Deciphering the Magnitude of Current Steps in Electrochemical Blocking Collision Experiments and Its Implications

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ABSTRACT

The magnitude of the current steps due to blocking collisions is shown to be proportional to the square of the particle size, the concentration of the redox mediator, and inversely proportional to the size of the indicator electrode. A theoretical model and a simple analytical expression have been developed that allow for estimation of the average value of the current step magnitude in blocking collisions. Thus, it is now possible to directly relate the size of the analyte to the size of the average current step without worrying about the edge effect. It is proposed that by using the developed model and equations one could monitor the state of analyte species in solution, i.e., whether it is aggregated or not.

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1. Introduction

Stochastic electrochemical detection has become important in the analysis of individual analyte species, making it an intense area of interest in electrochemistry [1–21]. This method of electrochemical detection has been used in recent years for the detection of single nanoparticles, emulsion droplets, vesicles, biological macromolecules, and single ions. Boika, Thorgaard, and Bard report on the detection of single silica and polystyrene nanoparticles by their blocking of the flux of ferrocenemethanol to the surface of a Pt ultramicroelectrode (UME) [2]. Dick et al. employed this same method in the detection of a single murine cytomegalovirus [3,10]. Furthermore, a similar method was used by Dick, Renault, and Bard in the detection of single protein and DNA macromolecules [4]. In these experiments the arrival of an analyte at the surface of an UME creates a sudden drop in current, resulting in staircase-like features in a chronoamperogram. Such a method does not employ electrochemistry of the particles themselves; rather the detection is based on the blocking of the flux of a redox mediator by the analyte particles. Another approach used by Zhou et al. employs the direct oxidation of silver particles at the surface of an UME [5]. In this method, upon the oxidation of individual silver particles, current spikes are observed in a chronoamperogram. Sepunaru et al. extended their work by using silver particles to tag single influenza viruses thus allowing for their detection [6]. Kim et al. used both methods (direct oxidation at the surface of an UME and blocking of the flux of a redox mediator) for characterization of emulsion droplets [7]. Lebègue et al. extended the use of both methods to the detection of phospholipid vesicles [8].

In the discussed blocking collision experiments it has been shown that the collision frequency is proportional to the magnitude of the faradaic current [2,20]. In this publication we expand on our previous findings and the knowledge from other groups, and use experimental data to show that the step height is dependent on the electrode size, the size of the analyte species, and concentration of the redox mediator. In the past, several groups have considered the magnitude of current steps in blocking collisions. Lemay et al. reported that the size of the current steps relative to the faradaic current (recorded with an indicator electrode) scales with the ratio of an electrode to particle radii [16]. Later, Boika and co-workers showed by numerical simulations that the height of current steps also depends on the concentration of redox mediator [2]. Most recently, Dick et al. presented a simple expression to estimate the size of the analyte from the experimentally measured average current step magnitude and compared it to the crystallographic data [4]. However, these earlier reports [2,16] did not present a complete picture, while the approach by Dick et al. [4] neglected the edge effect. Another issue

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that we are tackling in this work is that, when the ratio between the electrode size and analyte size is too large, not all collision events may be successfully discerned against the background noise. Being able to determine the electrode size to be used to see all discrete collision events before performing collision experiments presents an advantage in the field of stochastic electrochemical detection. Thus, we propose a simple analytical expression, supported by the results of the numerical simulations and experiments, for determining the expected average step height in a typical blocking collision experiment. We have compared the findings, obtained with our model, to the experimental results reported by Dick et al. [4], and determined that their theoretical approach to data analysis, in certain cases, may suffer from analyte aggregation. The issue of aggregation has also been investigated previously by the Compton group on the example of dissolution of magnetite nanoparticles [22]. In the presented work, we expand the methodology to include the case of blocking collisions.

2. Experimental

2.1. Materials and Instrumentation

The particles used in the performed collision experiments were aqueous suspensions of carboxylated polystyrene beads purchased from Bangs Laboratories, Inc. (Fishers, IN, catalog numbers PC04N, PS03N). The working electrodes used were 4, 5, 7, 10, and 22 μm diameter Pt disks fabricated by sealing a Pt wire in glass. The 4, 5, and 7 μm diameter electrodes were prepared by sealing a 25 μm Pt wire purchased from Alfa Aesar (Ward Hill, MA) in a quartz capillary purchased from Drummond Scientific Company (Broomall, PA) using a Laser Puller from Sutter Instruments Company (Novato CA, model P-2000), which produced needle-like nanoelectrodes. These electrodes were polished to size using a World Precision Instruments beveler (Sarasota, FL, model 1300-m), fit with 0.1 μm diamond lapping film from Allied High Tech Products Inc. (Rancho Dominguez, CA). A connection between a Pt microwire and a tungsten rod (FHC, Bowdoin, ME) was made with a silver paste purchased from Resin Technology Group LLC (Easton, MA). The 10 and 22 μm diameter electrodes were prepared by sealing a Pt wire of the respective size in borosilicate capillaries purchased from World Precision Instruments (Sarasota, FL) using a microelectrode puller (Stoelting Company, Wood Dale, IL). A connection was made using copper wire and the silver paste mentioned above. The 10 and 22 μm diameter electrodes were polished using 1200 Grit MicroCut™ discs from Buehler (Lake Bluff, IL) and mirror-like polishing was accomplished using a solution of 0.3 μm, then 0.05 μm alumina micropolish powder purchased from CH Instruments Inc. (Austin, TX). The redox species used in the electrochemical cell was ferrocenemethanol (FcCH$_2$OH) purchased from Sigma-Aldrich (St. Louis, MO). It was recrystallized twice from hexane. The supporting electrolyte was potassium nitrate, which was purchased from Sigma-Aldrich. All solutions were prepared with water from a Milli-Q Integral 5 purification system (Millipore, Bedford, MA) and sonicated for at least thirty minutes using a VWR Symphony bath sonicator (VWR International Radnor, PA). Electrochemical data were collected using a CHI760E potentiostat purchased from CH Instruments, Inc. (Austin, TX).

2.2. Experimental procedure

The electrochemical cell was a typical three-electrode cell consisting of a Pt rod (0.3 mm diam.) auxiliary electrode, Ag|AgCl reference electrode (saturated KCl inner solution), and the working electrodes mentioned above. Chronoamperometry was performed with the working electrode potential set at +0.5 V.

All glassware used was rinsed with large amounts of deionized water and not reused between experiments. Before each experiment, the working electrode was cleaned in a piranha solution before being introduced into the electrochemical cell. Before filling the cell, the solution was filtered using a 0.02 μm PTFE filter purchased from Whatman Inc. (Florham Park, NJ). To ensure collisions observed were due to the polystyrene spheres, chronoamperograms were recorded for 300 s before the introduction of the spheres. For all experiments, no steps were observed before the introduction of the spheres.

A stock solution of spheres was prepared using deionized water and introduced to the experimental cell via an autopipette to achieve the required concentration of spheres. The cell was then stirred for approximately 15 s and sat for approximately 60 s prior to running chronoamperograms to ensure a uniform concentration of spheres in the cell. Multiple chronoamperograms were recorded for 300 s for each experiment, and the working electrodes were cleaned with piranha solution and rinsed with large amounts of deionized water before restarting each experiment.

3. Theory

3.1. Simulations

The main simulation algorithm was the same as previously described [2]. In brief, we have investigated the dependence of the current step height on the size of the analyte particles, the electrode radius and the concentration of redox species; the findings are presented in Figs. S1–S3 in the Supporting Information. These results were further used to develop analytical relationships as described in Section 3.2.

The simulations were performed using the 'transport of diluted species' application mode of COMSOL Multiphysics v5.2. The Nernst–Planck equation, written out for a 2D axisymmetric coordinate system, assumes diffusion and migration mass transfer modes as shown below:

$$J_i(r,z) = -D_i \nabla C_i(r,z) - \frac{z_i F}{RT} D_i C_i(r,z) \nabla \varphi(r,z) \tag{1}$$

where J_i is the flux of the species i, D_i is the diffusion coefficient, C_i is the concentration, z_i is the charge on the species in signed units of electronic charge, F is the Faraday constant, φ is the electric potential responsible for the migration effect, and other symbols have their usual meaning. Note that for uncharged species, such as FcCH$_2$OH, $z = 0$ and the migration term does not enter the mass transfer equation.

3.1.1. Boundary conditions

For the electrode surface, a fully reversible redox process is considered (FcCH$_2$OH oxidation):

$$C_R(r,z) = 0 \quad C_O(r,z) = C_b \tag{2}$$

where C_R is the concentration of the redox species (FcCH$_2$OH) and C_O is the concentration of the reaction product (FcCH$_2$OH$^+$).

For the boundary in the bulk solution:

$$\lim_{r,z \to \infty} C_R = C_b \quad \lim_{r,z \to \infty} C_O = 0 \tag{3}$$

where C_b is the bulk concentration of the R species (FcCH$_2$OH).

For the axial symmetry axis, insulating particle ring, and a glass sheath,

$$\overline{n} \cdot \overline{J} = 0 \tag{4}$$

where $\overline{n}$ is the normal vector, $\overline{J}$ is the flux of the redox species (R, O) given by the Nernst–Planck equation above.