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Double layer effects in voltammetric measurements with scanning electrochemical microscopy (SECM)

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A B S T R A C T

Scanning electrochemical microscopy (SECM) operating as a variable gap ultra-thin layer twin-working electrode cell, has long been recognised as a powerful technique for investigating fast kinetics (heterogeneous electron transfer and homogeneous reactions coupled to electron transfer) as a consequence of high mass transport rates between the working electrodes when biased to promote redox shuttling. Recently, SECM has advanced technically and nanogap cells with dimensions on the 10s of nm scale have been reported. In this paper, we consider double layer effects on voltammetric measurements in this configuration, outlining a comprehensive model that solves the Nernst-Planck equation and Poisson equation with charged interfaces. For supporting electrolyte concentrations that have been used for such measurements (50 mM and 100 mM), it is shown that for typical electrode charges and charge on the glass insulator that encases the ultramicroelectrode (UME) tip used in SECM, there are profound effects on the voltammetric wave-shapes for redox reactions of charged redox couples, in the common modes used to study electron transfer kinetics, namely the tip-voltammetry (feedback) mode and substrate-voltammetry (substrate-generation/tip-collection and competition) modes. Using the reduction and oxidation of a singly charged redox species to a neutral and doubly charged species, respectively, as exemplar systems, it is shown that the charge on the electrodes can greatly distort the voltammetric wave-shape, while charge on the glass that surrounds the UME tip can affect the limiting current. Analysis of SECM voltammograms using methods that do not account for double layer effects will thus result in significant error in the kinetic values derived and tip-substrate distances that have to be estimated from limiting currents in SECM. The model herein provides a framework that could be developed for further studies with nanogap-SECM (e.g. consideration of alternative models for the electrical double layer, other supporting electrolyte concentrations, potential of zero charge on the electrodes and charges on the redox couples). The model results presented are shown to qualitatively match to SECM voltammetric features from experimental data in the literature, and are further supported by experimental data for redox processes of tetrathiafulvalene (TTF), namely the TTF/TTF$^{\cdot +}$ and TTF$^{\cdot +}$/TTF^{2+} redox couples. This serves to demonstrate the immediate practical application of some of the ideas presented herein. For future applications of SECM, the use of different supporting electrolyte concentrations and a range of tip-substrate separations may allow the determination of both electron transfer kinetics and double layer properties.

1. Introduction

The electrical double layer (EDL) has a pivotal role in electrochemistry and interfacial science and was an area to which Roger Parsons made seminal contributions [1]. Since the initial description of the EDL by Helmholtz [2], many modifications have been proposed including the key early contributions of Gouy-Chapman [3] and Stern [4], resulting in models that have remained popular to this day [1]. In the Gouy-Chapman model, the surface charge is compensated by a diffuse layer of ions in solution and the decay of the electric potential away from the interface is characterised by the Debye length, typically scaling with the inverse square root of the solution ionic strength [5,6]. Note that the Debye length represents the distance over which the electric potential decays to a factor of $1/e$ of the potential difference between the interface and bulk solution, and does not cover the full dimension of the double layer. Consequently, surface charge effects can be seen at greater distances than the Debye length. The EDL is increasingly recognised to have significant impact on nanoscale electrochemical systems, for which the characteristic diffusion layer size, for a redox reaction involving solutes, approaches that of the EDL [7–20].

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The purpose of this paper is to consider the impact of surface charge on scanning electrochemical microscopy (SECM) measurements when configured to create a dual-working electrode thin layer electrochemical cell for kinetic measurements.

SECM has found considerable use in characterising fast heterogeneous electron transfer [21–24], homogeneous (solution) kinetics [25–27], detecting adsorbed species [28–30] and measuring lateral charge transfer [31–35], amongst a wide range of applications. In many of these studies, the gap between the tip and substrate has usually been at the micron or larger scale and, with the excess supporting electrolyte concentrations used, EDL effects are negligible, because the EDL size is very small compared to the gap size (which defines the concentration boundary layer between the two working electrodes). However, recent technical advances have enabled SECM gaps as small as a few 10s of nm to be realised between a parallel dual-working electrode arrangement (so-called "nanogap-SECM") [36,37], which provides ultrafast diffusion rates of redox species between the two working electrodes as seen in other nanogap devices [15,38,39]. In principle, this is highly advantageous for the study of fast kinetics, but the high surface area to solution volume ratio of such devices magnifies certain physicochemical effects, including adsorption [30,40] and, as we show herein, EDL phenomena. EDL effects have been explored very recently for dual-electrode nanogap devices [15,16], and for SECM [17] but in the latter case with the focus on the active part of the tip and substrate electrodes and for the highly charged $Fe(CN)_6^{4-/3-}$ couple. These studies highlight that the voltammetric wave-shape recorded at the dual-electrodes can be significantly modified by EDL properties, with the effect being most noticeable (as expected) at low electrolyte concentration and/or small gap size where the EDL size is non-negligible. However, EDL effects are still seen at ionic strengths that are more typically used in voltammetry (e.g. 0.1 to 1.0 M 1:1 electrolyte concentration in both aqueous solution [16,17] and acetonitrile [15]).

The ultramicroelectrode (UME) tip in SECM is encased in an insulating sheath that is often fabricated from glass or quartz and has traditionally been considered to be 'inert' [41]. However, in a recent paper [30], we have demonstrated that the glass sheath can influence transient mass transport during SECM measurements [30]. Given the strong ion current rectification (ICR) effects that are seen in glass and quartz nanopipettes [42–45] of characteristic dimensions similar to, and larger, than the gap size in nanogap-SECM, and that surface induced ion current rectification (SIR) phenomena are seen in scanning ion conductance microscopy (SICM) studies of charged interfaces [46–50], at ionic strengths similar to those used in typical SECM voltammetric measurements, it is essential to investigate surface charge and EDL effects from the glass sheath of the SECM tip, as well as from the electrodes. Primarily through modelling, but also with some experiments, we demonstrate that EDL effects in nanogap-SECM are very significant and need to be accounted for when analysing SECM data from a variety of different modes, e.g. the tip-voltammetry [21,22] and substrate-voltammetry [23,30] modes. We also point out instances in the literature where features arising from the models outlined herein are clearly evident in experimental voltammetric data, but have either been ignored or interpreted in terms of other phenomena.

2. Theory and simulations

COMSOL Multiphysics 5.2a (COMSOL, Stockholm, Sweden) finite-element method (FEM) modelling software was used to describe the time-dependent mass transport problem in a 2D-axisymmetric cylindrical SECM configuration shown in Fig. 1.

For this purpose, the Nernst-Plank equation was solved to describe the mass transport of all species in solution:

$$\frac{\partial c_i}{\partial t} = \nabla . \left(D_i \nabla c_i + z_i \frac{F}{RT} D_i c_i \nabla \phi \right) \tag{1}$$

and the Poisson equation described the electrical potential, ϕ:

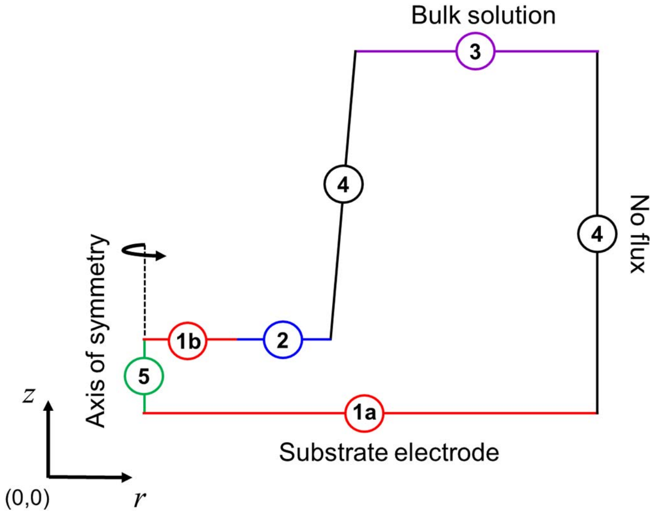

Fig. 1. Schematic of the 2D-axisymetric SECM simulation domain (not to scale), with labelled boundaries 1a and 1b (red) being the substrate and tip electrode surfaces, respectively, label 2 (blue) represents the glass surface that encapsulates the UME tip, label 3 (purple) is the bulk solution, label 4 (black) is a no-flux boundary and label 5 (green) is the axis of symmetry. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$$\nabla^2 \phi = -\frac{F}{\varepsilon \varepsilon_0} \sum z_i c_i \tag{2}$$

where c_i, D_i and z_i denote the concentration, diffusion coefficient and charge of species i in solution, respectively. ε is the solvent dielectric constant (38 for acetonitrile, 78 for water) and ε_0 is the vacuum permittivity (8.85×10^{-12} F m^{-1}). F, R and T are the Faraday constant (96,485 C mol^{-1}), gas constant (8.31 J mol^{-1} K^{-1}) and absolute temperature (298 K), respectively.

We first consider tetrathiafulvalene (TTF), which undergoes two sequential single electron oxidation processes in acetonitrile media [51], as an exemplar, for which we also report experimental data (vide infra):

$$\mathrm{TTF} \underset{k_{\mathrm{red},1}}{\overset{k_{\mathrm{ox},1}}{\rightleftarrows}} \mathrm{TTF}^{\bullet+} \underset{k_{\mathrm{red},2}}{\overset{k_{\mathrm{ox},2}}{\rightleftarrows}} \mathrm{TTF}^{2+} \tag{3}$$

where k_{ox} and k_{red} are the first-order heterogeneous oxidation and reduction rate constants, respectively. Subscripts 1 and 2 refer to the TTF/$\mathrm{TTF}^{\cdot+}$ and $\mathrm{TTF}^{\cdot+}/\mathrm{TTF}^{2+}$ redox processes, respectively.

Both the TTF/$\mathrm{TTF}^{\cdot+}$ and $\mathrm{TTF}^{\cdot+}/\mathrm{TTF}^{2+}$ redox processes are studied in the tip-voltammetry mode of SECM. This follows from a previously reported total shielding approach [25,52] where a large substrate electrode was held at a potential, E_{sub}, ($E^{0'}_{\mathrm{TTF/TTF^{\bullet+}}} > E_{\mathrm{sub}} > E^{0'}_{\mathrm{TTF^{\bullet+}/TTF^{2+}}}$). This creates a quasi-steady-state diffusion layer of $\mathrm{TTF}^{\cdot+}$ extending from the substrate electrode surface and shields the UME tip, which is placed close to the substrate surface, from the bulk TTF solution. $\mathrm{TTF}^{\cdot+}$ reduction to TTF, on the one hand, and oxidation to TTF^{2+}, on the other, at the UME tip can thus be investigated from the gap solution essentially free from the influence of the comproportionation reaction, between TTF (from bulk solution) and TTF^{2+} (tip-generated) species [25,52]. In this way, $\mathrm{TTF}^{\cdot+}$ reduction and oxidation reactions, under the same (mass transport) conditions [53], would be expected to yield equal but opposite limiting currents if diffusional mass transport alone were operating. The electrolyte solution (acetonitrile) also contains a supporting electrolyte comprising of 0.1 M tetrabutylammonium hexafluorophosphate ($\mathrm{TBAPF_6}$).

The first-order heterogeneous oxidation and reduction rate constants are described by the Butler-Volmer relationship, but with the plane of electron transfer (PET) taken to be the Outer Helmholtz Plane (OHP), located 0.6 nm from the actual electrode surface, as considered in recent work from other groups [15–17]. The flux at the substrate PET