Methanol Oxidation at Single Platinum Nanoparticles

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Abstract

The methanol oxidation reaction is studied at the single nanoparticle scale under aqueous alkaline conditions. Upon impacting a potentiostated electrode and after ≤1 ms a steady-state reaction limited catalytic current is induced to occur at the platinum nanoparticle (nominal diameter 50 nm); the magnitude of the current is close to that seen for both larger arrays of nanoparticles and polycrystalline 'bulk' material suggesting that single entity activity is preserved in ensembles of nanoparticles. This catalytic rate reaches a maximum at a potential of +0.05 V (vs Ag/AgCl; 3.4M KCl) with a current density of 0.3±0.2 mA cm^{-2}. However, at very short timescales (< 1 ms) the single nanoparticle response reveals the occurrence of an initial rapid charge injection event. This charge injection is consistent with the one-electron oxidation of a monolayer of methanol prior to establishment of the steady-state.

Keywords: electrochemistry, nanoparticles, methanol oxidation, catalysis, nano-impact

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1. Introduction

Methanol fuel cells are commonly operated under acidic conditions; however, on platinum the methanol oxidation reaction (MOR) is over an order of magnitude faster in alkali, as opposed to acidic, environments.[1] This increased rate predominantly reflects the greater availability of hydroxide to electro-adsorb onto the catalytic interface to form OH_{ads}. Under alkali conditions this surface oxygen species (OH_{ads}) plays an integral role in the methanol oxidation process.[1-3] Herein, we demonstrate for the first time how this energy transformation reaction can be studied at the single nanoparticle scale and reveal the material's associated catalytic activity.

Single entity electrochemistry[4-6] studies electrocatalytic particles using an electrode which is relatively inert to the process of interest.[7] When the catalytically active particle makes electrical contact with the electrode the electrocatalytic reaction is newly driven to occur at the individual nanoentity. This electrocatalytic reaction can – under suitable conditions – lead to a measurable change in the current. There are three primary processes that may limit the single nanoparticle catalytic turnover rate and hence control the magnitude of the recorded current; mass-transport of reagents and/or products to/from the catalytic interface,[4] the electrical connectivity of the material to the electrode[8] or the inherent catalytic activity of the material.[9] In early work the magnitude of the resulting current transient was often analysed on the basis of the electrocatalytic reaction being limited by the mass-transport of the reagent to the individual nanoparticle. Consequently, the catalytic current was analysed using the expression for the steady-state flux to a sphere supported on an inert surface:[10]

$$i_{ss} = 4\pi \ln 2\, nFDCr_{NP} \qquad (1)$$

where n, is the stoichiometric number of electrons transferred, D is the diffusion coefficient ($m^2\ s^{-1}$) of the reagent, F the Faraday constant (96485 C mol^{-1}), C is the solution phase concentration of the reagent (mol m^{-3}) and r_{NP} is the radius of the impacting nanoparticle (m). From this analysis the magnitude of the current was 'shown' to be consistent with arising from the arrival of individual nanoparticles.[4] However, nanoparticle agglomeration/aggregation in such electrochemical systems can be a significant issue.[11] Agglomeration leads to the presence of larger nanoentities in the solution phase which, when they impact, give larger current responses and render the use of equation (1) for the analysis of the current response invalid. This propensity for the nanoparticle suspension to agglomerate means that the stability of the suspension must be carefully controlled. In recent work it is common that solutions with only millimolar electrolyte concentrations are employed. Further caution is needed with the use of low pHs or other reagents (such as hydrazine) that may significantly interfere with the stability of the suspension.

In terms of nanocatalysis platinum based materials are of both industrial and academic importance. Prof. Feliu and the Alicante group have been leading the forefront of modern platinum electrochemistry;[12-16] providing extensive experimental and theoretical insights into the fundamental role of the crystal structure in controlling the material's electrocatalytic activity. More recently this work has been extended to considering platinum interfacial structure at the nanoscale.[17, 18] Through the use of pristine nanoparticle structures they have been able to experimentally demonstrate the link between measurements made on the macro (single crystal) and the nano (particle ensembles) scale. In this work we demonstrate how a nanoparticle's activity can be investigated at the individual entity scale, demonstrating for the methanol oxidation reaction under alkaline conditions how the single nanoparticle activity directly relates to that measured for a large ensemble of particles and further how this single particle technique can allow different experimental timescales to be experimentally probed.

2. Experimental

2.1 Chemicals and Reagents

All chemicals were purchased and used without further purification. Citrate-capped mesoporous 50 nm platinum nanoparticles (nanoComposix, San Diego, USA), sodium hydroxide (NaOH, Fisher Scientific, ≥99.3%), methanol (Sigma-Aldrich, ≥99.9%) and nitrogen (BOC, Surrey, UK) were used as received. The deionized water with a specific resistance of 18.2 MΩ·cm at 298 K was obtained by Synergy water purification system, EMD Millipore.

2.2 Electrochemistry experiments

A three-electrode system contained within a Faraday cage was employed to perform all the electrochemical experiments. The working electrode was either a gold (radius: 5.0 μm, purchased from ALS, Tokyo, Japan) or a platinum microelectrode (radius: 5.0 μm, purchased from Princeton Applie Research, Oak Ridge, TN, USA) and was polished with alumina slurries of decreasing sizes: 1.0, 0.3, and 0.05 μm (Buehler, Lake Bluff, IL, USA). The counter electrode was a graphite rod and the reference electrode was a leakless Ag/AgCl electrode (in 3.4 M KCl, eDAQ, E = 0.205 V vs. RHE). 10 mM NaOH was used as supporting electrolyte in all the experiments.[19] In this work a comparatively high concentration of methanol (10 M) is used throughout, a lower concentration of the reagent could have been used; however, the high concentration was beneficial in unambiguously confirming that the reaction rate is not under mass-transport control, *vide infra*. To avoid agglomeration or aggregation, PtNPs involved solutions were used for only 20 min each time. All electrochemical measurements were conducted with a lab built low noise, highly stabilized (1 kHz bandwidth) potentiostat at 25 ± 0.5 °C. An NI USB-6289 data acquisition (DAQ, National Instruments, Austin, TX, USA) was controlled by Python 3.5 (Canopy from Enthought, Austin, TX, USA), and connected to a computer interface via an USB. The working electrode was held at virtual ground where a low-noise current amplifier Axopatch 200B (Molecular Devices, San Jose, CA, USA) was employed to amplify the current and filtered at an analogue frequency of 5 kHz. The DAQ device oversampled and digitized the incoming analogue signal at a stream rate of 625 kHz, and the digitized signal was filtered at a bandwidth of 250 Hz afterwards. The filter and measurement systems used in this work conserves the charge passed.[20]

3. Results and Discussion

In this work 50 nm diameter platinum nanoparticles are used. A representative TEM image is shown in SI Section 1. The platinum nanoparticles are overall quasi-spherical in shape and are comprised of an aggregation of smaller crystallites of sizes in the range of 2-5 nm. In this work they are studied in 0.01M NaOH, in which they are stable with respect to agglomeration (see SI section 2).

Initially methanol oxidation was studied at both platinum and gold microelectrodes, Figure 1 a) depicts their voltammetric responses. For the platinum electrode in the presence of methanol a broad oxidation peak is observed from -0.2 to +0.2 V (vs Ag/AgCl; 3.4 M KCl). As seen in the inlay of Figure 1 a) in the absence of methanol no oxidation wave is observed in this potential range and only the oxidation (>0.1 V) and reduction (<0.0 V) of the platinum surface is observable. The methanol oxidation peak on platinum reaches a maximum catalytic turnover rate of 89±14 A m^{-2} (where the electrochemical surface area has been estimated from the under potential deposition of hydrogen[21]) at a potential of 0.05 V vs Ag/AgCl; the magnitude of this peak is far below the 'mass-transport' limit. Hypothetically were the oxidation of the 10 M methanol to be limited by the mass-transport of the material the electrochemical current would be at least three orders of magnitude larger. Whilst the methanol is in very large excess as compared to the supporting electrolyte, due to the comparatively low current densities the ionic strength is sufficient to allow the oxidation process to proceed without significant Ohmic drop occurring through the solution phase. As evidence via Tafel analysis (see SI Section 3) of the foot of the catalytic peak which yields a transfer coefficient of ~0.4. This value is in good agreement with literature reported values[22] and supports the inference that the voltammetric response is not Ohmically distorted.

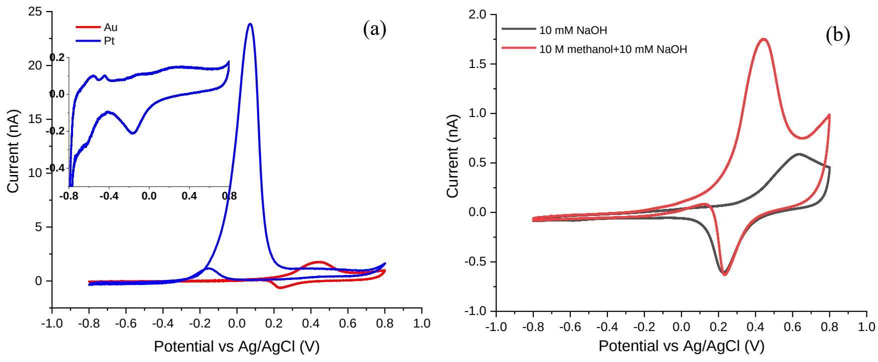

Figure 1. The oxidation of methanol on both gold and platinum microelectrodes. a) depicts the response of a platinum (blue) and gold (red) microelectrode in the presence of 10 M methanol and 10 mM NaOH. Inlay depicts the response of the platinum electrode in 10 mM NaOH; b) a comparison of the voltammetric response of a gold microelectrode with (red) and without (black) methanol present in solution.

The methanol oxidation reaction rate on platinum peaks at approximately +0.05 V. The cause of the decrease at higher potentials is evident from the inset in Figure 1(a) where it is seen to correspond to the onset of oxide formation as noted in the absence of methanol. More positive than ~0.2 V the oxidation of methanol still occurs on the oxidised platinum surface but at a significantly lower rate (4.2 A m^{-2}). Figure 1 b) depicts the response of the gold electrode in the presence (red) and absence (black) of methanol. Although the current density is significantly smaller, the gold interface is able to drive the methanol oxidation reaction. However, the peak in the gold activity is both markedly lower (21.5 A m^{-2}; relative to the geometric area of the electrode) and also occurs at a distinctly higher overpotential (0.2-0.6 V vs Ag/AgCl). This difference in activity between gold and platinum will be used in the following sections to enable study of the electrochemical behaviour of the platinum nanoparticles towards methanol oxidation.

A gold microelectrode was submerged into a platinum nanoparticle (6.7 pM) suspension (10 mM NaOH, 10 M methanol, 0.24 mM sodium citrate) and repeatedly cycled between -0.5 and +0.8 V (vs Ag/AgCl). The results are shown in Figure 2. Initially upon immersion of the electrode into the nanoparticle suspension the figure shows the response of a bare gold electrode (black line), where a voltammetric peak corresponding to the gold catalyzed oxidation of the methanol is observed at ~+0.5 V. As time progresses a secondary peak at ~+0.05 V increases in magnitude with increasing time. This new peak at +0.05 V corresponds to the electrocatalytic oxidation of methanol on the newly arrived platinum nanoparticles. During the course of the experiment platinum nanoparticles present in the solution phase impact with and adsorb to the gold interface.

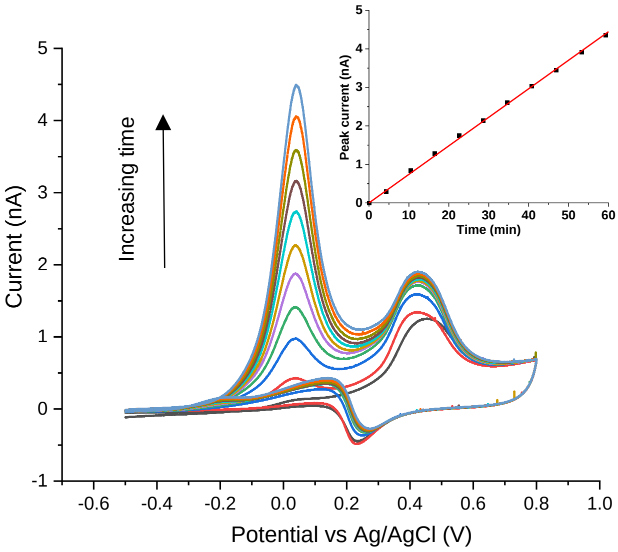

Figure 2. Successive voltammetric response of a gold microelectrode immersed in a suspension of 50 nm platinum nanoparticles (10 mM NaOH, 10 M methanol). Inlay: a plot of the platinum catalysed peak current against experimental time.

Hence, as the experiment progresses platinum nanoparticles accumulate at the interface forming a random array, this platinum nanoparticle array catalyses the methanol oxidation reaction. Tafel analysis of the resulting voltammetric response yields a transfer coefficient of 0.36 (see SI section 3), close to the value obtained for the platinum microelectrode, indicating that the nanoparticle/electrode contact is of a low enough resistance such that the nanoparticle holds the same potential as the underlying substrate even while catalysing the MOR. If the nanoparticle/electrode contact was too resistive the measured transfer coefficient would be lower and there would be a significant shift in the potential of the oxidative peak. The apparently low contact resistance plausibly reflects the fact that a gold electrode has been used; previous work studying the catalytic behaviour of nanoparticles impacting a carbon substrate has evidenced the nanoparticle response to be influenced by the contact resistance between the substrate and the nanoparticle.[8]

On the basis of the nanoparticle concentration the steady-state diffusion controlled rate of accumulation of the nanoparticles at the interface is ~50 min^{-1}. The inlay of Figure 2 plots the platinum catalysed peak current as a function of the time. From the slope of this plot and on the basis of the predicted accumulation the average catalytic current is found to be 1.54 pA NP^{-1}. For this per nanoparticle current to be compared to the platinum microelectrode it is necessary to account for the nanoparticle's porosity. Larger platinum nanostructures have a propensity to form via an aggregation pathway leading to the formation of 'open' nanoparticulate structures.[23] The TEM image in SI Section 1 shows how the used nanoparticles are comprised of aggregates of smaller 2-5 nm crystallites. The surface area per nanoparticle was determined by measuring the underpotential deposition of hydrogen onto the nanointerface. For this nanoparticle sample the average nanoparticle surface area is 0.03 μm^2.[24] Hence, the platinum nanoparticle catalysed methanol oxidation reaction has a peak activity (at 0.05 V) of 51±16 A m^{-2} (see Table 1). This value for the peak catalytic current density is less than that measured for the bulk polycrystalline material. That nanoparticles are in some case less catalytically active towards methanol oxidation has been previously reported and is attributed to the differing ratio of crystal facets exhibited by the nanomaterial.[1] During the course of the voltammograms presented in Figure 2, a number of spike and step like features are observable super imposed on top of the voltammetric response. In the data presented in Figure 2 these features are most apparent at high overpotentials. These small current transients are associated with the arrival of new nanoparticles during the voltammetric experiment. We next focus on the measurement and analysis of these small single particle transients and their sensitivity to the applied electrode potential.

A gold microelectrode was submerged into a nanoparticle suspension again containing 10 mM NaOH and 10 M methanol. A chosen potential was held upon the electrode and the resulting current measured as a function of time. On top of the transient associated with background processes small steps and spikes in current were observed. The SI section 4 presents examples of the full chronoamperometric profile. Figure 3 shows two representative examples of individual current transients as measured at (a) +0.7 V and (b) +0.05 V (vs Ag/AgCl). These small current transients are due to the arrival of new platinum nanoparticles to the gold interface and the change in current directly reflects the electrochemical processes occurring at the newly arrived particle. At +0.7 V single spike like features are observed. Under these experimental conditions the oxidation of platinum is both kinetically and thermodynamically favourable above ~+0.1 V. At +0.7 V the average charge passed during a single event is 0.06 pC. Assuming that the platinum oxidation process involves the transfer of two electrons then this amount of charge only represents a partial oxidation of the nanoparticle surface (ca. 48%). Note similar spike like features are observed at higher potentials and in the absence of methanol corroborating the conclusion that these high potential features are associated with the direct oxidation of the impacting nanomaterial.

Figure 3 b) depicts a representative nano-impact feature as recorded at +0.05 V and in the presence of 10 M methanol. The nano-impact exhibits both spike (blue hashed area) and step (orange lines) like features, where at this potential the average step size is found to be 0.9±0.4 pA. This step in current is a direct measure of the single nanoparticle steady-state catalytic methanol oxidation rate. Furthermore at this potential of 0.05 V the average charge passed during the initial spike is 5 femtocoulombs. Figure 3 c) plots the average spike charge and step current measured for the nano-impact events over a range of potentials. The inlay of Figure 3 c) plots the spike charge across a wider range of potentials, showing that at high potentials the spike charge is over an order of magnitude greater than that recorded at or below +0.05V (vs Ag/AgCl). As discussed above, at these high overpotentials (≥0.1 V vs Ag/AgCl) the spike represents the partial oxidation of the impacting platinum nanoparticle.

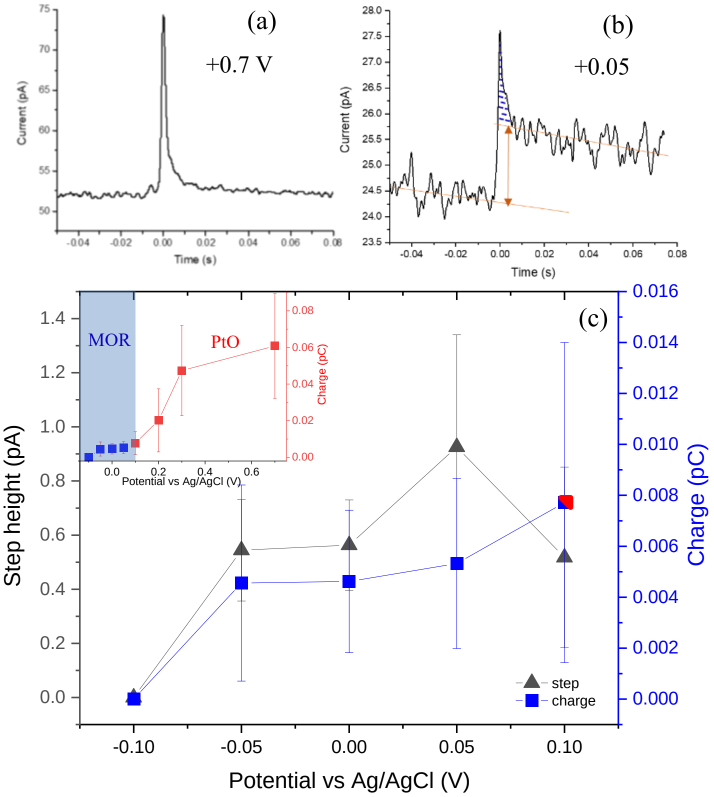

Figure 3. Representative single nanoparticle transients as measured at a) +0.7 and b) 0.05 V (vs Ag/AgCl). c) Quantification of the variation in the single platinum particle responses as a function of the applied electrode potential. Black, the measured average magnitude of the single particle catalytic current associated with the MOR. Blue, the average magnitude of the single particle impact spike charge. Inlay in c): a plot of the variation of the average charge per impact transient as a function of applied potential in both MOR and PtO region.

	Nano-impact	Nano-array	Pt microelectrode
Current per particle (pA)	0.93±0.41	1.54±0.01	-
Current density ($A\ m^{-2}$)	28.1±22	51.3±15.7	89.4±14

Table 1. Comparison of the platinum catalysed MOR peak rates as measured for polycrystalline bulk material and 50 nm platinum nanoparticles.

As can be seen from the data presented in Figure 3 c) the magnitude of the step current reaches a maximum at 0.05 V, where above +0.1 V steps in current were no longer observed. Note the large uncertainties presented in Figure 3 c) represent not just the experimental error but also the intrinsic heterogeneity of the nanoparticle sample (SI Section 1 for the particle size distribution). The magnitude of this step in current represents the catalytic methanol oxidation rate at a single nanoparticle and as is the case for the platinum microelectrode the rate determining step is the surface catalysed MOR. Notably, if the reaction was limited by the mass-transport of methanol to the nanoparticle then, in accordance with equation 1, a steady-state current of 210 nA is expected per nanoparticle; this is more than 5 orders of magnitude larger than experimentally measured, rather the step in current directly reflects the activity of an individual nanoparticle towards the MOR. Table 1 compares this single particle measured catalytic rate to the measurements made using the nanoparticle array and the microelectrode. Although very comparable to the current measured using the nanoparticle array, the single nanoparticle measurements yield a current density that is approximately 50% less than found using the latter ensemble measurements. This difference in activity most likely simply reflects the differing experimental conditions; for both the platinum nanoparticle array (Figure 2) and the platinum microelectrode (Figure 1) the platinum in these experiments has been repeated voltammetrically cycled. Redox cycling of the platinum material, causing the repeated oxidation and reduction of the electrode surface, will essentially clean and active the platinum surface leading to higher current densities for the methanol oxidation reaction. SI section 5 demonstrates how for the platinum microelectrode redox cycling of the electrode increases its activity 1.5 fold over the course of a few scans.

Having ascertained the origin of the observed steps in current, the question remains as to the mechanistic cause of the initial spike in current as shown on the current transient depicted in Figure 3 b). This spike in current is very rapid. SI section 6 demonstrates that the spike shape reflects the bandwidth of the used electronics and that the charge is passed in less than 1 millisecond when measured at a bandwidth of 5 kHz, note the data represented in Figure 3 is shown at a filtering rate of 250 Hz. Hence the initial spike in current is longer in duration (ca. 10 ms) than the actual event occurring at the nano-interface; the spike transient shape reflects the lower filtering bandwidth. This lower bandwidth is beneficial for resolving the step in current which would not be observable at higher filtering frequencies due to the lower signal-to-noise ratio. As shown in Figure 3 c) the charge passed during the spike is essentially the same in the range from -0.05V – 0.05V, with a value of 5 fC. This value is approximately an order of magnitude smaller than the platinum oxidation features observed at high overpotentials, further platinum oxidation is not thermodynamically feasible at these low potentials indicating that these spikes cannot be associated with the formation of platinum oxide. The marginally higher spike charge at +0.1V (as shown in Figure 3c) likely reflects the onset of platinum oxidation. If this spike in current was associated with the capacitative charging of the nanoparticle the magnitude of the charge would be strongly sensitive to the applied electrode potential. Consequently, we conclude that the spike in charge corresponds to the charge passed during the establishment of the steady-state reaction. The magnitude of the charge is equivalent to the passage of one electron for approximately every ten platinum atoms on the surface of the nanoparticle. It has been previously reported that the methanol dehydrogenation requires at least four neighbouring active platinum sites at the surface.[25] Hence, the magnitude of the spike is consistent with arising from the initial electro-adsorption of methanol to the catalytic interface.

4. Conclusion

This work has demonstrated how the MOR can be studied at an individual particle scale where the magnitude of the resulting steady-state current reflects not the geometric size of the impacting nanoparticle but its catalytic activity. Uniquely the single nanoparticle experiment reveals that prior to establishment of steady-state a charge injection event occurs. The magnitude of this rapid charge injection processes is consistent with arising from the oxidation of a monolayer of methanol. Similar levels of catalytic activity are seen in ensembles as at the single entity level.

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