

Discussion

Comments on ‘Spurious potential dependence of diffusion coefficients in Li^+ insertion electrodes measured with PITT’

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Abstract

Deiss [Electrochim. Acta 47 (2002) 4027] claimed that the diffusion coefficient of electrochemical systems is potential-independent and apparent dependency is just related to the experimental errors. In this commentary paper, based on solid arguments, it was demonstrated that it is not a correct conclusion. The diffusion coefficient is strongly potential-dependent as can be understood from statistico-mechanical standpoint. This is well known from more than a century with convincing theoretical formulations. Of course, the possible experimental errors mentioned by Deiss are true, but not responsible for potential dependency of the diffusion coefficient.

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1. Introduction

In this recent paper [1], Deiss notified the ignorance of electrochemists in using classical electrochemistry for the practical cases. This is indeed a brilliant contribution and we do not aim to criticize it, but to modify its conclusion. The fact that determination of diffusion coefficient by potentiostatic intermittent titration technique (PITT) is accompanied by experimental due to invalid assumption (of classical electrochemistry) is indisputable, but the conclusion of potential-independency of the diffusion coefficient [1,2] is not correct. Sometimes, inappropriate use of electrochemical methods for the determination of diffusion coefficient lacking phenomenological standpoint is observed in the literature. For instance, Gobal et al. [3] have reported differences of the diffusion coefficients of a typical redox system at slow and fast scans of cyclic voltammetry. It is evident that the value of diffusion coefficient is independent of measurement conditions (otherwise the method is no longer reliable), but it is

not true for potential-dependency as it has phenomenological reasoning.

2. Variation of diffusion coefficient

First of all, we note a simple mistake in the theoretical consideration made in [1], which provided an apparent agreement with the experimental results reported in the literature (a comprehensive list has been cited in [1]). Deiss, based on solid theoretical argument, shows that the diffusion coefficient at redox potential is nine times smaller than the real one owing to invalidity of PITT assumptions. On the other hand, potential-dependency of the diffusion coefficient detected in various papers published in the literature (cf. the references cited in [1]) are about one order of magnitude [4]. This agreement apparently suggests that the differences observed in experimental measurements are purely related to the methodology problem mentioned by Deiss [1]. However, this $1/9D$ value is not true.

In Section 2.2 of [1], Deiss calculates that the charged transferred for a spherical particle-based electroactive film is equal to $nF\Delta cp(4\pi r_1^3/3)$, which is correct. But the expression

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that the surface area is equal to $p(4\pi r_1^2)$ is incorrect, as it is just valid for individually dispersed particles. The closely packed particles in a film electrode is significantly different from this, which is indeed an ideal model. On one hand, it should be taken into account that the distance between individual particles should be significantly smaller than the diffusion layer thickness, otherwise another problem appears as the diffusion is no longer one-dimensional toward the electrode surface (as assumed in classical electrochemistry) [5]. The importance of film density for the case of LiMn_2O_4 has been reported [6]. In other words, the surface area of a particle-based film is at least few times smaller than that of individual particles. This means that the parameter of 1/9 introduced in Eq. (5) of [1] is not practical and indeed approaches 1 (but not ideally 1). In fact, this problem associated with the methodology (due to invalidity of basic assumption of linear diffusion in a semi-infinite system) results in a tiny difference in the diffusion coefficient, not as large as nine times.

Of course, we emphasize that the problem of surface area is an obstacle for using the Cottrell equation, even more important than that expressed by Deiss since the surface structure of the electroactive particles is subject of severe changes upon insertion/extraction process [7]. On the other hand, internal structure of the particles packed together is responsible for the occurrence of diffusion through empty pores and channels existing between individual particles [8].

3. Potential-dependency of diffusion coefficient

Since the potential-dependency of the diffusion coefficient is evident from theoretical point of view, we just address some solid theoretical considerations reported in the literature. From classical era, it was known that diffusion processes are nonlinear [9–11]. Nernst emphasized invalidity of Fick's linear law [12]. This is indicative of concentration-dependency of the diffusion coefficient [13]. In an electrochemical redox system, this concentration-dependency is equivalent to potential dependency [14]. This is a logical behavior from statistical mechanical point of view. It can be found that ion–ion interactions of the diffusing species have a significant influence on the activation energy, leading to dependency of the diffusion coefficient upon concentration.

However, the most rigid reason for potential-dependency of the diffusion coefficient can be concluded from thermodynamical consideration. This issue has been well established by Chen and Ho [15,16]. According to solid thermodynamical consideration, they concluded that nonlinear potential-dependency of the diffusion coefficient is attributed to a corresponding concave-down excess energy–potential characteristic, which results in the maximum excess energy and suppresses the random mixing. This behavior can also be revealed by means of Monte Carlo simulation as simulates the diffusion at different concentrations from statistical point of view [17].

In general, both theoretical and experimental results reported by various researchers over a century are indicative of potential-dependency of the diffusion coefficient. Even, the Deiss' contribution does not provide a theoretical formulation that the diffusion coefficient is independent of potential.

4. The pros and cons of Deiss' contribution

The strategy of study followed in [1] is truly appreciable. It reminds an important failure in modern electrochemistry. This issue is indeed worth of further attention. For the case of the determination of the diffusion coefficient by means of PITT, the theoretical considerations elaborated by Deiss [1] clearly indicate the methodology failure. We agree with the generalization made in the Section 4.5 of [1], as this failure is also applicable for other electrochemical methods since the basic assumptions of classical electrochemistry are not completely fulfilled in real electrodes.

Unfortunately, Deiss made haste to come to a simple conclusion that this failure is exclusively responsible for the nonlinear potential-dependency observed in experimental measurements. In other words, Deiss has no solid reason for potential-independency of the diffusion coefficient. Whereas, there are several arguments and theoretical considerations developed in the literature in favor of potential-dependency (i.e. a kind of nonlinear concentration dependency) of the diffusion coefficient. Deiss does not present sufficient reason to deny commonly accepted potential-dependency of the diffusion coefficient, but introduces another source of nonlinearity of the diffusion coefficient (i.e. due to experimental error originating from the methodology failure).

Not only because of the theoretical consideration addressed here but also according to numerous experimental results reported in the literature, Deiss is unable to convince electrochemists that diffusion is potential-independent. However, modifying the claim of Deiss' contribution, which is the aim of the present note, is of practical important. It advises the researchers to consider severe experimental errors appearing in the course of PITT (or other experiments) for the determination of the diffusion coefficient. We wish to emphasize this issue in complimentary to the brilliant contribution of Deiss [1].

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