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The voltammetric responses of nanometer-sized electrodes in weakly supported electrolyte: A theoretical study

Yuwen Liu, Qianfan Zhang, Shengli Chen*

Hubei Electrochemical Power Sources Key Laboratory, Key Laboratory of Analytical Chemistry for Biology and Medicine (Ministry of Education), Department of Chemistry, Wuhan University, Wuhan 430072, China

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ABSTRACT

The effect of the supporting electrolyte concentration on the interfacial profiles and voltammetric responses of nanometer-sized disk electrodes have been investigated theoretically by combining the Poisson–Nernst–Planck (PNP) theory and Butler–Volmer (BV) equation. The PNP-theory is used to treat the nonlinear couplings of electric field, concentration field and dielectric field at electrochemical interface without the electroneutrality assumption that has been long adopted in various voltammetric theories for macro/microelectrodes. The BV equation is modified by using the Frumkin correction to account for the effect of the diffuse double layer potential on interfacial electron-transfer (ET) rate and by including a distance-dependent ET probability in the expression of rate constant to describe the radial heterogeneity of the ET rate constant at nanometer-sized disk electrodes. The computed voltammetric responses for disk electrodes larger than 200 nm in radii in the absence of the excess of the supporting electrolyte using the present theoretical scheme show reasonable agreements with the predications of the conventional microelectrode voltammetric theory which uses the combined Nernst–Planck equation and electroneutrality equation to describe the mixed electromigration-diffusion mass transport without including the possible effects of the diffuse double layer (Amatore et al. [25]). For electrodes smaller than 200 nm, however, the voltammetric responses predicated by the present theory exhibit significant deviation from the microelectrode theory. It is shown that the deviations are mainly resulted from the overlap between the diffuse double layer and the concentration depletion layer (CDL) at nanoscale electrochemical interfaces in weakly supported media, which will result in the invalidation of the electroneutrality condition in CDL, and from the radial inhomogeneity of ET probability at nanometer-sized disk electrodes.

1. Introduction

In the past two decades, quantitative electrochemical measurements utilizing electrodes of nanometer dimensions have been the subject of extensive studies because of its high spatio/temporal resolution, ultra fast mass transport rate and unique electrochemical properties [1–14]. The interpretation of experimental data requires theoretical models describing the electrochemical behaviors of nanometer-sized electrodes. A simple way is to apply the conventional voltammetric theories developed for microelectrodes. However, it has been long argued that nanoelectrodes cannot be considered simply as smaller microelectrodes since some qualitative changes may arise upon reducing the electroactive size of an electrode into nanoscales [15–20]. For instance, with the comparable electrode size to the thickness of the electric double layer (EDL), significant overlap between the mass transport layer and the diffuse EDL would induce diffuse double layer effect on the mass transport of the electroactive molecules and the electron transfer between the electrode and the electroactive molecules [16,17]. In addition, the electroneutrality conditions that have been long used in voltammetric analysis of microelectrodes may become questionable.

As having been shown in recent experimental and theoretical studies [5,14,19], the voltammetric responses of nanoelectrodes, at least the limiting current densities in the presence of the excess of the supporting electrolyte, may deviate inconspicuously in quantity from the predication of the conventional voltammetric theory. The electrode-size dependent voltammetric features may only become visible when the electrode size is below 10 nm [14]. However, the experimental observations in the absence of excess supporting electrolyte have shown that, even at electrodes a few tens of nanometers in radii, significant deviation from the predications of the conventional microelectrode voltammetric theories may occur [4,10,12]. So far, most of the theoretical studies on nanoelectrodes

* Corresponding author.
E-mail address: slchen@whu.edu.cn (S. Chen).

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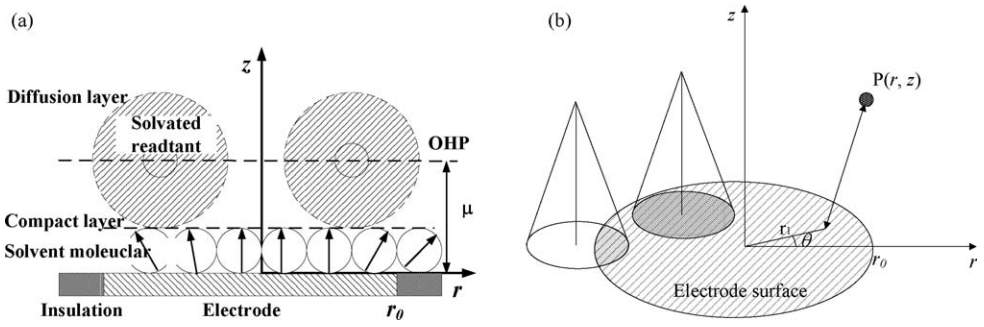

Fig. 1. The schematic diagrams of (a) the cross section of the electrochemical interface at a disk electrode of r_0 radius embedded in an infinite insulating sheath and (b) the radial heterogeneity of the electron-tunneling probability between the electrode and the redox molecules. The outer Helmholtz plane is at $z = \mu$ and the polarization of water near the edge is different from that in the center of the electrode.

have been concentrated on the deviation of the voltammetric responses from the conventional diffusion-based voltammetric theory when excess of supporting electrolyte is present in the solution [15–20]. By modeling the dynamic electrochemical interface with the Poisson–Nernst–Planck (PNP) theory, the effects of the diffuse EDL on the mass transport and charge transfer can be treated in a rather precise manner. However, the PNP-based theoretical study on the voltammetry of nanoelectrodes in solutions with low supporting electrolyte concentrations has been rather rare [16,21,22], especially when the effects of the EDL and the electrode geometry are concerned. In earlier theoretical studies dealing with the voltammetries of microelectrodes in weakly supported electrolyte, the attentions were mainly paid on the effect of electromigration on the mass transport of electroactive molecules. The theoretical scheme in these studies mostly consists of the Nernst–Planck equation and the electroneutrality equation [22–31]. The use of the electroneutrality condition can significantly simplify the formulization and computation. Using such a theoretical scheme, Amatore and Fosset [25] have derived analytical formulations describing the effects of the electric field on the limiting transport rate of electroactive ions toward microelectrodes in the absence of the excess of the supporting electrolyte. In addition, Hyk and Stojek [22] and Garay and Barbero [31] discussed the influence of diversity in redox species diffusivities on electrochemical processes on electrodes with conventional sizes in weakly supporting electrolyte. The validity of the electroneutrality assumption for ultrasmall spherical electrodes has been investigated using PNP equations by Oldham and Bond [18]. The authors paid special attentions on the charge separation in the mass transport layer, but the possible diffuse EDL effects were ignored. They concluded that detectable charge separation in depletion layer only occurs as the electrode diameter is less than 10 nm even in the absence of supporting electrolyte, which is obviously inconsistent with the recent experimental findings. In addition to neglecting the diffuse double layer effect, these authors have also assumed that the electrochemical reactions are Nernst type, i.e., electrochemically reversible. In reality, most of the electrochemical reactions would become rather irreversible at electrodes of nanometer scales due to very high mass transport rates.

With typical experimental current in the order of 10^{-12} A, nanometer-sized electrodes offer new opportunities for electrochemical measurements in solutions containing no (or low concentrations of) supporting electrolyte in which the ohmic potential drop through the solution will become a problem when larger electrodes are used. Rational theoretical models for voltammetric responses of nanometer-sized electrodes in weakly supported electrolyte would be highly appreciated for such electrochemical applications of nanoelectrodes. In present study, we modeled the dynamic electrochemical interface at nanometer-sized disk electrodes in solutions containing various concentrations of supporting electrolyte by using PNP equations and Butler–Volmer equation, with attentions being especially paid on the effects of the radial heterogeneities of the electric field, dielectric properties of solvents and the electron-tunneling probability at nanometer-sized disk electrodes. The computed results reveal how and to what extent the concentration of supporting electrolyte and the electrode sizes will render the voltammetric responses of nanoelectrodes deviate from those of microelectrodes.

2. Theoretical model and computations

The interface at disk electrodes can be modeled with a cylindrical coordinate system of axial symmetry (Fig. 1a). In present study, we consider an outer-sphere one-electron reduction of O^x to R^{x-1} at interfaces of disk electrode with radius r_0 embedded into an insulating sheath of infinite thickness and in solutions with various concentrations of supporting electrolyte A^+B^-. For simplicity, we assume that the diffusion coefficients of O^x and R^{x-1} are the same as each other and that the effects of the finite sizes of ions and the solvent noncontinuum can be ignored. We also make the following assumptions: the counter ion accompanying the reactant O^x is either A^+ or B^- depending on the sign of the reactant charge x. Therefore, certain amount of A^+ (for $x < 0$) or B^- (for $x > 0$) is included in the solution to maintain the electroneutrality of the solution; none of the ions in the solution specifically adsorbs on the electrode surface and all the ions have the same plane of closest approach at the outer Helmholtz plane (OHP, $z = \mu$ with μ referring to the thickness of compact double layer) so that no charge resides in the compact part of the double layer; the potentials are measured with respect of that in the bulk solution, which is assumed to be equivalent to the potential of zero charge (PZC).

The Poisson's equation is used to describe the local electric potential (ϕ) in a dielectric medium, which in cylindrical coordinate system has the following form:

$$\nabla^2\phi = \frac{\partial^2\phi}{\partial r^2} + \frac{1}{r}\frac{\partial\phi}{\partial r} + \frac{\partial^2\phi}{\partial z^2} = -\frac{\rho}{\varepsilon_0\varepsilon_r} \quad (1)$$

where ε_r refers to the local dielectric constant, ε_0 is the permittivity of vacuum respectively, and ρ is the local charge density. It should be noted that the local dielectric constant ε_r depends on the electrical field intensity due to the dielectric saturation effect [32]. In the absence of the specific adsorption of ions, we have $\rho = 0$ in the compact part of the double layer ($0 < z < \mu$). In the diffuse part of the interface, however,

$$\rho = \sum x_i c_i F \quad (2)$$

where x_i and c_i are the charge and the local concentration of ion i, respectively.