Electrochimica Acta 55 (2010) 5629–5635

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Reference values of the chronoamperometric response at cylindrical and capped cylindrical electrodes

Dieter Britz [a,*], Ole Østerby [b], Jörg Strutwolf [c]

[a] Department of Chemistry, Aarhus University, 8000 Århus C, Denmark
[b] Department of Computer Science, Aarhus University, 8200 Århus N, Denmark
[c] Tyndall National Institute, Lee Maltings, Cork, Ireland

ARTICLE INFO

Article history:
Received 10 February 2010
Received in revised form 20 April 2010
Accepted 24 April 2010
Available online 4 May 2010

Keywords:
Computational electrochemistry
Finite difference digital simulation
Cylindrical electrodes
Reference currents
Cylindrical transport

ABSTRACT

This work provides accurate solutions of the cylinder flux function $I(0, 1; T)$, first solved by Jaeger and Clarke, which can serve as reference values for electrochemical amperometric diffusion limited currents at a cylinder, as well as heat fluxes under equivalent conditions (fixed temperature at the cylinder surface). For the capped cylinder of varying lengths, reference values of time-dependent electrochemical currents are provided. Steady state currents at capped cylinders are presented and a function is provided that fits the simulated values to within 1%. All of these are more accurate than in previous works.

1. Introduction

This paper is concerned with cylindrical electrodes, both the infinitely long cylinder and what will be called the "capped cylinder", as seen in Fig. 1. The electrode is protruding from a planar insulating base of infinite extent and has radius a and height h. Both the cap and shank are conducting and thus, as pointed out by Dickinson et al. [1] and Ferrigno et al. [2], who simulated the chronoamperometric response of capped cylinders, there are contributions to the current from both. As h becomes smaller, the electrode approaches the form of a planar protruding disk [2,3] and, at the limit $h \to 0$, it becomes an embedded disk. If h is large compared with a, we have "whiskers" [4]; these are often made from carbon fibres cut with a scalpel [5–8] or carbon-coated metal wires used for hot-wire electrochemistry [9]. As $h \to \infty$, the capped cylinder approaches an infinite cylinder, which we will simply refer to as a cylinder in the following. The extensive series of articles of the Wightman and coworkers [10–15] (to cite just a few) on the use of cylindrical electrodes in neuroscience attest to the application of these electrodes in practice. McNally et al. [16] developed a conical-tip electrode (recently simulated [17]) which they considered as close to cylindrical and applied an approximate analytical solution due to Amatore [18]. They later used this electrode as a probe into rat brains [19].

Capped cylinders have a steady state current response, whereas cylinders do not, although the response of a cylinder decays very slowly at long times. For this reason, the cylinder response at long times is sometimes called "quasi-steady state" [20].

There have been simulation studies of cylinders [21] and capped cylinders [1,2]. Szabo et al. [21] presented a table of cylinder current responses to a diffusion limiting potential step, within a certain range of time values. They related these to the analytical solution found by Jaeger [22], in the form of an infinite integral, tabulated by Jaeger and Clarke [23], see below.

We find (as did Aoki et al. [24]) that the tables of Jaeger and Clarke [23] contain some inaccuracies at longer times, and they only presented three decimal figures over a limited time range. There have been, to our knowledge, no published accurate steady state current values for capped cylinders nor accurate time-dependent current responses at capped cylinders. Ferrigno et al. [2] provided steady state currents for only five H values and we believe these to be very approximate. Dickinson et al. [1] provided only a graph of steady state current densities.

The aim of this paper is thus to provide reference values for all of these over a wide time range and steady state current responses over a large range of h/a, and to test the accuracy of those values that have been published previously.

* Corresponding author. Tel.: +45 89423874; fax: +45 86196199.
E-mail addresses: britz@chem.au.dk (D. Britz), oleby@cs.au.dk (O. Østerby), jorg.strutwolf@tyndall.ie (J. Strutwolf).

0013-4686/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2010.04.096

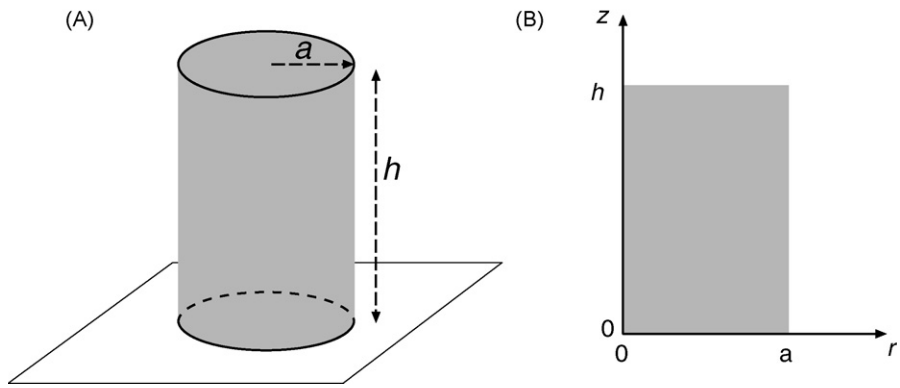

Fig. 1. Capped cylinder electrode (A); geometry for simulation (B).

2. Theory

As seen in Fig. 1(B), we have cylindrical coordinates r in the radial direction and z along the cylinder axis. The capped cylinder has radius a, and height h above the insulating plane. The following normalisations are convenient:

$$C = \frac{c}{c^*} \tag{1a}$$

$$Z = \frac{z}{a} \tag{1b}$$

$$R = \frac{r}{a} \tag{1c}$$

$$T = \frac{Dt}{a^2} \tag{1d}$$

$$H = \frac{h}{a} \tag{1e}$$

where c is the concentration of the diffusing species, c^* its bulk value, D the diffusion coefficient and t the time.

The diffusion equation for the cylinder is then, in dimensionless form,

$$\frac{\partial C}{\partial T} = \frac{\partial^2 C}{\partial R^2} + \frac{1}{R}\frac{\partial C}{\partial R} \tag{2}$$

(the coordinate Z is not involved here, as no gradients in that direction are assumed, and H is not relevant). Boundary conditions for a diffusion limiting chronoamperometric experiment are

$$T < 0, \;\; \text{all } R > 1: \quad C = 1 \tag{3a}$$

$$T \geq 0, R = 1: \quad C = 0 \tag{3b}$$

$$T \geq 0, R \to \infty: \quad C = 1. \tag{3c}$$

The dimensionless current I_{cyl} per unit length is given by

$$I_{cyl} = 2\pi \left.\frac{\partial C}{\partial R}\right|_{R=1} \tag{4}$$

which yields the actual current at a cylinder section of length l

$$i_{cyl} = 2\pi nFDla \left.\frac{\partial c}{\partial r}\right|_{r=a} = nFDlc^* I_{cyl} \tag{5}$$

in which n is the number of electrons transferred in the reaction and F is the Faraday constant.

For the capped cylinder we must also consider the cap, and the system now involves the coordinate Z, so that the diffusion equation is

$$\frac{\partial C}{\partial T} = \frac{\partial^2 C}{\partial Z^2} + \frac{\partial^2 C}{\partial R^2} + \frac{1}{R}\frac{\partial C}{\partial R} \tag{6}$$

with boundary conditions for a diffusion limiting chronoamperometric experiment being

$$T < 0, \; 0 \leq Z \leq H, \; R > 1: \quad C = 1 \tag{7a}$$

$$T < 0, \; Z > H, \; \text{all } R: \quad C = 1 \tag{7b}$$

$$T \geq 0, \; 0 \leq Z \geq H, \; R = 1: \quad C = 0 \tag{7c}$$

$$T \geq 0, \; Z = H, \; 0 \leq R \leq 1: \quad C = 0 \tag{7d}$$

$$T \geq 0, R \to \infty, \; Z \to \infty: \quad C = 1. \tag{7e}$$

The dimensionless current for the capped cylinder I_{cap} is the sum of the contributions from the shank and top,

$$I_{cap} = 2\pi \int_0^H \left.\frac{\partial C}{\partial R}\right|_{R=1} \mathrm{d}Z + 2\pi \int_0^1 R \left.\frac{\partial C}{\partial Z}\right|_{Z=H} \mathrm{d}R \tag{8}$$

yielding the actual current as

$$i_{cap} = nFDc^* I_{cap}. \tag{9}$$

The capped cylinder has a steady state, unlike the infinite cylinder. This can be computed by solving the equation

$$0 = \frac{\partial^2 C}{\partial Z^2} + \frac{\partial^2 C}{\partial R^2} + \frac{1}{R}\frac{\partial C}{\partial R} \tag{10}$$

with the boundary conditions

$$0 \leq Z \leq H, \; R = 1: \quad C = 0 \tag{11a}$$

$$Z = H, \; 0 \leq R \leq 1: \quad C = 0 \tag{11b}$$

$$R \to \infty, \; Z \to \infty: \quad C = 1. \tag{11c}$$

3. Some solutions

3.1. The cylinder case

The partial differential Eq. (2) also applies to heat transport and in that area has been considered much earlier. Jaeger [22] and Jaeger and Clarke [23] presented solutions to the problem, with essentially the same Dirichlet conditions as given by (3a)–(3c). They cite even earlier work on the analytical solution by others (and Jaeger), for example, Nicholson [25], who derived (almost) the same function. In the present context, we have the solution for the dimensionless current at a unit length of the cylinder, following Szabo et al. [21],

$$I_{cyl} = 2\pi f(T) \tag{12}$$

where [22]

$$f(T) = \frac{4}{\pi^2} I(0, 1; T) \tag{13}$$