The Hydrogen Oxidation Reaction on Platinum Nanoparticles: Understanding the Kinetics of Electrocatalytic Reactions via ‘Nano- Impacts’

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Abstract

The kinetics of the hydrogen oxidation reaction (HOR) on platinum nanoparticles (PtNPs) is explored. The steady-state current for HOR on individual PtNPs is measured via the nano-impact approach. Adopting the Tafel-Volmer mechanism, the adsorption rate constant for HOR on PtNPs is calculated as $0.020 \pm 0.008 \text{ m s}^{-1}$. The HOR is also studied on electrodes where PtNPs are immobilized via drop-casting on the supporting substrate prior to experimentation and the kinetic parameters contrasted with those from the nano-impact experiments. The distinction in the kinetic parameters between the nano-impact and the drop-casting approaches reveals that the measurement on an individual nanoparticle is required in order to correctly understand the electrochemical reaction catalysed by nanoparticles, because the aggregation or loss of the nanoparticles drop-casted on the electrode leads to unavoidable errors in the measurement.

1 Introduction

The physical and chemical properties of a material can change dramatically when the size decreases from the macro-scale to the nano-scale, leading to potential applications for nanoparticles in the fields of biotechnology, catalysis and energy¹⁻⁴. In the area of catalysis, the small size provides large surface-to-volume ratio and often a high density of defects, which may alter the catalytic properties of nano-scale materials⁵. Furthermore, the investigations of nanoparticles lead to new insights into the structure-activity relationship of catalysts⁶⁻⁷ and help to understand the principles of the catalysis and heterogeneous reactions.

The electrocatalytic activity of nanoparticles is commonly studied as an ensemble effect by immobilising a large number of nanoparticles on an inert, conductive substrate.⁸ Inherent in such work is the assumption that the structure and the morphology of the nanoparticles on the surface are well known. However, the coverage of the nanoparticles may change in the experiment due to the aggregation or loss of the nanoparticles, misleading the analysis of experimental phenomena observed on the nanoparticle ensemble.⁹⁻¹¹

In recent years, the electrochemical characterization of nanoparticles has developed rapidly.¹²⁻¹⁴ On dispersing nanoparticles into solution, an individual nanoparticle can collide with an electrode due to its Brownian motion. Impacts are revealed by current spikes or steps at the electrode. The current can be generated from two possible sources: one is the oxidation or reduction of the nanoparticle itself when it hits the supporting substrate (for instance, $\text{Ni(NP)} - 2\text{e}^- \rightarrow \text{Ni}^{2+}$);¹⁵ the other is from the electrochemical reactions catalysed on the surface of the collided nanoparticle (for instance, proton reduction on platinum nanoparticles $\text{H}^+ + \text{e}^- \rightarrow 1/2 \text{H}_2$).¹⁶⁻¹⁷ The so-called “nano-impact” or “single nanoparticle collision” approach using individual nanoparticles allows the characterization of the properties and components of nanomaterials,¹⁸⁻²⁰ as well as the detection of target species

in the solution.²¹⁻²² This electroanalytical approach also provides information about the electrolyte-electrode interface and reaction kinetics.²³⁻²⁵

In this work, the kinetics of the hydrogen oxidation reaction (HOR) on Pt nanoparticles (PtNPs) is investigated. This reaction system is selected because it is a paradigmatic example of an inner sphere reaction and is of both fundamental and commercial interest.²⁶ Our study of the hydrogen oxidation reaction is implemented both on ensembles of PtNPs and at individual PtNPs. The adsorption rate constant for the hydrogen oxidation reaction on individual PtNPs is measured to be $0.020 \pm 0.008 \text{ m s}^{-1}$. It is further found that the kinetics for HOR on PtNPs detected from an ensemble of PtNPs is significantly underestimated, emphasizing the importance of applying the nano-impact technique to correctly understand electrocatalytic reactions on nanoparticles. Physical insights into the differences between single nanoparticle and ensemble behaviour are drawn.

2 Experimental

2.1 Chemicals

Hydrogen ($\geq 99.98\%$ H_2) was supplied from BOC, Surrey, U.K. Potassium nitrate ($\geq 99.0\%$, KNO_3) was obtained from Sigma-Aldrich, Dorset, U.K. Citrate-capped platinum nanoparticles (PtNPs) were provided by nanoComposix, San Diego, CA, U.S.A with a reported size 25 nm and concentration 3.5×10^{13} particles L^{-1} . All solutions were prepared with ultrapure water from Millipore with a resistivity of not less than 18.2 $\text{M}\Omega$ cm at 298 K.

2.2 Electrochemistry

2.2.1 Drop-casting Experiments

A three electrode system in a Faraday cage was used for all drop cast electrochemical experiments. A μ Autolab III from Metrohm Autolab B.V., Utrecht, The Netherlands, was employed as a potentiostat. The working electrode was a gold macrodisk electrode of radius 1.01 mm from BASi, West Lafayette, IN, U.S.A and the electrode was polished with alumina powders from Buehler, Lake Bluff, IL, U.S.A in a size sequence: 1.0 μm , 0.3 μm and 0.05 μm . The reference electrode was a standard mercury/mercurous sulfate electrode (MSE) [$\text{Hg}/\text{Hg}_2\text{SO}_4$, K_2SO_4 (saturated; + 0.64 V vs standard hydrogen electrode, SHE)] from BASi, West Lafayette, IN, U.S.A. The counter electrode was a graphite rod of diameter 6 mm from Sigma-Aldrich, Dorset, U.K. All experiments were conducted under a hydrogen atmosphere. All electrochemical and UV/Vis spectroscopy measurements were thermostatted at 25 ± 0.5 $^\circ\text{C}$.

Nanoparticle modification of the gold macroelectrode was achieved through drop casting 1 μL of the stock PtNP suspension, directly from the manufacturer, onto the electrode surface. The electrode was subsequently allowed to dry under flowing nitrogen prior to experimentation.

2.2.2 Nano-impact Experiments

All nano-impact electrochemical experiments were performed on a three electrode system in a Faraday cage. The working electrode was a gold microdisc electrode of diameter 10.0 μm from ALS, Tokyo, Japan and the electrode was polished with alumina powders from Buehler, Lake Bluff, IL, U.S.A of decreasing sizes: 1.0 μm , 0.3 μm and 0.05 μm . A leakless silver/silver chloride electrode [Ag/AgCl, 1.0 M KCl] from Cypress Systems, Lawrence, KS, U.S.A functioned as a reference electrode (measured as -0.006 V vs saturated calomel electrode, SCE, [Hg/Hg₂Cl₂, KCl (saturated)], which is equivalent to $+0.235\text{ V}$ vs SHE). A platinum foil from Goodfellow, Cambridge, U.K. acted as a counter electrode. All solutions were thoroughly saturated with hydrogen prior to both electrochemical and UV/Vis spectroscopy experiments. All measurements were made under thermostatted conditions at $25.0 \pm 0.5\text{ }^{\circ}\text{C}$.

An in-house built low noise potentiostat²⁰ was employed for both potentiostatic control and impact current measurement. A computer interface allowed analogue-digital conversion via a USB connected NI USB-6003 data acquisition (DAQ) device from National Instruments, Austin, TX, U.S.A. The DAQ device was controlled by a script written in Python 2.7 and run through the IDE Canopy from Enthought, Austin, TX, U.S.A. A low-noise current amplifier LCA-4K-1G from FEMTO, Messtechnik GmbH, Germany measured currents at the working electrode (running to ground), where its output bandwidth was limited by two cascaded passive RC-filters (100 Hz). The outcoming analogue signal was oversampled and digitized by the DAQ device at a stream rate of 4 kHz. A highly stabilized (1 kHz bandwidth) classic adder potentiostat²⁷ provided potentiostatic control. It is noted that a high quality operational amplifier, LMC6001 from Farnell, Leeds, U.K, with an ultra-low-input bias (25 fA) was used for the reference buffer; and a high quality low-noise operational amplifier, AD797 from Farnell, Leeds, U.K, controlled the potential at the counter electrode.

In the experimental data report below, all potentials are converted to the SHE scale.

2.3 Characterisation

The stock PtNP samples were characterised via transmission electron microscopy (TEM) and ultraviolet-visible (UV/Vis) spectroscopy.

2.3.1 TEM

TEM (JEOL JEM-3000F FEGTEM, 300 kV accelerating voltage) was performed to determine the size of nanoparticles. Samples were prepared by depositing a drop of the stock PtNP suspension, with concentration 3.5×10^{13} particles L^{-1} , onto a carbon TEM grid coated with holey carbon film from Agar Scientific, Stansted, U.K. Air drying was allowed before any further examination. ImageJ software²⁸ developed at the National Institutes of Health, U.S was used to analyse the TEM images. Clearly defined PtNPs were measured and their radii calculated. Example images are shown in Figure 1. The particles were found to be made up of an aggregation of smaller particles with size about 5 nm. A total count of 165 PtNPs gave a mean radius of 24.3 ± 1.6 nm, close to the value of 25 nm provided by the manufacturer. To clarify, in this paper, the “PtNP” refers to the 25 nm particle; the “small nanoparticles” are components of a PtNP; and the “PtNP modified electrode” is an inert, conductive electrode (gold) modified by electroactive PtNPs via either drop-casting or the nano-impact approach, where the electrochemical reaction only occurs on the PtNPs.

Figure 1 (a) TEM bright field image of PtNPs. (b) High-resolution TEM image of one PtNP. (c) Size

distribution of the PtNPs with an average radius of 24.3 ± 1.6 nm.

2.3.2 UV/Vis Spectroscopy

For UV/Vis (Shimadzu UV-1800 UV/Vis Spectrophotometer) measurements, the stock PtNP suspension was diluted by a factor of 2 with ultrapure water to obtain absorbance in an analytically meaningful range. Both deuterium and halogen light sources were used, with the sample being scanned from 900 to 200 nm. A broad surface plasmon peak around 295 nm was recorded indicating the presence of PtNPs.²⁹

3 Theory and Simulation

The simulation model for the PtNPs modified electrode and the mechanism of the hydrogen oxidation reaction on Pt are discussed in this section. Different geometries of the PtNP are compared in order to explore a suitable and simple simulation model for the HOR on PtNPs.

3.1 Simulation for the PtNP modified electrode

As shown in the TEM image of Figure 1, a PtNP can be regarded as a sphere with an average radius of 25 nm. For the PtNP modified electrode, the PtNPs are assumed to be regularly dispersed on a supporting substrate. Although a regular distribution of the PtNPs is an idealised model, it has been previously applied successfully in the simulation for the drop-casting experiments, especially at low nanoparticle coverages³⁰⁻³⁴. Therefore, the PtNP modified electrode is treated as a regular array in this work. For a nanoparticle array, the geometry of the nanoparticle also plays a crucial role. There is previous work discussing the influence of the particle geometry in the simulation for nanoparticle modified electrodes³⁵. Here two geometries are discussed in the study of HOR on PtNPs: a 'sphere model' and a 'disc model'.

Figure 2 illustrates the 'sphere model' for the PtNP modified electrode. Figure 2a shows the regular distribution of the spherical PtNPs dispersed on the supporting substrate. The simulation space for each individual PtNP is estimated on the basis of the diffusion domain approximation.^{34, 36-37} It has been shown that the diffusion domain approximation turns the 3-dimensional problem into a simpler 2-dimensional problem while attaining similar accuracy^{30, 34, 36-37}. Figure 2b shows the simulation space under a 2-dimensional cylindrical coordinate for a spherical PtNP. In the cylindrical coordinate system, r is the coordinate parallel to the supporting electrode surface and z is that perpendicular to the supporting electrode. d_{NP} is the average centre-to-centre distance between two adjacent PtNPs, which can be inferred from the particle coverages used in the experiment. The distribution of the particles is

approximated by a hexagonal packing arrangement and the simulating area for an individual PtNP on the supporting substrate is considered as a circular cell with a radius of $0.5258 d_{\text{NP}}$ ³⁸. The radius of the particle is r_{NP} and the radius of the simulation cell is r_0 . Thus the d_{NP} and the coverage of PtNPs have the relationship:

$$\text{coverage} = \frac{r_{\text{NP}}^2}{(0.5258 d_{\text{NP}})^2} \quad (1)$$

As the simulation area for one PtNP is symmetric, only half of the space needs to be calculated and the three-dimensional space in Figure 2b can be converted to a two-dimensional cell as shown in Figure 2c³⁹. Figure 2c displays the simulation geometry and the calculation grids for a PtNP, based on the approach in the literature⁴⁰⁻⁴². Within the area where $r < r_{\text{NP}}$ and $z < 2^* r_{\text{NP}}$, the grids are given by:

$$\begin{aligned} r_m &= r_{\text{NP}} \sin(\theta_m), \theta_m = 0, \frac{\pi}{200}, \dots, \frac{99\pi}{200}, \frac{\pi}{2} \\ z_n &= r_{\text{NP}} (1 - \cos(\theta_n)), \theta_n = 0, \frac{\pi}{200}, \dots, \frac{199\pi}{200}, \pi \end{aligned} \quad (2)$$

where m, n are the indexes of r and z directions. θ is the angle shown in Figure 2c. In our simulation, the angle from 0 to π in the sphere is evenly separated into 200 parts. For the rest, general expanding grids are applied⁴³. Figure 2d is an example of the concentration profile for an individual spherical PtNP, showing how the concentration of the reactant gradually changes from the bulk solution to the electroactive surface.

An alternative but more approximate approach to simulate the PtNPs modified electrode is to apply a disc geometry for the PtNP and keep the equivalent electroactive surface area to the PtNP sphere³⁵. For the sphere model, the radius of the PtNP sphere r_{NP} is the average radius for real PtNPs, 25 nm. But as the PtNP disc should have the same surface area with the spherical one, the radius of the PtNP disc r_{NP}' is taken as equal to $2 r_{\text{NP}}$, 50 nm. The simulation space and the calculation grids are shown in Figure 3, also with an example of

the concentration profile for the reactant on an individual disc PtNP. As the geometry is relatively simple in the disc model, general expanding grids are applied in the (r, z) space. In the r direction, as the boundaries are located at $r = 0$ and $r = r_{\text{NP}}$, the grids symmetrically expand from both 0 and r_{NP} to the middle point $0.5r_{\text{NP}}$.

Figure 2 Simulation for the PtNPs modified electrode with the sphere model. (a) Distribution of the PtNPs on the supporting electrode, where the blue circles are PtNPs and the dashed line shows the simulation area for each PtNP; (b) Simulation space for one PtNP, where the blue sphere is the PtNP; (c) Calculation grids applied in a simulation cell, where the red points are the boundary of a PtNP; (d) An example concentration profile of the reactant.

Figure 3 Simulation for the PtNPs modified electrode with the disc model. (a) Simulation space for one PtNP disc, where the blue sphere is the electroactive area for the PtNP; (b) Calculation grids applied in the simulation cell, where the red line shows the position of the electroactive area; (c) An example concentration profile of the reactant.

3.2 The Mechanism of the Hydrogen Oxidation Reaction

The hydrogen oxidation reaction on Pt electrodes is widely thought to follow the Tafel-Volmer mechanism, where the hydrogen molecule first adsorbs and dissociates to two adsorbed H atoms before electron transfer:^{7, 44-47}

where H(ads) is the hydrogen atom adsorbed on the Pt, k_a and k_d are the adsorption and desorption rate constants, k_{ox} and k_{red} are the oxidative and reductive electron transfer rate constants. In the following electron transfer step (4), k_{ox} and k_{red} are assumed to follow the Butler-Volmer equation:

$$k_{\text{ox}} = k_0 \exp\left(\frac{\beta F}{RT} \left(E - E_{\text{f, H}^+/\text{H(ads)}}\right)\right) \quad (5)$$

$$k_{\text{red}} = k_0 \exp\left(-\frac{\alpha F}{RT} \left(E - E_{\text{f, H}^+/\text{H(ads)}}\right)\right) \quad (6)$$

α and β are the cathodic and anodic transfer coefficients and $\alpha+\beta=1$.⁴⁸⁻⁴⁹ For the HOR, the values of both transfer coefficients are assumed to be 0.5. $E_{\text{f, H}^+/\text{H(ads)}}$ is the formal potential for $\text{H}^+/\text{H(ads)}$ redox couple, which can be derived from the Gibbs energy balance in HOR:

$$E_{\text{f, H}^+/\text{H(ads)}} = E_{\text{f, H}^+/\text{H}_2} + \frac{RT}{2F} \ln\left(\frac{k_a c^0}{k_d}\right) \quad (7)$$

where c^0 is the standard concentration, equal to 1 mol dm^{-3} . $E_{\text{f, H}^+/\text{H}_2}$ is the formal potential for the HOR with the H^+/H_2 redox couple. Under our experimental conditions, $E_{\text{f, H}^+/\text{H}_2}$ is -0.0991 V.⁵⁰

The reaction rate equations for the HOR at a PtNP are:

$$j_{\text{H}_2}(\vec{r}_{\text{surf}}, t) = -k_a c_{\text{H}_2}(\vec{r}_{\text{surf}}, t) \left[\frac{\Gamma_{\text{M}}(\vec{r}_{\text{surf}}, t)}{\Gamma_{\text{max}}} \right]^2 + k_d \left[\frac{\Gamma_{\text{H(ads)}}(\vec{r}_{\text{surf}}, t)}{\Gamma_{\text{max}}} \right]^2 \quad (8)$$

$$\begin{aligned} \frac{\partial \Gamma_{\text{H(ads)}}(\vec{r}_{\text{surf}}, t)}{\partial t} = & 2k_a c_{\text{H}_2}(\vec{r}_{\text{surf}}, t) \left[\frac{\Gamma_{\text{M}}(\vec{r}_{\text{surf}}, t)}{\Gamma_{\text{max}}} \right]^2 - 2k_d \left[\frac{\Gamma_{\text{H(ads)}}(\vec{r}_{\text{surf}}, t)}{\Gamma_{\text{max}}} \right]^2 \\ & - k_{\text{ox}} \left[\frac{\Gamma_{\text{H(ads)}}(\vec{r}_{\text{surf}}, t)}{\Gamma_{\text{max}}} \right] + k_{\text{red}} \left[\frac{\Gamma_{\text{M}}(\vec{r}_{\text{surf}}, t)}{\Gamma_{\text{max}}} \right] c_{\text{H}^+}(\vec{r}_{\text{surf}}, t) \end{aligned} \quad (9)$$

$$j_{\text{H}^+}(\vec{r}_{\text{surf}}, t) = k_{\text{ox}} \left[\frac{\Gamma_{\text{H(ads)}}(\vec{r}_{\text{surf}}, t)}{\Gamma_{\text{max}}} \right] - k_{\text{red}} c_{\text{H}^+}(\vec{r}_{\text{surf}}, t) \left[\frac{\Gamma_{\text{M}}(\vec{r}_{\text{surf}}, t)}{\Gamma_{\text{max}}} \right] \quad (10)$$

where $\vec{r}_{\text{surf}}$ refers to surface of the PtNP:

$$\vec{r}_{\text{surf}} \begin{cases} r^2 + (z - r_{\text{NP}})^2 = r_{\text{NP}}^2 & \text{PtNP sphere} \\ r \leq r_{\text{NP}}, z = 0 & \text{PtNP disc} \end{cases} \quad (11)$$

The parameters r and z are the cylindrical coordinates used in section 3.1. t is time, Γ_i is the surface coverage (mol m^{-2}) and $\Gamma_i/\Gamma_{\text{max}}$ is the fractional surface coverage (unitless). Γ_{max} is the maximum surface coverage at the electrode surface and $\Gamma_{\text{max}} = \Gamma_{\text{H(ads)}}(\vec{r}_{\text{surf}}, t) + \Gamma_{\text{M}}(\vec{r}_{\text{surf}}, t)$. The maximum surface coverage reported in the literature for a monolayer hydrogen adsorption is about $2.2 \times 10^{-5} \text{ mol m}^{-2}$ on polycrystalline Pt.⁴⁵ The same maximum surface coverage value is applied below in the simulations for PtNP clusters. Considering the rough surface of the PtNPs, the kinetic parameters defined in Eqs.(8)-(10) are “combined” parameters in which the variation of Γ_{max} is taken into consideration.^{47, 51}

On the surface of the inert supporting substrate and the edge of the simulation cell, a reflective boundary condition is applied:

$$\left. \frac{\partial c_i(\vec{r}, t)}{\partial \vec{r}} \right|_{\vec{r}_{\text{sub}}, \vec{r}_{\text{edge}}} = 0 \quad (12)$$

$\vec{r}_{\text{sub}}$ is the supporting substrate:

$$\vec{r}_{\text{sub}} \begin{cases} z = 0 & \text{PtNP sphere} \\ z = 0, r > r_{\text{NP}} & \text{PtNP disc} \end{cases} \quad (13)$$

$\vec{r}_{\text{edge}}$ is the edge of the simulation cell where $r = r_0$ in both sphere and disc simulation models.

As the electrolyte applied in our experiment to ensure the electrochemical reaction is fully supported and hence the mass transport can be taken to be “diffusional”.⁵² The mass transport of the redox species H_2 and H^+ in the solution is described by Fick’s second law:

$$\frac{\partial c_i(\vec{r}, t)}{\partial t} = D_i \nabla^2 c_i(\vec{r}, t) \quad (14)$$

where i refers to H_2 or H^+ and D is the diffusion coefficient. The diffusion coefficients of H_2 and H^+ applied in this work are the values measured in KNO_3 electrolyte,^{50, 53} which are $5.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $9.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, respectively.

Before the electrochemical reaction ($t = 0$), the chemisorption of H_2 on Pt before the electrochemical reaction is assumed to follow the Langmuir isotherm:

$$\frac{\left(\Gamma_{H(\text{ads})}(\vec{r}_{\text{surf}}, t = 0) / \Gamma_{\text{max}} \right)^2}{\left(1 - \Gamma_{H(\text{ads})}(\vec{r}_{\text{surf}}, t = 0) / \Gamma_{\text{max}} \right)^2} = \frac{k_a c_{H_2}(\vec{r}_{\text{surf}}, t = 0)}{k_d} \quad (15)$$

The initial concentrations of H_2 and H^+ are:

$$\begin{aligned} c_{H_2}(\vec{r}, t = 0) &= 0.77 \text{ mM} \\ c_{H^+}(\vec{r}, t = 0) &= 0 \end{aligned} \quad (16)$$

The electrolyte solution in the experiment is saturated with H_2 and the hydrogen solubility at standard pressure as given by the Henry's law constant is 0.77 mM.⁵⁰

During the cyclic voltammetry scanning, the electrode potential E and the time t are linked by:

$$\begin{aligned} t < t_{\text{switch}}, E &= E_{\text{ini}} + \nu t \\ t > t_{\text{switch}}, E &= E_{\text{switch}} - \nu(t - t_{\text{switch}}) \end{aligned} \quad (17)$$

where E_{ini} and E_{switch} are the initial and the switching potentials, t_{switch} is the time at which the direction of sweep is switched, and ν is the scan rate.

By solving the diffusion equations (14) with the known initial conditions (15) and (16) and boundary conditions (8)-(13), the flux densities j of the redox species H_2 and H^+ can be calculated from:

$$j_i = -D_i \frac{\partial c_i(\vec{r}, t)}{\partial \vec{r}} \bigg|_{\vec{r}_{\text{surf}}} \quad (18)$$

where i refers to H_2 or H^+ . Hence the cyclic voltammogram can be simulated:

$$I(E) = F \int_{\text{surf}} j_{H^+}(E) dA \quad (19)$$

where A is the surface area of the PtNP.

The resulting problem was solved numerically by means of the Newton-Raphson method and the alternating direction implicit (ADI) method, the details of which can be found in the literature.⁴³ In this work, cyclic voltammograms are simulated for the HOR on PtNP modified electrodes. The differences between the sphere model and the disk model will be discussed in next subsections. The simulation was written in C++ with OpenMP for multithreading and simulations were performed using an Intel(R) Xeon(R) 3.60G CPU. The runtime varied between approximately 20 minutes to 20 hours per voltammogram, depending on the mesh and the simulation parameters applied to reach convergence.⁵⁴

3.3 The HOR on PtNP Arrays for Different Geometry Models

Generally the diffusion conditions, determined by the experimental timescale and the coverages of the nanoparticles, can be divided into four limiting categories, defined as “cases 1~4” in the literature.^{35, 38} In cases 1 and 2, the diffusion zones for each particle are separated. But the diffusion zone is perpendicular to the surface of each individual particle for case 1 while it is radial from the surface for case 2. In cases 3, the radial diffusion zones for each individual particle overlap somewhat. In case 4, the diffusion zones for each particle fully overlap such that the overall diffusion region becomes planar and linear to the whole

electrode. However, as in our experiments the size of the PtNP (25 nm) and the scan rate for HOR in the cyclic voltammetry (0.1 V s^{-1}) is fixed, the diffusion condition is determined by the coverage of the PtNPs on the supporting substrate and the reaction kinetics. Thus the case 1 which only occurs under an ultrashort experimental timescale will not be discussed in this work, while cases 2~4 are shown in the Figure 4.

In addition to the diffusion conditions, different reaction kinetics are considered as well: one where the reaction rate of HOR is fast and the limiting factor for the reaction rate is diffusion, the other where that the reaction rate of the HOR is limited by slow adsorption. From a previous study of HOR on Pt, it is known that on microsize electrodes, the reaction rate of HOR is limited by the slow dissociative adsorption of H_2 and the electron transfer rate is relatively fast.⁵¹ Therefore, only the adsorption kinetics and the diffusion of the reactant are taken into consideration as possible limiting factors for the HOR on the PtNP array.

Figures 4 a-c illustrate the diffusion conditions for three different coverages of PtNPs, that is, cases 4, 3 and 2 respectively. The diffusional cases for the three situations are distinct and thus lead to various voltammetric features. Figures 4 d-f and Figures 4 g-i are simulated with different kinetics: the reaction rate is “fast” in Figures 4d-f and the reaction is limited by the slow adsorption process in Figure 4 g-i. When the reaction is fast and the reaction rate is only limited by the diffusion of the reactant, these diffusion-controlled voltammograms change with different PtNP coverages, as shown in Figures 4 d-f. The “case 4” voltammetry of Figure 4d, corresponding to linear diffusion in Figure 4a, appears when the centre-to-centre distance between two adjacent PtNPs is small (compared to the diffusion layer thickness) and the diffusion layers for each PtNP are overlapped. In contrast, the fully steady-state (“case 2”) voltammetry of Figure 4f, corresponding to the convergent diffusion in Figure 4c, can be observed when the distance between particles is large (compared to the diffusion layer thickness) and the diffusion regions for each particle are separated. In the diffusion condition of Figure 4b, the “case 3” voltammetric waveshape is between the “case 4” voltammetry and the “case 2” one, as shown in Figure 4e.

Figures 4g, 4h and 4i show the “case 4”, “case 3” and “case 2” voltammograms under the adsorption-limited reactions. Although the diffusion-controlled voltammograms and the adsorption-limited ones have similar voltammetric features under the same PtNP coverage, the formation of the waveshapes and the steady-state currents are distinct. In the voltammograms of Figures 4d, 4e and 4f, the diffusion process is the limiting factor for the reaction while in Figures 4g, 4h and 4i, the slow adsorption process of H₂ prevents the increase of the current with the overpotential. Compared to the diffusion-controlled situation for one-electron-transfer reaction on nanoparticle arrays, which has been well-established in the literature,^{35, 42} the HOR has a more complex CE mechanism (C: chemical step; E: electrochemical step). As can be seen from Figure 4, the voltammetric responses for the CE reaction on nanoparticle arrays are strongly dependent on the reaction kinetics.

In Figure 4, the two simulation geometries, the spherical model of Figure 2 and the disc model of Figure 3, are also compared with respect to various distribution densities of the nanoparticles and different reaction kinetics. The simulated voltammograms based on the sphere model are shown in black lines while those from the disc are in red. The electroactive areas for HOR on spherical and disc PtNPs are the same in the two simulation models. The voltammograms of the HOR in Figures 4d, 4e, 4f are simulated with fast and reversible reaction kinetics. In this case, the waveshapes for PtNP spheres and discs are very similar in “case 4” (Figure 4d) and “case 3” (Figure 4e) voltammograms. But the diffusion-controlled steady-state currents (“case 2”, Figure 4f) for an isolated nano-sphere and an isolated nano-disk are different. In the steady state, the analytical diffusion-controlled steady-state currents for HOR on the isolated sphere and the isolated disk of equivalent surface areas can be expressed by^{38, 55}:

$$I_{\text{diff, disk}} = 4nFr_{\text{NP}}'c_{\text{H}_2}^*D_{\text{H}_2} \quad (20)$$

$$I_{\text{diff, sphere}} = 4\pi nFr_{\text{NP}}c_{\text{H}_2}^*D_{\text{H}_2} \ln 2 \quad (21)$$

where r_{NP} in Eq.(21) is the average radius of the PtNP sphere and r'_{NP} is the radius of the nano-disk, equal to $2r_{\text{NP}}$.

The “case 4”, “case 3” and “case 2” voltammetries, for cases where the reaction rate is limited by the adsorption kinetics, are shown in Figures 4g, 4h and 4i. When the coverage density of the particles is high on the supporting substrate, the forward peaks of the two simulated geometries overlap and the backward peaks have similar waveshapes and peak currents, as shown in Figures 4g and 4h. For the steady-state voltammetry in Figure 4i, in contrast to the results of Figure 4f, the kinetics-limited steady-state current is insensitive to the change of the geometry of the electroactive PtNP. Therefore, the alternative of the sphere model by the disc one is suitable for the kinetics-limited steady-state voltammetry. In steady state, when the adsorption process is a limiting factor, the adsorption-limited current I_{ad} on a disc microelectrode or nanoelectrode can be expressed as a function of k_a ⁵¹:

$$I_{\text{ad}} = I_{\text{diff}} \frac{\frac{k_a r_{\text{NP}}}{D_{\text{H}_2}}}{\frac{4}{\pi} + \frac{k_a r_{\text{NP}}}{D_{\text{H}_2}}} \quad (22)$$

which is also valid for an isolated PtNP sphere. But when applying to an isolated PtNP sphere it needs to be noted that I_{diff} used in Eq.(22) is the diffusion current in the planar geometry model, calculated from Eq.(20).

Figure 4 Comparison between the voltammograms with the sphere model (shown by the black lines) and the disc model (shown by the red lines). The reaction rates in (a), (b) and (c) are limited only by the diffusion process and $k_a = 1 \text{ m s}^{-1}$. The reaction rates in (d), (e) and (f) are limited by the adsorption of H_2 and $k_a = 0.001 \text{ m s}^{-1}$. k_d is $1.0 \text{ mol m}^{-2} \text{ s}^{-1}$ and k_0 is 1.0 m s^{-1} . r_{NP} in the nano-sphere model is 25 nm and r_{NP} in the nano-disk model is 50 nm . $c_{\text{H}_2}^*$ is 0.78 mM . D_{H_2} is $5.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. D_{H^+} is $8.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

4 Results and Discussions

In this section, the drop-casting and the nano-impact techniques are applied to study the hydrogen oxidation reaction (HOR) on platinum nanoparticles (PtNPs). By combining the experimental results with the numerical simulations, kinetic information is collected from both experiments, and then analysed, contrasted and discussed.

4.1 Aggregation Study of PtNPs

UV/Vis analysis was performed prior to electrochemical measurements, in the presence of electrolyte (20 mM KNO_3) and gas (air, nitrogen or hydrogen) to monitor any aggregation of the PtNPs²⁹. In particular hydrogen, H_2 , dissociatively adsorbs strongly on platinum and so may displace the capping agent (citrate in the case of interest). It has been reported⁵⁶ that in the presence of hydrogen PtNPs are more susceptible to aggregation: The lower surface charge is thought to decrease the stability of the PtNPs in solution and promote aggregation. Changes in the surface plasmon signals were measured via UV/Vis spectroscopy at a wavelength of 295 nm. Note that the aggregation can be affected by size, shape of the nanoparticles and the experimental environment (capping agent, solvent)⁵⁷⁻⁶⁰.

As shown in Figure 5, in both case of air and saturated nitrogen, no significant variations of the surface plasmon peak were observed during the experimental timescale, indicating stability of PtNPs. With a long exposure time in the presence of saturated hydrogen, the recorded surface plasmon signal attenuated and red shifted, indicating the aggregation of the nanoparticles. However over a period of 30 mins, the difference between the signals in the presence of hydrogen, nitrogen or air were tiny and peak heights were closely similar, suggesting little, if any, aggregation happened. Hence in the following, the PtNPs were concluded to be stable over this timescale. Consequently, electrochemical measurements were conducted within 30 minutes in the presence of hydrogen to avoid aggregation.

Figure 5 Plot of the absorbance against the experimental time measured at a wavelength of 295 nm. Black square, blue triangle and red circle represent PtNPs in 20 mM KNO_3 with air, nitrogen and hydrogen, respectively. Inlay: UV/Vis spectrum of PtNPs in 20 mM KNO_3 with hydrogen. The very first absorbance in all three situations and the dotted UV/Vis curve in inlay were PtNPs data collected in 20 mM KNO_3 with air, before bubbling any nitrogen or hydrogen. All five points overlaid to give a reproducible UV/Vis measurement.

4.2 HOR on Individual PtNPs

The nano-impact technique enables the study of electrochemical reactions at individual nanoparticle.¹²⁻¹⁴ In this work, the hydrogen oxidation reaction on individual PtNPs is explored via the nano-impact approach as described in the experimental section. A gold micro-disc electrode (radius $5.0\ \mu\text{m}$) was employed and immersed in a 20 mM KNO_3 solution saturated with hydrogen gas. PtNPs were added into the electrolyte solution; when a PtNP strikes and sticks on the supporting Au electrode, current 'spikes' and 'steps' are observed in the chronoamperograms.

Figure 6 shows a typical current-time profile corresponding to the HOR on individual PtNPs. Figure 6a provides the chronoamperograms of 50 s duration at an overpotential of 0.44 V versus the standard hydrogen electrode, SHE. The black line is the

chronoamperogram measured in the presence of 20 pM PtNPs, while the red line shown for comparison is the blank chronoamperogram where no PtNP was added to the electrolyte. As shown in the inner panel of Figure 6a, current “steps” are recorded in the chronoamperogram in the presence of PtNPs. In the ‘blank’ chronoamperogram, no signal steps are visible. In the chronoamperogram with PtNPs added, current “steps” are only observed in the presence of H₂, indicating that steps are related to the oxidation of hydrogen on the PtNPs. For the case where both H₂ and PtNPs are present, the stepped nature of the responses suggests that the PtNPs are irreversibly adsorbed on the Au electrode.

Figures 6b and 6c show two representative current steps for HOR on individual PtNPs recorded at 0.34 V and 0.44 V (vs SHE), respectively. The current difference between the point at 150 ms from the starting point and the background (illustrated by the red lines in Figure 6b and 6c) is regarded as the steady-state current for HOR to an individual PtNP at a certain potential. By averaging the currents measured from several steps, the influence of the noise level on the signal caused by potentiostat is minimised. The average steady-state current is thus measured as 18.6 ± 6.3 pA at 0.34 V and 19.9 ± 7.1 pA at 0.44 V, where the standard deviation somewhat reflects not only the possible experimental noise/error but also the distribution of nanoparticle sizes. As the reacting current does not increase with the potential from 0.34 V to 0.44 V, the assumption that the current is indeed at steady state is reasonable and the steady-state current can be taken ca. 20 ± 7 pA. According to Eq.(21), if the HOR on an individual PtNP is diffusion-controlled, the diffusional steady-state current I_{diff} would be expected to be 164 pA. The measured steady-state current on isolated PtNPs is clearly smaller than the diffusion-controlled value, showing that even on nano-size Pt, the reaction rate of the HOR is kinetically limited probably by the slow adsorption kinetics. Eq.(22) describes the relationship between the adsorption rate constant k_a and the adsorption-limited steady-state current I_{ad} . The adsorption rate constant for HOR on an individual PtNP can be therefore calculated as 0.020 ± 0.008 m s⁻¹.

Figure 6 (a) chronoamperograms for a 5.0 μm Au microelectrode in 20 mM KNO_3 saturated with H_2 ; (b) and (c) are typical individual PtNP signals seen at 0.34 V and 0.44 V (vs SHE), respectively.

The adsorption rate constant k_a for HOR measured on polycrystalline Pt microdisc electrodes is reported as $5 \times 10^{-4} \text{ m s}^{-1}$.⁴⁷ As we have estimated, the steady-state current in Figure 6 implies an approximate k_a value of 0.02 m s^{-1} for HOR on the nano-size platinum. k_a thus approximately increases by 40 times from the polycrystalline Pt electrodes to the PtNPs. This may be because that compared to bulk Pt, the PtNP has much higher effective surface area. The k_a defined in the Tafel-Volmer mechanism is a “combined” adsorption rate constant⁵¹, which is not only dependent on the property of the catalyst but also related to the maximum surface coverage Γ_{max} . For the same material, when Γ_{max} increases, the value of the “combined” k_a increases as a function of the square of Γ_{max} . Thus, the enhancement of k_a from $5 \times 10^{-4} \text{ m s}^{-1}$ to 0.02 m s^{-1} may suggest an increase of Γ_{max} . The simulation constant $\Gamma_{\text{max}} = 2.2 \times 10^{-5} \text{ mol m}^{-2}$ is only valid if the surface of the PtNP can be regarded as smooth as the poly-crystalline surface. However, as can be seen from the TEM images (see above), the surface of the PtNP is composed of many smaller nanoparticles and is likely much ‘rougher’ than a polished poly-crystalline Pt surface. Therefore, a PtNP with a rough surface likely has a larger surface density of active sites for HOR than the smooth Pt electrode, indicating why the combined adsorption rate constant changes by ca. 40 times from the poly-crystalline Pt to the PtNP.

4.3 HOR on Drop-casted PtNPs

To further explore the kinetics of the hydrogen oxidation reaction on nano-sized Pt, the HOR was next studied using PtNPs drop-casted on a gold electrode with various coverages via both experiment and numerical simulation. In contrast to the nano-impact experiments, the PtNPs are first immobilized on the supporting Au macro-electrode (radius 1.01 mm) prior to experimentation. Eight drop-casted electrodes with different coverages of PtNPs were employed in this work. The coverage is the percentage of the area occupied by all the PtNPs in the overall area of the substrate:

$$\text{Coverage of PtNPs (\%)} = \frac{N_{\text{NP}} \times (\pi r_{\text{NP}}^2)}{\pi r_{\text{Au}}^2} \times 100 \quad (23)$$

where N_{NP} is the number of PtNPs and r_{Au} is the radius of the substrate Au electrode. The kinetic study of the HOR on the drop-casted electrodes is more complicated than on individual PtNPs, as the voltammetric features (for instance, the peak current) cannot be described by a simple equation but have to be modelled by numerical simulation. The simulation for the HOR on drop-casted PtNP electrodes has been introduced in section 3. Since the HOR on PtNPs is known to be adsorption-limited, the disc model is applied in the simulation of the PtNP ensemble for convenience.

As mentioned above, the aggregation or loss of the drop-casted nanoparticles can affect the experimental results measured from the drop-casted electrodes.⁹ For this reason, the reproducibility of the HOR on various drop-casted PtNPs was tested and two of them are taken as examples: one is the electrode with a relatively high coverage of PtNPs (ca. 4.0%) and the other has a low coverage (ca. 0.06%). Figure 7 shows the reproducibility of the cyclic voltammograms for the HOR on the two electrodes. For both coverages, three voltammograms were recorded independently. Reasonable reproducibility is observed, especially for high coverage. The variability likely arises from some loss of the material.

Therefore, the cyclic voltammograms with the highest signals were taken as represented of the coverages expected.

Figure 7 Cyclic voltammograms of the HOR on two drop-casted electrodes with different coverages of PtNPs: (a) 4.0 %; (b) 0.06 %. The electrolyte is 0.2 M KNO_3 , the bulk concentration of hydrogen is 0.78 mM and the scan rate is 0.1 V s^{-1} . The substrate Au electrode has a 1.01 mm radius.

Figure 8 (a) Cyclic voltammograms for HOR on PtNPs drop-casted electrodes. The coverages of PtNPs from high to low are 4.0%, 2.0%, 1.0%, 0.50%, 0.25%, 0.12%, 0.06%, 0.03%. Detailed calculation of the experimental coverages can be found in the Supporting Information (SI); (b) Experimental and simulated forward peak currents varying as a function of the coverage of PtNPs. The black square points are from Figure 8a. The blue, red and yellow circle points are from numerical simulations with k_a equal to 0.06, 0.02 and 0.007 m s^{-1} .

The experimental cyclic voltammograms for the HOR on various drop-casted electrodes are shown in Figure 8a. The coverage of PtNPs varies from 0.03% to 4.0%. From Figure 8a, for large PtNP coverages, the cyclic voltammogram shows an apparent peaked waveshape. When the coverage of the PtNP decreases, the peak becomes less observable. Figure 8b shows the dependence of the forward peak current on the coverage of PtNP. The black line represents the experimental peak currents of Figure 8a while the blue, red and yellow lines are the peak currents obtained via the numerical simulation with different adsorption rate constants k_a , 0.06 m s^{-1} , 0.02 m s^{-1} and 0.007 m s^{-1} . In the simulation, when the value of k_a changed, we assigned the desorption rate constant k_d (unit: $\text{mol m}^{-2} \text{ s}^{-1}$) and the standard heterogeneous rate constant k_0 (unit: m s^{-1}) the same number as k_a (unit: m s^{-1}). The detailed discussion about the choice of k_d and k_0 for the cyclic voltammetry simulation can be found in the SI. Among the simulated results shown in Figure 8b, those shown for the 0.02 m s^{-1} k_a are the peak currents simulated with the adsorption rate constant measured in the nano-impact experiments. However, in Figure 8b, the experimental peak currents for HOR on the drop-casted PtNPs clearly fit better with the simulated results of 0.007 m s^{-1} than 0.02 m s^{-1} , indicating the adsorption rate constant measured on the drop-casted PtNPs appears significantly less than that on the individual PtNPs.

It is now recognized^{9-10, 61} that the drop-casting method leads to aggregation on surfaces and also that electrical contact between the nanoparticles and the substrate electrode cannot be guaranteed. The disagreement between the kinetic data inferred from the two techniques likely, again, points to the limitation of the drop-casting approach. Applying the idealised nanoparticle coverages will thus lead to an underestimation for the kinetics of the electrochemical reaction. On the contrary, the nano-impact technique provides the opportunity to measure the reacting current occurring on an individual, active nanoparticle and thus the kinetic parameters determined from the nano-impact experiment are more likely to reflect the physical reality.

Conclusions

Two different electrochemical approaches, cyclic voltammetry on drop-casted electrodes and nano-impacts are used to determine the kinetics of the hydrogen oxidation reaction (HOR) on platinum nanoparticles (PtNPs). The adsorption rate constant for HOR on PtNPs can be quantified via the steady-state current measured on individual PtNPs in the nano-impact chronoamperometry or the voltammetric responses on the drop-casted PtNP ensembles with various PtNP coverages. In comparison with the adsorption rate constant measured on the bulk platinum electrodes,⁴⁷ the adsorption rate for the HOR is larger on the PtNPs. This is likely a consequence of the high effective surface area of the nanoparticle as evidenced by the TEM data. At same time, the kinetic parameter obtained from the drop-casted PtNP ensembles (ca. 0.007 m s^{-1}) differs from the value on the individual PtNPs (ca. 0.02 m s^{-1}), reflecting that the kinetics of the electrocatalytic reaction can be misinterpreted and underestimated if the measurement is implemented on an ensemble of nanoparticles rather than at individual nanoparticles. The underestimation is attributed to aggregation or loss of the nanoparticle on the electrode surface in the drop-casting experiments. The nano-impact technique which allows the detection of individual nanoparticles has merits in the study of kinetics for electrocatalytic reactions.

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Notes

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Supporting Information

The Supporting Information is available free of charge on the website. The detailed calculation of the coverages of the drop-casted PtNPs and the discussion about the influence of the kinetic parameters k_a , k_d and k_0 on the cyclic voltammograms for the HOR on PtNP arrays can be found in the Supporting Information.

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