Mini review

Electrochemical insight from nanoparticle collisions with electrodes: A mini-review

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A B S T R A C T

The field of particle impact electrochemistry has grown rapidly in the few years since its development, with discoveries including: detection, characterisation, and quantification of nanoparticles (NPs); solution and surface aggregation of NPs; kinetics of redox reactions of NPs and of species at NPs; and information on surface chemistry of NPs. This mini-review aims to briefly cover the many advances made since the end of 2011.

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1. Introduction

The first electrochemical report of collisions of particles with electrode surfaces was in 1995 with Heyrovsky's work on colloidal semiconductors [1–4]. The phenomenon appeared sporadically in the literature for the next decade through the work of Scholz [5–7] and Compton [8–11] until the studies on Faradaic charge transfer by Heyrovsky and Korshunov [12] and Bard and Xiao [13] in 2006 and 2007 respectively. In excess of 50 papers that have been published since, particle-impact electrochemistry has become one of the fastest growing areas of activity in fundamental electrochemistry: to the extent that a previous review from early 2012 [14] is already considerably out of date.

The concept of the particle-collision experiment is straightforward: a nanoparticle (NP), usually travelling under thermal Brownian motion in a fully supported solution of inert electrolyte, is allowed to strike an inert microelectrode surface (typically a carbon fibre or mercury-plated platinum microelectrode). The particle may rebound immediately, or adsorb to the surface either temporarily or permanently. Depending on the material of the nanoparticle and the potential of the substrate electrode, the nanoparticle may either (i) be reduced or oxidised itself, or (ii) act as a nanospherical electrode to oxidise or reduce an electroactive species in solution (see Fig. 1). These two 'modes' of impact experiment are often loosely termed as 'direct' particle voltammetry and 'indirect' particle voltammetry respectively, and can be used to probe the nanoscale in different ways.

2. Direct oxidation/reduction of nanoparticles: characterisation & kinetics

The initial experiments in this field were on the (destructive) oxidation of silver nanoparticles (AgNPs), where the AgNPs were shown to

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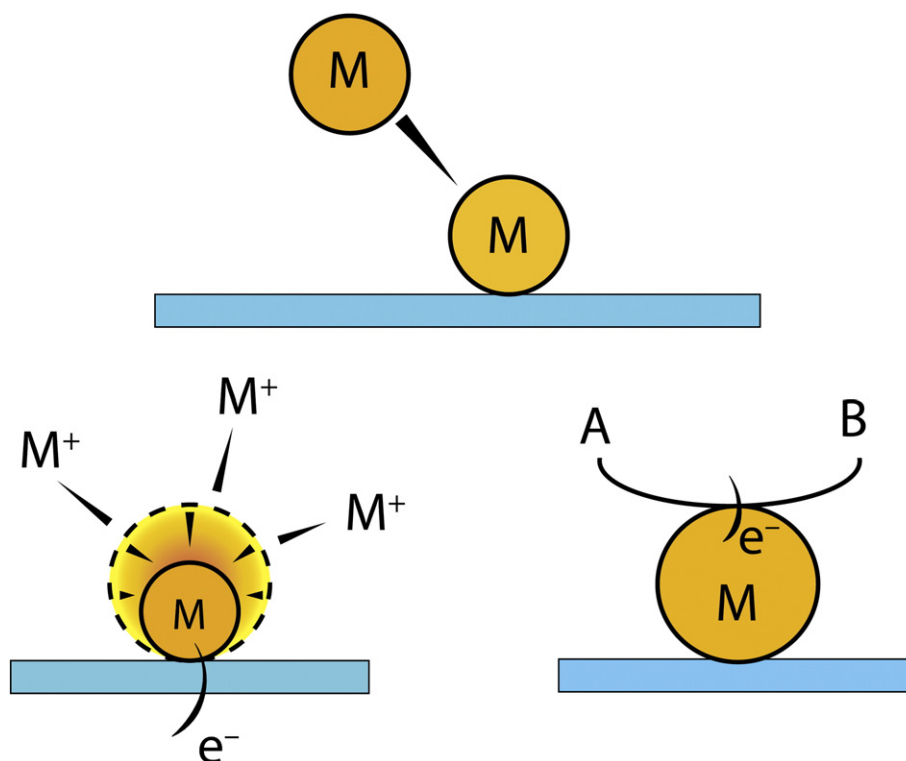
Fig. 1. Basic forms of particle-impact electrochemistry: direct oxidation/reduction of the nanoparticle and surface catalysed reaction of solution species.

be detected, and size and agglomeration distributions derived [15,16]. Further work by Zhou et al. demonstrated that the same properties could be deduced for AuNPs via oxidative impacts in chloride solution, where the dissolution of gold was facilitated through formation of the $AuCl_2^-$ and $AuCl_4^-$ ions [17].

Analogous oxidative studies were reported by Haddou et al. for copper and nickel NPs [18,19]. In addition to sizing the NPs, in [18], theoretical results were derived for fully reversible and irreversible kinetics of oxidation (see [18] for definition of symbols):

Reversible case: $E_{1/2} - E_f^0 = \frac{RT}{nF} \ln\left\{\frac{\rho r_i^2}{3.746 M D t_L}\right\}$.

Irreversible case: $E_{1/2} - E_f^0 = \frac{RT}{(n'+\beta)F} \ln\left\{\frac{\rho r_i}{4.847 M k_0 t_L}\right\}$.

It was shown that both the 1 electron oxidation Cu/Cu^+ and the 2 electron oxidation Cu/Cu^{2+} exhibit irreversible (i.e. slow) kinetics. In contrast, it was then found that the 1 electron Ag/Ag^+ oxidation was reversible and the 2 electron Ni/Ni^{2+} oxidation was irreversible [19].

Nanoparticle mixtures were investigated in [20], where AgNPs and NiNPs were shown to be individually identifiable through their oxidative impact transients. Size distributions for both species were obtained from the same experiment and expressions were derived that enabled the (unknown) concentrations of both nanoparticle species to be determined, via fitting the cumulative number of transient events as a function of time as an integrated chronoamperogram.

Whilst the majority of direct particle voltammetry reported is for the oxidation of NPs, Tschulik et al. [21] demonstrated that reduction of NPs can equally be used to infer details of the NP. In that paper, Fe_3O_4 (magnetite) NPs were sized by anodic (oxidative) and cathodic (reductive) impacts, with excellent agreement.

Most recently, the direct oxidation of organic NPs has been reported by Cheng et al. [22,23], using the coupled 2-electron, 2-proton reduction of indigo to leuco-indigo as a test system. In [22], it was shown that organic NPs can be accurately sized via impact voltammetry using the same procedure and theory as metallic NPs. The kinetics of the indigo NP reduction was then derived in [23] by considering the average

charge per reductive transient impact as a function of electrode potential as a measure of the change in NP radius, given by (see [23] for definition of symbols):

$$r_f = r_i - \frac{M t_L k_0 C_0}{\rho} \exp\left[\frac{(n'+\alpha)}{RT}\left(E_f^0 - E\right)\right]$$

via $|Q| = \frac{4\pi n F \rho}{3M}\left(r_i^3 - r_f^3\right)$.

3. Indirect electrochemistry of nanoparticles: kinetics of solution/surface reactions

The use of impacting NPs as proxies for single nanospherical electrodes was first investigated by Bard in a series of papers from 2007, based on the reduction of protons at PtNPs and hydrazine oxidation at AgNPs and AuNPs. Other systems included the oxidation of water at IrOx NPs [13,24–27].

The realisation that transient signals from indirect electrochemistry could be used to determine the kinetics of those surface reactions at single nanoparticles, and hence gain insight on the altered kinetics (if any) at the nanoscale came with Kahk et al.'s study into proton reduction occurring at PtNPs and AuNPs during impacts [28]. By plotting the average impact transient current as a function of potential, a trace is obtained that is entirely analogous with a steady-state voltammogram of a nanosphere on a surface. This can be modelled using a Butler–Volmer methodology to obtain unambiguous kinetic data, separating kinetic effects from mass-transport effects: Kahk et al. showed that proton reduction was not subject to a catalytic effect from AuNPs but was for AgNPs.

In a similar study Zhou and co-workers considered the reduction of protons at Ni@NiO NPs. By modelling the electrochemically irreversible process as occurring at a sphere on a plane, they found that the kinetic acceleration in the rate was due to surface NiO and not due to a size effect [29].

The application of the Marcus–Hush model electrode kinetics to such systems has been presented theoretically [30], and a startling