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Impact of alignment defects of rotating disk electrode on transport properties

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ABSTRACT

The rotating disc electrode (RDE) is by far the most popular of the hydrodynamic electrodes, in which the transport of electroactive species is enhanced by a controlled flow; one of the reasons of this success is its resilience, as the rate of transport of actual RDEs are close to the theoretical predictions. However, if this is true for defect-free electrodes, little is known about the effect of defects on the transport properties of actual RDEs. In this paper, we use state-of-the-art finite volumes computational fluid dynamics simulations to investigate the transport properties of a defect-free cylindrical RDE, and of three RDEs presenting defects that commonly arise from imperfect construction, handling or even just ageing. We show that, while the transport toward the defect-free cylindrical RDE can be considered homogeneous, this is not the case for the other electrodes. We found that the presence of defects has only a minor effect on the average rate of mass-transport of the electrodes, which is what matters for analytical purposes, but that they significantly increase the heterogeneity of mass transport. This heterogeneity can have a significant impact in the context of kinetic studies, especially those in which the response is non-linear with respect to the concentration, like the study of immobilized enzymes using protein film voltammetry.

1. Introduction

Among hydrodynamic electrodes, in which mass-transport of electroactive species toward the electrode is enhanced by a flow of the electrochemical buffer [1–3], the rotating disc electrode (RDE), in which the electrochemical buffer is put in motion by the rotation of the electrode, is by far the most popular. The keys of its success are multiple. RDEs are easy to setup, and have been commercialized for a long time. Their flow and transport properties are very well characterized: Von Karman [4] and later Chochran [5] solved the equations of the movement of a fluid around an infinite planar rotating electrode, and proposed numerical solutions for the velocity fields and developments in the vicinity of the electrode [5]. Levich used these solutions to integrate the diffusive-convective equations for the mass-transport of an electroactive species toward a RDE, yielding the so-called Levich equation [1,6].

While the original equations were derived for an infinite plane, they also apply to real electrodes. The transport properties of actual RDEs were found not to depend much on the details of their implementations: a number of geometries have been used, such as simple rotating cylinders, bell-shaped [7] or conical shaped electrodes [8]. Blurton and Riddiford conducted an extensive experimental study of the influence of the electrode shape on the transport properties, and found only minute differences between the transport properties of the electrodes they tested and the predictions of the Levich equation, in general less than a 5% deviation [9], in spite of large qualitative changes in the flow pattern away from the electrode. Prater and Adams demonstrated that the immersion depth of the electrode has also little effect on mass transport [10]. This resilience arises from the fact that the transport properties are determined by the velocity profiles in a very thin layer of fluid in the vicinity of the electrode, the diffusion boundary layer, which is hardly affected by the specifics of the flow pattern remote from the electrode.

Flow and transport characteristics of real RDEs were also studied using numerical simulations. Using finite volume methods, Mandin and coworkers [11], and Gonzalez and coworkers [12] explored the

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effects of the finitude of the bath on the overall flow. Their results are in good agreement with the flows described by Cochran in the vicinity of the electrode, even if they found large discrepancies with the theoretical predictions in the bulk. Dong and coworkers, using finite elements simulations, obtained similar results [13]. Alexiadis and coworkers addressed the case of a chemical reaction creating bubbles of gas on the surface of the electrode [14]. Overall, the flow patterns predicted by computation fluid dynamics agree well with the very few studies in which the local velocities were measured, be it using Doppler laser anemometry [11] or magnetic resonance imaging [15]. Numerical simulations have also been successfully employed for similar setups, like rotating cylinder (hollow) electrodes [16,17] or rocking disc electrodes [18].

The transport properties of RDEs have so far only been studied on a global scale, by relating an overall current, or an average flux, to the rotation rate and other geometrical properties. Very few studies have considered the possibility of heterogeneous mass transport, probably because this is very hard to address experimentally. From a theoretical point of view, Albery and Bruckenstein showed that the infinite RDE is uniformly accessible, which means that the rate of mass transport is uniform on the electrode surface [19]. Using numerical simulations, Mandin and coworkers noticed that, while the flux towards a cylindrical RDE is mostly homogeneous, it is slightly greater at the center of the electrode [11].

Some authors have also studied the effect of the presence of defects in the electrode, namely the case in which the electroactive part of the rotating cylinder is not centered on the rotation axis (eccentric electrodes). These defects were studied analytically, using the expressions of the velocities derived by Cochran, and confirmed experimentally [20,21]; the studies showed that, up to a certain critical eccentricity, the defect did not impact the transport properties. Note, however, that these studies were based on the flow of an infinite disc. To the best of our knowledge, other kinds of defects have not been studied.

In the present work, we use state-of-the-art finite volume computational fluid dynamics methods to compute the velocity fields and the concentration profiles in a finite cell with an ideal, finite, cylindrical RDE. By cylindrical RDE, we designate the most common shape for commercial RDEs, in which the electrode is a filled cylinder within which a conductor is encased (Fig. 1, this configuration was referred to as “wire electrode” by Azim and Riddiford [7]). We determine the local rate of mass-transport, and show that practical RDEs can also be considered uniformly accessible. We also study electrodes with three distinct defects: an eccentric electrode (in which the rotation axis and symmetry axis are just parallel, not identical), an electrode whose surface is inclined from the normal to the rotation axis, and an electrode whose symmetry axis is inclined with respect to its rotation axis. We show that the presence of defects affects the overall transport properties, and result in possibly large heterogeneities in the local rate of mass transport, especially for the last two defects, despite only moderate changes in the average mass transport rate.

2. Theory for an infinite rotating disc electrode

2.1. Fluid motion

Let us first consider an infinite planar electrode rotating at an angular velocity ω. This geometry was first addressed by Von Karman [4] and then Cochran [5], who showed that the radial (v_r) and axial (v_z) components of the velocity can be put under the following form, in cylindrical coordinates:

$$v_r = r\omega F(\zeta) \tag{1}$$

$$v_z = (\nu\omega)^{1/2} H(\zeta) \tag{2}$$

where r and z are the respectively the radial and axial cylindrical coordinates, $\zeta = (\omega/\nu)^{1/2} z$ is the dimensionless distance normal to the surface of the electrode, F is the dimensionless radial velocity; ν is the kinematic viscosity and H is the dimensionless axial velocity. Cochran solved these equations using the following boundary conditions:

$$\text{At } \zeta = 0;\ F(0) = H(0) = 0 \tag{3}$$

$$\text{At } \zeta = \infty;\ F(\infty) = 0 \tag{4}$$

He computed numerically the values of $F(\zeta)$ and $H(\zeta)$ and derived the following asymptotic expressions for $H(\zeta)$ for the low and the high values of ζ:

$$H(\zeta) = -0.51\zeta^2 + \frac{1}{3}\zeta^3 - \frac{0.616}{6}\zeta^4 + \ldots \text{for } \zeta \ll 1 \tag{5}$$

$$H(\zeta) = -H_\infty = -0.88446 \text{ for } \zeta \gg 1 \tag{6}$$

As the axial velocity tends to a constant at high distances from the electrode, the flow can be considered as a jet [5].

Feldberg and coworkers [22] proposed an interpolation of Cochran's numerical results for $H(\zeta)$ that is valid for all values of ζ:

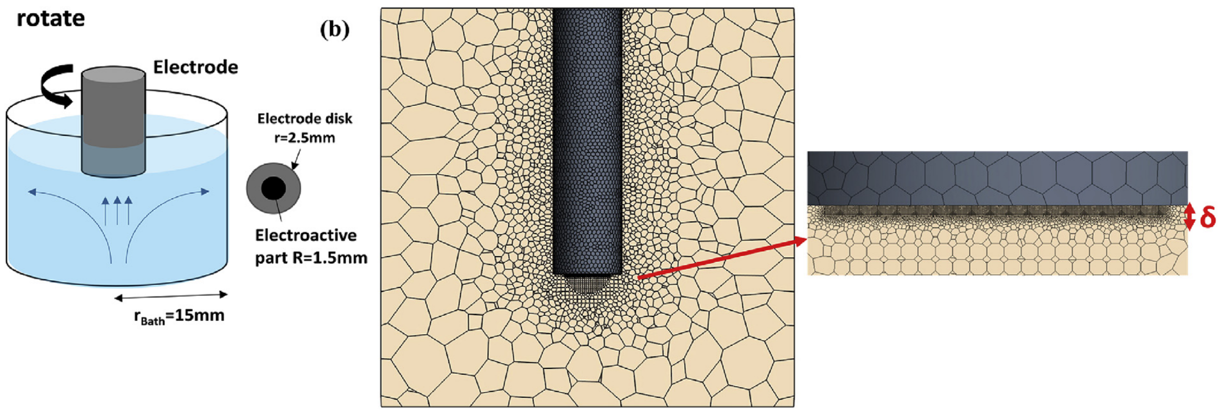

Fig. 1. (a) Schematic presentation of an electrochemical cell making use of a perfectly cylindrical electrode (b) Representation of the 3D mesh used in our calculations, with a detailed view near the electrode bottom surface showing the high number of mesh elements within the diffusion boundary layer.