



Cyclic Voltammetry Characterization of Microparticle Monolayers



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ABSTRACT

We have demonstrated the applicability of cyclic voltammetry and rotating disk electrode techniques for the characterization of microparticle monolayers. We have tested experimentally the recently developed theoretical model for the determination of surface coverage of spherical particle monolayer by means of diffusion current measurements. We have verified our electrochemical results by means of optical microscopy. We have found that the model applicability range increases with the decrease of the adsorbed particle size. For the 1.16 μm particles we have found a good agreement between our theoretical and experimental results at the surface coverage larger than 0.45. Our results suggest that the voltammetric characterization of thin porous films may have practical applications for, e.g., detection and determination of surface coverage of bacteria, cells or other objects in the micron size range.

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1. Introduction

The continuing effort to develop a quantitative understanding of deposition of colloidal particles, macromolecules, and bioparticles onto solid surfaces is justified by the importance of the topic in a wide range of complex natural and technological processes. These are the protein, bacteria, or enzyme immobilization and separation, removal of pathological cells, conducting immunological assays, filtration, water treatment, membrane biofouling, artificial organ implantation, fabrication of optical elements, etc. Therefore, studies of the deposition mechanism and properties of deposited layers, such as the particle surface concentration and layer porosity, are necessary and very important from a practical point of view. The experimental characterization of deposited colloidal films under natural conditions (without, e.g., drying it out) is particularly important.

In the case of nanoparticles, deposited layers can be characterized by means of atomic force microscopy (AFM), ellipsometry, reflectometry, fluorescence methods, streaming potential measurement, isotope labeling, or the quartz crystal microbalance [1]. A common experimental method for quantitative description of micron-sized particle monolayers is optical microscopy. However, its application is limited to monolayer structures only and we cannot use this technique for the characterization of multilayers.

Recently, following the application of electrochemical techniques in studies of ion transport through gel layers [2], we have

proposed a novel method for quantitative description of colloidal particle monolayers, based on cyclic voltammetry (CV) measurements of limiting diffusion current at rotating disk electrode (RDE) [3–5]. The main advantage of this method is that it could potentially be applied to particle multilayers. The underlying theoretical framework, however, has been limited to systems where the flow penetration depth is much less than the deposited layer thickness. Therefore, e.g., the cyclic voltammetry determination of particle surface coverage in monolayers of 3 μm particles is limited to dense layers at the surface coverage higher than 0.7 [5]. In general, however, we can expect that the range of applicability of the model can change with the particle size determining the layer permeability, as well as with the layer thickness, which in thick layers is much larger than the flow penetration depth. The aim of this paper is to experimentally verify the hypothesis by comparison of predicted and measured parameters of deposited monolayers for smaller particles of the diameter 1.16 μm .

2. Theoretical model

The theoretical basis of our model the reader can find in Ref. 5, as well as detailed derivations of equations used below. Here, in brief, we have presented just essential information. The subject of our consideration is a highly porous thin film of non-conductive, monodisperse, spherical particles of radius a , deposited on a homogeneous surface of disk electrode. Let us first define the dimensionless measure of particle surface concentration

$$\theta = \pi a^2 N/S, \quad (1)$$

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which we have called the particle surface coverage. Here, N and S denote the number of deposited particles and the electrode surface area, respectively.

In what follows we have assumed that the electrode rotates in a solution of electrochemically active species with a constant angular frequency ω . We have considered steady-state mass transfer of the solute that is consumed quantitatively at the surface of the disk electrode. If the radius of the disk is large compared to the diffusion boundary layer, edge effects can be neglected and only variations of chemical concentration in the direction perpendicular to the disk surface need to be considered. Assuming an infinitely fast reaction at the electrode surface, the electric current at the RDE has been determined by convective diffusion of the active species in the diffusion boundary layer and in the porous particle monolayer. If convection in the porous film is negligibly small and the particle size much larger than that of the diffusing species, we can describe the variation of limiting diffusion current with the particle surface coverage in terms of the equivalent thickness of stagnant solution layer or, for short, equivalent layer thickness [5]:

$$\lambda(\theta) = a \left[1 + \left(\frac{\pi}{2} - \frac{5}{3} \right) \theta + \frac{\theta + 1}{\sqrt{\theta(1-\theta)}} \arctan \sqrt{\frac{\theta}{1-\theta}} \right]. \quad (2)$$

This parameter is related to the limiting diffusion current I at the RDE by the equation [5]:

$$\lambda(\theta) = d \left(\frac{I_0}{I} - 1 \right) \quad (3)$$

where I_0 is the limiting diffusion current at the bare RDE and d is the thickness of the diffusion boundary layer, which is given by [6]:

$$d = 1.61D^{1/3}\omega^{-1/2}\nu^{1/6}. \quad (4)$$

Here D is the active species diffusion coefficient in the solution, ν is the solution kinematic viscosity, and ω is the disk angular frequency.

Thus, in principle, measuring the limiting diffusion currents at a given angular frequency of bare and covered electrode, we can determine the equivalent layer thickness of the porous layer. Then, solving Eq. (2) numerically, we can calculate the particle surface coverage. In practice, however, it is better to conduct a series of current measurements at various angular frequencies. This way we can not only improve the accuracy of our results, but also verify the assumption of negligible convection and quality of electrochemical measurements by testing the stability of λ , which should be independent of ω .

To compare results for different particle sizes, it is convenient to normalize λ by the particle monolayer thickness:

$$\Lambda(\theta) = \frac{\lambda(\theta)}{2a}. \quad (5)$$

From Eqs. (3) and (5) we can estimate the relative error in Λ to be

$$\sigma_{\Lambda} \approx \sigma_a + \sigma_d + \left(\frac{d}{2a\Lambda} + 1 \right) \sigma_{I_0/I}, \quad (6)$$

where σ_x denotes the relative error in the quantity x . It is easy to see that in case of thin highly porous layers, where Λ can be close to unity and $d \gg 2a$, the major contribution to the error in Λ can come from the error in the diffusion current ratio. Typically, d is of the order of 10 μm . Therefore, to determine the surface coverage of a monolayer of micron-sized particles with error less than 1%, we need to determine the diffusion current ratio with error less than 0.1%. This is a consequence of the decrease of porous layer effect on the limiting diffusion current with the decrease of that layer's thickness.

Let us emphasize that in case of thin highly porous layers the determination of λ from Eq. (3) has several advantages over the method based on the linear regression of the function $I^{-1}(\omega^{-1/2})$, described in Ref. 5. In that method we calculated Λ from the constant term of the linear function, determined by the least-square method under the assumption of independence of the equivalent layer thickness and disk angular frequency. In contrary, here we have calculated λ for various values of ω to determine if it is constant at given θ . This way we can more accurately verify the assumption of negligible convection and to determine the range of applicability of our theoretical model. Second, because of system non-ideality and finite-size effects [7,8], deviations of the limiting diffusion current from its theoretical values can exceed 0.1% and therefore the accuracy of coverage determination by the linear regression method can be poor. In contrary, the accuracy of the ratio I_0/I can be much better, because the effect of thin porous layer on the hydrodynamics is negligible and the deviations of I_0 and I cancel each other out. Finally, using Eq. (3) we do not need to determine accurately the electrode surface area and reactant concentration, which can be problematic in some systems.

3. Experimental

3.1. Electrochemical measurements

We have performed the cyclic voltammetry experiments in the measurement system as described previously [5]. The working electrode in our measurements has been a gold rotating disk electrode (Au RDE). Before each experiment, the gold surface has been polished for about 20 minutes with a 0.05 μm Al_2O_3 MasterPrep Polishing Suspension (Buehler) with addition of isopropanol (POCH, p.a.) on a polypropylene nonwoven fabric at a pressure about 2.4 kPa, using a custom made polishing machine. After polishing, we have rinsed it with ultrapure water and cleaned it in a mixture of ultrapure water and isopropanol (1:1) using an ultrasonic cleaner for about 5 min. to remove polishing residues. Then, we have carried out the CV measurements for the bare Au RDE. We have conducted the CV experiments in an equimolar aqueous 1 mM $\text{K}_3[\text{Fe}(\text{CN})_6] + \text{K}_4[\text{Fe}(\text{CN})_6]$ solution (POCH, p.a.) containing 1 M KCl (POCH, p.a.) as a base electrolyte. We have used ultrapure water (Direct-Q 3 System, Millipore) for the preparation of all solutions. We have determined the kinematic viscosity of the electrolyte solution at 298.15 K by means of Ubbelohde viscometer to be $\nu = (8.46 \pm 0.04) \times 10^{-7} \text{ m}^2/\text{s}$. The value of diffusion coefficient of hexacyanoferrate(III) ions, used in our calculations, equals $(7.39 \pm 0.01) \times 10^{-10} \text{ m}^2/\text{s}$ [5,9].

We have deoxygenated the electrolyte solution before the measurements by bubbling it with 5.0 argon (Linde Gas Poland) for about 20 minutes. We have carried out the CV measurements in the solution under argon atmosphere at $298.15 \pm 0.01 \text{ K}$. The temperature has been controlled in the electrochemical cell using the thermostat (VWR, AD 7L R-20) with an external temperature sensor. We have recorded cyclic voltammograms (I vs. E) of both bare and covered RDE for the rotational frequency $f = 30 \omega/\pi$ equal 1000, 1600, 2200, 2200, 1600, 1000 rpm. We have not used lower frequencies to avoid large values of d and errors in λ (see Eqs. (4) and (6)). At higher frequencies, on the other hand, the flow intensity grows and we can expect a variation of λ with f . We have conducted two measurements of the limiting diffusion current at each of the three frequencies to evaluate the rate of molecular surface contamination and particle desorption. We have limited the number of measurements to six because with its increase we have observed a growing molecular surface contamination of the bare

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