



# Mass-transport impedance at channel electrodes: accurate and approximate solutions



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## ABSTRACT

Accurate numerical electrochemical impedance spectra at channel electrodes are obtained using commercial finite element method software. These agree with experimental measurements on the hexammineruthenium(II/III) reversible redox couple. The numerical solutions are used as a benchmark to test the validity of some common analytical approximations for the mass-transport impedance.

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## 1. Introduction

Improved microfluidic fabrication methods have led to a resurgence of devices using channel flow electrodes [1], and it is important to quantitatively understand the mass transport in these systems. Channel electrodes do not have uniform accessibility, which makes them mathematically more difficult than the analogous rotating disk electrode (RDE). One approach is use to the finite element method (FEM) to give accurate numerical solutions, and its implementation in the program Comsol Multiphysics® [2] has found wide use in electrochemistry [3]. Another approach to accurate solutions is to use semianalytic methods, which have recently been used for band electrodes with and without flow [4–6]. More commonly, approximations are applied to get simplified analytical expressions: (i) axial diffusion (in the channel direction) is neglected, and/or (ii) the Lévêque approximation is applied, i.e., the velocity profile is assumed to be linear.

Electrochemical impedance spectroscopy is well known as a powerful method for studying electrode processes, but the convective-diffusion problem under a.c. conditions must be

properly understood in order to make progress. Even for the much-studied RDE, the convective-diffusion impedance is typically modeled by approximate analytical solutions, sometimes with different expressions for high and low frequency regions [7–12], and comparison of these with numerical solutions is available, e.g., [13,14]. For channel electrodes, the two above-mentioned approximations have been used to get analytical treatments [15–18]. Alternatively, convection has been neglected altogether [19]. Approximate and experimental treatments of higher harmonics have also been reported [20]. Comparisons of approximate treatments with experiment have typically been restricted to the regimes where the approximations are valid. Experiments and theory are lacking in some important parameter regimes, in particular for low flow rates and low-height channels.

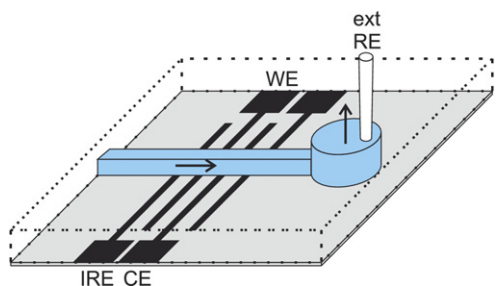
There is therefore the need for accurate numerical impedance solutions for channel electrodes. These can be directly compared with experiment, or can be used to establish the validity of various approximate analytical methods. Both of these objectives are achieved here, where we compare numerical solutions from Comsol with experiment and literature approximations, for the simple redox reaction, Eq. (1).



The experiments used the Ru<sup>II</sup>/Ru<sup>III</sup> hexammine redox couple with  $n = 1$ . Only a few FEM simulations of impedance have been

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**Fig. 1.** Diagram of the cell. Channel and outlet reservoir shown in blue, with arrows showing the fluid flow direction. IRE and ext RE are the internal and external reference electrodes.

reported before, e.g., [21,22], none of which treat channel electrodes.

## 2. Methods

### 2.1. Microfluidics

The microfluidic flow cells, Fig. 1, were made in the NorFab facilities (Trondheim, Norway). The electrodes were prepared on clean glass slabs by a photoresist method using ma-405 photoresist and ma-D331/s developer (Micro Resist Technology GmbH). Titanium (10 nm) and platinum (190 nm) were evaporated onto the developed glass slides (Pfeiffer Vacuum Classic 500) and excess metal was removed with mr-REM 600 (Micro Resist Technology GmbH).

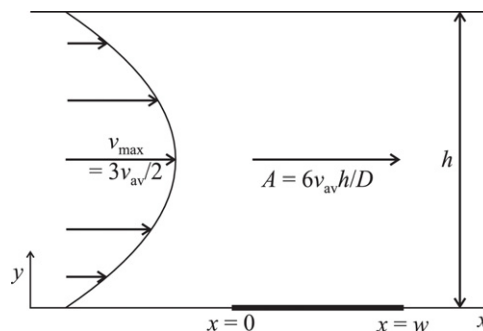
The PDMS channels were made from a channel master on a Si slide. The master was fabricated by applying photoresists SU8-5 and SU8-2100 (both MicroChem Corp.), developing the pattern, and removing excess material with Mr-DEV 600 (Micro Resist Technology GmbH). The wafer was then hard baked. The PDMS was made by mixing base (Lindberg and Lund AS) and curing agent (Dow Corning S.A). The mixture was degassed and poured on top of the Si master. The finished PDMS channel was assembled by making inlet and outlet holes, activating the surface using a plasma cleaner, and then mounting on the electrode glass slide.

Wires were connected by soldering, and a reservoir for collecting the electrolyte and holding the external reference electrode was added, see Fig. 1. The cells produced had 100  $\mu\text{m}$  wide electrodes in a 100  $\mu\text{m}$  high channel with a depth of 1 mm.

### 2.2. Electrochemistry

To avoid oxygen, the microfluidic cell was mounted in a chamber that was purged with argon (Praxair Ultra High Purity 5.0). The absence of oxygen was confirmed by cycling the electrode between oxygen evolution and hydrogen evolution in 0.5 M  $\text{H}_2\text{SO}_4$  (Seastar Chemicals, Baseline grade). Solutions were made up with Millipore Milli-Q water. All electrochemistry was performed with a Gamry Ref. 600 potentiostat. The external reference electrode used during electrochemistry in 0.5 M  $\text{H}_2\text{SO}_4$  was a reversible hydrogen electrode mounted in the outlet reservoir, which consisted of a Pt wire sealed in glass and exposed to the solution and a trapped hydrogen bubble.

To further minimize the effect of oxygen, an iodine monolayer was deposited on the electrodes by holding at 0.4 V vs RHE for 6 minutes in 0.5 M  $\text{H}_2\text{SO}_4$  + 4 mM KI ( $\geq 98.5\%$  Caledon) electrolyte. The quality of the iodine layer was checked using cyclic voltammetry (CV) in  $\text{H}_2\text{SO}_4$ , by comparing the magnitude of the capacitive current between 0.3 and 0.7 V vs RHE. The layer was deemed sufficient if the capacitive current had dropped to below 0.01  $\text{mA cm}^{-2}$  for a scan rate of 200  $\text{mV s}^{-1}$ .



**Fig. 2.** Geometry of the channel electrode in 2-D. Flow is from left to right, with one electrode (bold) in the bottom of the channel. The parabolic velocity profile is also shown, with the relationship between the average and maximum velocities.

The data reported in this paper used the reversible  $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$  hexaammine redox couple. The aqueous solution was prepared from nominally 5 mM  $\text{Ru}^{\text{II}}(\text{NH}_3)_6\text{Cl}_2$  ( $\geq 98\%$  Sigma-Aldrich) and 5 mM  $\text{Ru}^{\text{III}}(\text{NH}_3)_6\text{Cl}_3$  ( $\geq 99.9\%$  Sigma-Aldrich) in 0.1 M  $\text{K}_2\text{SO}_4$  electrolyte ( $\geq 99.5\%$  AnalaR). The ruthenium hexaammine complexes degrade if there is oxygen present in the solution, and so argon was purged for 10 minutes before the complexes were introduced, and then purged again after introduction. The electrolyte was always made fresh on the day of the experiments and properly stored to avoid oxygen introduction. Despite this, slight degradation of ruthenium hexaammine did occur, and the actual concentrations were estimated as 4.0 mM by adjusting the Comsol modeled results to give a satisfactory fit for all flow rates.

The  $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$  hexaammine redox couple was used as an internal reference electrode (IRE, about 0.45 V vs SHE). It was the first (most upstream) electrode in the microfluidic channel. Potentiostatic impedance spectra were collected at the  $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$  reversible potential as determined from the average of the anodic and cathodic peak potentials in CVs. This potential was slightly offset from 0.0 V vs IRE (see Fig. 3). The ac amplitude was 5 mV (rms), and the frequency range was from 100 kHz to ca. 0.1 Hz at 20 points per decade. The lower frequency limit was chosen by noting when the impedance was not significantly changed on decreasing the frequency. The flow rate was varied between 1  $\mu\text{L min}^{-1}$  and 300  $\mu\text{L min}^{-1}$  using a syringe pump (Harvard Apparatus PHD 2000).

### 2.3. Modeling

The geometry modeled is shown in Fig. 2, introducing the two dimensionless parameters,  $A (= 6v_{\text{av}}h/D)$ , which is a Péclet number, and  $B (= w/h)$ , which is a geometric parameter. Here,  $v_{\text{av}}$  is the average velocity in the channel,  $h$  is the channel height,  $D$  is a diffusivity, and  $w$  is the electrode width. To model diffusional impedance on a channel electrode, one has to solve the convective-diffusion equation for a 2-D channel, Eq. (2), which assumes laminar flow with a parabolic (Poiseuille) velocity profile.

$$\frac{\partial c_i(x, y, t)}{\partial t} = D_i \frac{\partial^2 c_i(x, y, t)}{\partial x^2} + D_i \frac{\partial^2 c_i(x, y, t)}{\partial y^2} - \frac{6v_{\text{av}}}{h^2} y(h-y) \frac{\partial c_i(x, y, t)}{\partial x} \quad (2)$$

Here,  $c_i$  is the concentration of reactant or product species  $i = \text{R}, \text{P}$ , and  $D_i$  is the diffusivity of species  $i$ . In the presence of the ac perturbation of angular frequency  $\omega$ , the concentration will have the form of Eq. (3).

$$c_i(x, y, t) = c_{i, \text{ss}}(x, y) + \tilde{c}_i(x, y) \exp(i\omega t) \quad (3)$$

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