrochemical surface of a ring electrode of an RRCE is the curved outer surface of the frustrum of the cone.

Collection experiments, where the disc-generated species is observed at the ring, are generally carried out with an RRDE. Recently, an RRCE has been used to determine the supersaturation concentration of oxygen at an oxygen-evolving electron [1].

The collection efficiency of an RRDE is well-known and can be calculated from its geometry, since it depends only on the radius of the disc electrode, the inner radius of the ring electrode and the outer radius of the ring electrode. The collection efficiency is independent of the angular velocity of the electrode, the concentration of the electro-active species in the bulk of solution, the diffusion coefficient of the active species and the kinematic viscosity of the solution [7].

Mass transfer to an RRCE has been extensively studied by Nijborg [8]. His theoretical work supports the relations derived by Newman and Mohr [4, 5]. Moreover, he has found that the collection efficiency for an RRCE is similar to that for an RRDE and does not depend on the apex half-angle of the cone.

The collection efficiency, N_0, for an RRCE is given by the same mathematical relation as that for an RRDE if the radius of the disc, the inner radius of the ring and the outer radius of the ring are substituted by r_1, r_2 and r_3, respectively, [8] where these radii are indicated in Fig. 1.

The aim of this investigation is to verify experimentally the theoretical relations for the mass transfer to the cone and the collection efficiency of an RRCE, and, particularly, the effect of the apex half-angle of the cone on the characteristics of an RRCE.

The mass transfer experiments were carried out with the well-known indicator redox couple $Fe(CN)_6^{3-}$ / $Fe(CN)_6^{4-}$ in alkaline solution.

The collection efficiency coefficient, N_0, for an RRDE is given by a rather complex equation [7]. Values of the collection efficiency coefficient are given for various ratios of r_2/r_1 and r_3/r_2 in the literature [9].

Table 1. Parameters of RRCE, calculated and experimental values h_C, $\beta^{2/3}$ and N_0

Apex half-angle of cone (degree)	*9.8*	*19.7*	*30*	*60*	*90*
r_1/mm	2.730	2.695	2.745	2.715	4.005
r_2/mm	2.985	2.980	3.010	2.930	4.203
r_3/mm	3.370	3.415	3.440	3.435	4.335
h_1/mm	15.1	7.25	4.69	1.58	0
h_2/mm	2.23	1.23	0.72	0.28	0
h_3/mm	1.41	0.77	0.45	0.13	0
A_C/mm^2	131.5	65.5	46.8	29.1	50.4
A_R/mm^2	44.2	20.6	17.8	11.6	4.55
β (calculated)	0.57	0.68	0.65	0.77	0.12
β (experimental)	0.64	0.62	0.62	0.68	0.13
$10^3\ h_C$/A s$^{1/2}$ rad$^{-1/2}$ (theoretical)	1.06	0.74	0.63	0.47	0.94
$10^3\ h_C$/A s$^{1/2}$ rad$^{-1/2}$ (experimental)	1.00	0.74	0.65	0.43	0.85
N_0 (calculated)	0.26	0.27	0.27	0.31	0.11
N_0 (experimental)	0.25	0.29	0.26	0.27	0.13

2. Experimental details

The experiments were carried out in a simple cell divided into two compartments by a cation exchange membrane. The working electrode assembly was a Pt ring–Ni cone electrode (RRCE), a schematic diagram of this type of RRCE has already been published [1]. For economic reasons the cone of the RRCE was made from nickel and the ring from platinum. Some parameters of the RRCE used are given in Table 1.

A flat platinum electrode of about 5 cm^2 served as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode to which all potentials are referred.

All experiments were carried out in a 1 M KOH solution containing 0.040 M $K_3Fe(CN)_6$. The solution was kept at 298 K. The electrochemical measurements were performed with a bipotentiostat (Tacussel, type BI-PAD) and a voltage scan generator (Wenking model VSG 72). The potential-current curves were recorded with an X–Y recorder (Philips PM 8041).

The potential–current curves were recorded at a scan rate of 20 mV s^{-1} for the reduction of ferricyanide in the potential range between -0.20 and 0.45 V and for the oxidation of ferrocyanide between 0.23 and 0.49 V. Ferrocyanide formed at the cone of the RRCE was detected at the ring of the RRCE.

3. Results and discussion

3.1. *Rate of mass transfer*

The potential–current curve for the reduction of ferricyanide shows that the current attains a limiting value at potentials between 0 and -0.2 V; this limiting value is indicated by $I_{g,Fe(III)}$. During a series of experiments the rotation speed of the RRCE was decreased from 402 to 6.28 rad s^{-1} by steps.

It had been found that for a nickel electrode the $I_{g,Fe(III)}/\omega^{1/2}$ relation is slightly curved. The deviation from a linear relationship is caused by a small effect of

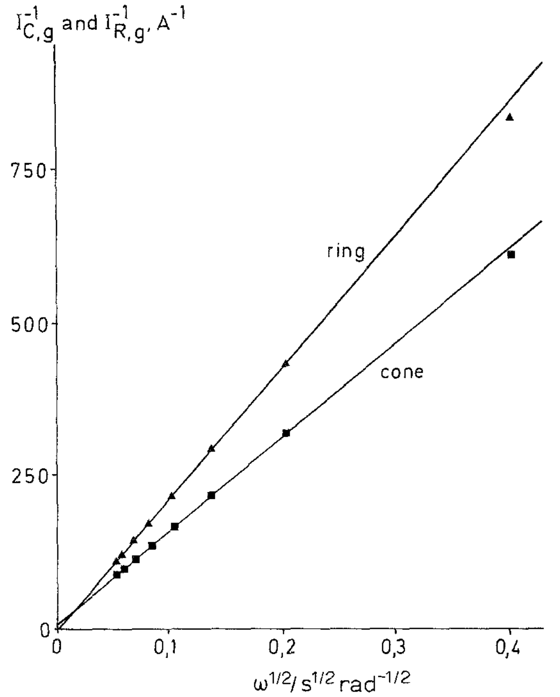

Fig. 2. The inverse of the limiting current for reduction of ferricyanide at a cone electrode and at a ring electrode where $I_C = 0$ as a function of the inverse of the square root of rotation speed for an RRCE with an apex half-angle of 30°. Electrolysis conditions: 1 M KOH + 0.040 M $K_3Fe(CN)_6$ and 25° C.

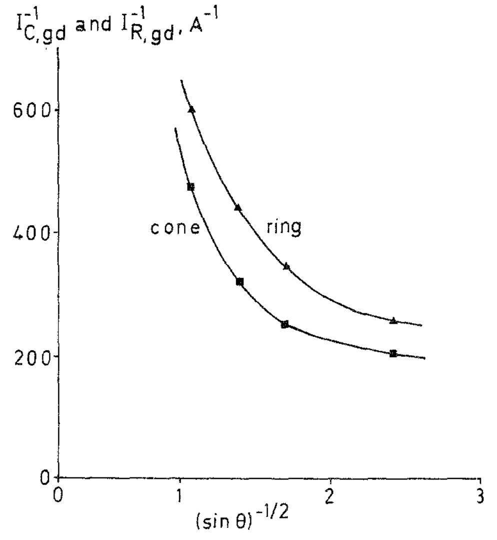

Fig. 3. The limiting diffusion currents for the reduction of ferricyanide at a cone electrode and at a ring electrode where $I_C = 0$ as a function of the inverse of $(\sin\theta)^{1/2}$. Electrolysis conditions: 1 M KOH + 0.040 M $K_3Fe(CN)_6$ and 25° C. The RRCEs were rotated with 8π rad s^{-1}.

the kinetics of electrode reaction. Plotting the reciprocal value of $I_{g,Fe(III)}$ against $\omega^{-1/2}$, a straight line plot was obtained. The slope of the $(I_{g,Fe(III)})^{-1}/\omega^{-1/2}$ plot for a cone electrode of RRCE is indicated by h_c.

In Table 1 the experimental h_c is tabulated for cone electrodes with various apex half-angles.

From Equation 1 it follows that the theoretical h_c is given by

$$h_c = 0.62nFc_b\pi r_1^2\left(\frac{\nu}{\sin\theta}\right)^{0.5}\left(\frac{D}{\nu}\right)^{0.67} \qquad (3)$$

Introducing $n = 1$, $F = 96484\,\mathrm{C\,mol^{-1}}$, $c_b = 40\,\mathrm{mol\,m^{-3}}$, $D_{Fe(III)} = 7.3 \times 10^{-10}\,\mathrm{m^2\,s^{-1}}$, $\nu = 1.073 \times 10^{-6}\,\mathrm{m^2\,s^{-1}}$ for 1 M KOH at 298 K and r_1 and θ from Table 1 into Equation 3 gives the theoretical h_c tabulated in Table 1. From Table 1 it follows that taking into account the inaccuracy in various parameters the theoretical and experimental h_c agree well.

To verify more clearly the effect of the apex half-angle on the rate of mass transfer to the cone electrode of an RRCE, $I_{gd,Fe(III)}$ was determined as a function of the apex half-angle θ. A characteristic result is given in Fig. 3 where $I_{c,gd,Fe(III)}$ is plotted against $(\sin\theta)^{-1/2}$. This figure shows a linear relationship between the parameters as predicted by Equation 1.

The limiting current for ferricyanide reduction was also determined for the platinum electrode of various RRCE with the cone electrode at open circuit potential. In contrast to nickel electrodes, the platinum electrode showed linear $I_{g,Fe(III)}/\omega^{1/2}$ plots. For a platinum disc electrode the same result has been obtained [1]. This means that for a platinum electrode $I_{g,Fe(III)} = I_{gd,Fe(III)}$.

In Fig. 3 $I^0_{R,gd,Fe(III)}$ is also plotted versus $(\sin\theta)^{-1/2}$ for a ring electrode of an RRCE with its cone electrode at open circuit ($I_C = 0$). Figure 3 shows that $I^0_{R,gd,Fe(III)}$ increases linearly with increasing $(\sin\theta)^{-1/2}$. Moreover, the ratio between $I_{C,gd,Fe(III)}$ and $I_{R,gd,Fe(III)}$ does not depend on the apex half-angle θ. The experimental parameter β, being $(I^0_{R,gd}/I_{C,gd})^{3/2}$, is given in Table 1 for various RRCE. Moreover, the theoretical β calculated from Equation 5, is also represented in Table 1. From Table 1 it follows that the experimental β agree satisfactorily with the theoretical values when the inaccuracies in the various cone parameters and in the experimental results are taken into account.

From the preceeding results it is concluded that the effect of the apex half-angle of an RRCE upon the rate of mass transfer is well described by the equations presented.

3.2. *Collection efficiency*

To determine the collection efficiency of an RRCE, two procedures were applied: one at varying I_C and constant ω, and the other at constant cone potential, E_C, where the limiting current of ferricyanide reduction takes place and at varying ω. For the method at constant ω, (25 rad s^{-1}) the cone was polarized with constant cathodic currents smaller than $I_{C,g,Fe(III)}$ and, at the same time, the potential–current curves were measured for the oxidation of ferrocyanide on the platinum ring. Since only the E_R/I_R curve for the cathodic sweep was a well-formed wave with a constant current plateau, this curve was used to obtain the limiting diffusion current for ferrocyanide oxidation [1].

The experimental collection efficiency, N_0, is calculated with $N_0 = I_{R,gd,Fe(II)}/I_{C,Fe(III)}$ and is given in Table 1 for various RRCE. Both methods used for the determination of N_0 give the same results. The theoretical collection efficiencies, N_0, are also given in Table 1. From this table it follows that the agreement between the experimental and theoretical collection is good. Moreover, the apex half-angle of the cone does not affect the N_0 of an RRCE. This supports the conclusion obtained by Nijborg in his theoretical approach.

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