Single-entity electrochemistry: Diffusion-controlled transport of an analyte inside a particle

Haonan Le, Chuhong Lin¹, Enno Kätelhön, Richard G. Compton*

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

Abstract

Recent progress in nanoparticle electrochemistry has enabled the detection of individual nanoparticles and the characterisation of nanoparticle populations. The nano-impact technique, in which individual nanoparticles diffusively reach and react at an electrode, has advanced to allow exciting insights into reaction mechanisms from inference of the progress of the reaction of an individual nanoparticle as reflected in the electrode current-time response.

This work characterises the diffusion-limited depletion of an analyte inside a nanoparticle which is initially doped with this analyte and, upon impact at the electrode, may deform, adsorb, and react. Two different theoretical models are contrasted and we reveal that key physical quantities such as the contact area of the particle and electrode can be extracted from experimental data in favourable cases. In addition, a dimensional analysis of the theoretical model is presented which simplifies the analysis of experimental data by reducing the number of required fitting parameters.

Keywords:

Single nanoparticle, Diffusion-controlled transport, Nano-impact, Modelling, Chronoamperometry

*Corresponding author

Email address: `richard.compton@chem.ox.ac.uk` (Richard G. Compton)

¹Current address: Institute of Intelligent Machines, Chinese Academy of Sciences, No. 350, Shushan Road, Hefei, Anhui, 230031, China

1. Introduction

During recent years, the nano-impact method has evolved into a powerful tool for the detection and characterisation of individual nanoparticles as discussed in the reviews[1–11]. This is not at least due to the method’s striking simplicity compared to other methods used in the characterisation of nanomaterials: An electrode is set in contact with a solution of analyte nanoparticles and biased versus the solution potential. By virtue of Brownian motion, individual nanoparticles may then reach the electrode where they may either react due to their intrinsic electrochemical properties or mediate a reaction between the electrode and species present in the solution. Throughout the experiment, individual nanoparticle reactions are monitored via the electrode current and provide valuable insights into the properties of the investigated solution. The rate of individual ‘nano-impacts’ can be measured to determine the particle concentration and, in many cases, the size distribution[12–14] of a nanoparticle population can be measured by simple integration of the overall charge transferred per spike.

More recently the analysis of spike shapes was explored theoretically[15] to enable the extraction of information beyond particle concentrations and size distributions from experimental data. Various methods have been validated and used for the analysis of diverse experiments including the study of the electro-doping[16] processes in individual nanoparticles, lithium deinsertion[17] processes in battery materials, the characterisation of the electro-dissolution[18] of individual silver nanoparticles, the detection of viruses via antibodies[19], the determination of reaction kinetics [8] and diffusion coefficients[20], the label-free detection of living bacteria[21] and an analysis of activity fluctuations of individual enzymes[22] near an electrode.

Nafion polymers have previously been modified with redox-functional ions such as methyl viologen dication (MV^{2+})[23, 24] and tris-(2,2’-bipyridyl)-dichlororuthenium dication ($Ru(bpy)_3^{2+}$)[25–27] to realise applications such as the catalysis of oxalate oxidation[25]. More recently, literature reported experimental work on the diffusion of MV^{2+} in MV^{2+} -doped ‘soft’ Nafion particles[28] and the application of such nanoparticles in the electro-catalytic reduction of oxygen [29]. The contact areas of these ‘soft’ particles with the electrode herein play a significant role in the electrochemical reaction as shown in studies of the contact resistance and contact area[30, 31] while related physiochemical processes still remain to be explored. Similar systems may further offer excellent opportunities to study three-phase [32] electro-

chemistry. To establish the theoretical basis of such experiments and to enable a more comprehensive analysis of related experimental data, we here discuss, investigate, and contrast two different mathematical models for diffusive depletion processes of analyte inside nanoparticles resulting from impacts on an electrode. Quantities that can be extracted from experimental data are identified and practical fitting parameters for data analysis presented. The presented work is closely linked to a recent publication[33], which employs one of the two theoretical models and the dimensionless conducted analysis at the end of this paper.

2. Theoretical Models

This work compares two theoretical models for the reaction of individual nanoparticles in impact electrochemistry with respect to their current responses. Both models describe diffusive depletion processes of an analyte within an individual polymer particle after its impact on the electrode surface where the particle adsorbs and the analyte reacts.

The impacting particle is assumed to be spherical with radius r_0 and to contain a homogeneous concentration of a species A^+ . Following the stochastic arrival of the particle via Brownian motion and its transient adsorption at the electrode, A^+ is reduced at the electrode-particle interface held at a sufficiently negative over-potential to drive the single-electron-transfer reaction $A^+ + e^- \rightarrow B^0$. The simulated time interval begins with the arrival of the particle at the electrode and ends with the complete reduction of A^+ before the particle either leaves the electrode or remains adsorbed. An illustration of the process can be found in Figure 1.

During the impact, a spike-shaped current signal can be measured at the electrode while A^+ is reduced to B . Assuming the particle remains electro-neutral at all time, the reduction is modelled in terms of either a slow charge hopping process within the particle alongside a fast ion exchange at its surface or rate-determining ion diffusion inside the particle. In the latter case, the electro-neutrality is realised by the diffusion of a negative ion species X^- from within the particle into the solution (Equation 1) or the diffusion of a positive ion species M^+ from the solution into the particle (Equation 2).

²We note that the reduction of A^+ to B has been chosen exemplarily and the model can be easily altered to describe other reactions.

Figure 1: Illustration of the impact process simulated in both theoretical models. The inset schematically depicts the current measured at the electrode during the reaction.

As illustrated below, both mechanisms result in equivalent mathematical models opening a wide range of possible applications of the here-presented theory.

Four further assumptions are made: First, the electrode is assumed to be held at a large over-potential to ensure fast reaction kinetics limited only by the diffusive mass transport of charge carriers towards the electrode. Second, the X^- and M^+ species do not participate in any reaction. Third, there is sufficient³ electrolyte in the solution to enable the facile ion insertion and de-insertion accompanied with Equation 1 or Equation 2. And fourth, the ion insertion or de-insertion rate of X^- or M^+ is fast enough to not be the rate-determining step.

While all the above applies to both theoretical models, the following contrasts the ‘truncated-sphere and the ‘undeformed-sphere models which differ in the considered particle geometries following the adsorption at the electrode surface.

³Related experiments are typically carried out at relatively large electrolyte concentrations. Yang et al. [28] used a phosphate buffer solution (pH 7.4) composed of 10 mM each of monobasic and dibasic potassium phosphate and 0.1M KCl. Chen et al. [33] used phosphate buffered saline (PBS) solution (pH 7.4) comprising 137 mM sodium chloride, 2.7 mM potassium chloride, 10 mM sodium phosphate dibasic, and 1.8 mM potassium phosphate monobasic.

Figure 2: Cross-section of the model for the depletion of A^+ within a truncated sphere. c^* is the initial uniform concentration of the analyte inside the particle, r_1 is the radius of the particle after the adsorption at the electrode surface, and r_e is the radius of the contact area with the electrode.

2.1. The ‘Truncated-Sphere’ Model

The first model assumes that, following the impact of the adsorption of the formerly spherical particle at the electrode surface, the particle adopts the shape of a truncated sphere as shown in Figure 2 where the contact area between the particle and the electrode is shown in red. The analyte particles are hence modelled to be soft and deformable. Such soft particles may for instance include polymer particles [28, 29, 33], red blood cells [34], micelles [35], viruses [19, 36], liposomes [37] and bacteria [21, 38].

In this model, the particle radius after the adsorption of the particle at the electrode surface is instantaneously adjusted to r_1 in a way that the particle volume and the initial uniform concentration c^* of the analyte remain unchanged for different contact areas:

$$\begin{aligned} V_p &= \int_{V_p} dV = V_p^{init} = \text{const.} \\ c^* &= c^{*, init} = \text{const.} \end{aligned} \quad \text{for all } r_e \quad (3)$$

where V_p is the particle volume, $\int_{V_p}$ is the integration over the volume of the particle, and the superscript *init* indicates volumes and concentrations before the deformation. The total amount of analyte contained in a particle is hence conserved during the deformation.

In Figure 2, the contact area between the particle and the electrode then features the shape of a planar circle of the radius r_e while the reaction exclusively takes place at this contact area.

Figure 3: Boundary conditions used in the truncated-sphere model. z_{max} is the upper boundary of the simulated space in z for $r = 0$ and is implicitly set through the choice of r_1 and r_e . $f(E)$ represents the boundary condition at the electrode surface which, here, is equivalent to $c = 0$ at a the large over-potential applied.

The depletion process is modelled using cylindrical coordinates (r, z, ϕ) , where r is the radial distance, z is the axial distance, and ϕ is the angle of the plane formed by the r -axis and the z -axis rotating around the z -axis. Since, due to the rotational symmetry of the system with respect to the z -axis, the concentration at a specific point in r and z is independent of the angle ϕ , we simplify the three-dimensional coordinate system (r, z, ϕ) to a two-dimensional coordinate system (r, z) . The diffusion equation can hence be simplified to:

$$\frac{\partial c}{\partial t} = D\nabla^2 c = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial z^2}\right) \quad (4)$$

where c is the number concentration of A^+ and D is the diffusion coefficient of A^+ inside the particle.

All boundary conditions are shown in Figure 3. We assume that a large negative over-potential is applied at the electrode enough to ensure that the concentration of A^+ can be approximated to equal 0 at all time and the rate of charge transfer is hence diffusion-controlled. No-flux boundaries are set everywhere else, obstructing any release of the analyte into solution during the impact.

Following Fick's first law, the current can be calculated as:

$$I = nFj \quad \text{where} \quad j = -2\pi D \int_0^{r_e} r \, dr \left. \frac{\partial c}{\partial z} \right|_{z=0} \quad (5)$$

Figure 4: Cross-section of the geometry considered in the ‘undeformed-sphere’ model. c^* indicates the uniform initial concentration of A^+ , Φ_0 defines the contact area shown in red, and r_0 is the radius of the particle.

where the n is the number of the electron transferred in the reaction, the F is the Faraday Constant, and the j is the consuming flux of the analyte.

2.2. The ‘Undeformed-Sphere’ Model

In the second model, the particle shape remains spherical upon the impact and adsorption. The contact area between the particle and the electrode is then curved as shown as the red area in Figure 4. In analogy with the previous model, the A^+ reacts only at this interface and is confined to the volume of the particle throughout the impact. The ‘undeformed-sphere’ model has recently been used in the analysis of transport processes in Nafion particles [33].

The diffusion of A^+ inside the particle is modelled in the spherical coordinates (r, Φ, ϕ) , where r is the radial distance, Φ is the polar angle and ϕ is the zenith angle. Due to the systems symmetry with respect to the zenith and as in the above model, only the concentration distribution in r and Φ are taken into consideration as the concentration is invariant with respect to the zenith angle ϕ . The diffusion equation inside the spherical particle is hence:

$$\frac{\partial c}{\partial t} = D\nabla^2 c = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r} + \frac{1}{r^2}\frac{\partial^2 c}{\partial \Phi^2} + \frac{1}{r^2 \tan \Phi}\frac{\partial c}{\partial \Phi}\right) \quad (6)$$

The simulation employs the geometry shown in the Figure 5. As in the previous model, a large electrode over-potential is assumed at the electrode so that the concentration of A^+ is set to zero at the electrode surface, and no-flux boundaries are set everywhere else to prevent any release of the analyte into the solution surrounding the particle.

Figure 5: Boundary conditions used in the undeformed-sphere model. As in the truncated-sphere model, $f(E)$ represents the boundary condition at the electrode surface which, here, is equivalent to $c = 0$ at a the large over-potential applied.

The total current across the contact area is calculated on the basis of Fick's first law:

$$I = nFD \frac{\partial}{\partial t} (2\pi \int c r \sin \Phi dr d\Phi) \quad (7)$$

2.3. Computational Methods

The partial differential equations for the two models are solved via two different finite difference approaches. For the ‘truncated-sphere model, custom code was developed in *C++* which makes use of the alternating direction implicit (ADI) method[39–41] to simplify the resulting systems of linear equations to tri-diagonal matrix equations which are then solved via the Thomas algorithm[42]. Results are visualised via Python scripts using the *NumPy* and *matplotlib* libraries. The ‘undeformed-sphere model was realized and visualised in *MATLAB* R2018a where the ADI method was adopted to solve the matrix system , see [33] for further details. An expanding time grid is used to for both models for better accuracy at short time scales. Further details can be found in the textbook[43] by Compton et al.

We recognise the importance of the software testing and validation[44] and have carried out comprehensive tests including convergence studies and the studies of error of mass conservation.

2.4. Dimensionless Parameters

For simplicity of presentation and to enable an easier comparison with experimental data, dimensionless parameters are used throughout this study

Table 1: Conversion of dimensional parameters to their dimensionless counterparts where r_0 is the radius of the spherical particle before the impact and throughout the entire simulation for the ‘truncated-’ and the ‘undeformed-sphere’ model, respectively, f_c is the dimensional frequency which is defined as $\frac{1}{t}$, F is the Faraday Constant, $\mathbf{R}$ is the Universal Gas Constant, and $\mathbf{T}$ is the temperature.

Parameter	Conversion
Concentration of species j	$C_j = \frac{c_j}{c^*}$
Diffusion coefficient of species j	$d_j = \frac{D_j}{D}$
Radial distance	$R = \frac{r}{r_0}$
Axial distance	$Z = \frac{z}{r_0}$
Time	$T = \frac{Dt}{r_0^2}$
Frequency	$F_c = \frac{r_0^2 f_c}{D}$
Potential	$\theta = \frac{F}{\mathbf{RT}}(E - E_f^0)$
Current	$J = \frac{I}{F r_0 D c^*}$

and respective transformations are shown in Table 1.

Since the particle volume and the overall amount of A^+ it contains are conserved during the deformation process, see Equation (3), the dimensionless particle radius R_1 is a function of the contact area and $R_1 \geq 1$ in the ‘truncated-sphere’ model. In contrast and as the particle is not deformed in the ‘undeformed-sphere’ model, $R_0 = 1$ independent of the contact angle Φ_0 .

Typical values for dimensional parameters can be found in a recent experimental study [33] by Chen *et al.* which makes use of one of the two theoretical models.

3. Results and Discussion

The following section is divided into three parts. We first focus on the truncated-sphere model and discuss simulation results with respect to concentration profiles, the electrode current, and the impact analogue signal processing in a typical experimental set-up may have on the measurement. Second, we compare both theoretical models before, finally, we conduct a dimensional analysis to establish two useful fitting parameters for the analysis of experimental data.

3.1. The ‘truncated-sphere’ model

A series of simulations is performed for the truncated-sphere model while the size of the contact area between the electrode and the sphere is varied and the concentration profiles of A^+ are investigated, see Figure 6. The figure reveals a significant dependency of the temporal evolution of the depletion on the size of the contact area: For large contact areas the analyte depletion progresses much faster than for smaller areas. At the time $T = 1$, for instance, about 70% of the initial mass has been consumed for a contact area of 2 while only about 35% has been consumed at the same time for a contact area of 0.5. This large difference suggests that the contact area might be inferred from the current transient measured at the electrode.

To further investigate the depletion process, we analyse the temporal evolution of the current alongside the mass remaining within the particle in Figure 7. The data shown confirms the strong dependency of the current response on the contact area anticipated on the basis of Figure 6: The larger is the contact area, the greater⁴ is the current at short times after the impact and the faster the depletion progresses. Despite the initial greater current for greater contact areas, the current response simulated for smaller contact areas exceeds the response calculated for larger contact areas at long time scales. This can be understood considering that the overall amount of analyte inside the particle remains unchanged with different contact areas and an initial lower current hence necessarily results in a larger current at long time scales.

To further rationalise the simulated current responses, we compare the modelled data with the Cottrell equation[45] which describes the temporal evolution of the current I at large overpotentials in one-dimensional chronoamperometry. In its dimensional form⁵, Cottrell equation is given by:

$$I = nFAc^* \sqrt{\frac{D}{\pi t}} \quad (8)$$

⁴We note that for very short time scales, the simulated geometry resembles a one-dimensional geometry, i.e. $I \propto 1/\sqrt{t}$ and hence $I \rightarrow \infty$ for $t \rightarrow 0$. As infinite current cannot be modelled via the finite differences method, the simulated data for very short time scales can only be of a qualitative nature. Convergence studies are provided in the Supplementary Information

⁵The dimensionless form representation is: $J = \frac{\sin^2 \Phi_0}{2\sqrt{\pi T}}$

Figure 6: Temporal evolution of the concentration profiles simulated for four different contact areas. Plots are arranged in a way that the time increases from the left to the right while the contact area increases from the top to the bottom and simulations for $Ar = 0.5, 1.0, 1.5, 2.0$ are depicted. The values plotted as red insets indicate percentage of the initial mass remaining in the particle at the respective simulated time. Video illustration of temporal evolution of the concentration profiles are shown as Video S1.

where n is the number of electrons transferred, F is the Faraday Constant, A is the area of the electrode, c^* is the initial concentration of the analyte, D is the diffusion coefficient, and t is the time. We note that the simulated current in the ‘truncated-sphere’ model differs from the Cottrell model as it is not exclusively limited by linear diffusion. However, at short-time scales, when radial diffusion does not have a large influence on the mass transport

Figure 7: Temporal evolution of the electrode current (left) and the mass remaining within the particle (right) in the ‘truncated-sphere’ model.

towards the electrode, the simulated current is expected to converge to the production of the Cottrell equation.

The current evolutions calculated for two different contact areas ($Ar = 0.5, 1.0$) are compared in Figure 8 where the x -axis depicts $1/\sqrt{T}$ and hence the regions ① to ④ and ⑤ to ⑧ are reached in ascending order with time, i.e. ① $\rightarrow$ ② $\rightarrow$ and so forth, and ⑤ $\rightarrow$ ⑥ $\rightarrow$ and so forth. A direct comparison between the simulated currents and Cottrell equation reveals that at short times, in the regions ② and ⑥, the simulated currents approach the Cottrell equation as the geometry resembles the one-dimensional diffusion case as modelled by Cottrell. In the regions ③ and ⑦, radial diffusion additionally contributes to the current which then exceeds the corresponding value of the Cottrell equation. At the end of the simulated time, ④ and ⑧, the current drops to zero due to the limited amount of analyte within the particle which is now entirely consumed. At very short times ① and ⑤ we find a deviation between the simulated data and the Cottrell equation which results from intrinsic limitations of the finite differences method and can be understood along the lines of the footnote in Section 3.1. We though note that the time scale at which we observe these artefacts is of no experimental relevance as illustrated below in the discussion of the experimental signal processing.

Prior literature[16, 46] has shown that the shapes of current spikes measured in impact electrochemistry often reflect the signal processing characteristics of the potentiostat than the temporal evolution of the actual charge process at the electrode surface. In order to compare the simulated currents with an experimental data, the signal transfer function of the potentiostat

Figure 8: Comparison between Cottrell equation and our simulation results for different Ar , $Ar = 0.5$ and $Ar = 1$. Cottrell equation and simulation results are depicted in blue and black, respectively.

- for many experiments a simple low-pass filter - must hence be included in the simulation. To this end, we apply a digital first-order **Bessel-type** low-pass filter to the simulated current to model bandwidth limitations of the potentiostat. The key parameter is herein the filter's cut-off frequency which is a measure for the signal bandwidth **which, depending on the experimental system, typically features values between 1 Hz and 1 KHz (A recent work[33] used a cut-off frequency of 50 Hz.)**. If the frequency of a spectral signal component is larger than the cut-off frequency, the contribution of this component to the output signal is attenuated whereas other signal components experience only small changes in terms of their contribution. In addition, despite of no relevance in this work, we do note the the cut-off frequency has a influence on the phase shift of the individual spectral components.

Figure 9 compares the current evolutions before and after the application of digital filter for different contact areas $Ar = 0.5, 1.0, 1.5, 2.0$ and a dimensionless cut-off frequency of 100. The x -axes on the left and right depict the dimensionless time T and $\text{Log}_{10}T$, respectively, while the same data is shown. In the figure we find that immediately after impact all currents are attenuated significantly while in the following filtered currents slightly exceed their unfiltered equivalents before, finally, both converge to the same value. Prior literature has shown that for this type of filter, the overall charge transferred, i.e. the integral of the current, is conserved[9]. The above discussed intrinsic inaccuracy of our simulations at very short time scales is hence of negligible practical relevance for the shape of the spike after the filtering. Most notably,

Figure 9: Evolution of the current response before and after a digital filter operated at a dimensionless cut-off frequency of 100. Different contact areas are investigated and, for clarity, the same data is plotted versus both T and $\text{Log}_{10}(T)$.

the current response significantly depends on the contact area even after the filter and, in the context of this theoretical model, can hence be used to extract the contact area as well as the degree of the particle deformation from experimental data.

In order to further investigate the influence of the cut-off frequency, the current transients before and after filtering are compared for different dimensionless cut-off frequencies, $F_c = 25, 50, 100, 150, 200$, when the contact area is set to be 1. From the Figure 10, we can see that when the cut-off frequency is set to a low value, the signal is masked by the filter and only little information can be retained as higher-bandwidth features are attenuated. In contrast and at higher cut-off frequencies, the potentiostat is less limiting, though experimentally the signal may be masked by other sources of noise so that the cut-off frequency needs to be chosen carefully to sufficiently suppress external noise while still retaining spectral information of interest.

3.2. Comparison between the ‘Truncated-’ and the ‘Undeformed-sphere’ Model

For the comparison between the ‘truncated-’ and the ‘undeformed-sphere’ model, we consider four different cases as shown in Figure 11. The red and green areas represent the contact areas simulated for the ‘truncated-’ and the ‘undeformed-sphere’ model, respectively. The angles Φ_0 , which define the contact areas in both models, feature identical values in corresponding simulations for both models. Currents are evaluated for four different angles Φ_0 , $\sin\Phi_0 = 0.399, 0.561, 0.679, 0.774$, which are labelled **A**, **B**, **C**, and **D** in the

Figure 10: Current Evolutions before and after filtering evaluated for different cut-off frequencies and a contact area of 1.

Figure 11: Comparison of different simulated contact areas for two models. Red and green areas show the ‘truncated-’ and the ‘undeformed-sphere’ model, respectively.

Figure and correspond to the above four surface areas $Ar = 0.5, 1.0, 1.5, 2.0$ in the ‘truncated-sphere’ model. As discussed above, the total volume of the particles remains unchanged for different angles and particle radii R_1 of deformed particles in the ‘truncated-sphere’ model hence increase accordingly as the particle is deformed upon the impact.

The dimensionless contact areas can be calculated from the angle Φ_0 for the ‘truncated-sphere’ model:

$$Ar = \pi R_e^2 = \pi R_1^2 \sin^2 \Phi_0 \quad (9)$$

and the ‘deformed-sphere’ model:

$$Ar = 2\pi R_0 H \quad \text{where} \quad H = R_0(1 - \cos \Phi_0) \quad (10)$$

where R_e is the radius of the contact area in the ‘truncated-sphere’ model and H is the height of the missing cap of the truncated sphere.

Figure 12: Comparison of the temporal evolutions of the current responses in the ‘truncated-’ and the ‘undeformed-sphere’ models evaluated for different Ar .

The current signals for the ‘truncated-’ and the ‘undeformed-sphere’ model are compared in Figure 12 where we find that the smaller is the contact angle, the smaller is the difference in the current response. This can be rationalised considering that for small contact angles $\Phi \rightarrow 0$ both models converge to the same geometry. We further observe very similar current responses at intermediate- and long time scales despite clear differences at the short time-scales. The latter however do not feature any experimental relevance in the light of the bandwidth limitations imposed experimentally and can therefore be neglected. To illustrate this, Figure 13 additionally contrasts the same current signals after the signal filtering which feature significant similarities at all time scales. When analysing experimental data it is hence not possible to distinguish between the two theoretical models solely on the basis of the spike shape which leaves us with the convenience of a choosing one of the two models for the estimation of the contact area angle Φ_0 from experimental data in favourable cases where the values of the below introduced fitting parameters can be determined with sufficient accuracy.

3.3. Dimensional Analysis and Fitting Parameters

In the above definition of both theoretical models, four different fitting parameters must be considered when comparing measured dimensional currents with simulated data: The diffusion coefficient D of the analyte A^+ , the radius of the particle r_0 before the impact and adsorption⁶, the concen-

⁶For polymer particles, we note that as the material may adsorb water and swell in solution[47, 48], the real values of r_0 and c^* are therefore difficult to determine in solution.

Figure 13: Comparison of the current responses found in the ‘truncated-’ and the ‘undeformed-sphere’ models when evaluated for different Ar after signal filtering at a dimensionless cut-off frequency of 100.

tration c^* of the analyte within the particle, and the contact area angle Φ_0 . The large number of parameters obviously complicates the comparison with experimental data where exact values may be unknown. It is therefore desirable to reduce the number of parameters as well as to use quantities that are more accessible from experimental data. To this end, this section conducts a dimensionless analysis to establish a set of less and more convenient parameters for the theoretical modelling. **The presented analysis follows and elaborates the analysis presented in [33].**

We first consider the relation between the dimensional current and the dimensionless current as provided in Table 1:

$$I = Fr_0 D c^* J \quad (11)$$

Using this transformation, the dimensionless currents calculated on the basis of Fick’s first law can be written:

$$J_t = \frac{\partial C_t}{\partial Z} \Big|_{Z=0, R < R_e} \quad (12)$$

$$J_f = \frac{\partial C_f}{\partial R} \Big|_{R=1, \Phi < \Phi_0} \quad (13)$$

where the subscripts t and f label the ‘truncated-’ and the ‘undeformed-sphere’ model, respectively.

Via the transformations given in Table 1 we further obtain the partial differential equation for the temporal evolution of dimensionless concentration

from Fick's second law:

$$\frac{\partial C}{\partial T} = \nabla_{R,Z}^2 C \quad (14)$$

Analogously, we transform the boundary conditions defined in Figures 3 and 5, namely no-flux boundaries of the form:

$$\vec{n} \cdot \nabla_{R,Z} C = 0 \quad (15)$$

where $\vec{n}$ is the normal vector of the respective boundary, and most notably set the dimensionless concentration at the electrode to 0:

$$C_t = 0 \mid_{Z=0, R < R_e} \quad (16)$$

$$C_f = 0 \mid_{R=1, \Phi < \Phi_0} \quad (17)$$

The above Equations 12 to 17 represent a complete definition of the theoretical models solved in this work.

A closer investigation reveals that the dimensionless currents in both models solely depend on two parameters:

$$J_t = f_t(T, R_e) \quad (18)$$

$$J_f = f_f(T, \Phi_0) \quad (19)$$

For the 'truncated-sphere' model, we can further express R_e as a function of R_1 and Φ_0 :

$$R_e = R_1 \sin \Phi_0 \quad (20)$$

where R_1 is the particle radius following the deformation in the 'truncated-sphere' model. Since, in this model, we can calculate the dimensionless volume of a particle before and after the adsorption:

$$V_0 = \frac{4}{3} \pi R_0^3 \quad (21)$$

$$V_1 = \frac{\pi}{3} (3R_1 - H) H^2 \quad (22)$$

where H is the height of the missing cap of the truncated sphere as defined

in Figure 11, we express the dimensionless R_e as a function of Φ_0 :

$$\begin{aligned} R_e &= \sqrt[3]{\frac{R_0^3 \sin^3 \Phi_0}{2 - 3\cos \Phi_0 + \cos^3 \Phi_0}} \\ &= \sqrt[3]{\frac{\sin^3 \Phi_0}{2 - 3\cos \Phi_0 + \cos^3 \Phi_0}} \end{aligned} \quad (23)$$

The current response in both models, Equation 18 and 19, can hence be expressed in the form:

$$J = f(T, \Phi_0) \quad (24)$$

Substituting the definition of the dimensionless time:

$$T = \frac{Dt}{r_0^2} \quad (25)$$

and Equation 11, the dimensional current can be written:

$$I = Fr_0 D c^* f\left(t \cdot \frac{D}{r_0^2}, \Phi_0\right) \quad (26)$$

where the shape of the current transient is solely defined by only two parameters, $D \cdot r_0^{-2}$ and Φ_0 , and an additional proportionality factor, $r_0 \cdot D \cdot c^*$.

To further simplify this factor, we write the overall charge of all analyte Q within the particle as:

$$Q = c^* FV \quad (27)$$

where V is the total dimensional volume of the particle before the impact which can be calculated by:

$$V = \frac{4}{3}\pi r_0^3 \quad (28)$$

Substitution of Equations 27 and 28 simplifies Equation 26 to:

$$\begin{aligned}
I &= \frac{r_0 D Q}{V} f\left(t \cdot \frac{D}{r_0^2}, \Phi_0\right) \\
&= \frac{3}{4\pi} \cdot \frac{D}{r_0^2} \cdot Q \cdot f\left(t \cdot \frac{D}{r_0^2}, \Phi_0\right)
\end{aligned} \tag{29}$$

This equation features three parameters, $D \cdot r_0^{-2}$, Φ_0 , and the overall charge Q which is readily available from the integration of the respective current spike. The above dimensional analysis hence reduces the number of fitting parameter from four to three, one of which is directly accessible from the experimental data. There are hence only two parameters left that must be fitted simultaneously for the comparison of experimental currents with simulated data.

4. Conclusions

We have investigated the diffusion-controlled electrochemical depletion of an analyte inside a nanoparticle adsorption at an electrode. Two theoretical models are **discussed** and contrasted that differ in the assumed particle shape upon adsorption. Simulated electrode currents are rationalised and discussed in the light of bandwidth limitations that are typically imposed by experimental measurement set-ups. Our analysis reveals that, in cases where simulated data can be fitted to experimental data with sufficient accuracy, the size of the contact area between the particle and the electrode can be extracted from experimental data while the deformation of the particle hardly affects the measured current transients. In addition, we present a dimensional analysis to reduce the number of fitting parameters in both theoretical models.

Acknowledgement

The research leading to these results has received partial funding from the European Research Council under the European Union's Seventh Framework Programme (FP/20072013) / ERC Grant Agreement no. [320403].

[Titles of newly added references are highlighted.]

References

- [1] V. A. Hernández, F. Scholz, **The Electrochemistry of Liposomes**, Israel Journal of Chemistry 48 (34) (2008) 169–184. doi:10.1560/IJC.48.3-4.169.
- [2] W. Cheng, R. G. Compton, Electrochemical detection of nanoparticles by nano-impact methods, TrAC Trends in Analytical Chemistry 58 (2014) 79–89. doi:10.1016/j.trac.2014.01.008.
- [3] M. Pumera, Impact electrochemistry: Measuring individual nanoparticles, ACS Nano 8 (2014) 7555–7558. doi:10.1021/nn503831r.
- [4] C. Batchelor-McAuley, E. Kätelhön, E. O. Barnes, R. G. Compton, E. Laborda, A. Molina, Recent advances in voltammetry, Chemistry-Open 4 (2015) 224–260. doi:10.1002/open.201500042.
- [5] P. H. Robbs, N. V. Rees, Nanoparticle electrochemistry, Physical Chemistry Chemical Physics 18 (2016) 24812–24819. doi:10.1039/C6CP05101D.
- [6] M. V. Mirkin, T. Sun, Y. Yu, M. Zhou, Electrochemistry at one nanoparticle, Accounts of Chemical Research 49 (2016) 2328–2335. doi:10.1021/acs.accounts.6b00294.
- [7] Y. Wang, X. Shan, N. Tao, Emerging tools for studying single entity electrochemistry, Faraday Discussions 193 (2016) 9–39. doi:10.1039/C6FD00180G.
- [8] E. N. Saw, M. Kratz, K. Tschulik, Time-resolved impact electrochemistry for quantitative measurement of single-nanoparticle reaction kinetics, Nano Research 10 (2017) 3680–3689. doi:10.1007/s12274-017-1578-3.
- [9] S. V. Sokolov, S. Eloul, E. Kätelhön, C. Batchelor-McAuley, R. G. Compton, Electrodeparticle impacts: A users guide, Physical Chemistry Chemical Physics 19 (2017) 28–43. doi:10.1039/C6CP07788A.
- [10] K. J. Stevenson, K. Tschulik, A materials driven approach for understanding single entity nano impact electrochemistry, Current Opinion in Electrochemistry 6 (2017) 38–45. doi:10.1016/j.coelec.2017.07.009.

- [11] L. K. Allerston, N. V. Rees, Nanoparticle impacts in innovative electrochemistry, *Current Opinion in Electrochemistry* 10 (2018) 31–36. doi:10.1016/j.coelec.2018.03.020.
- [12] Y.-G. Zhou, N. V. Rees, R. G. Compton, The electrochemical detection and characterization of silver nanoparticles in aqueous solution, *Angewandte Chemie International Edition* 50 (2011) 4219–4221. doi:10.1002/anie.201100885.
- [13] Y.-G. Zhou, N. V. Rees, J. Pillay, R. Tshikhudo, S. Vilakazi, R. G. Compton, Gold nanoparticles show electroactivity: Counting and sorting nanoparticles upon impact with electrodes, *Chemical Communications* 48 (2012) 224–226. doi:10.1039/C1CC16407D.
- [14] H. S. Toh, R. G. Compton, nano-impacts: An electrochemical technique for nanoparticle sizing in optically opaque solutions, *ChemistryOpen* 4 (2014) 261–263. doi:10.1002/open.201402161.
- [15] E. Kätelhön, E. E. Tanner, C. Batchelor-McAuley, R. G. Compton, Destructive nano-impacts: What information can be extracted from spike shapes?, *Electrochimica Acta* 199 (2016) 297–304. doi:10.1016/j.electacta.2016.02.031.
- [16] E. Kätelhön, A. Feng, W. Cheng, S. Eloul, C. Batchelor-McAuley, R. G. Compton, Understanding nano-impact current spikes: Electrochemical doping of impacting nanoparticles, *The Journal of Physical Chemistry C* 120 (2016) 17029–17034. doi:10.1021/acs.jpcc.6b04289.
- [17] G. Zampardi, C. Batchelor-McAuley, E. Kätelhön, R. G. Compton, Lithium-ion-transfer kinetics of single LiMn_2O_4 particles, *Angewandte Chemie International Edition* 56 (2017) 641–644. doi:10.1002/anie.201610485.
- [18] K. J. Krause, F. Brings, J. Schnitker, E. Kätelhön, P. Rinklin, D. Mayer, R. G. Compton, S. G. Lemay, A. Offenhäusser, B. Wolfrum, The influence of supporting ions on the electrochemical detection of individual silver nanoparticles: Understanding the shape and frequency of current transients in nano-impacts, *Chemistry – A European Journal* 23 (2017) 4638–4643. doi:10.1002/chem.201605924.

- [19] J. E. Dick, A. T. Hilterbrand, A. Boika, J. W. Upton, A. J. Bard, Electrochemical detection of a single cytomegalovirus at an ultramicroelectrode and its antibody anchoring, *Proceedings of the National Academy of Sciences* 112 (2015) 5303–5308. doi:10.1073/pnas.1504294112.
- [20] E. N. Saw, N. Blanc, K. Kanokkanchana, K. Tschulik, **Time-resolved impact electrochemistry - A new method to determine diffusion coefficients of ions in solution**, *Electrochimica Acta* 282 (2018) 317 – 323. doi:10.1016/j.electacta.2018.06.013.
- [21] J. Y. Lee, B.-K. Kim, M. Kang, J. H. Park, Label-free detection of single living bacteria via electrochemical collision event, *Scientific Reports* 6 (2016) 30022. doi:10.1038/srep30022.
- [22] C. Lin, L. Sepunaru, E. Kätelhön, R. G. Compton, Electrochemistry of single enzymes: Fluctuations of catalase activities, *The Journal of Physical Chemistry Letters* 9 (2018) 2814–2817. doi:10.1021/acs.jpcclett.8b01199.
- [23] J. G. Gaudiello, P. K. Ghosh, A. J. Bard, Polymer films on electrodes. 17. the application of simultaneous electrochemical and electron spin resonance techniques for the study of two viologen-based chemically modified electrodes, *Journal of the American Chemical Society* 107 (1985) 3027–3032. doi:10.1021/ja00297a006.
- [24] R. J. Mortimer, J. L. Dillingham, Electrochromic 1,1'-dialkyl-4,4'-bipyridilium-incorporated nafion electrodes, *Journal of the Electrochemical Society* 144 (1997) 1549–1553. doi:10.1149/1.1837639.
- [25] I. Rubinstein, A. J. Bard, Polymer films on electrodes. 5. Electrochemistry and chemiluminescence at nafion-coated electrodes, *Journal of the American Chemical Society* 103 (1981) 5007–5013. doi:10.1021/ja00407a006.
- [26] C. R. Martin, I. Rubinstein, A. J. Bard, Polymer films on electrodes. 9. Electron and mass transfer in nafion films containing tris(2,2'-bipyridine)Ruthenium²⁺, *Journal of the American Chemical Society* 104 (1982) 4817–4824. doi:10.1021/ja00382a014.

- [27] D. A. Buttry, F. C. Anson, Electrochemical control of the luminescent lifetime of $\text{Ru}(\text{bpy})_3^{2+}$ incorporated in nafion films on graphite electrodes, *Journal of the American Chemical Society* 104 (1982) 4824–4829. doi:10.1021/ja00382a015.
- [28] H. Yang, X. Li, C. Batchelor-McAuley, S. V. Sokolov, R. G. Compton, Nafion particles doped with methyl viologen: Electrochemistry, *Physical Chemistry Chemical Physics* 20 (2018) 682–689. doi:10.1039/c7cp06764j.
- [29] L. Chen, C. Lin, R. G. Compton, Single entity electrocatalysis: Oxygen reduction mediated via methyl viologen doped nafion nanoparticles, *Physical Chemistry Chemical Physics* 20 (2018) 15795–15806. doi:10.1039/c8cp02311e.
- [30] X. Li, C. Batchelor-McAuley, L. Shao, S. V. Sokolov, N. P. Young, R. G. Compton, Quantifying single-carbon nanotube-electrode contact via the nanoimpact method, *The Journal of Physical Chemistry Letters* 8 (2017) 507–511. doi:10.1021/acs.jpcclett.6b02899.
- [31] A. Krittayavathananon, X. Li, S. V. Sokolov, C. Batchelor-McAuley, M. Sawangphruk, R. G. Compton, The solution phase aggregation of graphene nanoplates, *Applied Materials Today* 10 (2018) 122 – 126. doi:10.1016/j.apmt.2018.01.001.
- [32] U. Schröder, K. B. Oldham, J. C. Myland, P. J. Mahon, F. Scholz, **Modelling of solid state voltammetry of immobilized microcrystals assuming an initiation of the electrochemical reaction at a three-phase junction**, *Journal of Solid State Electrochemistry* 4 (2000) 314–324. doi:10.1007/s100080000130.
- [33] L. Chen, C. Lin, R. G. Compton, **Electrochemical characterisation and comparison of transport in Nafion films and particles**, *Phys. Chem. Chem. Phys.* (2019) –doi:10.1039/C8CP06504G.
- [34] L. Sepunaru, S. V. Sokolov, J. Holter, N. P. Young, R. G. Compton, **Electrochemical Red Blood Cell Counting: One at a Time**, *Angewandte Chemie* 128 (33) (2016) 9920–9923. doi:10.1002/ange.201605310.

- [35] H. S. Toh, R. G. Compton, **Electrochemical detection of single micelles through nano-impacts**, *Chemical Science* 6 (2015) 5053–5058. doi:10.1039/c5sc01635e.
- [36] L. Sepunaru, B. J. Plowman, S. V. Sokolov, N. P. Young, R. G. Compton, **Rapid electrochemical detection of single influenza viruses tagged with silver nanoparticles**, *Chemical Science* 7 (2016) 3892–3899. doi:10.1039/C6SC00412A.
- [37] W. Cheng, R. G. Compton, **Investigation of Single-Drug-Encapsulating Liposomes using the Nano-Impact Method**, *Angewandte Chemie International Edition* 53 (50) (2014) 13928–13930. doi:10.1002/anie.201408934.
- [38] L. Sepunaru, K. Tschulik, C. Batchelor-McAuley, R. Gavish, R. G. Compton, **Electrochemical detection of single E. coli bacteria labeled with silver nanoparticles**, *Biomaterials Science* 3 (2015) 816–820. doi:10.1039/C5BM00114E.
- [39] D. Peaceman, H. Rachford, Jr., The numerical solution of parabolic and elliptic differential equations, *Journal of the Society for Industrial and Applied Mathematics* 3 (1955) 28–41. doi:10.1137/0103003.
- [40] J. Heinze, Diffusion processes at finite (micro) disk electrodes solved by digital simulation, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* 124 (1981) 73 – 86. doi:10.1016/S0022-0728(81)80285-9.
- [41] J. A. Alden, R. G. Compton, A general method for electrochemical simulations. 1. Formulation of the strategy for two-dimensional simulations, *The Journal of Physical Chemistry B* 101 (1997) 8941–8954. doi:10.1021/jp9719366.
- [42] W. H. Press, S. A. Teukolsky, B. P. Vetterling, William T. and Flannery, *Numerical Recipes : The Art of Scientific Computing (Third Edition)*, Cambridge University Press, 2007.
- [43] R. G. Compton, E. Laborda, K. R. Ward, *Understanding Voltammetry: Simulation of Electrode Processes*, Imperial College Press, 2013.

- [44] E. Kätelhön, R. G. Compton, Testing and validating electroanalytical simulations, *Analyst* 140 (2015) 2592–2598. doi:10.1039/c4an02276a.
- [45] F. G. Cottrell, *Zeitschrift für Physikalische Chemie* 42 (1903) 385.
- [46] K. Kanokkanchana, E. N. Saw, K. Tschulik, **Nano Impact Electrochemistry: Effects of Electronic Filtering on Peak Height, Duration and Area**, *ChemElectroChem* 5 (20) (2018) 3000–3005. doi:10.1002/celec.201800738.
- [47] G. Gebel, P. Aldebert, M. Pineri, Swelling study of perfluorosulphonated ionomer membranes, *Polymer* 34 (1993) 333 – 339. doi:10.1016/0032-3861(93)90086-P.
- [48] M. H. Eikerling, P. Berg, Poro-electroelastic theory of water sorption and swelling in polymer electrolyte membranes, *Soft Matter* 7 (2011) 5976–5990. doi:10.1039/C1SM05273J.