Available online at www.sciencedirect.com
SCIENCE DIRECT®
Electrochimica Acta 51 (2006) 2977–2979
ELECTROCHIMICA Acta
www.elsevier.com/locate/electacta

Discussion article

Reply to “Comments on the papers: Electrochimica Acta 49 (2004) 445 and Electrochimica Acta 49 (2004) 2569, by M. Arun Prasad and M.V. Sangaranarayanan”—On the dependence of the Nernst diffusion layer thickness on potential and sweep rate for reversible and of the thickness of the charge transfer layer for irreversible processes studied by application of the linear potential sweep method by J. Gonzalez Velasco (EAST05-391)

M. Arun Prasad*

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

Received 18 August 2005; received in revised form 15 September 2005; accepted 20 September 2005
Available online 18 November 2005

The authors appreciate having an opportunity to respond to the comments of Velasco for re-examining some aspects of the articles [1,2] leading to an interesting discussion on the subject which can be categorized in to (i) diffusion layer thickness in linear sweep voltammetry (LSV) and (ii) conductance associated with reversible/irreversible charge transfers in LSV

(i) Diffusion layer thickness in LSV:

First, the authors regret that Fig. 3 in [1] is not representing Eq. (9) of [1]. As per Eq. (9) [1], the diffusion layer thickness (δ) varies inversely with the square root of the scan rate (υ), however, the figure implies the other way due to wrong marking of the axes while drawing in a graphical software. Fig. 1 given in here shows the correct variation of δ both with scan rate and potential (E) drawn according to Eq. (9) of [1]. On comparing Fig. 1 given here and Fig. 2 of the Comment [3], one may see that the results according to the Eq. (9) of [1] and that of the Comment match each other very well. In the case of irreversible electrode reactions [2], even though the relationship between δ and υ is not illustrated diagrammatically, the inverse relationship of δ with $\sqrt{\upsilon}$ is obvious in Eq. (23) of [2].

(ii) Conductance associated with reversible/irreversible charge transfers in LSV:

There is a detailed discussion on conductance in LSV (C) in the Comment [3], wherein, the ratio between the current (i) and the potential (E) is suggested as the correct definition of conductance pertaining to LSV and the expression for conductance is formulated by multiplying the current equation with F/RT, viz. for the reversible electrode reactions, the conductance is expressed in the Comment as,

$$C = \frac{F}{RT}\left(nFAC_{\mathrm{O}}^{0}\sqrt{\frac{nF\upsilon\pi D_{\mathrm{O}}}{RT}}\chi(\sigma t)\right) \quad (1)$$

Further, it is claimed in the Comment [3] that the pattern of the conductance verses potential plot is similar to the corresponding voltammogram and the normalized conductance, C_{norm}, is an exact reproduction of the normalized voltammogram (Figs. 1 and 5 of the Comment).

The immediate shortcoming of this formulation can be illustrated as follows. Let us consider a voltammogram (neglecting the signs involved) and take two points a and b having same current values but referring to different potentials. The points a and b in Fig. 2 given here are having same current values but b is at higher potential than a. In this case, according to the definition of conductance suggested in the Comment [3], viz. $C = i/E$, one

DOI of original article:10.1016/j.electacta.2005.08.028.
* Tel.: +91 44 2257 4209; fax: +91 44 2257 0545.

doi:10.1016/j.electacta.2005.09.048

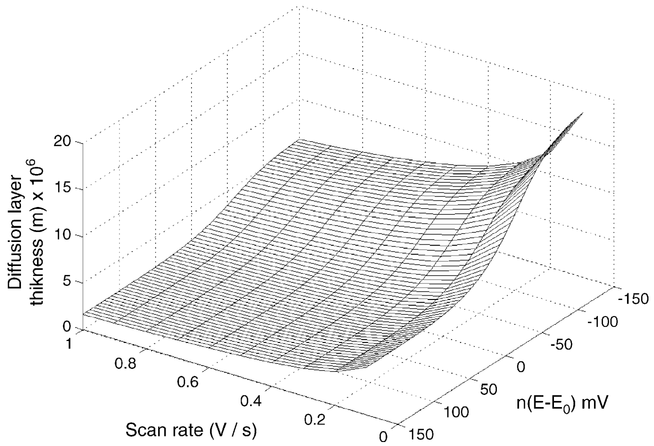

Fig. 1. Variation of the diffusion layer thickness with potential and scan rate obtained from Eq. (9) of [1]. The range of values chosen for the mesh plot are 0.1:0.1:1 for scan rate and −150:5:150 for potential, respectively. Other parameters are as follows: $n = 1$; $D = 10^{-10}$ m^2/s and $T = 298$ K.

can expect the conductance at b less than that at a, viz.

$$C_a = \frac{i_a}{E_a} > C_b = \frac{i_b}{E_b} \qquad (2)$$

since $i_a = i_b$ and $E_a < E_b$. However, the results of the Comment [3] leads to the inference that the conductance at a and b are exactly the same, viz. $C_a = C_b$ which is not logical. The expressions (16, the equation for conductance) and (24) in the Comment [3] are still the current equations (not divided by the potential variable) embodied in the dimension of conductance. Besides, one may question the validity of the definition $C = i/E$ in LSV, since, strictly speaking, $C = i/E$ is applicable only for the conducting media obeying Ohms law.

The paradox regarding conductance in LSV in [1,2] as noted in the Comment (viz. the conductance becomes zero or resistance infinite at the peak) can be explained as follows. It is pointed out [1,2] that the derivative of the current with respect to potential ($C = di/dE$) has been used as the definition for computing conductance in LSV (since the authors opine that the definition $C = i/E$ cannot be applied to non-linear i–E plots), which means that *the points in Fig. 4 in* [1,2] *represent the conductance at that instant of potential and not averaged over any segment of potential axis*. It is only at the particular instant of potential, regardless of previous history, the conductance is computed and hence it is not illegitimate to have conductance growing down to zero at some instant of potential (viz. the peak potential) regardless of previous values of the current.

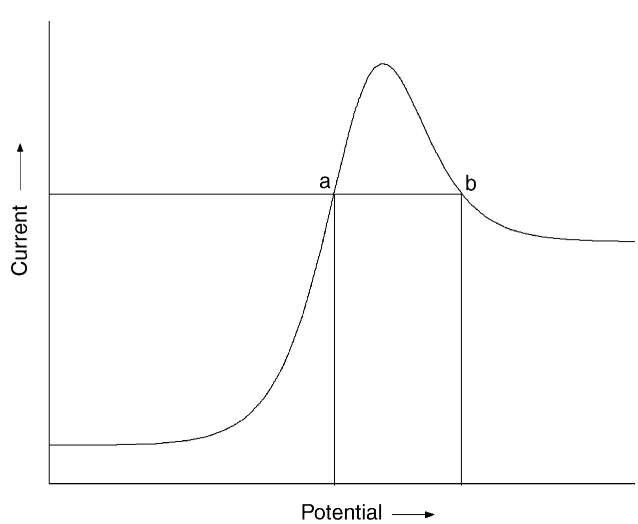

Fig. 2. A schematic voltammogram to illustrate that the conductance values at a and b are not equal.

There is an interesting remark in the Comment [3] as to why conductance becomes negative after the peak while the current does not change sign? Also, if the potential difference across a conducting medium is increased, one would normally expect the current flowing to increase; on the contrary, in LSV, increase in the potential (the driving force) after the peak leads to decrease in the current (viz. the negative slope after crossing zero) till the plateau is reached—this seemingly unphysical condition is reflected in the di/dE versus E plots in [1,2]. The conductance based on di/dE definition throws more light into the processes occurring at electrode. Initially, current grows with the potential (driving force) and a second force, opposing in nature that one can identify, also grows along with the potential which subsequently overwhelms the driving force exactly at the instant of peak potential (hence the resistance seems to be infinite at this instant of potential), so that the current, instead of growing further, starts decreasing till the plateau is reached. The interplay between the driving and opposing forces results in a beautiful wave-like current pattern, viz. the voltammogram and it is this particular feature which makes voltammetry sensitive to mechanistic details. The nature of this retarding force is well discussed and analyzed in the literature and the authors merely presented a different speculation of the same in [1].

Regarding the argument pertaining to equivalent circuit, it is true that in reversible electrode reaction, the diffusional component of the process governs the current response, however, what are the real equivalent circuit elements present in the 'Pseudoimpedance' is the question the authors wish to address in [1]. In [1], the discussion is confined to LSV studied in the context of applied linear potential perturbation and the resulting response of the electrode system in the form of current. In this respect, the authors suggested a circuit [1] that would reproduce the current pattern of the voltammogram and owing to its interesting resemblance with the general circuit of the electrode system, the various components of the former have been identified with the latter in [1] despite the fact that the circuit represents the diffusion component only. However, it has to be noted that except for the reproduction of the voltammetric pattern, the circuit suggested in [1] does not have complete electrochemical significance, for example, the inductance in the circuit does not imply any electrochemical significance.

1. Conclusions

The derivation to demonstrate that the diffusion layer thickness is inversely proportional to the square root of the scan rate has been provided in [1,2] and the same dependence has been again given in the Comment [3]. Fig. 3 of [1] has an incorrect marking of the scan rate axis which has now been rectified in the Reply (Fig. 1). The authors are not in agreement with the conductance definition for LSV suggested in the Comment.

References

[1] M. Arun Prasad, M.V. Sangarnarayanan, Electrochim Acta 49 (2004) 445.
[2] M. Arun Prasad, M.V. Sangarnarayanan, Electrochim Acta 49 (2004) 2569.
[3] J. Gonzalez Velasco, Electrochim. Acta (EAST05-391).