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The effect of near wall hindered diffusion on nanoparticle–electrode impacts: A computational model

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ABSTRACT

The influence of near wall hindered diffusion of nanoparticles on anodic particle coulometry (APC) is investigated. In an APC experiment, an electrode in a solution of nanoparticles is subject to a potential step from a value where no oxidation of nanoparticles occurs, to one where oxidative dissolution of nanoparticles is transport controlled. Nanoparticle–electrode impacts are then observed as spikes in the measured current. The area under these spikes corresponds to the charge transferred during the nanoparticle oxidation. A computational model is developed to simulate APC experiments, including the effect of near wall hindered diffusion. It is shown that this new, more complete picture is able to successfully simulate the experimental APC of nickel nanoparticles. It is also shown that a detailed, quantum mechanical tunnelling model is not required to describe the destructive oxidation of nanoparticles; an alternative simple impact model can successfully simulate experimental data.

1. Introduction

The detection and characterisation of metal nanoparticles is of great importance due to their potentially toxic effects on human health [1,2] and the environment [3,4]. In order to detect nanoparticles electrochemically, an understanding of their mass transport properties and mechanisms of oxidation is important.

“Anodic particle coulometry” (APC) has been used to characterise gold [5], silver [6,7], nickel [7] and copper [8] nanoparticles. In these experiments, a potential step is applied to an electrode in a solution containing nanoparticles from a potential where no current is measured to one where oxidation and dissolution of the nanoparticles occurs at a mass transport controlled rate, and the current passed measured as a function of time. When a nanoparticle approaches the electrode and is oxidised, a spike in the measured current is seen. This is shown schematically for a nickel nanoparticle in Fig. 1. The frequency of and charge under the spikes yields information about the nanoparticles under study. Measuring the charge passed gives information on the number of atoms in a nanoparticle, and hence its size and the degree of aggregation between nanoparticles. In the case of silver [6] and gold [5] this analysis showed significant aggregation occurring between nanoparticles, but not in the case of nickel [7]. Fig. 2a shows a schematic of typical nanoparticle APC experimental results. The area under the spikes corresponds to the charge transferred during the impact event. Fig. 2b shows a schematic of the cumulative number of spikes observed and total charge passed over time in an APC experiment (the charge passed is the integral of the current time plot minus the non-Faradaic background current, or the cumulative number of spikes observed times the charge passed per nanoparticle oxidation). It has been shown that an analysis of the cumulative number of spikes observed over time can be used to estimate an unknown concentration of nanoparticles [7].

These previous electrochemical studies have assumed that the diffusion coefficient of nanoparticles of a given size is constant, whether the nanoparticle is near the electrode surface or in bulk solution. However, it has been shown theoretically [9–11] and experimentally [12–14] that this is not the case, and that the diffusion of spherical particles in solution is hindered near a solid wall, due to hydrodynamic drag [13]. The diffusion coefficients must be multiplied by a hindrance factor:

$$D(r) = \lambda D(\infty) \tag{1}$$

where $D(r)$ is the diffusion coefficient at distance R from the wall, $D(\infty)$ is the diffusion coefficient infinitely far from the wall (given by the Stokes–Einstein equation), and λ is the hindrance factor. For motion perpendicular to a wall, the hindrance factor is given by:

$$\lambda = \frac{6h^2 + 2ah}{6h^2 + 9ah + 2a^2} \tag{2}$$

where a is the radius of the nanoparticle, and h is the distance between the edge of the nanoparticle and the wall. Note that, when a is zero, λ is equal to 1 for all values of h. It is reasonable to expect that this must affect the analysis of the electrochemistry of nanoparticles, and this paper investigates whether or not this is the case.

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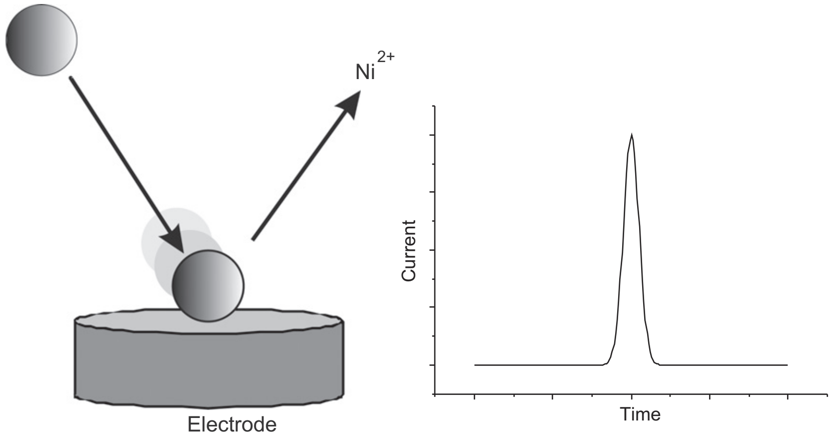

Fig. 1. Schematic diagram of a single impact event. As the nanoparticle approaches the electrode, it is oxidised and dissolved, resulting in a spike in the current time plot.

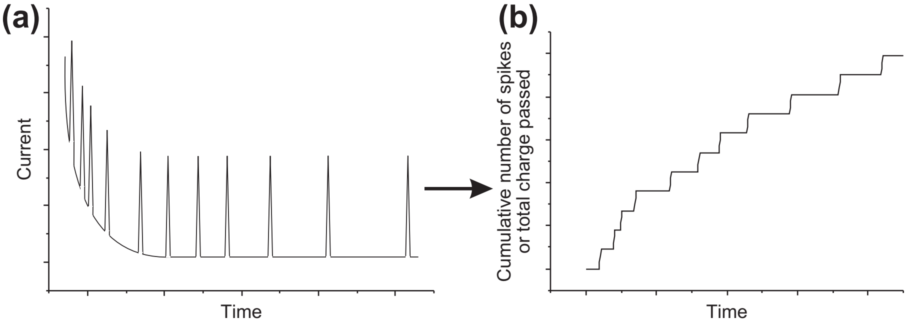

Fig. 2. (a) Schematic of a nanoparticle APC experiment. Each spike corresponds to a nanoparticle impact. (b) Schematic of the cumulative number of spikes observed or the total charge passed as a function of time.

In this paper, we study the APC of nickel nanoparticles (NiNPs), and develop a more complete computational model to simulate these experiments, including near-wall hindered diffusion in the model for destructive oxidation of the nanoparticles. The model is used to successfully simulate APC experiments by measuring the flux of nanoparticles approaching the electrode.

2. Theory

We develop a model to simulate the destructive oxidation of nanoparticles, via anodic particle coulometry (APC), including the effects of hindered diffusion at a hemispherical electrode. In an APC experiment, the potential applied to the electrode is stepped from one where no oxidation occurs, to one where oxidation is transport controlled.

Approximating the nanoparticle's transport to behave in a statistical manner [15,16] we can apply Fick's second law (in spherical coordinates) and avoid time consuming stochastic calculations:

$$\frac{\partial c}{\partial t} = \nabla(D\nabla c) \tag{3}$$

which in spherical space, and assuming D is a function of r, is given by:

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r}\right) + \frac{\partial D}{\partial r}\frac{\partial c}{\partial r} \tag{4}$$

where c is concentration, t is time, r is the radial distance from the centre of the electrode, and D is the diffusion coefficient. All symbols are defined in Table 1.

Since we are using a Fickian model of diffusion rather than a stochastic one, the simulations will generate a smooth, continuous current rather than discrete impact spikes. We can convert the current produced into the cumulative number of impact spikes expected in a simple way. The current, I, can be converted into a number of particles per second, P:

$$P = \frac{N_A I}{F} \tag{5}$$

where N_A is the Avogadro constant and F is the Faraday constant. This direct proportionality means that the currents produced by the simulations can readily be thought of as directly reflecting impact spike frequency. The cumulative number of impact spikes expected in the APC experiment at time t, $N(t)$, can the be calculated by integrating P with respect to t:

Table 1
Dimensional parameters.

Parameter	Description	Units
a	Nanoparticle radius	m
D	Diffusion coefficient	$m^2\ s^{-1}$
D^{bulk}	Bulk diffusion coefficient	$m^2\ s^{-1}$
C	Concentration	$mol\ m^{-3}$
C^*	Bulk solution concentration	$mol\ m^{-3}$
η	Solution viscosity	Pa s
h	Electrode to nanoparticle edge distance	m
J	Flux	$mol\ m^{-2}\ s^{-1}$
k_B	Boltzmann constant ($\approx 1.3806 \times 10^{-23}$)	$J\ K^{-1}$
n	Number of electrons transferred	Unitless
r_e	Electrode radius	m
t	Time	s
T	Temperature	K