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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 $Au_xCu_{100-x}@Au_{2ML}@Pt_{ML}$ 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 was to move us closer toward establishing more uniform and rigorous protocols in measuring and reporting the ORR rates on Pt alloys.

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 kW/g_{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). Additional effects in ORR measurements have also been reported to impact catalyst performance and potentially even cause discrepancies in measured activity, for instance the voltage scan rate [16], impurities and measurement protocols [17] and the incorporation of Nafion in catalyst film [18]. 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

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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 [19]. 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 [20,21]. 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 [22,23]. This is due to the modified electronic properties of the Pt surface sites [24–29]. 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 [11,24,30].

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 $Au_xCu_{100-x}@Au_{2ML}@Pt_{ML}$ and comparing these to standard monometallic Pt nanoparticle 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 [13,31–33], unbiased measurements of Pt-alloy ECSA have remained largely unaddressed and, unfortunately, overrating of surface-specific ORR rates is rather prevalent in the literature. Benchmarking criteria designed specifically for oxygen evolution and hydrogen evolution electrocatalysts have been reported recently [34], and they have helped standardize the methods used to compare objectively the performance of water splitting catalysts. Our objective here was to move us closer toward 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 min. At this time, 20–30 mg of $Cu(acac)_2$ 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 h 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 min 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 h. Supported nanoparticles were then collected by centrifugation (3 washes with IPA at 8000 rpm for 8 min). 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 Supporting Information (Figs. S.1 and S.2). Powders were thermally treated for 5 h 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) [29,35]. 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 $Hg/HgSO_4$ (sat. K_2SO_4) reference electrode) in a 5 mM solution of $CuSO_4$ with a 50 mM supporting electrolyte of H_2SO_4. 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 MΩ cm (Millipore)) and deposited into a solution containing either 1 μM $AuCl_3$ or K_2PtCl_4 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 Ref. 3000 potentiostat/galvanostat/frequency response analyzer. The Ref. 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 Ref. 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 μl droplets onto a 5 mm glassy carbon electrode (GCE, Pine Instruments) dried with rotation at 700 rpm [36]. The GCE was polished with 0.05 μl 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 $HClO_4$ prepared by dilution of 70% perchloric acid stock solution (Merck Suprapur) with Millipore water (18.2 MΩ cm). Uncompensated resistance of ∼25 Ω was consistently measured with high-frequency electrochemical impedance spectroscopy, which was then corrected for in all the reported data. All potentials are