Journal of Applied Electrochemistry **30**: 1087–1090, 2000.

Short communication

On the determination of limiting current density from uncertain data

C. PONCE-DE-LEÓN[1]* and R.W. FIELD[2]
[1]*Universidad Autonoma Metropolitana-Izt, Departamento de Química, Apdo Postal 55-534, 09340 México, D.F., México*
[2]*University of Bath Department of Chemical Engineering, Bath, Claverton Down BA2 7AY, Great Britain*
(**author for correspondence, e-mail: cpla@xanum.uam.mx*)

Received 23 December 1998 accepted in revised form 27 March 2000

Key words: ferric cyanide, limiting current, mass transfer, oxygen

List of symbols

A	electrode area (m^2)
A_e	electrode area per unit volume (m^2 m^{-3})
C_O	concentration of reactant (mol cm^{-3})
E	electrode potential vs SCE (V)
$(E/I)_{max}$	maximum resistance (Ω)
F	faradaic constant (96 500 C mol^{-1})
I_L	limiting current (A)
I	current (A)
k_L	mass transfer coefficient (m s^{-1})
n	number of electrons
v_e	cathode volume
V_e	electrode potential (V)
V_c	concentration potential (V)
V_p	polarization potential (V)
R	solution resistance (Ω)

1. Introduction

In a number of electrodialysis and electrolysis applications, polarization limits the amount of current that can be passed through the cells. By convention, 'limiting current' designates the value at which the current is diffusion limited. The concept of limiting current given in the literature is expressed by [1]:

$$I_L = -nFAk_LC_O \tag{1}$$

The technique for determining the limiting current from I/E curves is normally simple. However, in the absence of a clearly defined plateau it is not straightforward. In a recent study of the concentration of nitric acid by electro-electrodialysis (membrane electrolysis), Robbins [2] plotted the normalized resistance $(E/I)/(E/I)_{max}$ against the reciprocal current density $(1/I)$ corrected for catholyte acid concentration, in order to elucidate the cathodic reactions. He based his plot upon the work of Kuppinger et al. [3] but was unable to find a theoretical basis for the apparent relationship between the minimum point in the curves and the mass transfer coefficient.

The purpose of this paper is twofold. First, it is to reintroduce the E/I against $1/I$ plot as a basis for the determination of the limiting current. Second, it is to show that the previously presented method using this approach [4] is mathematically incorrect. In fact, the authors never justified their mathematical methodology but stated that the point at which the negative slope cuts the positive slope in the curve E/I against $1/I$, is designated as a 'limiting current density' because of its apparent relation (our emphasis) to diffusion. The point of intersection used by them will be clearly defined later and contrasted with other methodologies.

Our proposed approach was tested for the reduction of oxygen and $Fe(CN)_6^{3-}$. The reduction of ferric cyanide ions was carried out in a commercially available laboratory electrolyser, the FM01-LC cell supplied by ICI, and oxygen reduction was carried out in a conventional flow cell constructed in our laboratory, both on a reticulated vitreous carbon electrode (RVC).

2. Methodology

The only previous work that has made extensive use of the E/I against $1/I$ plot to determine limiting currents justified the approach on empirical grounds [4]. The voltage drop across an electrodialysis cell consists of an electrode potential V_e, concentration potentials V_c, polarization potentials V_p and an ohmic voltage IR. Hence,

$$E/I = R + (V_e + V_c + V_p)/I \tag{2}$$

This indicates that a plot of E/I against $1/I$ would be used to obtain information from a current potential curve. Others [4] have pointed out that it would give the cell resistance as an intercept, and the slopes would give information about the potentials. Furthermore, it was noted that the change in the direction of the slope corresponded to the onset of diffusion limited performance. It was suggested that one slope be extended to intercept the other and that this point corresponds to the limiting diffusion current density. This approach is entirely pragmatic and as is shown below, it is not the best method of determining the limiting current from E/I against $1/I$ plots since it will always give an estimate of the limiting current. It should be noted that the voltage balance in Equation 2 is not valid if there is a spatial distribution of the reaction current; as would be the case for certain porous electrodes [5, 6].

Although the data used below is for the reduction of oxygen and ferric cyanide through a RVC porous electrode, this electrode was sufficiently thin for the voltage to be taken to be constant. (See, for example, [7–12]).

2.1. *Determination of limiting current from E/I against 1/I plots*

If we consider that $I = f(E)$, then the following equations are true:

$$\frac{\mathrm{d}(E/I)}{\mathrm{d}(1/I)} = \frac{\mathrm{d}(E/I)}{\mathrm{d}(I)} \times \frac{\mathrm{d}(I)}{\mathrm{d}(1/I)} \tag{3}$$

$$= -I^2\left[\left(\frac{1}{I}\right) \times \frac{\mathrm{d}(E)}{\mathrm{d}(I)} - \frac{E}{I^2}\right]$$

$$= -I\left[\left(\frac{\mathrm{d}(I)}{\mathrm{d}(E)}\right)^{-1} - \frac{E}{I}\right] \tag{4}$$

The term in square brackets increases when the change of current (I) with potential (E) decreases, that is, as the conditions of limiting current are approached. Under these conditions, the curve in an E/I against $1/I$ plot is very steep. Ideally a limiting current would correspond to $\mathrm{d}(I)/\mathrm{d}(E) = 0$, and so the upward curve in the E/I against $1/I$ plot would be vertical. Under certain experimental conditions this is masked by the start of a second reaction or by IR drop, and so the determination of the condition corresponding to mass transfer limitation has been taken to be the mid-point between the two turning points. The first turning point corresponds to the point at which the value of $\mathrm{d}(I)/\mathrm{d}(E)$ is sufficiently low for the term in square brackets in Equation 4 to be zero. As the electrical potential increases further $\mathrm{d}(I)/\mathrm{d}(E)$ becomes smaller and the term in brackets becomes strongly positive. The second turning point occurs when the value of $\mathrm{d}(I)/\mathrm{d}(E)$ increases sufficiently for the term in square brackets to become negative again. Placing the mass transfer limitation in the middle of the region where the following inequality is valid gives a reasonable estimate of this condition. In contrast, the extrapolation method can imply that the limitation occurs before

$$\left(\frac{\mathrm{d}(I)}{\mathrm{d}(E)}\right)^{-1} > \frac{E}{I} \tag{5}$$

Thus the extrapolation method can give an underestimate, as shown later. Both methods give the same result for ideal data.

3. Experimental details

3.1. *Reduction of oxygen in a reticulated vitreous carbon electrode*

The reduction of oxygen was carried out in a flow-through cell [9–12] with a 60 pores per inch (ppi) reticulated vitreous carbon electrode. An air saturated solution of 1 M aqueous NaOH was used in this experiment. The data are presented in conventional form in Figure 1, using different flow rates, and with resistance (E/I) against reciprocal current ($1/I$) in the inset. Two reduction waves are observed, suggesting that oxygen reduction occurs in two steps, giving hydrogen peroxide in the first process and water in the second. For the first wave ($E_{1/2} \sim -460$ mV), the limiting current does not change significantly with the linear flow velocity. On the other hand, for the second wave ($E_{1/2} \sim -970$ mV), the limiting current increases with flow rate. The analysis of the reduction products has been given in the literature [11].

A comparison of our procedure for evaluating the limiting current for the second wave with that of Cowan and Brown [4] is given, in which the limiting current was determined by the interception of lines and the determination of local maximum and minimum points. The calculated values are presented in Table 1.

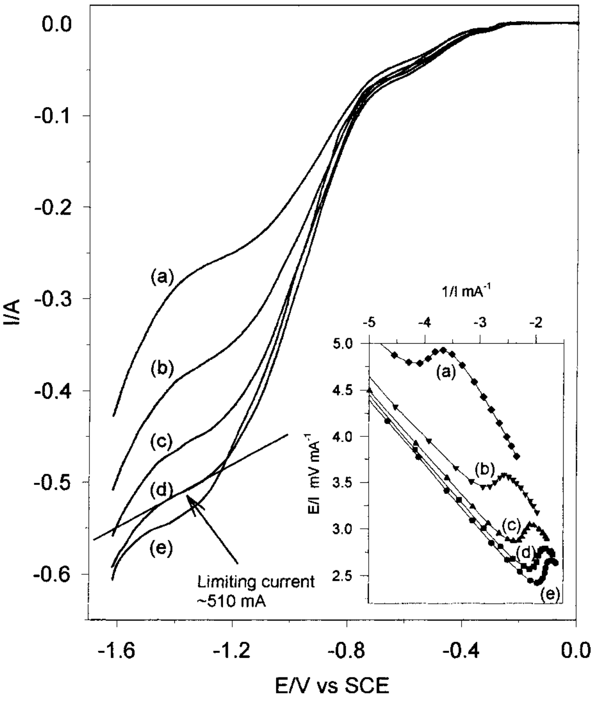

Fig. 1. Current potential curves for oxygen reduction at 60 ppi RVC electrode in 1 M NaOH in an air saturated solution. Catholyte linear flow velocity: (a) 0.016, (b) 0.045, (c) 0.09, (d) 0.13, (e) 0.17 m s^{-1}, $T = 25$ °C. Inset: curves E/I against $1/I$ from the main Figure.

Table 1. Current values taken from the inset of Figure 1 for the reduction of oxygen in 1 M NaOH air saturated solution at different flow rates

Flow rate /m s^{-1}	Current/mA		Limiting current/mA	
	Minimum	Maximum	This method	Method [4]
(a) 0.016	−244	−273	−259	−235
(b) 0.045	−340	−390	−365	−340
(c) 0.09	−418	−476	−447	−416
(d) 0.13	−475	−550	−513	−478
(e) 0.17	−508	−591	−549	−517

In Figure 1 the gradient d(I)/d(E) is positive at all points. A clear definition of the limiting current is that current at which there is either a plateau or a point of inflexion in the I/E curve. For curve (d) in the example used, the limiting current is −510 mA as is shown in the Figure 1. On the other hand, Figure 2 shows curve (d) of the inset in Figure 1. In the alternative plot of E/I against $1/I$ for curve (d), the minimum corresponds to −475 mA, whilst the local maximum corresponds to −550 mA. The average of these two values 513 mA, gives a good estimate of the limiting current at the actual point of inflection. The turning points, i.e., the maximum and minimum in the E/I against $1/I$ curve, are easy to identify.

In the above example, E and I are negative, d(I)/d(E) is positive and E/I is positive. In the region of the limiting current, when d(I)/d(E) is small, the overall effect is to make the gradient of a E/I against $1/I$ plot positive. Elsewhere d(I)/d(E) is greater than I/E and so, in this region, the gradients are negative. The choice of an E/I against $1/I$ plot has thus generated a curve that changes from a negative slope to a positive slope and back again to a negative slope. These clear changes in the sign of the slope lead to easy identification of the limiting current region.

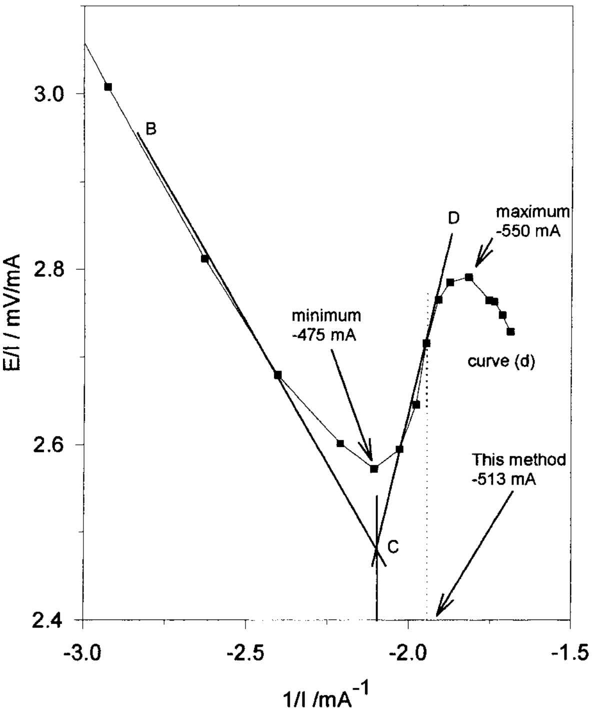

Fig. 2. Illustration of procedures for determining the limiting current. For curve (c), Cowan and Brown method [4], curve (d), present method based on local minimum and maximum points.

In the case of an oxidation process when E and I are both positive, the gradient changes from a positive slope to a negative slope and back to a positive slope. Again, identification of the limiting current region is straightforward. Difficulties only arise if there is a change of sign in either E or I, in which case discontinuities arise in the E/I against $1/I$ plot.

In earlier work, [4] straight lines were drawn through the two pairs of points D–C and B–C in Figure 2 to give an intercept in the region of the local minimum at C. It is readily appreciated that this corresponds to a larger value of the reciprocal current and hence a smaller value of current. The approach of these earlier researches [4] generates a value that corresponds to the beginning of the diffusion limited region. The comparison of the two approaches shows that the present methodology offers both: (a) a clear procedure for accurately estimating the plateau region, and (b) the values of E and I corresponding to the limits of the diffusion controlled region.

3.2. *Reduction of $Fe(CN)_6^{3-}$ in the FM01 cell*

The data used in this section were obtained from the reduction of ferricyanide on a 10 ppi RVC electrode in the FM01-LC cell. A full description of this cell is available in the literature [13–16]. The concentration of ferricyanide ions was 10 mM in 1 M of NaOH as an electrolyte. Figure 3 shows the I against E and the E/I against $1/I$ curves. As in the previous example, the region of the limiting current in the I/E curves is not apparent visually. However, the plot of E/I against $1/I$ identifies the minimum and maximum points as well as the intersection of both negative and positive slopes. Calculated values for the limiting currents are presented in Table 2 and compared with the Cowan and Brown method [4].

Mass transfer coefficients were calculated from the limiting current values, assuming that the entire cathode surface is active, in which case, for a RVC electrode the Equation 1 may be rewritten as $I_L = -nFA_e k_L v_e C_O$, where A_e is the electrode area per unit volume and v_e is the cathode volume. The values of k_L were obtained by considering the area per unit volume already reported in the literature for RVC material 60 ppi [9, 17, 18]. The calculated values are reported in Table 3 together with k_L values obtained from a literature correlation developed for a similar experimental apparatus [19]. It can be seen that the mass transfer coefficients calculated with the method proposed in this paper are in between those values calculated using the other two methods. As expected the extrapolation method [4] gives an underestimate because it is focussed upon that part of the

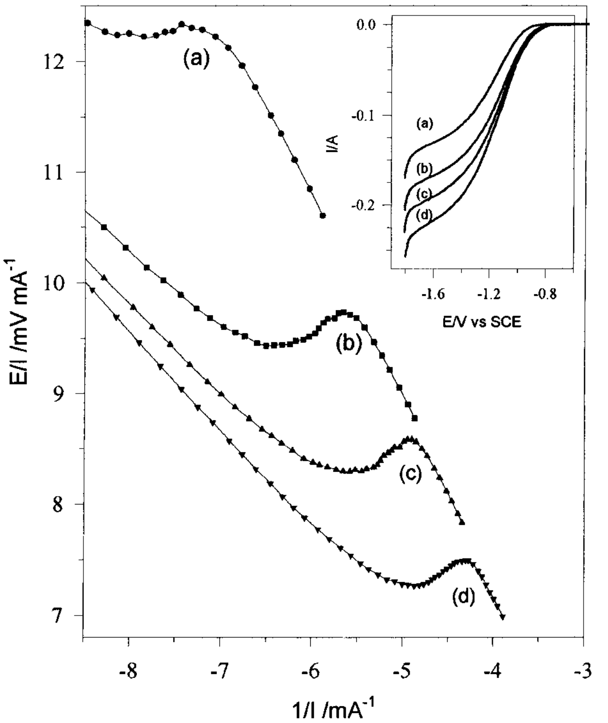

Fig. 3. E/I against $1/I$ curves for 10 mM of $Fe(CN)_6^{3-}$ in 1 M NaOH carried out in the FM01-LC electrolyser. Catholyte linear flow velocity (a) 0.062, (b) 0.106, (c) 0.15, (d) 0.195 m s^{-1}, $T = 25$ °C. Inset: E against I curves used to construct the main Figure.

Table 2. Currents from E/I against $1/I$ curve for the reduction of 10 mM $Fe(CN)_6^{3-}$ in 1 M NaOH in a FM01-LC cell at different flow rates

Flow rate /m s^{-1}	Current/mA		Limiting current/mA	
	Minimum	Maximum	This method	Method [4]
(a) 0.062	−127	−134	−130	−125
(b) 0.106	−154	−177	−165	−157
(c) 0.150	−183	−202	−192	−179
(d) 0.195	−206	−232	−219	−204

curve corresponding to the onset of the limiting current region. The correlation developed in [19] was based upon visual determination of a particular potential that coincided with those regions of the potential curves for which the change of current with potential was smallest. From this one potential, the limiting currents were estimated and the k_L correlation developed. Table 3 shows that this methodology generated k_L values that were consistently higher than those generated by the new method. For a true plateau all three methods would give the same value.

Table 3. Comparison of the calculated values of k_L
Data from the literature corresponds to the reduction of 1 mM $Fe(CN)_6^{3-}$ in 1 M NaOH solution on a 60 ppi reticulated carbon electrode

Flow rate /m s^{-1}	k_L/cm s^{-1} 10^4		
	Calculated from [19]	This method	Method [4]
(a) 0.062	1.4	1.2	1.1
(b) 0.106	1.8	1.6	1.4
(c) 0.150	2.1	1.7	1.6
(d) 0.195	2.3	1.9	1.8

4. Conclusion

It has been shown that a plot of E/I against $1/I$ from I/E data can be used to determine the value of the limiting diffusion current. The analysis is concerned with the extraction of limiting current from a polarization curve in which the plateau current is masked by a secondary reaction not affected by mass transfer. The analysis is constrained by the need to assume that the whole of the electrode is at a constant voltage. As the examples show, the limiting current region is clearly defined as the midpoint of the positive branch of an E/I against $1/I$ plot. On the other hand, the extrapolation of the two sloping lines defines approximately a point corresponding to the minimum in the E/I against $1/I$ curve and no use is made of the maximum.

References

1. D. Pletcher and F.C. Walsh, 'Industrial Electrochemistry', (Chapman & Hall, London 1990).
2. B.J. Robbins, R.W. Field, S.T. Kolaczkowski and A.D. Lockett, *J. Membrane Sci.* **118** (1996) 101 and, B.J. Robbins PhD thesis, Bath University, UK (1996).
3. F. Kuppinger, W. Neubrand and G. Eigenberger, 'Fundamentals of Electro-membrane Processes', Comett course, University of Stuttgart, 11–14 Oct. 1993.
4. D.A. Cowan and J.H. Brown, *Ind. & Eng. Chem.* **51** (1959) 1445.
5. J.A. Trainham and J. Newman, *J. Electrochem. Soc.* **124** (1977) 1528.
6. J.S. Newman and C.W. Tobias, *J. Electrochem. Soc.* **109** (1962) 1183.
7. M.S. El-Deab, M.M. Saleh, B.E. El-Anadouli and B.G. Ateya, *J. Electrochem. Soc.* **146** (1999) 208.
8. M. Matlosz and J. Newman, *J. Electrochem. Soc.* **133** (1986) 1850.
9. D. Pletcher, F.C. Walsh, I. Whyte and J.P. Millington, *J. Appl. Electrochem.* **21** (1991) 659.
10. D. Pletcher, F.C. Walsh, I. Whyte and J.P. Millington, *J. Appl. Electrochem.* **21** (1991) 667.
11. C. Ponce de Leon and D. Pletcher, *J. Appl. Electrochem.* **25** (1995) 307.
12. C. Ponce de Leon and D. Pletcher, *Electrochim Acta.* **41** (1996) 533.
13. D. Robinson, *in* J.D. Genders and D. Pletcher (eds), 'Electrosynthesis from laboratory, to pilot, to production' (The Electrosynthesis Co., Lancaster, NY, 1990), p. 219.
14. C.J. Brown, D. Pletcher, F.C. Walsh, J.K. Hammond and D. Robinson, 'Electrochemical cell design and optimization procedures', *Dechema Monographs* **123** (1991), p. 299.
15. C.J. Brown, D. Pletcher, F.C. Walsh, J.K. Hammond and D. Robinson, *J. Appl. Electrochem.* **22** (1992) 613.
16. C.J. Brown, D. Pletcher, F.C. Walsh, J.K. Hammond and D. Robinson, *J. Appl. Electrochem.* **23** (1993) 38.
17. S. Langlois and F. Coeuret, *J. Appl. Electrochem.* **19** (1989) 43.
18. 'Reticulated Vitreous Carbon Data Sheets' (The Electrosynthesis Co., New York, 1976).
19. C. Ponce de León, PhD thesis, University of Southampton, UK (1994).