



# Equality of diffusion-limited chronoamperometric currents to equal area spherical and cubic nanoparticles on a supporting electrode surface



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## ABSTRACT

We computationally investigate the chronoamperometric current response of spherical and cubic particles on a supporting insulating surface. By using the method of finite differences and random walk simulations, we can show that both systems exhibit identical responses on all time scales if their exposed surface areas are equal. This result enables a simple and computationally efficient method to treat certain spherical geometries in random walk based noise investigations.

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## 1. Introduction

Random walk simulations provide a versatile tool for a variety of applications in electrochemistry [1–5]. Recent advances in computational power and the wide availability of multi-core systems [6] and massively parallelised graphics processing units (GPUs) [7,8] opened up new options for high-performance simulations involving large numbers of molecules as well as a high resolution. Hereby, random walks can particularly be employed to model mesoscopic effects as well as noise characteristics of nanoscale sensors that cannot be simulated through numerical methods based on solutions of differential equations.

However, even though random walks are successfully applied in many studies, their use may still remain challenging in certain geometries. Difficulties mostly arise from the general concept of the random walk: in random walk simulations, molecules are typically displaced by a random vector of a fixed length  $dr$  at a frequency of  $1/dt$ , where  $dr$  and  $dt$  fulfil

$$dr = \sqrt{2nDdt} \quad (1)$$

in the  $n$ -dimensional case, where  $D$  represents the diffusion coefficient. However, this equation is a direct consequence of the general solution of the diffusion equation, which is only valid in absence of physical boundaries. While this can be compensated in the case of flat surfaces [6], rough or porous surfaces can only be modelled provided  $dr$  is significantly smaller than the investigated structure and appropriate boundary conditions have been applied. Furthermore,

surfaces that are curved in regard to the displacement vector's coordinate system are difficult to model, since boundary conditions have to be separately defined for every single grid point. This is, for instance, the case for the later discussed geometry of a spherical electrode in a Cartesian coordinate system.

An alternative approach to electrochemical simulations is given by the method of finite differences, which has been used in a wide range of applications during recent years [9–14]. In comparison to random walks, it is a relatively fast method for the investigation of electrochemical systems. However, since the locations of single molecules are described through probability density functions that spread across the whole simulated space, stochastic processes in the mesoscopic regime and, hence, noise characteristics of electrochemical sensors cannot be analysed.

Here, we address the modelling of nanosphere electrodes through random walks. Investigated spheres are mounted on an insulating flat surface, which is a typical experimental setting for electrodes that are modified with nanoparticles or certain nanoimpact setups. While previous attempts at equivalence problems focused on the comparison between microdisc- and hemispherical electrodes [15] and demonstrated that in this case equal 'superficial radii' lead to equal steady-state voltammograms [16], we here find an equivalent for the direct modelling of the sphere electrode through the random walks in Cartesian coordinates. We first calculate an exact solution for a single sphere via finite differences before we fit this result to cubic electrodes that were modelled through random walks. By this method, we find an equivalent cube that features an identical chronoamperometric current response. The presented equality holds true on all time scales and is independent of the electrode size. Hence, all findings are equally applicable to microparticles or even larger particles.

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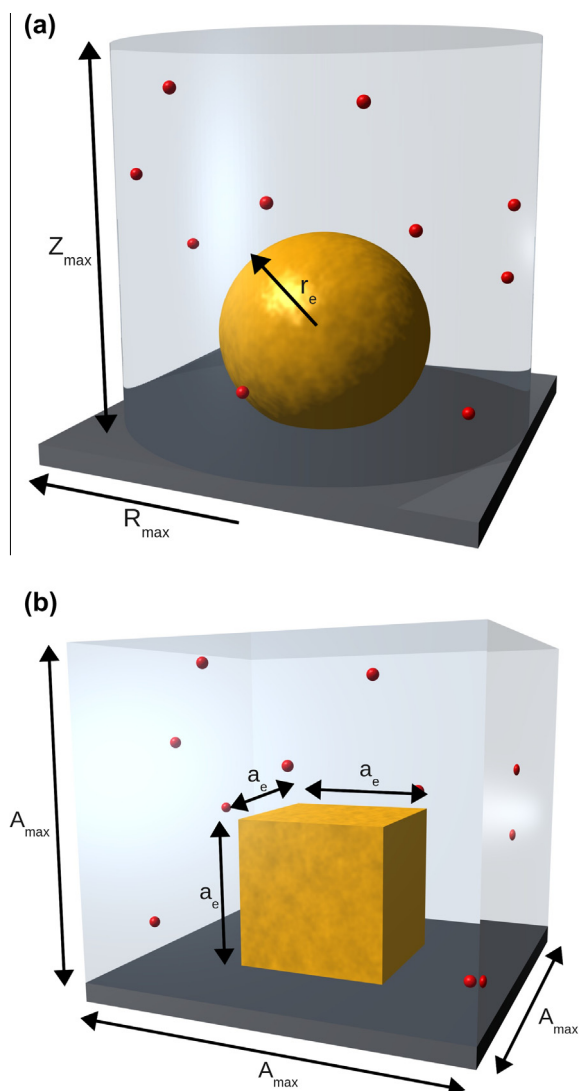
## 2. Theoretical model

The model considered is a simple one-electron reduction process,



where molecules are assumed to react immediately and fully upon contact with the electrode, that is to say the process is diffusion controlled. An excess amount of supporting electrolyte is also considered to be present in solution, suppressing electric fields and ensuring that mass transport is limited to diffusive processes. Hence, electrode currents are solely limited by the analyte's diffusive mass transport towards the electrode surface, which is a good approximation for many diffusion-limited chronoamperometric experiments.

In this Letter, we investigate two electrode geometries: a spherical and a cubic electrode on an insulating surface, as shown in Figure 1. For the sphere on an insulating surface, cyclic voltammetry has previously been simulated [17] using a Fickian diffusion model and the finite difference method, which is here modified to simulate chronoamperometry. A stochastic random walk model



**Figure 1.** Schematic of the two simulated geometries: a spherical (a) and a cubic (b) electrode on a supporting, electrochemically inactive surface. Dimensions are not to scale.

is used to simulate chronoamperometry at a cubic electrode, and the correspondence between the two cases is investigated. Simulation and computational procedures are detailed below.

### 2.1. Finite differences

In order to simulate electrochemistry at an isolated spherical electrode resting on an insulating surface, symmetry can be exploited to reduce the problem to two dimensions. A schematic illustration of this is shown in Figure 2.

Fick's second law for diffusion in cylindrical space is given by:

$$\frac{\partial c}{\partial t} = D \left( \frac{\partial^2 c}{\partial r^2} + \frac{\partial^2 c}{\partial z^2} + \frac{1}{r} \frac{\partial c}{\partial r} \right) \quad (3)$$

To simplify the model, dimensionless parameters are used in simulations. Concentrations are taken relative to the bulk concentration of the electroactive species ( $c^*$ ), and the relevant diffusion coefficient taken to be unity. Dimensionless parameters are defined in Table 1.

Substituting these parameters into the mass transport equation, the following equation is obtained:

$$\frac{\partial C}{\partial \tau} = \left( \frac{\partial^2 C}{\partial R^2} + \frac{\partial^2 C}{\partial Z^2} + \frac{1}{R} \frac{\partial C}{\partial R} \right) \quad (4)$$

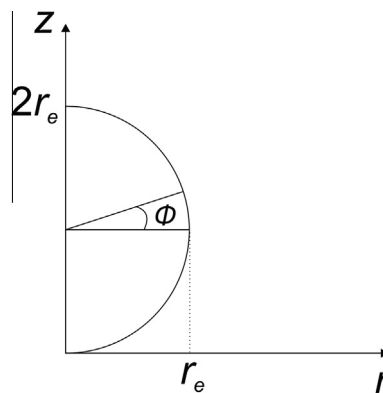
This must be solved over all space subject to appropriate boundary conditions. After the beginning of the experiment at  $\tau = 0$ , the electrode is biased to a potential to oxidise the electroactive species at a mass transport controlled rate. The concentration at the electrode surface can therefore be defined as zero:

$$C_{R^2+(Z-1)^2=1} = 0 \quad (5)$$

The outer edges of the simulation space are set to be well outside the depletion layer around the electrode:

$$R_{\max} = 1 + 6\sqrt{\tau_{\max}} \quad (6)$$

$$Z_{\max} = 2 + 6\sqrt{\tau_{\max}} \quad (7)$$



**Figure 2.** Schematic diagram of the simulation space used to simulate an isolated spherical electrode on an insulating surface.

**Table 1**  
Normalised parameter definitions.

Normalised parameter	Definition
$C$	$\frac{c}{c^*}$
$\tau$	$\frac{D}{r_e^2} t$
$R$	$\frac{r}{r_e}$
$Z$	$\frac{z}{r_e}$

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