Pitfalls and best practices in measurements of the electrochemical surface area of platinum-based nanostructured electro-catalysts

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Abstract

Platinum-based nanoparticles are the most active and stable catalysts for electrochemical oxygen reduction reaction (ORR). Objective evaluation of the specific activity of Pt-based electro-catalysts requires a rigorous measurement of their electrochemical surface area (ECSA), which provides the link between measured currents and per-site turnover. Most common implementations of existing voltammetry methods for evaluating the ECSA often lead to overrated performance levels for Pt-based electro-catalysts and even inflated relative performance compared to pure Pt. We illustrate these uncertainties by evaluating the ECSA and ORR rates of a Pt-monolayer (ML) electro-catalyst of the form $\text{Au}_x\text{Cu}_{100-x}@\text{Au}_{2\text{ML}}@\text{Pt}_{\text{ML}}$ and comparing these to commercial Pt nanoparticles. We develop and discuss some reasonable practices that could be employed to address these problems in order to assess the activity of Pt-alloy nano-catalysts more rigorously. Our objective is to move us closer towards establishing more uniform and rigorous protocols in measuring and reporting the ORR rates on Pt alloys.

Keywords: Electrochemical surface area; platinum-based catalysts; oxygen reduction reaction; electrocatalysis; voltammetry

1. Introduction

Low temperature proton exchange membrane fuel cells have attracted significant attention as efficient alternatives for portable power generation and transportation applications [1,2]. Despite significant progress made in the field [3,4], widespread commercialization of fuel cells has been hindered largely by low efficiencies of Pt-based

nanoparticle electro-catalysts used to catalyze the cathodic oxygen reduction reaction (ORR) [5]. It has been established that optimal performance per mass of monometallic Pt nanoparticle electro-catalysts is achieved for 3-5 nm nanoparticles [5,6]. When supported on carbon these electro-catalysts achieve a peak power output of $\sim 1 \text{ kW/g}_{\text{Pt}}$, which is about an order of magnitude lower than that required for viable large-scale implementation [6,7]. Most research efforts have focused on improving the intrinsic activity, *i.e.*, the electro-catalytic turnover, of Pt by alloying it with other transition metals and creating more active Pt surface sites [6,8–11]. To conclusively establish the relative performance of these Pt alloys and benchmark them against commercial standards and the U.S. Department of Energy (DOE) performance targets [4,12], it is critical to accurately measure the intrinsic surface-specific rates of ORR. Surface-specific rates of ORR on various Pt and Pt-alloy electro-catalysts are most often measured using the rotating disk electrode (RDE) setup [5,13,14]. In this setup, a thin-film of active electro-catalysts is deposited on a glassy carbon electrode and RDE voltammetry is performed in a non-adsorbing electrolyte solution, typically HClO_4 [13,15]. The kinetic rates of ORR are de-convoluted from mass transfer-limited rates using Koutecky-Levich approach [14,15]. The kinetic rates are typically reported at 0.9 V *vs.* the reversible hydrogen electrode (RHE) as a standard metric of evaluating the performance of ORR electro-catalysts.

Measuring specific kinetic ORR rates using the RDE methodology and comparing these to Pt nanoparticle standards has multiple potential sources of error. These error sources include varying external (from solution to the surface of the catalyst film) and internal (through the porous network of the catalyst thin film) reactant mass transport

rates for different electro-catalyst geometries, making it difficult to conclusively compare the specific kinetic rates on different architectures of electro-catalysts such as nanoparticles versus other designs (*e.g.*, mesoporous networks, nanowires, nanoframes). Another potential source of error is the measurement of electrochemical surface area (ECSA) of high-surface-area electro-catalysts. For metal electrodes, the most common method of evaluating ECSA involves integration of the voltammetric peak (current evolved) associated with the electrochemical desorption (‘stripping’) of the overlayer of a carefully selected adsorbate from the surface [16]. The most commonly used adsorbates in the evaluation of ECSA are the H atom and CO molecule. These adsorbates are selected since their adsorption and desorption on pure Pt materials have been studied extensively, and clear correlations have been established between the surface area and the current evolved during the desorption of these species from pure Pt [17,18]. On the other hand, for Pt-alloy catalysts adsorption energies of these probe species are different from, and in general less characterized than, those on monometallic Pt nanoparticles [19,20]. This is due to the modified electronic properties of the Pt surface sites [21–26]. These differences could lead to overlaps with other potential-dependent (adsorption/desorption) processes, sometimes resulting in undervalued ECSAs and overestimation of specific activity for Pt alloys [11,21,27].

In this contribution, we demonstrate by a way of a concrete example the inherent uncertainties and potential difficulties in measuring the ECSA of Pt-alloy nanoparticles and therefore surface-specific ORR rates. We illustrate these uncertainties by evaluating the ECSA and ORR rates of a Pt-monolayer (ML) shell electro-catalyst of the form $\text{Au}_x\text{Cu}_{100-x}@\text{Au}_{2\text{ML}}@\text{Pt}_{\text{ML}}$ and comparing these to standard monometallic Pt

nanoparticles samples. We also discuss some reasonable practices that could be employed to address these problems in order to assess the activity of Pt-alloy nano-catalysts more rigorously. While some shortcomings of the most common ECSA evaluation methods for various Pt surfaces have been previously identified [13,28–30], unbiased measurements of Pt-alloy ECSA have remained largely unaddressed and, unfortunately, overrating of surface-specific ORR rates are rather prevalent in the literature. Benchmarking criteria designed specifically for oxygen evolution and hydrogen evolution electrocatalysts have been reported recently [31], and they have helped standardize the methods used to compare objectively the performance of water splitting catalysts. Our objective here is to move us closer towards establishing more uniform and rigorous protocols in measuring and reporting the ORR rates on Pt alloys.

2. Experimental Methods

2.1. Synthesis of $Au_xCu_{100-x}@Au_{2ML}/Pt_{ML}/C$ Nanoparticles

The multi-metallic electro-catalysts were synthesized in a two-step process. In the first step, the internal AuCu alloy cores were prepared by a thermal reduction of gold(III) chloride trihydrate ($AuCl_3 \cdot 3H_2O$, Sigma Aldrich) and copper acetylacetonate ($Cu(acac)_2$, Fisher) precursors in 20 mL of oleylamine under reflux conditions. In a typical synthesis, 150 mg of $AuCl_3 \cdot 3H_2O$ was added to a 100-mL round bottom flask containing 20 mL of oleylamine heated to 40 °C. The reflux condenser was sealed and fed a positive pressure of Ar. Complete reduction of the Au precursor to Au nanoparticles was accomplished by keeping the flask at 110 °C with magnetic stirring and for 4. The flask was then removed from the silicone oil bath and allowed to cool for at least 10-15 minutes. At this time, 20-

30 mg of $\text{Cu}(\text{acac})_2$ was added to the Au nanoparticle solution. The flask was immersed back into the oil bath and gradually heated to 280 °C under excess flow of Ar through the condenser. After 1 hour at 280 °C, the flask was removed from the heated oil bath and allowed to cool. The nanoparticle suspension was rinsed with methanol (Fisher), and the nanoparticles were then collected by centrifugation (8 minutes at 8000 rpm). Following three methanol washes, the nanoparticles were suspended in n-hexane (Sigma).

The alloy nanoparticles were deposited on pre-treated carbon support (Vulcan XC72R, Cabot) at roughly 20 wt. % loading in hexane and allowed to mix under continuous stirring for at least 24 hours. Supported nanoparticles were then collected by centrifugation (3 washes with IPA at 8000 rpm for 8 minutes). The samples were collected in pure ethanol (Fischer) and allowed to dry in an oven overnight. Structure of the AuCu/C nanoparticles was characterized by X-ray diffraction, inductively-coupled plasma-atomic absorption spectroscopy, and transmission/scanning transmission electron microscopy (STEM) to verify the successful synthesis of the intermetallic AuCu nanoparticles. The STEM and energy-dispersive X-ray spectroscopy characterizations are shown in the Supporting Information (Figures S.1-S.2). Powders were thermally treated for 5 hours in air at 185 °C prior to electrochemical preparation.

The monolayers of Au and Pt were grown epitaxially on supported AuCu cores via the spontaneous galvanic replacement of a sacrificial monolayer of underpotentially-deposited Cu (Cu UPD) [26,32]. In the Cu UPD process, the electrode was held at a set potential slightly above the bulk Cu^{2+}/Cu redox potential (-0.35 V against Hg/HgSO₄ (sat. K₂SO₄) reference electrode) in a 5 mM solution of CuSO₄ with a 50 mM supporting electrolyte of H₂SO₄. At this potential, only a monolayer (ML) of Cu was deposited onto

AuCu alloy surface because the deposition of multiple Cu layers was unfavorable. Multiple sweeps to higher potentials were performed to verify similar amount of Cu were deposited on consecutive scans. After removing the electrode under potential control, the electrode was rinsed with ultrapure water (18.2 M Ω ·cm (Millipore)) and deposited into a solution containing either 1 μ M AuCl₃ or K₂PtCl₄ for galvanic displacement of the Cu UPD monolayer. In the galvanic replacement step, 2/3 ML of Au or 1 ML Pt deposited for every 1 ML of Cu removed, so three Au and one Pt depositions were performed to prepare the AuCu@Au_{2ML}@Pt_{ML} structures. After depositing Au and Pt layers, the electrode was rinsed with ultrapure water to remove excess metal precursors before performing the subsequent depositions or beginning electrochemical testing. Samples were characterized with electron microscopy before and after the electrochemical measurements.

2.2 Electrochemical Testing Protocols

Electrochemical measurements were performed at room temperature in a custom-made three-electrode cell using a Gamry Instruments Reference 3000 potentiostat/galvanostat/frequency response analyzer. The reference electrode (Ag/AgCl in 3 M KCl, Radiometer Analytical) was housed in an external container connected to the electrochemical cell *via* a capillary bridge to minimize Cl⁻ contamination in the reactive ORR environment. Additionally, the potential of the reference electrode was calibrated against the RHE scale prior to start of each experiment. The counter electrode (Pt wire, Alfa Aesar) was placed in an isolated compartment in the cell with long diffusion path from the working electrode chamber. Working electrodes were prepared by ultrasonication of catalyst powders in 99.9% ethanol (Fischer) at 0.75 mg/mL for at least an

hour, and then depositing four 10 μ l droplets onto a 5 mm glassy carbon electrode (GCE, Pine Instruments) dried with rotation at 700 rpm [33]. The GCE was polished with 0.05 μ l alumina paste and sonicated in ultrapure water prior to use. Commercial 3 nm Pt/C standard was purchased from Alfa Aesar.

For all experiments, the electrolyte solution was 0.1 M HClO₄ prepared by dilution of 70% perchloric acid stock solution (Merck Suprapur) with Millipore water (18.2 M Ω cm). Uncompensated resistance of $\sim 25 \Omega$ was consistently measured with high-frequency electrochemical impedance spectroscopy, which was then corrected for in. All potentials are reported against the RHE scale ($V_{\text{RHE}} = V_{\text{NHE}} + 0.0591 \text{ pH (NHE, normal hydrogen electrode)}$), calibrated by H₂ oxidation equilibrium at the pH of the solution. All currents have been corrected for potential-independent capacitance effect as described in *Section 3.3.1*.

Following the conditioning scans, the ORR polarization curves were obtained *via* linear sweep voltammetry (LSV) at 50 mV/s between 0.05 and 1.0 V_{RHE} at 400, 900, 1600, and 2500 rpm in O₂-saturated solution. Immediately following the LSV measurements, the solution was purged with Ar for about 20 minutes, after which time cyclic voltammograms of the materials were recorded at 50 mV/s between 0.05 and 1.0 V_{RHE}. Upon completion of this step, CO stripping voltammetry was performed by holding the electrode potential at 0.05 V_{RHE} for 4-5 minutes while CO was flowed into the working chamber at 30 sccm flow rate. While maintaining the electrode potential, the chamber was then purged with Ar for about 20 minutes to remove excess CO. The potential was then scanned to 1.0 V_{RHE} at 10 mV/s, and cycled between 1.0 and 0.05 V_{RHE} for five complete cycles. Observation of a CO stripping peak (at around 0.8 V_{RHE})

in only the first oxidizing sweep suggested the successful removal of the entire CO adlayer. In all subsequent sweeps, the general features of CV on Pt (*e.g.*, H_{UPD} , oxide formation) appeared. The ECSA of the material was determined from analysis of these voltammetry scans as described in *Sections 3.3* and *3.4*.

2.3 Catalyst Characterization

Aberration-corrected scanning transmission electron microscopy (STEM) imaging and energy-dispersive X-ray spectroscopy (EDS) were performed at the Center for Nanophase Materials Sciences at Oak Ridge National Laboratory with a JEOL 2200FS TEM/STEM equipped with a CEOS aberration (probe) corrector and operated at a 200 kV accelerating voltage. The microscope was operated in bright field as well as high angle annular dark field (HAADF)-STEM imaging mode, and was equipped with a Bruker AXS X-Flash 5030 silicon drift detector. The probe size was ~ 0.7 Å and the probe current was ~ 30 pA during HAADF-STEM imaging. When collecting the EDS spectra, the probe current was increased to ~ 280 pA and the probe size was ~ 2 Å.

3. Results and Discussion

3.1. Synthesis

We discuss our findings by a way of an example where we compare the ORR performance of a multi-layer Pt-monolayer electrocatalyst ($Au_{85}Cu_{15}@Au_{2ML}@Pt_{ML}$) against commercial monometallic Pt nanoparticles electrocatalyst. The multi-layer Pt-based nanostructures were synthesized by a combination of colloidal and copper-mediated electrochemical methods. In the first step, the AuCu alloy core nanoparticles were prepared by a sequential thermal reduction of gold and copper precursors. The

composition of the alloy nanoparticles was controlled by the molar ratio of the Au and Cu precursors. The AuCu alloy nanoparticles were then deposited on carbon (Vulcan) support. Following the synthesis of the AuCu core nanoparticles, an ink of the AuCu/C powder in pure ethanol was deposited on a pre-polished glassy carbon electrode RDE tip. The droplets were spun cast using the inverted RDE method [33]. To prepare the $\text{Au}_x\text{Cu}_{100-x}@\text{Au}_{2\text{ML}}@\text{Pt}_{\text{ML}}$ electro-catalysts, the monolayers of Au and Pt were grown on the AuCu/C cores via the spontaneous galvanic replacement of a sacrificial monolayer of underpotentially-deposited Cu (Cu UPD) [26,32]. While the exact atomistic structure of these materials is not relevant to the arguments presented below, successful synthesis of these nanostructures was verified by scanning transmission electron microscopy (STEM) and elemental energy-dispersive X-ray spectroscopy (EDS) (Figures S.1 and S.2). The metal loading of both electrocatalysts on carbon support was ~ 20 wt. %. The Pt-monolayer nanoparticles used in these studies were $\sim 14.1\pm 3.3$ nm, while the commercial Pt standards were 1.75 ± 0.24 nm in diameter. We also performed analogous experiments on standard Pt nanoparticles of larger size (4.51 ± 1.10 nm); in this paper we will make comparisons with the smaller sized Pt standard due to generality of observations.

3.2. Normalization of Rates by the Geometric Area of the Electrode

The ORR performance of the Pt-monolayer and monometallic Pt electrocatalysts was investigated using the thin film RDE configuration. The polarization curves of $\text{Au}_{85}\text{Cu}_{15}@\text{Au}_{2\text{ML}}@\text{Pt}_{\text{ML}}$ and monometallic Pt samples are shown in **Figure 1**, where the measured currents are normalized by the geometric area of the RDE tip ($\sim 0.196 \text{ cm}^2$). The data in **Figure 1** show the typical features of Pt-based electro-catalysts in thin-film RDE configuration: an overpotential of ~ 300 mV before any current can be drawn, a

region mainly controlled by reaction kinetics (*ca.* 0.75-0.95 V_{RHE}), and the transport-limited region (potential < 0.75 V_{RHE}). The limiting currents of both the Pt-monolayer and pure Pt reach the expected transport-controlled values [5], and their agreement suggests similar selectivity for the two catalysts. Levich analysis suggested that a pathway to H₂O is the dominant oxidation channel for both materials. A visual inspection of **Figure 1** suggests that the Pt-monolayer nanoparticle catalyst has an earlier onset and a more positive half-wave potential, indicating higher ORR activity than pure Pt. However, normalizing the kinetic currents by the disk area neglects the likely difference in the number of active surface sites packed in the different electro-catalysts on the RDE tip. This difference can be due to different loading of the active surface sites or even due to the potential catalyst surface poisoning by the organic stabilizers used in colloidal synthesis of the nanoparticles. The true influence of catalyst structure and composition can be examined objectively only if activity benchmarks are unambiguous, a requirement that is not satisfied by using the geometric electrode area. While the practice of benchmarking Pt-based electrocatalysts based on the current normalization with respect to the electrode geometric area is infrequent, it is worth noting that this approach is used regularly in the benchmarking of the performance of various carbon-based electrocatalysts as well as transition metal sulfides, phosphides and nitrides, often leading to significant overestimation of the performance of these materials.

Figure 1. IR- and capacitance-corrected RDE polarization curves (potentials relative to the RHE) taken in O₂-saturated 0.1 M HClO₄ for the Pt-monolayer and pure Pt electrocatalysts. Only the positive-going (0.05 to 1.0 V_{RHE}) sweeps are shown. Scan rate: 50 mV/s. Rotation speed: 1600 rpm.

To quantify the oxygen reduction kinetics of the Pt-monolayer and pure Pt – which in turn would allow comparisons to be made beyond the rather qualitative assessments afforded by the data shown in **Figure 1** – the kinetic and transport effects were de-convoluted through a Koutecky-Levich (K-L) analysis [34,35]:

$$\frac{1}{|I|} = \frac{1}{|I_K|} + \frac{1}{|I_L|} \Rightarrow |I_K| = \left(\frac{1}{|I|} - \frac{1}{|I_L|} \right)^{-1}$$

Equation 1

where I is the measured current (unit: mA), I_K is the kinetic current, and I_L is the limiting current. The surface-specific kinetic rates are then obtained through normalizing the kinetic currents I_K by the ECSA. The question is how to objectively estimate the ECSA. In *Section 3.3* we describe the voltammetric methods commonly employed in the community to evaluate the ECSA of Pt-based electrodes, and illustrating some shortcomings of these methods for accurate and unbiased measurements. In *Section 3.4*, we present a practical solution that could be used to overcome the shortcomings of these commonly used methods.

3.3. Evaluation of the ECSA from Voltammetric Methods

3.3.1. H_{UPD} method

Most commonly, the ECSA of metal (*e.g.*, Pt-based) electrodes is determined by taking advantage of surface-limited reactions involving adsorption/desorption of a probe species on the electrocatalysts surface [16–18]. In this method, the charge associated with desorption (‘stripping’) of the probe species derived from corresponding cyclic voltammograms is used to estimate the ECSA. The most commonly used probe species for Pt-based electrodes is the hydrogen atom (H) [11,36]. In this method, the ECSA is determined from the charge evolved in the process of desorbing an adlayer of underpotentially-deposited H (H_{UPD}) ($H_{UPD}^* \rightarrow H^+ + e^-$) from the exposed Pt surface. For Pt-based electro-catalysts in acidic solution (*e.g.*, $HClO_4$), the H_{UPD} charge is usually determined by integrating the H_{UPD} desorption peak from *ca.* 0.05 to 0.4 V_{RHE} as shown in **Figure 2a**. We note that in any approach to the ECSA evaluation, the contribution of the background, double layer capacitive current needs to be removed. For all the measurements discussed below in the text, the potential-independent contribution to the

double layer capacitive current was taken to be one-half of the difference in the limiting currents between the positive- and negative-going sweeps in O₂-saturated electrolyte at 100 mV/s. We note that we measured similar values for this capacitive current in the absence of O₂ by subtracting the argon CV, consistent with previous observations [14,37]. We then accounted for this potential-independent capacitive current contribution by shifting all the voltammograms up (negative-going sweeps) or down (positive-going sweeps) in current by exactly this amount. We accounted for the measurements performed with different potential scan rates by taking advantage of the linear dependency of the potential-independent capacitive current on the scan rate,

$$i_{cap} = C \times dV/dt$$

Equation 2

where i_{cap} is the potential-independent capacitive current, C is the double layer capacitance, and dV/dt is the scan rate.

The measured H_{UPD} charge yields an estimate of the ECSA of the material, assuming a conversion factor 210 $\mu\text{C}/\text{cm}^2$ which corresponds to the estimated charge evolved with the desorption a monolayer of adsorbed H on a smooth Pt surface [13,14,38–40]. From this method, the H_{UPD} charge of the Pt-monolayer and monometallic Pt electro-catalysts were calculated to be 59.70 and 210.0 μC , respectively. Using these H_{UPD} stripping charges, the RDE polarization curves shown in **Figure 1a** were adjusted to an equal-area basis. This is necessary because the onset and half-wave potentials are invariant characteristics of a material, but differences in catalyst loading (thus ECSA) create apparent shifts in these quantities [13]. **Equation 1** was first used to extract the

raw kinetic current I_K (unit: mA). Then **Equation 3** was used to regenerate the RDE current density j_{RDE} (units: mA/cm²) curve on a zero-roughness (superficial area) basis as:

$$|j_{RDE}| = \left(\frac{A_{ECSA}}{|I_K|} + \frac{A_{Geo}}{|I_L|} \right)^{-1}$$

Equation 3

where A_{ECSA} is the ECSA value as measured by each protocol described in the text (H_{UPD} for this section), A_{Geo} is the projected geometric area of the electrode (~ 0.196 cm²), and I_L is the limiting current. In practice, small particle loadings (typically 40 µl of a 0.75 mg/mL catalyst ink) were used to keep roughness between 1-3 so that the correction was small.

Upon performing these adjustments, Tafel plots of kinetic current density versus potential, shown in **Figure 2b**, were extracted through the K-L analysis. The data show that for both catalysts the Tafel plots exhibit double Tafel slope usually observed for the Pt surfaces [41,42]. The specific kinetic rates of the Pt-monolayer and pure Pt samples at 0.9 V_{RHE} are 5.93±1.62 and 0.66±0.21 mA/cm², respectively, as shown in the inset of **Figure 2b**.

Figure 2. (a) CVs of the Pt-monolayer and pure Pt electro-catalysts recorded in Ar-purged 0.1 M HClO₄. The voltammograms have been corrected for uncompensated resistance. The dashed lines indicate the voltage-independent (horizontal) and voltage-dependent (slanted) baselines used to evaluate the H_{UPD} ECSA. Scan rate: 50 mV/s. Voltammograms were recorded without electrode rotation. (b,c) Tafel plot of the ORR kinetic current density using the voltage-independent and voltage-dependent baselines, respectively, for evaluating the H_{UPD} ECSA of the Pt-monolayer and pure Pt samples.

Insets show kinetic current densities at 0.9 V_{RHE}. Scan rate: 50 mV/s. Rotation speed: 1600 rpm.

An implicit assumption in the above method of correcting for the background capacitive current of H_{UPD} is that this current is constant across all potentials. Mayrhofer *et al.* [13], Binniger *et al.* [30], and others [39,43] have shown that this procedure might have some inaccuracies, since there are potential-dependent background currents (not related to the desorption of H_{UPD}) that could overlap with the H_{UPD} desorption and impact significantly the ECSA measurements. This potential-dependent background current can be observed in the voltammograms in **Figure 2a** as a sloping baseline in the H_{UPD} region (particularly for the Pt-monolayer electro-catalyst), consistent with the reports of others [13,43].

We analyzed how the ORR kinetic current densities of the Pt-monolayer and standard Pt electro-catalysts change if a voltage-dependent slanted baseline current was subtracted from the H_{UPD} desorption voltammograms instead of the horizontal double-layer capacitive one. Using the same set of CVs but instead integrating the H_{UPD} desorption peak with slanted baselines (see **Figure 2a**), the H_{UPD} desorption charges were calculated to be 86.33 and 225.20 μC for the Pt-monolayer and Pt standard samples, respectively. Comparing these results to the surface areas obtained using a horizontal baseline leads us to conclude that the measured surface areas increased by nearly 50% for the Pt-monolayer sample while it remained nearly the same for the pure Pt sample. These changes impact the absolute values of the ORR kinetic rates on both catalysts. The Tafel plots, extracted from the equal-area adjusted polarization curves, are shown in **Figure 2c**.

The data indicate that the Pt-monolayer electro-catalyst yielded enhanced kinetics across all potentials of interest (0.75-0.95 V_{RHE}). As shown in the inset of **Figure 2c** and **Figure 6**, using these ECSA values leads to lower specific activities at 0.9 V_{RHE}: 4.67 ± 1.61 and 0.62 ± 0.19 mA/cm² for the Pt-monolayer and pure Pt, respectively. Although using a slanted baseline for H_{UPD} peak integration does survey the surface area of a greater number of active sites than when using a horizontal baseline, the choice of the slope of the line is rather subjective, and therefore potentially subject to systematic errors. We will illustrate in *Section 3.4* another, potentially more rigorous and systematic procedure to eliminate this potential-dependent contribution to the H_{UPD} background currents.

Even if care is taken to completely eliminate the contributions of the potential-dependent and independent background currents, the accuracy of the H_{UPD} method for calculating the ECSA for alloys of Pt remains the subject of increasing concerns [11,13,21,28]. In calculating the ECSA from the integrated H_{UPD} charge, the measured evolved charge is divided by the conversion factor of 210 μC/cm², which corresponds to the surface-specific charge of a monolayer of adsorbed H. This manipulation implicitly assumes that the saturation surface coverage of H_{UPD} on the Pt sites is independent of alloying or catalyst surface structure. Recent studies have found that the surface areas derived from H_{UPD} were underestimated significantly for various Pt-alloys compared to pure Pt even when identical surface structures are probed (*i.e.*, the (111) surface), thus leading to the overestimation of specific activity. For example, underestimation of H_{UPD}-ECSA as high as 50% have been observed for Pt₃Ni(111) compared to Pt(111) [11]. This is not surprising considering that alloying changes the electronic structure of surface Pt atoms and therefore the binding characteristics (*i.e.*, the adsorption energy) of H_{UPD}

compared to pure Pt. More rigorous calculation of the H_{UPD} -ECSA should consider that the true coverage θ_H of the H_{UPD} overlayer might not necessarily be one monolayer. More generally the H_{UPD} ECSA can be computed using **Equation 4**:

$$H_{\text{UPD}} - \text{ECSA} = \frac{Q_H}{q_H \cdot 210 \frac{\text{mC}}{\text{cm}^2}}$$

Equation 4

where Q_H is the charge evolved during the process of H_{UPD} desorption. We note that rigorous estimation of θ_H is a non-trivial task. In the literature, most of the ECSA evaluations from H_{UPD} were calculated with θ_H assumed to be unity; only a few reports assumed a fractional hydrogen coverage, *e.g.*, 0.77 of a monolayer [40].

3.3.2. CO stripping method

To bypass altogether the inherent biases of H_{UPD} adsorption on measuring the surface area of Pt-alloys, alternative surface-sensitive reactions (probe species) have been investigated. ECSA estimations from the desorption charge of CO [13,21,40] and Cu [44,45] have been found to survey a greater number of surface Pt sites. Compared to CO, the use of underpotentially-deposited Cu is not very common since it has the major disadvantage that the electrochemical cells, as well as the counter and reference electrodes, are difficult to clean afterwards and that residual copper ions strongly impact the catalytic reaction [13].

In our CO stripping experiments, an adlayer of CO was adsorbed on the Pt surface by holding the potential at a negative limit (0.05 V_{RHE}). The working cell was then purged with argon to remove excess (un-bound) CO. We note that due to the strong Pt-CO_{ad} interactions, CO molecules stay on the Pt surface while the electrolyte is purged

[14,21]. Sweeping the potential in the oxidizing direction resulted in the removal of the CO adlayer at $\sim 0.7\text{-}0.8\text{ V}_{\text{RHE}}$ for the Pt surfaces, and the stripping charge was used to calculate the ECSA. Here, we assume a conversion factor $420\text{ }\mu\text{C}/\text{cm}^2$ corresponding to a monolayer of adsorbed CO, which is in accordance with spectroscopy results indicating a CO monolayer adsorption on the Pt on-top sites [40,46]. In both acid and alkaline media, the electro-oxidation of CO adsorbed on Pt has been suggested to proceed through a Langmuir-Hinshelwood mechanism [40,47–49] where adsorbed CO_{ad} reacts with an adsorbed oxygenated surface intermediate, usually considered to be OH_{ad} [48,50–52], liberating two electrons (this mechanism has also been verified by *in situ* vibrational spectroscopy [53]):

Cyclic voltammetry experiments have shown that, unlike in the case of the H_{UPD} desorption, Pt alloys and monometallic Pt catalysts under the relevant electrochemical conditions have approximately equal saturation surface coverage of CO on the Pt surface sites [21,22]. Therefore, the CO stripping procedure tends to lessen the inherent uncertainties involved in evaluating the ECSA compared to the H_{UPD} method.

The CO stripping voltammograms are shown in **Figure 3a**. The electro-oxidation peak of CO on the Pt-monolayer is observed at lower potential than on pure Pt, owing to the weaker interaction of the surface Pt atoms with CO due to the modified electronic properties of the surface Pt sites. The integrated CO stripping charge for the Pt-monolayer was found to be $306.90\text{ }\mu\text{C}$, and for the pure Pt sample it was $784.0\text{ }\mu\text{C}$. Using these values, the ORR polarization sweeps were re-adjusted to an equal-area basis, which then allowed extraction of the Tafel curves shown in **Figure 3b**. Similar to the previous

case, we see that both samples have similar Tafel features. Data also show that the Pt-monolayer electrocatalyst outperforms monometallic Pt across all potentials. At 0.9 V_{RHE}, the ORR activity of the Pt-alloy electro-catalyst is 1.96 ± 0.20 mA/cm², while that of the Pt standard is 0.39 ± 0.11 mA/cm².

Figure 3. (a) CO stripping voltammograms for the Pt-monolayer and pure Pt samples measured in Ar-purged 0.1 M HClO₄ electrolyte. The CO adlayer was adsorbed by bubbling CO gas into the electrolyte solution at 30 sccm while fixing the potential of the working electrode at 0.05 V_{RHE}. Scan rate: 10 mV/s. Voltammograms were recorded without electrode rotation. (b) Tafel plot of the ORR kinetic current density using the CO stripping ECSA of the Pt-monolayer and pure Pt samples. Inset shows kinetic current

densities at 0.9 V_{RHE}. Scan rate: 50 mV/s. Rotation speed: 1600 rpm. (c,d) CO stripping profiles of the Pt-monolayer and pure Pt samples. The voltammograms indicate the return of the usual CV features of Pt in HClO₄ in subsequent potential cycles (2nd-5th).

3.4. Correcting for potential-dependent background current

We pointed out that in addition to the potential-independent, background capacitive current i_{cap} (**Equation 2**), there is also a potential-dependent contribution to the background current arising from the possible adsorption/desorption of different species on the working electrode. For example, in the case of CO stripping (**Figures 3c,d**), there is a background current that is higher than the potential-independent capacitive current. This current is presumably due to the initial onset of the deposition of the O-containing species on the Pt sites (OH and Pt oxidation). The question is how to remove these contributions from the surface area measurements.

In the CO stripping surface area measurement method, complete removal of the CO adlayer in the first anodic sweep is assumed. This assumption was confirmed by cycling the potential (negative and positive scans) four additional times as shown in **Figures 3c,d** which showed the return of the usual CV features of Pt in perchloric acid [5,14]. One way to remove the contribution of the potential-dependent background current from the CO stripping ECSA measurements is to subtract an anodic wave, measured after the CO stripping wave (CO-free electrode surface), from the CO stripping sweep (CO-covered surface). This subtraction removes the background current from the CO-stripping voltammogram and yields the net current of the electro-oxidation of CO. The resulting voltammograms are shown in **Figure 4a**. The potential-independent

contribution to the background current was separately accounted for (**Equation 2**). Upon accounting for the potential-dependent background current, the CO stripping charges of the Pt-monolayer and pure Pt electro-catalysts were found to be 295.69 and 922.57 μC , respectively. Compared to the CO stripping charges obtained without correcting for the potential-dependent current (306.90 and 784.0 μC , respectively), there is a $\sim 4\%$ and $\sim 15\%$ decrease in CO stripping charge. We note that Shao *et al.* have reported a $>16\%$ decrease in the CO stripping charge for PtNi/C nanoparticles upon correcting for this difference in the oxide reduction charge [43]. Using the CO stripping ECSAs obtained upon correcting for the potential-dependent and potential-independent background currents, the ORR Tafel curves were re-generated as shown in **Figure 4b**. Specific activity of the Pt-monolayer and pure Pt electro-catalysts at 0.9 V_{RHE} were calculated to be 2.07 ± 0.20 and 0.35 ± 0.08 mA/cm^2 , respectively.

Figure 4. (a) Subtraction of the potential-dependent background (‘bkgd.’ in figure) contribution to obtain unbiased CO stripping voltammograms. The dashed lines are the 1st anodic wave of the CO stripping experiments (same as ‘1st cycle’ in **Figures 3c,d**), and the solid lines are the resulting voltammograms after subtracting the 5th anodic wave of the CO stripping experiments (‘5th cycle’ in **Figures 3c,d**). (b) Tafel plot of the ORR

kinetic current density using the background-subtracted CO stripping ECSA of the Pt-monolayer and pure Pt samples. Inset shows kinetic current densities at 0.9 V_{RHE}. Scan rate: 50 mV/s. Rotation speed: 1600 rpm.

We discussed in *Section 3.3.1* that an assumption of a constant, potential-independent double layer capacitance (excluding the potential-dependent background current) could also lead to errors in H_{UPD} ECSA measurements. We also introduced the concept of slanted baseline to address this problem. We demonstrate in **Figure 5a** another, unbiased way to account more properly for the potential-dependent background currents in the H_{UPD} measurements. The central idea here is that by depositing CO on the surface we selectively poison the Pt sites, preventing these from adsorbing hydrogen atoms from the solution in the potential window where the H_{UPD} adsorption takes place (*i.e.*, ~ 0 to ~ 0.4 V_{RHE}). By sweeping the potential to the H_{UPD} potential region with the CO adsorbed on the Pt surface, we should be able to account for the potential-dependent behavior of the system that is independent of the H_{UPD} process. We note that the potential-independent contribution to the double layer capacitance was separately accounted for by the procedure described earlier (**Equation 2**). The potential-dependent contributions to the background current were accounted for by subtracting the first anodic sweep (CO-covered electrode surface) from the fifth anodic sweep (CO-free surface). If we assume that CO is exclusively adsorbed on the Pt surface sites and that it blocks these sites against the H_{UPD} adsorption, then the subtraction process yields the net current of the electro-oxidation of H_{UPD}. The new voltammograms are shown in **Figure 5a**. Integration of the resulting H_{UPD} peaks (**Figure 5a**) allowed us to estimate the ECSA free from the

contribution of both the potential-independent and potential-dependent contributions of the double layer capacitance. Using this method, the H_{UPD} -charges were found to be 106.50 and 248.22 μC for the Pt-monolayer and pure Pt electro-catalysts, respectively, leading to the re-generated Tafel curves shown in **Figure 5b**. At 0.9 V_{RHE} , the specific activities of the electro-catalysts as normalized by these ECSAs were calculated to be 3.45 ± 1.16 and 0.54 ± 0.21 mA/cm^2 (inset of **Figure 5b**).

Figure 5. (a) Subtraction of the potential-dependent background (‘bkgd.’ in figure) contribution to obtain unbiased H_{UPD} stripping voltammograms. The dashed lines are the 5th anodic wave of the CO stripping experiments (same as ‘5th cycle’ in **Figures 3c,d**), and the solid lines are the resulting voltammograms after subtracting the 1st anodic wave of the CO stripping experiments (‘1st cycle’ in **Figures 3c,d**). (b) Tafel plot of the ORR kinetic current density using the background-subtracted H_{UPD} ECSA of the Pt-monolayer and pure Pt samples. Inset shows kinetic current densities at 0.9 V_{RHE} . Scan rate: 50 mV/s . Rotation speed: 1600 rpm.

Summary of the specific ORR activities measured at 0.9 V_{RHE} of the Pt-monolayer and pure Pt electro-catalysts obtained using the various ECSA evaluation

protocols is shown in **Figure 6**. All the data were corrected for potential-independent capacitive current and uncompensated solution resistance. As described above, some of the data were also corrected for the potential-dependent background processes. The data in **Figure 6** show that the highest kinetic current densities for both catalysts were obtained when the H_{UPD} ECSA measurements with the correction for only potential-independent capacitive current were employed. These measurements suggested the reaction rates that are approximately three times higher compared to the rates obtained using the CO stripping approaches. On the other hand, the measurements that utilized the H_{UPD} method to estimate the ECSA appear to be much more consistent with the CO-stripping results when a more careful analysis of potential-dependent background processes that overlap with the desorption of H_{UPD} is employed. This can be done by using the slanted baseline to subtract the potential-dependent background currents in the potential region where H_{UPD} desorbs. Even with this correction, the surface areas measured using H_{UPD} seem to be underestimated giving overestimated specific reaction rates. This issue is alarming particularly since the H_{UPD} method to measure ECSA is by far the most utilized, and overestimation of the reaction rates can lead to misleading statements about the potential usefulness of different Pt-based materials in commercialization of the fuel cell technology. The data in **Figure 6** also show that for all tested approaches to the ECSA measurements, the alloy electrocatalysts exhibit improved relative performance compared to the pure Pt. It should be noted, however, that difference in the performance of the alloy compared to pure Pt is dependent on the method used to measure ECSA, ranging from 5 to 9 times higher rates on alloys

compared to the 3 nm pure Pt; we note that the enhancements ranged from 1.3 to 3 for the larger (5 nm) pure Pt sample.

Figure 6. Specific activity of the Pt-monolayer and pure Pt electrocatalysts at 0.9 V_{RHE} following the indicated ECSA evaluation protocol. Error bars indicate standard deviation of ORR activity calculated from four independent experiments for the Pt-monolayer sample and three for the pure Pt sample.

4. Conclusions

We illustrated uncertainties in evaluating the electrochemical surface area of Pt-based oxygen reduction electrocatalysts that result in errors in the evaluation of the absolute kinetic rates of the pure Pt standards and Pt alloys. Due to these uncertainties, we believe that the most prudent way to report the data is to specifically report the rates for a number of different approaches to the measurement of ECSA. Furthermore, it would

be instructive for the scientific community to agree upon a specific protocol for reporting of the surface specific rates. Although readily accessible, the H_{UPD} method is prone to high relative error for alloys of Pt. Based on our analysis, we believe that the protocol that uses CO stripping with the subtraction of the potential-dependent and potential-independent background currents represents a reasonable compromise between the ease and accuracy of the measurements. This approach seemed to survey the largest number of the surface Pt sites, allowing us to establish a conservative estimate of the ORR rates on Pt alloys.

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