Mass transfer at rotating ring-cone electrodes

L. J. J. JANSSEN
Faculty of Chemical Engineering, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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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.

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

$$I_{gd,cone} = \frac{nF \omega \gamma}{\sin \theta} \left( \frac{v}{D} \right)^{0.5}$$

where $\theta$ 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

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

a geometric parameter $\beta$ 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 $I_{c} = 0$ and that for the disc electrode of an RRDE [7] is given by

$$\frac{I_{R,ring}}{I_{D,ring}} = \beta^{0.5}$$

The parameter $\beta$ 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

$$\frac{I_{R,ring}}{I_{D,ring}} = \beta^{0.5}$$

where $I_{R,ring}$ is the limiting diffusion current for the ring.
The nomenclature and geometry of RRCE.

$$\beta = \frac{r_2^3}{r_1^3} - \frac{r_3^3}{r_1^3}$$  \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, $N_o$, 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)$_6^{3-}$ in alkaline solution.

The collection efficiency coefficient, $N_o$, 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 $h_c$, $\beta^{0.5}$ and $N_o$

<table>
<thead>
<tr>
<th>Apex half-angle of cone (degree)</th>
<th>9.8</th>
<th>19.7</th>
<th>30</th>
<th>60</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_1$ (mm)</td>
<td>2.730</td>
<td>2.695</td>
<td>2.745</td>
<td>2.715</td>
<td>4.005</td>
</tr>
<tr>
<td>$r_2$ (mm)</td>
<td>2.985</td>
<td>2.980</td>
<td>3.010</td>
<td>2.930</td>
<td>4.203</td>
</tr>
<tr>
<td>$r_3$ (mm)</td>
<td>3.370</td>
<td>3.415</td>
<td>3.440</td>
<td>3.435</td>
<td>3.355</td>
</tr>
<tr>
<td>$h_1$ (mm)</td>
<td>15.1</td>
<td>7.25</td>
<td>4.69</td>
<td>1.58</td>
<td>0</td>
</tr>
<tr>
<td>$h_2$ (mm)</td>
<td>2.23</td>
<td>1.23</td>
<td>0.72</td>
<td>0.28</td>
<td>0</td>
</tr>
<tr>
<td>$h_3$ (mm)</td>
<td>1.41</td>
<td>0.77</td>
<td>0.45</td>
<td>0.13</td>
<td>0</td>
</tr>
<tr>
<td>$A_c$ (mm$^2$)</td>
<td>131.5</td>
<td>65.5</td>
<td>46.6</td>
<td>29.1</td>
<td>50.4</td>
</tr>
<tr>
<td>$A_0$ (mm$^2$)</td>
<td>44.2</td>
<td>20.6</td>
<td>17.8</td>
<td>11.6</td>
<td>4.55</td>
</tr>
<tr>
<td>$\beta$ (calculated)</td>
<td>0.57</td>
<td>0.68</td>
<td>0.65</td>
<td>0.77</td>
<td>0.12</td>
</tr>
<tr>
<td>$\beta$ (experimental)</td>
<td>0.64</td>
<td>0.62</td>
<td>0.62</td>
<td>0.68</td>
<td>0.13</td>
</tr>
<tr>
<td>$10^3 h_c/\text{A s}^{0.5} \text{rad}^{-1/2}$ (theoretical)</td>
<td>1.06</td>
<td>0.74</td>
<td>0.63</td>
<td>0.47</td>
<td>0.94</td>
</tr>
<tr>
<td>$10^3 h_c/\text{A s}^{0.5} \text{rad}^{-1/2}$ (experimental)</td>
<td>1.00</td>
<td>0.74</td>
<td>0.65</td>
<td>0.43</td>
<td>0.85</td>
</tr>
<tr>
<td>$N_o$ (calculated)</td>
<td>0.26</td>
<td>0.27</td>
<td>0.27</td>
<td>0.31</td>
<td>0.11</td>
</tr>
<tr>
<td>$N_o$ (experimental)</td>
<td>0.25</td>
<td>0.29</td>
<td>0.26</td>
<td>0.27</td>
<td>0.13</td>
</tr>
</tbody>
</table>

### 2. Experimental details

All 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$_3$Fe(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 $i_{Fe^3+/Fe^2+}$. 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 $i_{Fe^3+/Fe^2+}/\omega^{0.5}$ relation is slightly curved. The deviation from a linear relationship is caused by a small effect of...
the kinetics of electrode reaction. Plotting the reciprocal value of $I_{c, \text{Fe(III)}}$ against $\alpha^{-1/2}$, a straight line plot was obtained. The slope of the $(I_{c, \text{Fe(III)}})^{-1}/\alpha^{-1/2}$ plot for a cone electrode of RRCE is indicated by $h_1$.

In Table 1 the experimental $h_1$ is tabulated for cone electrodes with various apex half-angles.

From Equation 1 it follows that the theoretical $h_1$ is given by

$$h_1 = 0.62nF_\alpha \pi r_1^2 \left( \frac{v}{\sin \theta} \right)^{0.5} \left( \frac{D}{v} \right)^{0.60} \tag{3}$$

Introducing $n = 1$, $F = 96,484 \text{ C mol}^{-1}$, $c_0 = 40 \text{ mol m}^{-3}$, $D_{\text{Fe(III)}} = 7.3 \times 10^{-10} \text{ m}^2 \text{s}^{-1}$, $v = 1.073 \times 10^{-4} \text{ m}^2 \text{s}^{-1}$ for 1 M KOH at 298 K and $r_1$ and $\theta$ from Table 1 into Equation 3 gives the theoretical $h_1$ tabulated in Table 1. From Table 1 it follows that taking into account the inaccuracies in various parameters the theoretical and experimental $h_1$ 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, $I_{c, \text{Fe(III)}}$ was determined as a function of the apex half-angle $\theta$. A characteristic result is given in Fig. 3 where $I_{c, \text{Fe(III)}}$ 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 $I_{c, \text{Fe(III)}}/\alpha^{-1/2}$ plots. For a platinum disc electrode the same result has been obtained [1]. This means that for a platinum electrode $I_{c, \text{Fe(III)}} = I_{c, \text{Fe(III)}}$. 

In Fig. 3 $I_{R, \text{Fe(III)}}$ 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 $I_{R, \text{Fe(III)}}$ increases linearly with increasing $(\sin \theta)^{-1/2}$. Moreover, the ratio between $I_{c, \text{Fe(III)}}$ and $I_{R, \text{Fe(III)}}$ does not depend on the apex half-angle $\theta$. The experimental parameter $\beta$, being $(I_{R, \text{Fe(III)}}/I_{c, \text{Fe(III)}})^{3/2}$, is given in Table 1 for various RRCE. Moreover, the theoretical $\beta$ calculated from Equation 5, is also represented in Table 1. From Table 1 it follows that the experimental $\beta$ 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 preceding 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 $\omega$, and the other at constant cone potential, $E_c$, where the limiting current of ferricyanide reduction takes place and at varying $\omega$. For the method at constant $\omega$ (25 rad s$^{-1}$) the cone was polarized with constant cathodic currents smaller than $I_{c, \text{Fe(III)}}$ 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 $N_0 = I_{R, \text{Fe(III)}}/I_{c, \text{Fe(III)}}$ and is given in Table 1 for various RRCE. Both methods used for the determination of $N_0$ give the same results. The theor-
etical 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.

References


