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Diffusional impacts of nanoparticles on microdisc and microwire electrodes: The limit of detection and first passage statistics

Shaltiel Eloul, Enno Kätelhön, Christopher Batchelor-McAuley, Kristina Tschulik, Richard G. Compton *

Department of Chemistry, Physical and Theoretical Chemistry Laboratory, South Parks Road, Oxford University, Oxford OX1 3QZ, United Kingdom

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ABSTRACT

We derive approximate expressions for the average number of diffusive impacts/hits of nanoparticles on microdisc and microwire electrodes for the case where the impact leads to the loss of the nanoparticles from solution either via irreversible adsorption or complete electro-dissolution. The theory can also be applied to submicrometre size electrodes (nano-electrodes). The resulting equations can be utilised to analyse the number of impacts and its variance in the 'nano-impact' experiment. We also provide analytical expressions for the first passage time of an impact for dilute nanoparticle solutions in the continuum limit of Fickian diffusion. The expressions for the first passage times are used to estimate the lower limit of detection in ultra-dilute nanoparticle solutions for typical nano-impact experiments, and show the advantage of using microwire electrodes in ultra-dilute solutions or solutions containing larger nano-particles.

1. Introduction

Since nanoparticles are commonly used in many industrial and research applications, there is a strong demand for fast and cost-efficient characterisation methods on the respective particle's size and shape which are crucial requirements for understanding their physiochemical function in nanomaterials and, hence, for further developments in this field [1,2]. Alongside this, there is a growing interest in efficient ways to track and detect the large scale release of nanoparticles into the environment, especially in the light of rising concerns regarding the possible toxicity of various nano-sized particles [3,4].

The electrochemical detection of nanomaterials via the 'nano-impact' method offers significant advantages over conventional optical techniques, including the ability to analyse nanoparticles in-situ without the need for drying or modifying the investigated solution [5,6]. In the 'nano-impact' method, nanoparticles diffuse freely in an electrochemical cell, and are detected via their stochastic hits on an electrode, which may also be referred to as an 'impact'. Typically, micrometre sized electrodes are used to avoid large capacitance noise [7,8] or simultaneous impacts. During an impact event, the impacting particle may be involved in an electrochemical reaction at the electrode surface, which may result in a direct oxidation of the nanoparticle itself, while a corresponding current is measured [9–11]. Characteristics of the peak provide direct information about the individual nano-particle size, and the average number of impacts as a function of time can be described by Fick's diffusion equation, providing a practical way to measure the concentration of nanoparticles in a sample. Another possible reaction mechanism are mediated reactions, where, during the time of contact, an electrochemical reaction on the surface of the temporarily-biassed nanoparticle is enabled and recorded. This allows for the investigation of the electrocatalytic activity of the particle [6,12] and delivers information on the nanoparticle's Brownian motion at the electrode surface [13,14]. The nano-impact method has been used to identify various types of nanoparticles [15,5,10,16,17], and to provide fundamental insights into chemical mechanisms [18–22], agglomerations and aggregations [23,24], and the sensing at low nanoparticle concentrations for environmental studies [10].

Recently, we have derived probability expressions using Fick's second law to predict the number of diffusional impacts of nanoparticles that are fully dissolved on spherical and planar electrodes [25]. It was also shown how the variance of the probability expressions behaves in the Poisson limit [25]. Furthermore, analytical expressions were derived for the average first passage time as an indication of the lower concentration limit of detection. Having reported in depth the comparison between the radial and linear diffusion regime for the case of spherical and planar electrodes, in the present paper we adapt this method to microdisc and microcylinder geometries, as the importance of such electrodes for nano-impacts is enormous: The use

* Corresponding author.
E-mail address: richard.compton@chem.ox.ac.uk (R.G. Compton).

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of microdisc electrodes is the common way of measuring impacts in the radial diffusion regime [10,5,11,15], and by utilising microwire (microcylinder) electrodes the detection of nano-particles in the femto-molar concentration region is enabled [26]. This study is focused on impacts which lead to the loss of the nanoparticles from solution, either via irreversible adsorption or electro-dissolution. This assumption allows us to investigate the case of diffusion towards a fully absorbing wall [25].

2. Theory

This study is divided into the cases of (*i*) microdisc and (*ii*) microwire electrodes. In both cases we start with solutions of Fick's diffusion equation:

$$\frac{\partial c}{\partial t} = D\nabla^2 c \tag{1}$$

where c is the concentration and D is the diffusion coefficient of the nanoparticles. Previously known analytical expressions, which are approximate solutions for the mass transport in chronoamperometry, are employed as a starting point.

2.1. Microdisc electrode

We assume a diffusion controlled process of independent particles in a cell that contains a microdisc electrode. In cylindrical coordinates the diffusion equation is given by:

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

Since the considered system features symmetry with respect to the z-axis, we can neglect the angular terms of the Laplacian. Further assuming destructive impacts, the boundary conditions are given by a fully absorbing surface, where the concentration $c(r,0,t) = 0$, on the electrode surface and $\partial c/\partial z = 0$ at all other boundaries. Far from the electrode, at $z, r \to \infty$, we set the bulk concentration $c = c^*$ at any time and the concentration in all spaces is also set to c^* at $t = 0$. Saito found the steady state flux towards a disc electrode under such conditions to be [27]:

$$J(t\to\infty) = 4Dc^* r_d \tag{3}$$

where r_d is the disc radius. An approximate solution valid for all time is given by the Shoup and Szabo equation [28]:

$$J = 4Dc^* r_d f(\tau) \tag{4}$$

where

$$f(\tau) = 0.7854 + 0.8862\tau^{-1/2} + 0.2146\exp\left(-0.7823\tau^{-1/2}\right) \tag{5}$$

and τ is a dimensionless time parameter, which is defined as:

$$\tau = 4Dt/r_d^2. \tag{6}$$

This convenient expression is widely used and provides accuracy within 0.6% compared to simulations by Heinze [29]. Via a previously discussed approach [25], we utilise this solution to study the probability of finding $\hat{N}_{hits}(t)$ (we use the term 'hits' in the symbol for consistency with previous work [25], but in the text we refer to 'hit' as an 'impact') within the time t after the experiment was started. In particular, we replace the concentration with the probability density (p^*) of finding a particle at t_0 at a given position and the flux with the accumulated number of impacts ($\hat{N}_{hits}(t)$) in a dilute solution:

$$J = \frac{d\hat{N}_{hits}(t)}{dt} = 4Dp^* r_d f(\tau). \tag{7}$$

Integrating over time gives the accumulated number of impacts:

$$\hat{N}_{hits}(t) = \int_0^t 4Dp^* r_d f(\tau)dt. \tag{8}$$

In order to solve this equation, we transform the integration variable t to τ:

$$\hat{N}_{hits}(t) = \int_0^\tau p^* r_d^3 f(\tau)d\tau. \tag{9}$$

The integration of the Shoup–Szabo equation can be calculated via a power series expansion of the exponential term:

$$\begin{aligned}&\beta\exp\left(-\alpha\tau^{-1/2}\right)\\ &= \beta\left(1-\alpha\tau^{-1/2} + \frac{\alpha^2}{2!}\tau^{-1} - \frac{\alpha^3}{3!}\tau^{-3/2} + \ldots + \frac{(-\alpha)^n}{n!}\tau^{-n/2}\right).\end{aligned} \tag{10}$$

Integration then gives:

$$\hat{N}_{hits}(t) = p^* r_d^3 F(\tau) \tag{11}$$

where:

$$\begin{aligned}F(\tau) &= \tau + 1.437\sqrt{\tau} + 6.567\cdot 10^{-2}\ln\tau\\ &\quad + \frac{3.425\cdot 10^{-2}}{\sqrt{\tau}} - \frac{3.349\cdot 10^{-3}}{\tau}\end{aligned} \tag{12}$$

when taking into account the first five terms. This expression was already derived and is used for determining concentration in the 'nano-impact' experiment [10]. Under common experimental conditions, $\tau \gg 0$, it is only necessary to use the first three terms of the Taylor series, as the fourth and above terms add less than 0.6% to the accuracy. Therefore, the solution for the average number of impacts is:

$$\hat{N}_{hits}(t) = p^* r_d^3\left(\tau + 1.437\sqrt{\tau} + 6.567\cdot 10^{-2}\ln\tau\right),\ \tau = 4Dt/r_d^2. \tag{13}$$

The average first passage time can then be found by solving $\hat{N}_{hits}(t) = 1$:

$$\frac{1}{p^* r_d^3} = \tau + 1.437\sqrt{\tau} + 6.567\cdot 10^{-2}\ln\tau. \tag{14}$$

Boika and Bard recently suggested an approach to finding the first passage time of impacts on a microdisc electrode [30] and predict an inverse proportionality between the number of impacts and the nanoparticle concentration. The above analytical solution agrees with this finding under certain experimental conditions: At large τ, i.e. $\tau \gg 100$, Eq. (14) can be simplified to an inverse linear relation of concentration with time:

$$\frac{1}{4Dp^* r_d} = t. \tag{15}$$

If we, however, calculate τ for a typical nanoimpact experiment using a microdisc electrode of the radius 5 μm and a particle concentration of 5 pM, the average first passage time is found to be $\tau = 1.12$ using the approach presented here, while neglecting the non-linear terms in Eq. (14) leads to a value of $\tau = 2.65$, which deviates by more than 100%. The dependency of the first passage time on concentration is detailed later in the Discussion section.