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Short communication

A practical way to model convection in non-agitated electrolytes

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ABSTRACT

Many electrochemical experiments are performed in non-agitated or in non-controlled flow conditions. When such measurements are modelled considering convection, diffusion, migration and reactions, the problem of describing a suitable velocity field arises immediately. Based on the work of Amatore (2001), we present a workable approach that avoids solving the velocity fields in multi-ion modelling. The convection is treated as a diffusion term that becomes dominant from a certain distance from the wall (electrode). This implies that mass transfer becomes irrelevant from that distance on and that there is a fluent transition from the diffusion layer to the bulk of the solution. The theory is elaborated and two examples clearly show the applicability.

1. Introduction

In many experimental techniques like Scanning Vibrating Electrode Technique (SVET) or micro-potentiometric and micro-amperometric probes, in situ measurements are performed in small recipients with quiescent i.e. non-agitated electrolyte. Although quiescent, one cannot assume that the electrolyte velocity is zero. In simulations one would have too large diffusion layers that extend to the whole electrolyte volume. Flow is always induced by small variations in temperature [1,2], or concentrations (at electrodes), evaporation, small vibrations, air movement, etc. [3,4]. This leads after some time to a diffusion boundary layer.

Also often macroscopic electrochemical measurements are performed in hard to describe flow conditions except when devices are used that provide well-controlled flow conditions such as a rotating disc (RDE) or cylinder electrode (RCE).

So, in many cases numerical modelling of electrochemical systems is faced with the necessity to calculate the fluid flow [5,6] or to make approximations by defining a region of perfect electrolyte mix that is coupled with the diffusion layers close to electrodes and in which no flow is assumed, the so-called Nernst layers [7]. Considering distinct regions is unavoidable when the electrode configurations involve extended current density distributions. Both approaches, calculating the flow or defining subregions, implicate inaccuracies. The driving forces for flow are scarcely known and complex to solve for, certainly when induced for instance by electrode reactions in the electrolyte themselves (natural convection). Separating the electrolyte in diffusion controlled layers and a perfectly mixed electrolyte outside involves to define the a single diffusion layer thickness and to couple regions in which separated equations are to be solved [8]. In this communication we present a method that enables to reduce to a large extent the problem. The theoretical developments given by Amatore [3,9] for convection–diffusion problems of one species are extended/adapted for time dependent multi-ion transport driven by convection–diffusion–migration and homogenous reactions. These equations in the electrolyte are coupled with non-linear boundary conditions, e.g. Butler–Volmer, at the electrodes.

2. Theory

The mathematical model of ion transport in solutions is based on the balance equations [10]

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \vec{N}_i + R_i \qquad (1)$$

with $\vec{N}_i$ (mol m^{-2} s^{-1}) the flux of species i with concentration c_i (mol m^{-3}) and R_i (mol m^{-3} s^{-1}) the production/consumption rate of species i due to homogenous reactions. In dilute solutions the flux is

$$\vec{N}_i = \vec{v} c_i - D_i \vec{\nabla} c_i - z_i u_i F c_i \vec{\nabla} U \qquad (2)$$

with D_i (m^2 s^{-1}), z_i and $u_i = D_i/RT$ (mol s kg^{-1}) respectively the diffusion constant, charge and mobility of species i in total I species. F is the Faraday's constant, U the solution potential (V) and $\vec{v}$ the velocity (m s^{-1}) of the solvent.

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The electroneutrality condition provides the additional equation to solve for the potential U:

$$\sum_{i=1}^{I} z_i c_i = 0. \tag{3}$$

The local current density, obtained by summing up all ionic fluxes multiplied by Faraday's constant and the charge number z_i of each ion, yields (considering that z_i and D_i are constants)

$$J_{tot} = \vec{v} F \sum_{i=1}^{I} z_i c_i - F \vec{\vec{\nabla}} \sum_{i=1}^{I} z_i c_i D_i - \kappa \vec{\vec{\nabla}} U \tag{4}$$

in which

$$\kappa = \sum_{i=1}^{I} z_i^2 u_i F^2 c_i \tag{5}$$

is the electrical conductivity (S m^{-1}). Electroneutrality involves that convection cannot induce current density. Eq. (4) also shows that *in case all diffusion constants are equal*, electroneutrality can be invoked again such that there is also no contribution of diffusion to the total current density and only Ohm's law remains.

Even small spontaneous convection plays an important role in electrochemical systems. It is also known that due to the high Schmidt number, diffusion layers are about ten times smaller than thermal and hydrodynamic boundary layers. They are in general situated in the laminar sublayer [11]. When considering longer time ranges the effect of microscopic motion cannot be neglected. In order to avoid all flow simulations in what follows we extend/adapt the ideas of Amatore who replaces the convection flux by an equivalent diffusion flux [3]

$$N_{i\,\mu conv} = -D_{\mu conv} \vec{\vec{\nabla}} c_i. \tag{6}$$

Remark that this flux is only acting in the opposite direction of the concentration gradient. A micro-convection diffusion constant $D_{\mu conv}$ is introduced that is inherently species independent and space dependent but assumed here isotropic[1] in each point. In the viscous sublayer, the following expression that refers directly to the hydrodynamic properties of the solution can be derived [3,9]

$$D_{\mu conv} = D_{\mu conv}^{0} \left(\frac{y}{\Lambda}\right)^4 \tag{7}$$

with y the distance to the wall, Λ a scaling length such that $D_{\mu conv}$ equals $D^0_{\mu conv}$ at $y = \Lambda$.

In view of practical use Amatore [3] elaborated the following expression (Eq. (17) in [3])

$$D^i_{\mu conv} = D_{\mu conv} = D^0_{\mu conv} \left(\frac{y}{\Lambda}\right)^4 = 1.5072 D_i \left(\frac{y}{\delta}\right)^4 \tag{8}$$

with D_i the molecular diffusion of the reacting species, δ the thickness of the equivalent linearized Nernst diffusion layer of the same reacting species i and y the distance to the wall (electrode). This is fully justified as those parameters are directly linked to electrochemical measurements.

A problem arises when this expression is used for each species in the ion transport Eqs. (1) to (4). We have numerically observed that Eq. (8) couldn't be applied as such. Although the empirical approximation that δ is independent of the species is justified [3] for experiments, it is not valid in full multi-ion transport modelling. The total micro-convection current density becomes non-zero because electroneutrality is not applicable anymore, as it is explained further.

When applied in full ion transport models it is mandatory to make use of Eq. (7). For practical reasons of experimental determination, this can be rewritten as

$$D^{ref}_{\mu conv} = 1.5072 D_{ref} \left(\frac{y}{\delta_{ref}}\right)^4 \tag{9}$$

in which D_{ref} and δ_{ref} are respectively the molecular diffusion constant and the Nernst diffusion layer of the *reference* species that is chosen to characterize/measure the diffusion layer (e.g. H^+ or oxygen). D_{ref} and δ_{ref} are used for all species. This reveals clearly the link with expression (8): the choice of the reference species fixes the equivalent linearized Nernst diffusion layer.

One can write the total flux of any species i as

$$\vec{N}_{itot} = \vec{N}_{i\mu conv} + \vec{N}_i. \tag{10}$$

In contrast with Eq. (8), making use of expression (9), by virtue of electroneutrality, the total current density becomes independent of micro-convection:

$$\begin{aligned} J_{tot} &= -F \vec{\vec{\nabla}} \sum_{i=1}^{I} z_i D_i c_i - F \vec{\vec{\nabla}} \sum_{i=1}^{I} z_i D^{ref}_{\mu conv} c_i - \kappa \vec{\vec{\nabla}} U \\ &= -F \sum_{i=1}^{I} z_i D_i \vec{\vec{\nabla}} c_i - F D^{ref}_{\mu conv} \vec{\vec{\nabla}} \sum_{i=1}^{I} z_i c_i - \kappa \vec{\vec{\nabla}} U \\ &= -F \sum_{i=1}^{I} z_i D_i \vec{\vec{\nabla}} c_i - \kappa \vec{\vec{\nabla}} U. \end{aligned} \tag{11}$$

Remark that $D_{\mu conv}$ acts isotropically in any direction but its value is clearly space dependent: when close to the walls it is zero, but at distances larger than δ it becomes rapidly larger than all molecular diffusion constants. All values $D_i + D^{ref}_{\mu conv}$ become equal such that the total current density starts obeying Ohm's law. A fluent transition from diffusion-controlled transport near electrodes to migration-controlled transport in the bulk is obtained. This is also fully equivalent with what is found by Amatore et al. [3]. Outside the thus obtained diffusion layer other flow phenomena with larger recirculations might take place but at the end the effect remains the same: the electrolyte is perfectly mixed and justifies, for instance, the validity of the calibration equations used for SVET [12]. For that reason we believe that the approach might be suitable too for moderately agitated solutions provided that the transport of species tangential to electrodes is small with respect to one normal to their surfaces.

3. Calculations

Two examples show the validity of the developed theory.

The first example consists of the polarisation of a 1.2 mm diameter Pt disc in 10 mM $K_4Fe(CN)_6$ in 1 M KCl (pH 6), identical to the case presented by Amatore et al. [3] but solved now numerically with a multi-ion model. Polarisation data given by Van Parys et al. [13] are used and the diffusivities of species are as follows: $D_{H^+} = 9.31 \cdot 10^{-9}$ m^2 s^{-1}, $D_{OH^-} = 5.26 \cdot 10^{-9}$ m^2 s^{-1} [10], $D_{K^+} = 1.52 \cdot 10^{-9}$ m^2 s^{-1}, $D_{Cl^-} = 1.72 \cdot 10^{-9}$ m^2 s^{-1}, $D_{Fe(CN)_6^{4-}} = 5.70 \cdot 10^{-10}$ $m^2 s^{-1}$ and $D_{Fe(CN)_6^{3-}} = 6.00 \cdot 10^{-10} m^2 s^{-1}$ [3]. The initial bulk concentrations are $c_{K^+} = 1.04$ M, $c_{Cl^-} = 1$ M, $c_{H^+} = 10^{-6}$ M, $c_{OH^-} = 10^{-8}$ M, $c_{Fe(CN)_6^{4-}} = 10$ mM and $c_{Fe(CN)_6^{3-}} = 0$ M [3].

The second example deals with hydrogen evolution at an imposed current density of 13 A m^{-2} on an identical Pt disc in a 0.005 M NaCl (pH 6) solution, also a simple system that is often used to calibrate SVET devices. Polarisation data were imposed such that a constant current density distribution is obtained on the electrode. The diffusivities of species are: $D_{H^+} = 9.31 \cdot 10^{-9}$ m^2 s^{-1}, $D_{OH^-} = 5.26 \cdot 10^{-9}$ m^2 s^{-1}

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[1] In a more generalized theory the micro-turbulence can be anisotropic ($D_{x\,\mu conv} \neq D_{y\,\mu conv} \neq D_{z\,\mu conv}$).