

# Mass transfer at a rotating ring-cone electrode and its use to determine supersaturation of gas evolved

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# MASS TRANSFER AT A ROTATING RING-CONE ELECTRODE AND ITS USE TO DETERMINE SUPERSATURATION OF GAS EVOLVED

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**Abstract**—The rotating ring-cone electrode (*rrce*) is a useful electrode assembly to study electrochemical reactions, in particular, when gas bubble formation occurs. The aim of this study is to characterize the rate of mass transfer from the bulk to the cone of a *rrce*, to determine its collection efficiency,  $N$ , in the presence or absence of gas bubble formation, and to investigate its usefulness for determination of the oxygen supersaturation at an oxygen-evolving electrode. The mass transfer coefficient for the cone of a *rrce* increases linearly with increasing rate of oxygen evolution, while  $N$  declines sharply with increasing rate of oxygen evolution on the cone. In the absence of gas bubble formation  $N$  is determined by the *rrce* geometry factors except the cone angle. The *rrce* can be used successfully to determine the supersaturation concentration of oxygen on an oxygen-evolving electrode. The absorption of dissolved oxygen by bubbles during the transport of supersaturated solution from the cone to the ring will be, however, a rather complicating factor.

## NOMENCLATURE

$A$	surface area of working electrode
$c$	concentration
$c^*$	concentration in bulk of electrolyte
$c^0$	concentration on electrode surface
$c_s$	saturation concentration of oxygen at a pressure of 1 atm
$\Delta c$	supersaturation of dissolved oxygen on cone of <i>rrce</i>
$\Delta c_1$	$\Delta c$ when the absorption of dissolved oxygen by bubbles during the transport of solution is neglected
$\Delta c_2$	decrease of $\Delta c$ by absorption of dissolved oxygen by bubbles during the transport of solution
$D$	diffusion coefficient
$E$	electrode potential <i>vs sce</i>
$F$	Faraday constant
$i$	current density
$I$	current
$I^*$	current due to bulk concentration
$I^{*0}$	$I^0$ at $I_C = 0$ mA
$I_x$	$I$ for oxidation or reduction of species $x$
$\Delta I$	current due to supersaturation of solution at cone of <i>rrce</i>
$k_x$	mass transfer coefficient of species $x$
$n_x$	number of electrons involved in oxidation or reduction of 1 molecule $x$
$N$	collection efficiency of <i>rrce</i>
$N_0$	$N$ in absence of gas bubble formation
$r_C$	radius of the base of cone of <i>rrce</i>
$Sc$	Schmidt number
$\nu$	kinematic liquid viscosity
$\theta$	cone angle of <i>rrce</i>
$\omega$	rotation speed of <i>rrce</i>

### Subscripts

b	supporting electrolyte
C	cone of <i>rrce</i>
i	limiting conditions
R	ring of <i>rrce</i>
p	peak conditions

## 1. INTRODUCTION

A rotating cone electrode, *rce*, can be used successfully for electrochemical characterization, just as a rotating disc electrode, in particular when gas evolution occurs[1]. It is likely that a rotating ring-cone electrode offers similar possibilities for research as a rotating ring-disc electrode. Moreover, a rotating ring-cone electrode (*rrce*) has additional advantages during gas evolution.

Kirowa-Eisner and Gileadi[1] have found that the limiting current at a rotating cone electrode behaves according to a theoretical equation.

The first aim of this study is to characterize the rate of mass transfer to cone and ring and to find an expression for the collection efficiency  $N$  of a *rrce* when, whether or not, gas evolution on the cone occurs. It is well known that the solution at the surface of a gas-evolving electrode is supersaturated with the gas evolved. In a survey by Vogt[2] about supersaturation of the solution in the vicinity of gas-evolving electrodes, he stated that the experimental results varied considerably, even to a factor of 100.

The second aim of this study is, therefore, to investigate whether a *rrce* is useful to determine oxygen supersaturation of solution at the surface of an oxygen-evolving electrode.

## 2. EXPERIMENTAL

An ordinary electrolysis cell with working and counter electrode compartment, both about 100 cm<sup>3</sup>, is used. A cation exchange membrane is used to separate both compartments.

The experiments were carried out with a Pt ring–Pt cone electrode, represented in Fig. 1. The cone used is a right cone. The radius of its base is 2.73 mm and the area of its curved surface is 16.55 mm<sup>2</sup>. The ring is frustum of the right cone; the radius of its base is 3.34 mm and of its top 2.99 mm. The exposed area of the curved surface of the ring is 4.92 mm<sup>2</sup>. The thickness of the electrically insulating Kel-F layer is 0.18 mm. A flat platinum electrode of about 5 cm<sup>2</sup> 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 either a small quantity of K<sub>3</sub>Fe(CN)<sub>6</sub> or K<sub>4</sub>Fe(CN)<sub>6</sub>, or none of both. The electrolysis cell is kept at 298 K. The *rrce* is rotated by a rotator (Motomatic, model E-550-M). To determine the mass transfer to both cone and ring of the *rrce*, its collection efficiency *N* and the supersaturation concentration, potential–current 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). Unless otherwise stated, the scan rate is 10 mV s<sup>-1</sup>. The rate of mass transfer of Fe(CN)<sub>6</sub><sup>4-</sup> to the oxygen-evolving cone in a solution containing 0.04 M K<sub>4</sub>Fe(CN)<sub>6</sub> was obtained by iodometric determination of the quantity of Fe(CN)<sub>6</sub><sup>3-</sup> formed in a fixed period of electrolysis time[3].

### 3. RESULTS

#### 3.1. Mass transfer to, and collection efficiency, *N*<sub>0</sub>, of the *rrce* in the absence of gas evolution at the cone

The limiting rate of mass transfer of Fe(CN)<sub>6</sub><sup>3-</sup> ions to either the cone or the ring was determined as a function of the rotation speed for a 1 M KOH solution containing various concentrations of K<sub>3</sub>Fe(CN)<sub>6</sub>. It has been found that for both the cone and the ring electrode the limiting current for the reduction of Fe(CN)<sub>6</sub><sup>3-</sup> ions is proportional to the square root of the rotation speed. The experimental slope of  $dI_{C,L,Fe(III)}/d\sqrt{\omega}$  is  $0.255 \times 10^{-3} \text{ A rad}^{-1/2} \text{ s}^{1/2}$  for a 0.04 M K<sub>3</sub>Fe(CN)<sub>6</sub> in a 1 M KOH solution at 298 K. Here,  $I_{C,L,Fe(III)}$  is the limiting cone current. This value of slope is compared with the one calculated according to[1]:

$$\frac{dI_{C,L,Fe(III)}}{d\sqrt{\omega}} = n_{Fe(III)} F c_{Fe(III)}^* r_C^2 v^{1/2} S c^{-2/3} \sin^{1/2} \theta. \quad (1)$$

Substituting  $n_{Fe(III)} = 1$  electrons/molecule Fe(CN)<sub>6</sub><sup>3-</sup>,  $F = 96500 \text{ C mol}^{-1}$ ,  $c_{Fe(III)}^* = 4 \times 10^{-5} \text{ mol cm}^{-3}$ ,  $r_C = 0.273 \text{ cm}$ ,  $v$  for 1 M KOH at 298 K =  $0.01073 \text{ cm}^2 \text{ s}^{-1}$ ,  $Sc = 1358$  with  $D_{Fe(III)} = 0.79 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [3] and  $\sin \theta = 0.7071$ , into Equation (1) gives a slope of  $0.28 \times 10^{-3} \text{ A rad}^{-1/2} \text{ s}^{1/2}$ . The agreement between theory and experiment is good if

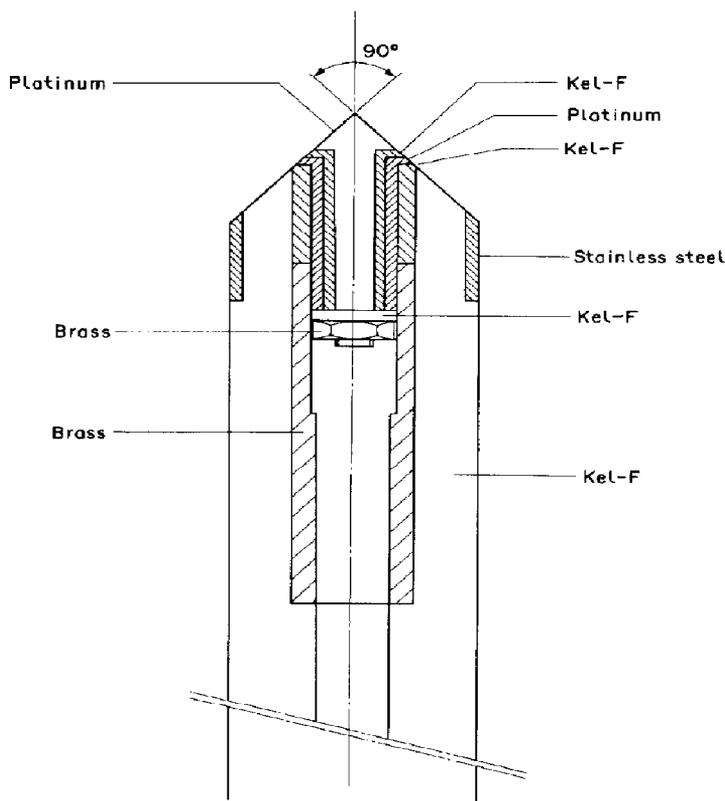


Fig. 1. Diagram of a ring–cone electrode.

taking into account the inaccuracy in some parameters like the radius  $r_c$ .

The collection efficiency  $N_0$  of the *rrce* was determined for various rotation speeds and for a 1 M KOH + 0.04 M  $K_3Fe(CN)_6$  solution at 298 K. The limiting current for the oxidation of  $Fe(CN)_6^{4-}$  ions on the ring,  $I_{R,L,Fe(II)}$ , is plotted vs the current for reduction of  $Fe(CN)_6^{3-}$  ions on the cone,  $I_{C,Fe(III)}$  in Fig. 2. This figure shows that  $I_{R,L,Fe(II)}$  has the same proportionality factor to  $I_{C,Fe(III)}$  for rotation speeds of 10, 20 and 40  $revs^{-1}$  i.e. the collection efficiency,  $N_0 = I_{R,L,Fe(II)}/I_{C,Fe(III)}$  (here = 0.25) does not depend on the rotation speed.

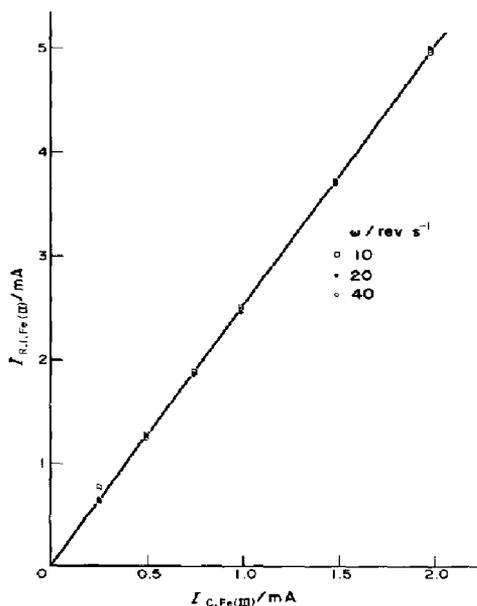


Fig. 2. Limiting ring current for oxidation of  $Fe(CN)_6^{4-}$  formed at the cone plotted vs the cone current for reduction of  $Fe(CN)_6^{3-}$  for a *rrce* in a 1 M KOH + 0.04 M  $K_3Fe(CN)_6$  at 298 K and various rotation speeds of *rrce*. During the measurement the potential of the ring is swept from 0.27 to 0.56 V with a scan rate of 20  $mVs^{-1}$ .

As known, the collection efficiency for a rotating ring-disc electrode (*rrde*) is characterized by three radii, viz the radius of disc electrode, and the inner and outer radius of the ring electrode[4], and is tabulated for different ratios of these radii[5]. Using table 8.1 of [5] and the radii for the cone base, the base and the top of the frustum of the cone (ring), it can be calculated that  $N_0 = 0.24$ , i.e. close to the experimental value. Consequently, it is likely that  $N_0$  for a *rrce* is characterized by similar factors as  $N_0$  for a *rrde*.

### 3.2. Mass transfer to, and collection efficiency, $N$ , of *rrce* at gas evolution on the cone

To investigate the mass transfer to, and the collection efficiency,  $N$ , of the *rrce* at oxygen evolution on the cone, experiments were carried out in a 1 M KOH + 0.04 M  $K_4Fe(CN)_6$  solution at 298 K. During

oxygen evolution on a platinum cone electrode in a 1 M KOH solution containing small quantities of  $Fe(CN)_6^{4-}$  ions, the concentration of  $Fe(CN)_6^{4-}$  ions at its surface is almost zero[3]. A fraction of the electric current on the cone is used for oxidizing  $Fe(CN)_6^{3-}$  ions to  $Fe(CN)_6^{4-}$  ions, the other part for oxygen evolution. Consequently,  $I_C = I_{C,H_2O} + I_{C,L,Fe(II)}$ . The mass transfer coefficient is defined as

$$k_{C,Fe(II)} = I_{C,L,Fe(II)}/n_{Fe(II)}FAcC_{Fe(II)}^*$$

The current  $I_{C,L,Fe(II)}$  was obtained from the quantity of  $Fe(CN)_6^{3-}$  ions formed during a 20 min electrolysis.

In Fig. 3  $k_{C,Fe(II)}$  is plotted vs  $i_{C,H_2O}$  for a rotation speed of 10  $revs^{-1}$  and in Fig. 4  $k_{C,Fe(II)}$  vs the square root of the rotation speed at  $i_C = 0.60 \text{ kAm}^{-2}$  for a 1 M KOH + 0.04 M  $K_4Fe(CN)_6$  solution at 298 K. For the experiments of Fig. 4 at a constant  $i_C$  value, viz  $0.60 \text{ kAm}^{-2}$ , the relative decline of  $i_{C,O_2}$  at increasing  $\omega$ , is small at  $\omega < 8 \text{ revs}^{-1}$  and rather high at  $\omega > 16 \text{ revs}^{-1}$ . For instance,  $i_{C,O_2}$  values are 0.54, 0.46, 0.36 and 0.20  $\text{kAm}^{-2}$  at, respectively,  $\omega$  values of 2, 8, 16 and 64  $revs^{-1}$ .

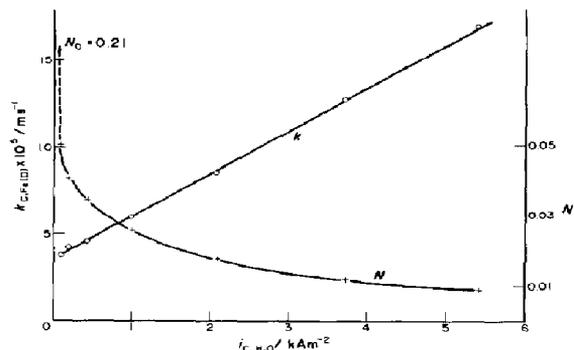


Fig. 3. The mass transfer coefficient for  $Fe(CN)_6^{4-}$  to the cone and the collection efficiency  $N$  for a *rrce* are plotted vs the current density of oxygen evolution on the cone. The experiments were carried out in a 1 M KOH + 0.04 M  $K_4Fe(CN)_6$  solution at 298 K; the rotation speed of the *rrce* was 10  $revs^{-1}$  and the potential scan rate 10  $mVs^{-1}$ .

In the beginning of the 20 min cone electrolysis current-potential curves at both decreasing and increasing ring potentials between 0.5 and  $-0.7$  V were recorded. The current  $I_{R,L,Fe(III)}$  was obtained from the curve at decreasing potential. (The limiting current, found from the curve at increasing potential, is slightly lower, probably due to electrode poisoning.) In Fig. 3, also the collection efficiency  $N$ , is plotted vs  $i_{C,H_2O}$  at  $\omega = 10 \text{ revs}^{-1}$  and so in Fig. 4 vs  $\omega$  at  $i_C = 0.60 \text{ kAm}^{-2}$ .

From Fig. 3 it follows that  $N$  declines strongly and  $k_{C,Fe(II)}$  increases almost linearly with increasing  $i_{C,O_2}$ . Figure 4 shows an almost linear increase of  $k_{C,Fe(II)}$  at increasing  $\sqrt{\omega}$  and the  $N/\omega^{1/2}$  curve has a clear minimum. This can be explained by three factors opposing each other, viz the increase of  $\omega$  diminishes  $N$ , the decline of  $i_{C,O_2}$  at increasing  $\omega$  enhances  $N$ , and by a change of behaviour of oxygen bubbles at increasing  $\omega$ .

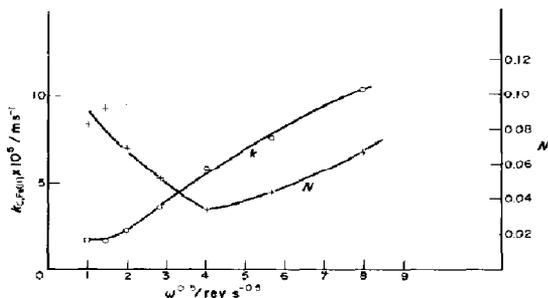


Fig. 4. The mass transfer coefficient for  $\text{Fe}(\text{CN})_6^{4-}$  to the cone and the collection efficiency  $N$  for a  $rrce$  are plotted vs the square root of the rotation speed at a cone current density of  $0.60 \text{ kA m}^{-2}$ . The experiments were carried out in a  $1 \text{ M KOH} + 0.04 \text{ M K}_4\text{Fe}(\text{CN})_6$  solution at  $298 \text{ K}$ ; the potential scan rate was  $10 \text{ mV s}^{-1}$ .

### 3.3. Supersaturation of oxygen

The concentration of oxygen at the surface of an oxygen evolving electrode,  $c_{\text{O}_2}^0$ , in a solution saturated with oxygen is higher than the concentration of oxygen in the bulk of the electrolyte,  $c_{\text{O}_2}^*$ . The latter is the

saturation concentration,  $c_s$ , at a pressure of  $1 \text{ atm}$ . The supersaturation concentration of dissolved oxygen on the cone electrode is  $\Delta c = c_{\text{O}_2}^0 - c_s$ .

As for a  $rrde$ , the collection efficiency,  $N_0$ , for a  $rrce$  does not depend on the nature of non-volatile compounds. If the bulk concentration of oxygen is not zero, there will be a finite limiting ring current at  $I_C = 0$ . Moreover, the mass transfer coefficient,  $k_{\text{C},\text{O}_2}$  for oxygen from the bulk of solution to the ring will depend on the rate of volumetric oxygen bubble evolution on the cone. To determine the ring current due to the saturation concentration of oxygen,  $\text{K}_3\text{Fe}(\text{CN})_6$  was added to the supporting electrolyte.

In Fig. 5 characteristic  $E_R$  vs  $I_R$  curves at various  $I_C$  are shown for a  $rrce$  in a  $1 \text{ M KOH} + 0.004 \text{ M K}_3\text{Fe}(\text{CN})_6$  solution saturated at  $1 \text{ atm}$  with oxygen. The cathodic voltammograms at  $-0.1 \text{ V} < E < 0.3 \text{ V}$  have a wave with a reasonable constant level for the reduction of  $\text{Fe}(\text{CN})_6^{3-}$ -ions, and at  $E < -0.1 \text{ V}$  have a wave with a small peak at about  $E = -0.45 \text{ V}$  for reduction of oxygen.

At a rotation speed of  $10 \text{ rev s}^{-1}$  and at  $I_C = 0 \text{ mA}$ , the limiting current  $I_{\text{R,L,Fe(III)}}$  increases only to a small extent with increasing potential scan rate. The peak current for the reduction of oxygen increases, however, strongly with increasing potential scan rate and ap-

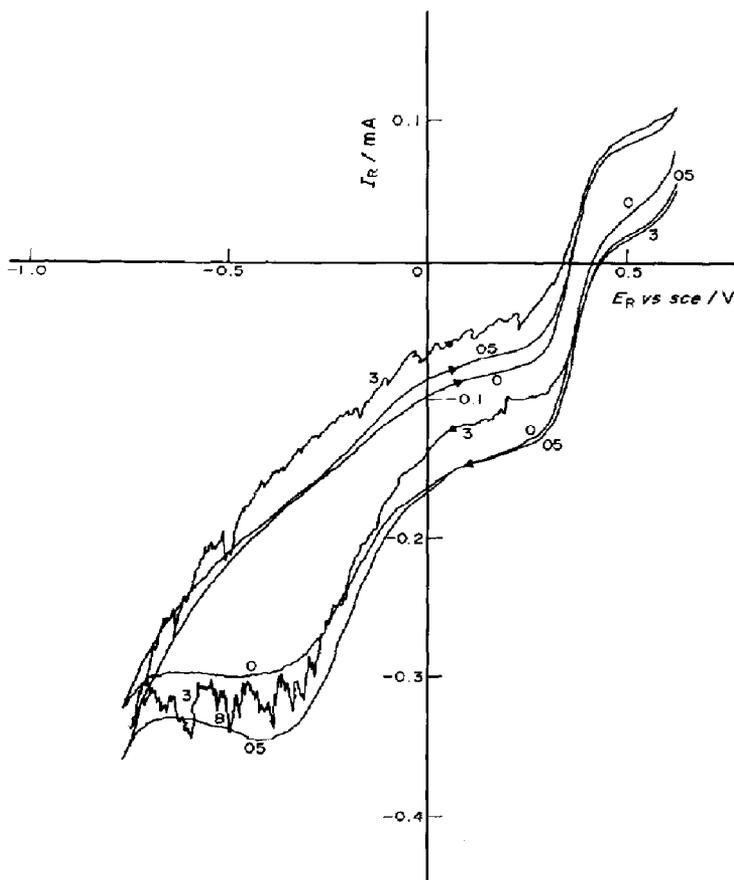


Fig. 5. Voltammograms for the ring of a  $rrce$  in a  $1.0 \text{ M KOH} + 0.004 \text{ M K}_3\text{Fe}(\text{CN})_6$  solution saturated with oxygen and at various anodic cone currents,  $298 \text{ K}$ , scan rate of  $10 \text{ mV s}^{-1}$ .

approach a constant value at a potential scan rate of about  $30 \text{ mV s}^{-1}$ . At high potential scan rates the voltammogram for the supporting electrolyte (1 M KOH) interferes with the voltammograms for oxygen and  $\text{Fe}(\text{CN})_6^{3-}$  reduction.

Weighing out these effects—*ie* decrease of oxygen peak current at decreasing scan rate and increase of the effect of supporting electrolyte and of oxides present on platinum electrodes at increasing scan rate—in order to determine the supersaturation of oxygen at the gas evolving cone electrode, the experiments were carried out at a potential scan rate of  $10 \text{ mV s}^{-1}$ . Assuming proportionality between peak and limiting current for the reduction of oxygen, then  $I_{R,p,O_2} = aI_{R,l,O_2}$ . From the relation for the rate of mass transfer at forced convection[7] and from  $n_{p,O_2} = an_{O_2}$  where  $n_{p,O_2}$  is the number of electrons involved in the reduction of 1 molecule  $O_2$  transferred by diffusion, it follows that for  $I_C = 0 \text{ mA}$

$$\frac{n_{p,O_2}}{n_{Fe(III)}} = \frac{I_{R,p,O_2}^*}{I_{R,l,Fe(III)}^*} \left( \frac{D_{Fe(III)}}{D_{O_2}} \right)^{2/3} \frac{c_{Fe(III)}}{c_s} \quad (2)$$

where  $I_R^*$  is the ring current due to bulk concentration and  $I_R^0$  is  $I_R^*$  at  $I_C = 0 \text{ mA}$ .

To determine  $n_{p,O_2}$ , the oxygen peak ring current  $I_{R,p,O_2}^0$  was obtained from experiments with an oxygen-free and an oxygen-saturated solution of 1 M KOH + 0.004 M  $K_3Fe(CN)_6$ . The oxygen peak ring current occurs at about  $-0.5 \text{ V}$ . It has been found that for the oxygen-free solution the ring current  $I_{R,b}$  at  $-0.5 \text{ V}$  is relatively small, *viz*  $0.025 \text{ mA}$  being about 15% of  $I_{R,p,O_2}^0$ . Consequently,  $I_{R,b}^0 = I_{R,p} - 0.025 \text{ mA}$  where  $I_{R,p}$  is the peak ring current at the potential of the oxygen peak, *viz*  $-0.5 \text{ V}$ .

A number  $n_{p,O_2} = 3.0$  is calculated by introducing in Equation (2):  $I_{R,p,O_2}^0$  at  $I_C = 0 \text{ mA}$ ,  $I_{R,l,Fe(III)}^0$  at  $I_C = 0 \text{ mA}$ , the saturation concentration of oxygen in 1 M KOH, *viz*  $0.89 \text{ mM}$ [6],  $c_{Fe(III)}$ , the diffusion coefficient of  $Fe(CN)_6^{3-}$ , *viz*  $0.79 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ [3], the diffusion coefficient of dissolved oxygen, *viz*  $1.59 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ [6], and  $n_{Fe(III)} = 1$  electron per molecule  $Fe(CN)_6^{3-}$  and  $n_{O_2} = 4$  electrons per molecule  $O_2$ .

Evolution of oxygen bubbles on the cone causes an additional flow of solution in the neighbourhood of the ring and will affect in the same degree the transfer of all dissolved species from the bulk of solution to the ring. Consequently,

$$I_{R,p,O_2}^* = I_{R,l,Fe(III)}^* I_{R,p,O_2}^0 / I_{R,l,Fe(III)}^0$$

The peak ring current for oxygen reduction due to supersaturation of the solution at the cone, is given by  $\Delta I_{R,p,O_2} = I_{R,p,O_2} - I_{R,p,O_2}^*$ . From  $\Delta I_{R,p,O_2}$  and the collection efficiency  $N$  and taking into account a difference between the number of electrons for the reduction of oxygen at the ring and the one for the formation of oxygen at the cone, it follows that the cone current used for the supersaturation of the solution at the cone is given by

$$\Delta I_{C,H_2O} = \frac{\Delta I_{R,p,O_2}}{N} \frac{n_{O_2}}{n_{p,O_2}} \quad (3)$$

If the concentration profile at the cone for dissolved oxygen is similar to that for  $Fe(CN)_6^{3-}$  formed by oxidation of  $Fe(CN)_6^{4-}$  during oxygen evolution, the

relation between  $\Delta I_{C,H_2O}$  and the oxygen supersaturation at the cone,  $\Delta c_1$  is given by

$$\Delta I_{C,H_2O} = n_{O_2} F k_{C,O_2} A_C \Delta c_1$$

Substitution of this relation for  $\Delta I_{C,H_2O}$  into Equation (3) gives

$$\Delta c_1 = \Delta I_{R,p,O_2} / n_{p,O_2} F N k_{C,O_2} A_C \quad (4)$$

Next, it is assumed that during the transport of supersaturated solution and oxygen bubbles from the cone to the ring electrode dissolved oxygen is not taken up by the bubbles transported.

The supersaturation concentration of oxygen at the gas evolving cone electrode has been calculated with the experimental results of  $\Delta I_{R,p,O_2}$ ,  $N$  (Fig. 3),  $k_{C,O_2} = k_{C,Fe(III)} D_{O_2}^{2/3} D_{Fe(III)}^{-1/3}$  (Fig. 3),  $n_{p,O_2} = 3.0$  electrons/molecule  $O_2$ ,  $A_C = 16.55 \text{ mm}^2$  and  $F = 96500 \text{ C mol}^{-1}$ . The results are given in Fig. 6 as a function of  $i_{C,H_2O}$ .

At very high current densities, *viz*  $i_{C,H_2O} > 4 \text{ kA m}^{-2}$ ,  $\Delta c_1$  was practically zero.

At a rotation speed of  $10 \text{ revs}^{-1}$  and at  $i_{C,H_2O} < 0.5 \text{ mA}$ , practically no oxygen bubbles could be observed on the cone electrode. With  $k_{C,O_2} = k_{C,Fe(III)} D_{O_2}^{2/3} / D_{Fe(III)}^{1/3}$  at  $i_{C,H_2O} = 0 \text{ kA m}^{-2}$  (Fig. 3) it was calculated that  $\Delta c = 1.7 \text{ mM}$  at  $i_{C,H_2O} = 0.03 \text{ kA m}^{-2}$ . From Fig. 6 it follows that  $\Delta c_1 = 1.9 \text{ mM}$  being in reasonable agreement with the former method.

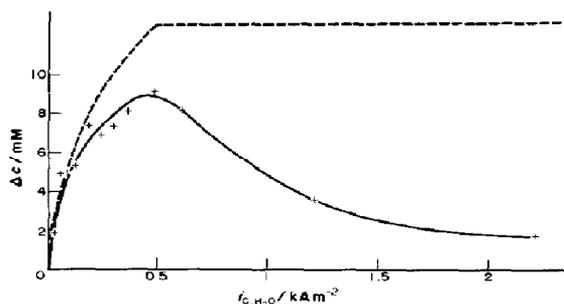


Fig. 6. Supersaturation concentration of oxygen neglecting the absorption of dissolved oxygen by bubbles during the transport of the supersaturated solution containing oxygen bubbles (solid line) and the supersaturation concentration of oxygen obtained by the first step of the approach process (dotted line) are given as a function of cone current density of oxygen evolution for a *rrce* in a 1 M KOH + 0.004 M  $K_3Fe(CN)_6$  solution saturated with oxygen and at 298 K.

## 4. DISCUSSION

### 4.1. Characterization of the *rrce*

In absence of gas evolution our experimental results for the mass transfer of indicator ions from the bulk of solution to the rotating cone electrode behaves according to the theoretical equations given by Kirova-Eisner and Gileadi[1].

From Section 3.1 it follows that the collection efficiency  $N_0$  for a *rrce* is determined by its geometrical factors except the cone angle. This conclusion is likely since for a *rrce* the ratios between the chord length of the cones are independent of the cone angle. Of course, theoretical verification is worth doing.

The mass transfer coefficient for a gas-evolving rotating cone electrode is strongly affected by the rate of gas evolution (Fig. 3) and the rotation speed (Fig. 4). At  $i_{C,H_2O} > 0.1 \text{ kA m}^{-2}$ , the mass transfer coefficient increases linearly with increasing  $i_{C,H_2O}$  (Fig. 3). This dependence reasonably agrees with the one found for both horizontally and vertically placed electrodes [3, 8].

The collection efficiency  $N$  for a *rrce* declines strongly with increasing  $i_{C,H_2O}$ . From the results of Fig. 4 it can be shown that in the  $i_{C,H_2O}$  range from 0.1 to  $1 \text{ kA m}^{-2}$   $\log N$  decreases linearly with increasing  $\log i_{C,H_2O}$ ; the slope of the  $\log N / \log i_{C,H_2O}$  curve is  $-0.30$ . The rotation speed strongly affects  $N$  for a *rrce* where gas is evolved at the cone (Fig. 4), and assuming a rotation speed independent slope of the  $\log N / \log i_{C,H_2O}$  curve, it can be shown that  $N$  decreases with increasing rotation speed up to  $\omega = 10 \text{ rev s}^{-1}$  and rises above  $\omega = 16 \text{ rev s}^{-1}$ .

#### 4.2. Supersaturation by oxygen

According to Fig. 6 the  $\Delta c_1 / i_{C,H_2O}$  curve has a sharp maximum at about  $i_{C,H_2O} = 0.3 \text{ kA m}^{-2}$ . At  $i_{C,H_2O}$  above  $0.3 \text{ kA m}^{-2}$ ,  $\Delta c_1$  strongly declines and approaches practically zero at high  $i_{C,H_2O}$ . However, it is likely that  $\Delta c_1$  will increase continuously with increasing  $i_{C,O_2}$ .

Several investigators [9, 10] have found that at moderate current densities the supersaturation on a gas-evolving electrode increases with increasing rate of gas evolution and that at high current densities, for instance at  $i_{C,H_2O} > 2 \text{ kA m}^{-2}$  for hydrogen evolution in acid solution [11], the supersaturation becomes practically constant.

The results of Fig. 6 at  $i_{C,H_2O} \geq 0.3 \text{ kA m}^{-2}$  have to be influenced by absorption of dissolved oxygen by oxygen bubbles during the transport of liquid and bubbles from the cone to the ring. At increasing  $i_{C,H_2O}$  the density of bubbles in the solution near the *rrce* increases. The rate of absorption of dissolved oxygen by bubbles must increase because of the increasing bubble population density and so the supersaturation of the liquid must decline with increasing  $i_{C,H_2O}$ . This means that the assumption made in Section 3.3 about the collection efficiency of dissolved oxygen is surely not true for  $i_{C,H_2O} \geq 0.3 \text{ kA m}^{-2}$ . Whether this assumption will be correct at  $i_{C,H_2O} < 0.3 \text{ kA m}^{-2}$ , has to be discussed, at least. Evidently, the rate of absorption of dissolved oxygen by bubbles decreases with decreasing  $i_{C,H_2O}$ . An estimation of this effect upon the experimental  $\Delta c_1$ , can be achieved by the following approach.

Because of oxygen absorption by bubbles,  $\Delta c$  values given by the solid curve of Fig. 6 are too low; also at low  $i_{C,H_2O}$ . It is assumed that the oxygen supersaturation at  $i_{C,H_2O} \geq 0.5 \text{ kA m}^{-2}$  is constant.

To obtain the  $\Delta c$  decrease,  $\Delta c_2$ , due to oxygen absorption by oxygen bubbles, we assume first that  $\Delta c_1 = 9 \text{ mM}$  at  $i_{C,H_2O} > 0.5 \text{ kA m}^{-2}$ , ie  $\Delta c_1$  at  $i_{C,H_2O} = 0.5 \text{ kA m}^{-2}$ . The difference between  $9 \text{ mM}$  and  $\Delta c_1$  of Fig. 6, being  $\Delta c_2$ , is plotted vs  $i_{C,H_2O}$  for  $i_{C,H_2O} = 1.2$  and  $2.4 \text{ kA m}^{-2}$ . Drawing a smooth curve through the origin and the two measuring points,  $\Delta c_2$  at  $i_{C,H_2O} < 0.5 \text{ kA m}^{-2}$  is obtained. This  $\Delta c_2$  is added to  $\Delta c_1$  at  $i_{C,H_2O} < 0.5 \text{ kA m}^{-2}$  and again it is assumed that  $\Delta c$  is

constant at  $i_{C,H_2O} > 0.5 \text{ kA m}^{-2}$ . The result of this summation is represented by the dotted line in Fig. 6. Repetition of this process gives  $\Delta c_2$  converging to  $4 \text{ mM}$  at  $i_{C,O_2} = 0.5 \text{ kA m}^{-2}$ . From the  $\Delta c_2 / i_{C,H_2O}$  plot obtained after this approach process, it follows that at  $i_{C,O_2} < 0.5 \text{ kA m}^{-2}$   $\Delta c_2$  is proportional to  $i_{C,H_2O}$ .

The supersaturation concentration of oxygen on the gas-evolving cone is given by  $\Delta c = \Delta c_1 + \Delta c_2$ . In Fig. 7  $\log \Delta c$  as well as  $\log \Delta c_1$  are plotted vs  $\log i_{C,H_2O}$ . In the  $i_{C,H_2O}$  range from 0.05 to  $0.5 \text{ kA m}^{-2}$  both relations can be given by a straight line. The slope of the  $\log \Delta c / \log i_{H_2O}$  line is 0.45.

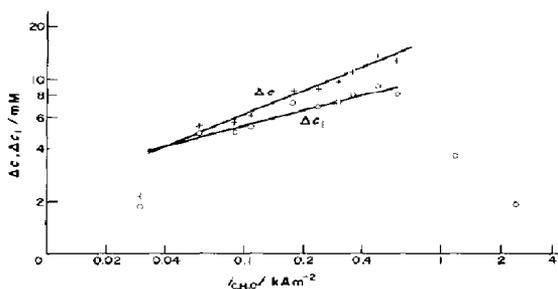


Fig. 7. Supersaturation concentration of oxygen is plotted on a double logarithmic scale vs the cone current density of oxygen evolution for a *rrce* in a  $1 \text{ M KOH} + 0.004 \text{ M K}_3\text{Fe(CN)}_6$  solution saturated with oxygen and at  $298 \text{ K}$ .

For oxygen evolving electrodes in a  $\text{KOH}$  solution only the results of Khomskaya and Kolosov [11] are well known, but their results obtained with *rrde* are not usable. In acidic media Shibata [9] has determined the supersaturation concentration as a function of oxygen evolution. Plotting his results as in Fig. 7, the slope of  $\log(\Delta c + c_s) / \log i_{H_2O}$  curve at  $0.05$  to  $1 \text{ kA m}^{-2}$  is  $0.41$ . This agrees well with the one of the straight line of Fig. 7. Shibata [9] found that  $\Delta c / c_s$  at  $0.5 \text{ kA m}^{-2}$  is about  $50$ . From Fig. 7 and  $c_s = 0.89 \text{ mM}$  it follows that  $\Delta c / c_s$  at  $0.5 \text{ kA m}^{-2}$  is about  $14$ .

From the experimental results it can be concluded that *rrce* can be used successfully to determine the supersaturation concentration on a gas-evolving electrode surface taking into account the effect of absorption of dissolved oxygen by bubbles during the transport of solution from the cone to the ring of the *rrce*.

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