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Experimental Methods for Quantifying the Activity of Platinum Electrocatalysts for the Oxygen Reduction Reaction

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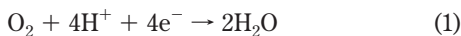
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A tutorial is provided for methods to accurately and reproducibly determine the activity of Pt-based electrocatalysts for the oxygen reduction reaction in proton exchange membrane fuel cells and other applications. The impact of various experimental parameters on electrocatalyst activity is demonstrated, and explicit experimental procedures and measurement protocols are given for comparison of electrocatalyst activity to fuel cell standards. (To listen to a podcast about this article, please go to the *Analytical Chemistry* multimedia page at pubs.acs.org/page/ancham/audio/index.html.)

Electrochemical energy conversion devices, ranging from fuel cells to metal-air batteries, require low cost, high activity, and durable electrocatalysts for the O₂ reduction reaction (ORR). High activity ORR catalysts are critical to proton exchange membrane fuel cells (PEMFCs), which make electricity efficiently by the electrochemical oxidation of H₂ fuel at their anodes and reduction of O₂ from air at their cathodes using nanoparticles of Pt or Pt-alloys as catalysts, usually supported on high surface area carbon blacks, such as Vulcan carbon or Ketjen black. The ORR in acid electrolyte (Equation 1) is a slow four-electron transfer reaction resulting in high overpotentials at the cathodes of PEMFCs, thus requiring high Pt catalyst loadings, which increase costs. New, highly active and durable electrocatalysts are crucial to the commercialization of PEMFCs for automotive



and stationary applications. Central to the research and testing of new electrocatalysts for the ORR are the experimental and analytical methods necessary for the meaningful evaluation of electrocatalyst activity.



Performance benchmarking of commercial catalysts with cyclic voltammetry (CV) in an inert atmosphere and rotating disk electrode (RDE) measurements in the presence of O_2 has been reported. The study showed that a three-electrode electrochemical cell can be used to predict performance trends of practical catalysts in membrane electrode assemblies of PEM-FCs.¹ CVs of the catalysts in an O_2 -free electrolyte measured the Pt electrochemical surface area of the hydrogen adsorption/desorption regions. Thin-film RDE measurements of the ORR in O_2 -saturated electrolyte performed at different rotation speeds isolated and estimated ORR kinetic currents. The results were normalized to the amount of Pt on the electrode and the Pt electrochemical surface area to calculate the Pt mass- and area-specific activities, which are the accepted measures of true ORR catalyst activity. Another recent publication has reported on methods to analyze CV and RDE data to determine whether the data are viable.²

The limitation of these benchmarking papers is that they give detailed instructions on how to analyze data, but not on exactly how to measure the data. The intent of this Feature is to share the simple—yet critical—information that is usually omitted from the experimental sections of papers, such as how to clean the electrochemical cell, build a stable reference electrode, and evaluate the topology and morphology (appearance) of a good catalyst-coated thin-film electrode. The results presented here will demonstrate the difference between “good” and “bad” data. This tutorial should enable more researchers to determine the three critical catalyst parameters: (1) electrochemical surface area, (2) Pt mass-specific activity (I_m), and (3) Pt area-specific activity (I_a), which are indispensable measures of true ORR catalyst activity.

PREPARATIONS AND MEASUREMENTS

The general procedure for evaluating a catalyst's electrocatalytic activity by the RDE methodology involves the casting of a catalyst thin-film of known concentration on the surface of a glassy carbon electrode substrate. Once this thin-film has dried, the catalyst electrocatalytic activity is evaluated in a standard three-electrode electrochemical cell with working, counter, and reference electrodes to obtain CVs in a de-aerated electrolyte and ORR polarization curves in an O_2 -saturated electrolyte. The execution of this procedure to obtain accurate and reproducible values requires a great deal of detailed preparation.

Method to clean glassware. The electrochemical cell, including glassware, stoppers, and o-rings, must be cleaned thoroughly of cationic, anionic, and organic impurities to obtain reproducible measurements that approach what is assumed to be the absolute value of the specific activity of Pt. The following simple methods are useful for cleaning these cells.

The electrochemical cell is filled with ~100 mL concentrated H_2SO_4 and turned from side to side to ensure that the entire glassware surface is wet and coated with the acid. The interior of the cell is then soaked in the concentrated H_2SO_4 overnight and is finally rinsed at least 8× with nanopure water (18 MΩ cm).

An alternative to this method is to wash the electrochemical cell thoroughly with a standard glassware surfactant (e.g., Spar-

kleen), vigorously rinse it with nanopure water to remove any residual surfactant, and finally, soak it in one of the following three acid cleaning treatments: (1) concentrated H_2SO_4 for eight hours, (2) 1:1 mixture of $\text{H}_2\text{SO}_4 + \text{HNO}_3$ for two to four hours, or (3) 1:1 mixture of $\text{H}_2\text{SO}_4 + \text{Nochromix}$ for four hours. Following acid treatment, the cell should be rinsed again with nanopure water, boiled twice in nanopure water (one hour each time), rinsed well with nanopure water, and then finally rinsed with the working electrolyte. This more extensive cleaning method is recommended biweekly or monthly if the glassware is contaminated or when testing low surface area electrodes. The success of the cleaning procedure can be benchmarked by evaluating a low-surface-area polycrystalline Pt disk in the cell; its specific activity at $E = 0.90$ V should be ~1500–3000 $\mu\text{A cm}^{-2}$. Polycrystalline Pt disks are highly sensitive to impurities, and high activities imply that one has met or exceeded the cleanliness levels needed to obtain good data using thin-films of high surface area catalysts as electrodes.

Reference electrode. ORR measurements require a stable reference electrode that does not contaminate the experiment and conversely is not contaminated by the experiment. Common reference electrodes include reversible H_2 electrodes (RHEs), dynamic H_2 electrodes (DHEs), saturated calomel electrodes (SCEs), and Ag/AgCl electrodes.

We prefer a RHE consisting of a high surface area Pt electrode immersed in H_2 -saturated 0.1 M HClO_4 electrolyte because such RHEs contain a low level of impurities and require no potential correction. An example of a sealed RHE is shown in Figure 1a, with a photograph of the RHE connected to the bridge shown in Figure 1b. The surface area of the Pt mesh can be increased significantly by platinization with Pt black. The design for the bridge was adopted from the literature.³ A fresh RHE should be prepared daily, using the same electrolyte (i.e., 0.1 M HClO_4) in the reference electrode and in the electrochemical cell. The RHE is filled completely via a syringe with 0.1 M HClO_4 with the glass capillary facing up. The RHE is then flipped down, placed into a beaker containing 0.1 M HClO_4 and a Pt counter electrode, and the 0.1 M HClO_4 is electrolyzed at ~30 V to fill the Pt mesh chamber halfway with H_2 (Figure 1a). The final RHE should have half of the Pt mesh in contact with the H_2 gas and the other half in the 0.1 M HClO_4 solution. An alternative RHE design is shown in Figure 1c: H_2 continuously flows over a high surface area Pt electrode, eliminating the need for electrolysis.

Alternatively, the DHE uses a load on Pt to constantly split water into H_2 and O_2 . Commercial SCE and Ag/AgCl reference electrodes can also be used successfully by incorporating a salt bridge. The salt bridge minimizes the intrusion of chloride or other ions from the SCE or Ag/AgCl reference electrode into the main compartment of the working electrode but can be cumbersome. The SCE and Ag/AgCl reference electrodes should be calibrated on a daily basis to ensure that their potential does not drift.

Chemical grades. All chemicals and gases must be high purity. Ultrahigh purity (UHP) Ar, N_2 (grade 5), and O_2 (grade 4); double distilled HClO_4 ; and nanopure water must be used. N_2 tends to have higher purity than Ar. High purity 0.1 M

Table 1. Comparison of the mass-specific (I_m) and area-specific activities (I_s) of Pt/Vulcan carbon films for the ORR at $E = 0.90$ V versus RHE determined from the anodic sweep (0.05 V→1.03 V) at 5 and 20 mV s⁻¹ for the films shown in Figure 2, and for a good film as function of Pt loading, electrolyte temperature, electrolyte purity and type

20% Pt/Vulcan carbon films	L_{Pt} $\mu\text{g}_{Pt} \text{ cm}^{-2}$	ECSA m^2 g_{Pt}^{-1}	$I_{m(0.90 \text{ V})}$, 20 mV/s A mg_{Pt}^{-1}	$I_{m(0.90 \text{ V})}$, 5 mV/s A mg_{Pt}^{-1}	$I_{s(0.90 \text{ V})}$, 20 mV/s $\mu\text{A cm}^{-2}_{Pt}$	$I_{s(0.90 \text{ V})}$, 5 mV/s $\mu\text{A cm}^{-2}_{Pt}$
Bad Film 0.1 M HClO ₄ , 30 °C	20	42	0.10	0.06	230	135
Intermediate Film 0.1 M HClO ₄ , 30 °C	20	57	0.15	0.10	272	175
Good Film 0.1 M HClO ₄ , 30 °C	20	61	0.21	0.16	347	261
Good Film Dirty 0.1 M HClO ₄ , 30 °C	20	61	0.15	0.05	239	89
Good Film 0.1 M HClO ₄ , 30 °C	14.3	66	0.21	0.16	305	200
Good Film 0.1 M HClO ₄ , 60 °C	14.3	66	0.20	0.13	304	199
Good Film 0.5 M H ₂ SO ₄ , 30 °C	20	68	0.04	—	53	—
Good Film 0.05 M H ₂ SO ₄ , 30 °C	20	65	0.07	—	105	—

L_{Pt} = the working electrode Pt loading. ECSA = Pt electrochemical surface area. $I_{m(0.90 \text{ V})}$, 20 mV/s = Pt mass-specific activity calculated at $E = 0.90$ V versus RHE for an ORR polarization curve measured at a scan rate of 20 mV s⁻¹. The mass activities are estimated via calculation of I_k (kinetic current) and normalization to L_{Pt} . $I_{m(0.90 \text{ V})}$, 5 mV/s = Pt mass-specific activity calculated at $E = 0.90$ V versus RHE for an ORR polarization curve measured at a scan rate of 5 mV s⁻¹. $I_{s(0.90 \text{ V})}$, 20 mV/s = Pt area-specific activity calculated at $E = 0.90$ V versus RHE for an ORR polarization curve measured at a scan rate of 20 mV s⁻¹. The area-specific activities are estimated via the calculation of I_k and normalization to ECSA. $I_{s(0.90 \text{ V})}$, 5 mV/s = Pt area-specific activity calculated at $E = 0.90$ V versus RHE for an ORR polarization curve measured at a scan rate of 5 mV s⁻¹.

variable and depend on the type of catalyst. The catalyst ink should be well-dispersed and not flocculate or settle. A small amount of Nafion ionomer is added to either the water/alcohol solution or directly to the dry thin-film to improve adhesion of the film to the electrode surface. Nafion films <0.2 μm thick on solid electrodes^{11,12} and Nafion films <0.1 μm thick on Pt/Vulcan-carbon-covered glassy carbon⁷ do not affect oxygen diffusion to the electrode. The alcohol type and content must also be optimized for each catalyst. Catalysts that are inherently hydrophobic, such as alloys or heat treated samples, may require inks with high alcohol (e.g., ethanol or isopropanol) to water ratios to obtain optimal dispersion.¹³ High isopropanol:water ratios as well as long ultrasonication times can yield inks that stay well dispersed and result in an electrode with higher measured electrocatalytic activity. Hydrophilic catalysts can disperse well in solutions with only the Nafion solution and water.

The following is a recipe for a thin-film electrode from a standard of 20% Pt on Vulcan carbon with an electrode Pt loading of 20 $\mu\text{g}_{Pt} \text{ cm}^{-2}$. A stock solution of 20% isopropanol and 0.02% Nafion ionomer is prepared by mixing 20 mL of isopropanol with 79.6 mL of nanopure water and 0.4 mL of 5 wt% Nafion ionomer solution (Ion Power, Liquion 1100) in a 100 mL volumetric flask. Next, 10 mg of the catalyst is measured into a 10 mL borosilicate vial and 5 mL of the stock isopropanol/Nafion solution is added; these are mixed thoroughly with a high shear mixer (IKA, T10Basic S1) for one minute. The catalyst ink is then transferred to an ultrasonicator (Branson, 2510) and sonicated for ≥ 60 minutes in a water bath temperature <40 °C.

The following is a recipe for a thin-film electrode from a standard of 46% Pt on Ketjen black with an electrode Pt loading of 17.3 $\mu\text{g}_{Pt} \text{ cm}^{-2}$. A 24% isopropanol solution is prepared by mixing 6 mL of isopropanol and 19 mL of nanopure water together in a 25 mL volumetric flask. Next, 18.5 mg of the Pt/Ketjen black catalyst is measured into a 50 mL volumetric flask, the 25 mL of 24% isopropanol solution is added, and finally, 100 μL of 5 wt% Nafion ionomer solution (Ion Power, Liquion 1100) is added to the Pt/Ketjen black/isopropanol solution. The catalyst ink is then placed in an ice bath and sonicated (Branson, 2510) for 30 minutes.

A 10 μL droplet of the well-dispersed ink is pipetted onto the clean, polished, glassy carbon electrode such that it completely covers the glassy carbon but does not cover any of the Teflon. The ink droplet should be dried in conditions that yield a smooth film that covers the entire surface of the glassy carbon electrode. The science of film drying has been studied extensively^{14,15} and is a function of alcohol type and content, Pt dispersion (sonication procedures), and ambient (temperature and humidity) conditions of the drying. One method is to cover the electrodes with a beaker to slow the drying. The film can also be dried under a low flow of N₂ at room temperature or at 40–60 °C for 30 minutes in air. Researchers should expect to dedicate some time to optimizing ink formulations and drying conditions to obtain the high quality thin-film electrodes needed for best performance.

Measurement temperature. The temperature of the cell is controlled by flowing heated/cooled water through the jacket of the electrochemical cell via a circulating water bath. Measurements should be made near room temperature (25–30 °C) because, besides being expeditious, it reduces wear on the equipment caused by the higher volatility of the acid at elevated temperatures. Prior work reports measurements at 60 °C¹, but HClO₄ decomposes over time, producing Cl⁻ ions, which inhibit the ORR.¹⁶ Because “room temperature” can be variable, a baseline temperature such as 30 °C can be chosen, though the impact of temperature on the results is very small (Table 1). Measurements at several controlled temperatures are needed to obtain an Arrhenius plot that produces a value of the activation energy for the ORR, which can subsequently determine the reaction order. CV measurements of the electrochemical surface area from H and CO adsorptions are always carried out near room temperature.

Electrochemical measurements. For every measurement, the clean electrochemical cell is filled with fresh 0.1 M HClO₄ and de-oxygenated with a steady stream of UHP N₂ for ≥ 25 minutes. During this time, the cell temperature is equilibrated (e.g., to 30 °C). The catalyst coated glassy carbon (the working electrode in this experiment) is wetted with nanopure water, attached to the shaft of the electrode rotator (e.g., Pine, AFMSRX electrode rotator), and guided into the electrolyte. The working electrode should be positioned at the same height

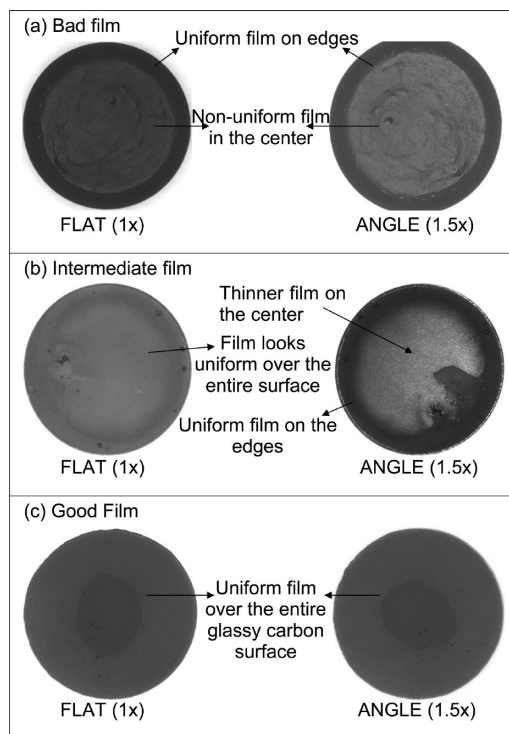


Figure 2. Optical micrographs of three films with different film quality, termed (a) bad, (b) intermediate, and (c) good. Left: “flat” picture (magnification: 1 \times); Right: “angle” picture (magnification: 1.5 \times).

for each experiment to keep the solution resistance between the working electrode and RHE lugging capillary similar. Gas bubbles attached to the working electrode surface can be dislodged by rotation at >3600 rpm. The gas flow rate is reduced during measurements to ensure that no additional bubbles stick to the working electrode surface. All electrodes are connected to the potentiostat (e.g., Autolab bipotentiostat, PGSTAT30) using appropriate shielded cables.

The working electrode must be first electrochemically cleaned via potential cycling prior to measuring the CVs for electrochemical surface area determination and the ORR. For example, a Pt/Vulcan carbon working electrode can be cycled between 0 and 1.20 V versus the RHE for 40 cycles at 200 mV s^{-1} or for 20 cycles at 100 mV s^{-1} . The upper limit of the CVs should be lower for catalysts containing leachable metals. The CV measurements for the Pt electrochemical surface area determination should be carried out by cycling $\geq 3\times$ at $20\text{--}100 \text{ mV s}^{-1}$ between 0.05 V and 1.20 V. The minimum potential should be just above the potential for H_2 evolution (Figure 3), which will be scan rate and catalyst dependent.

Upon completion of the CV measurements, the saturation gas is switched to O_2 , and the electrolyte is saturated for ≥ 25 minutes with O_2 . The rotator is set to the appropriate rotation rate and turned on. The rotation rate is typically 1600 rpm, except when collecting data for Levich-Koutecký curves,^{5,12} in which case the measurements are preferably made at rotation speeds of 400, 900, 1600, 2500, and 3600 rpm. Measurements are carried out at 5, 10 and/or 20 mV s^{-1} in a typical polarization program of $1.03 \text{ V} \rightarrow 0.05 \text{ V} \rightarrow 1.03 \text{ V}$. At lower sweep rates, the effect of impurities and the formation of surface oxides suppress the measured ORR activity; at scan rates $>20 \text{ mV s}^{-1}$, capacitive effects are higher. The background current is measured by

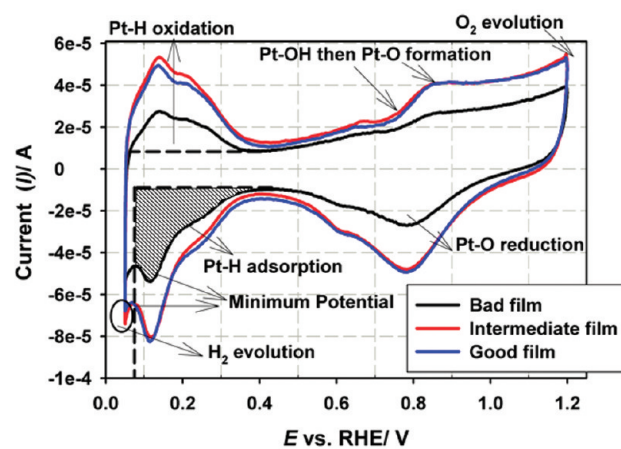


Figure 3. Comparison of CVs obtained with the bad, intermediate, and good films shown in Figure 2. CVs recorded at 20 mV s^{-1} in N_2 -saturated 0.1 M HClO_4 at 30°C . The shaded region shows the area integrated for hydrogen adsorption.

running the ORR sweep profile (e.g., $1.03 \text{ V} \rightarrow 0.05 \text{ V} \rightarrow 1.03 \text{ V}$ at 5 and 20 mV s^{-1} and 1600 rpm) in N_2 -purged 0.1 M HClO_4 either before or after the ORR measurements to account for capacitive current contributions. This background current is subtracted from the experimental ORR current to eliminate any contributions of capacitive current.

The measurement (and active compensation) of the solution resistance is also an important factor to take into consideration. If one assumes an uncompensated resistance of $10 \Omega \text{ cm}^{-1}$ and the distance between the working electrode and the RHE bridge capillary to be 1 cm, then the solution resistance will be 10Ω . At $E = 0.9 \text{ V}$ versus the RHE, the measured current density is typically $J = 2 \text{ mA cm}^{-2}$ or $\sim 0.4 \text{ mA}$ (geometric surface area of the glassy carbon = 0.196 cm^2). The potential is shifted by 4 mV, which, though a small amount, results in real difference in the activity. Therefore, evaluating the solution resistance and/or minimizing the distance between the RHE lugging capillary and the working electrode tip is important.

CATALYTIC ACTIVITY VERSUS FILM QUALITY

High quality ORR measurements require a thin, uniform film over the entire surface area of the glassy carbon. The quality of the film is determined by a delicate balance between alcohol content and type, Pt dispersion, drying conditions, and glassy carbon surface. The impact of film quality on electrochemical performance is shown quantitatively below. We compare the performance of the three different films shown in Figure 2, which we term as “bad”, “intermediate”, and “good” films.

Pt Electrochemical Surface Area Determination from CVs.

CVs for bad, intermediate, and good films are presented in Figure 3. The intermediate and good films show fairly similar CVs, whereas the response obtained for the bad film shows much lower currents over the entire potential region. The electrochemical surface area of the Pt in the working electrode is calculated using Equation 2 from the hydrogen adsorption charge ($Q_{\text{H-adsorption}}$) in the negative-going potential scan ($0.40\text{--}0.075 \text{ V}$) on CVs shown in Figure 3 after correction for double-layer charging (by subtracting the current at 0.40 V from the total current). This method has been validated versus CO adsorption and Cu under-

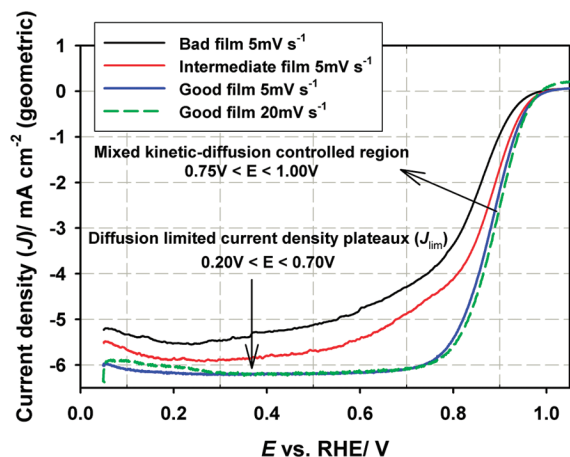


Figure 4. ORR polarization curves recorded with the bad, intermediate, and good films shown in Figure 2 during the anodic sweep (0.05 V → 1.03 V versus RHE) at 5 mV s⁻¹. The ORR polarization curve for the good film is also shown at 20 mV s⁻¹. Electrode rotation rate = 1600 rpm; O₂ saturated 0.1 M HClO₄; 30 °C; Pt loading = 20 μg_{Pt} cm⁻².

potential deposition methods for measuring the Pt electrochemical surface area.¹⁷ More details on the determination of the Pt electrochemical surface area are presented in ref. 2. The minimum potential is selected just above the potential of the H₂ evolution onset,¹⁷ as shown in Figure 3. The charge of full coverage for clean polycrystalline Pt is $Q_H = 210 \mu\text{C cm}^{-2}$ and is used as the conversion factor.^{6,18,19} The Pt electrochemical surface area (ECSA_{Pt,cat}) is reported in m² g_{Pt}⁻¹; L_{Pt} is the working electrode Pt loading (mg_{Pt} cm⁻²) and A_g (cm²) is the geometric surface area of the glassy carbon electrode (i.e., 0.196 cm²).

$$\text{ECSA}_{\text{Pt,cat}} (\text{m}^2 \text{g}_{\text{Pt}}^{-1}) = \left[\frac{Q_{H-\text{adsorption}} (\text{C})}{210 \mu\text{C cm}_{\text{Pt}}^{-2} L_{\text{Pt}} (\text{mg}_{\text{Pt}} \text{cm}^{-2}) A_g (\text{cm}^2)} \right] 10^5 \quad (2)$$

The electrochemical surface area results of films with different quality are tabulated in Table 1. The film quality affects the electrochemical surface area measurement and an electrochemical surface area of only 42 m² g_{Pt}⁻¹ is measured for the bad film, compared to 61 m² g_{Pt}⁻¹ for the good film.

ORR Comparison. Figure 4 compares the anodic sweep (0.05 V → 1.03 V) of the ORR polarization curves recorded with the bad, intermediate, and good films shown in Figure 2 at a scan rate of 5 mV s⁻¹ prior to background current subtraction. The ORR polarization curve for the good film is also shown at 20 mV s⁻¹. The ORR of the good films have a single, steep reduction wave with a mixed kinetic-diffusion control region 0.75 V < E < 1.00 V above a well developed (flat) diffusion limited current density plateau, J_{lim} , in the potential region 0.20 V < E < 0.70 V. The J_{lim} value of ~ -6 mA cm⁻² (geometric) is within the 10% margin of the theoretical diffusion limiting current² (i.e., -5.7 mA cm⁻²), which is calculated using the Levich equation, clearly indicating a negligible contribution from O₂ diffusion through the Nafion film. The form of the response for the good film is essentially identical to voltammograms recorded on a smooth polycrystalline Pt disk electrode and a carbon supported Pt catalyst in the same 0.1 M HCO₄ electrolyte at 60

°C.² The polarization curve obtained at 5 mV s⁻¹ gives lower activity for the ORR because its half-wave potential ($E_{1/2}$, the point half-way between zero current and the diffusion limited current density plateau) shows a 10 mV negative potential shift compared to the ORR activities obtained at 20 mV s⁻¹, as discussed above and in ref. 1.

The ORR polarization curves obtained for the intermediate and bad films are comparable to each other. A single reduction wave is visible in Figure 4, but the limiting current density plateau is not as well developed as the one obtained for the good film, indicating poor diffusion. Both the intermediate and bad films have lower activity towards the ORR (as observed from the magnitude of the current densities in the potential range 0.80 V < E < 1.00 V), with the bad film having the lowest current density and thus activity. The catalyst ORR activity can be visually benchmarked from its $E_{1/2}$. The $E_{1/2}$ for the bad film is 0.82 V, whereas the intermediate film and good film have $E_{1/2} = 0.85$ V and 0.89 V, respectively. The electrocatalyst's considerable activity is indicated by its high $E_{1/2}$ and is dependent on the quality of the catalyst cast film. The same trends are visible for the curves recorded at 20 mV s⁻¹ (not shown). Catalyst electrocatalytic activity towards the ORR is quantified at E = 0.90 V because interferences from mass-transport losses cannot be completely excluded at the higher current densities observed below E = 0.90 V.¹

The electrocatalytic activity of catalysts is best compared by their mass- and area-specific activities using the mass-transport correction for thin-film RDEs (Equation 3):¹

$$I_k (\text{A}) = \frac{I_{\text{lim}} (\text{A}) \times I (\text{A})}{(I_{\text{lim}} - I)} \quad (3)$$

where I_k is the kinetic current (A) and I_{lim} is the measured limiting current (A). First, the ORR polarization curves are corrected by subtracting background current measured under identical conditions under N₂ atmosphere without rotation. Then, I is the value of the curve at E = 0.90 V and I_{lim} is that at E = 0.40 V versus RHE. The Pt mass-specific activities are estimated via calculation of I_k and normalization to the Pt-loading of the disk electrode. For example, if 10 μL of ink is loaded onto the working electrode and the ink contains 10 mg of catalyst in 5 mL of the ink stock solution, then catalyst loading is 2 mg, of which 20% is Pt, resulting in a Pt loading of 4×10^{-3} mg. The Pt area-specific activities are estimated via the calculation of I_k and normalization to the Pt electrochemical surface area (Table 1) using Equation 4:

$$I_s (\mu\text{A cm}_{\text{Pt}}^{-2}) = \frac{I_k (\text{A})}{(Q_{H-\text{adsorption}} (\text{C}) / 210 \mu\text{C cm}_{\text{Pt}}^{-2})} \quad (4)$$

Alternatively, the kinetic currents may be calculated using the more rigorous but time-consuming approach of measuring the ORR polarization curves for at least four different rotation speeds (900, 1600, 2500, 3600 rpm), from which the current at infinite speed is extrapolated from a Koutecký-Levich plot.

The numerical values of the Pt mass-specific (I_m) and area-specific (I_s) activities at E = 0.90 V versus RHE derived from the ORR polarization curves shown in Figure 4 are detailed in

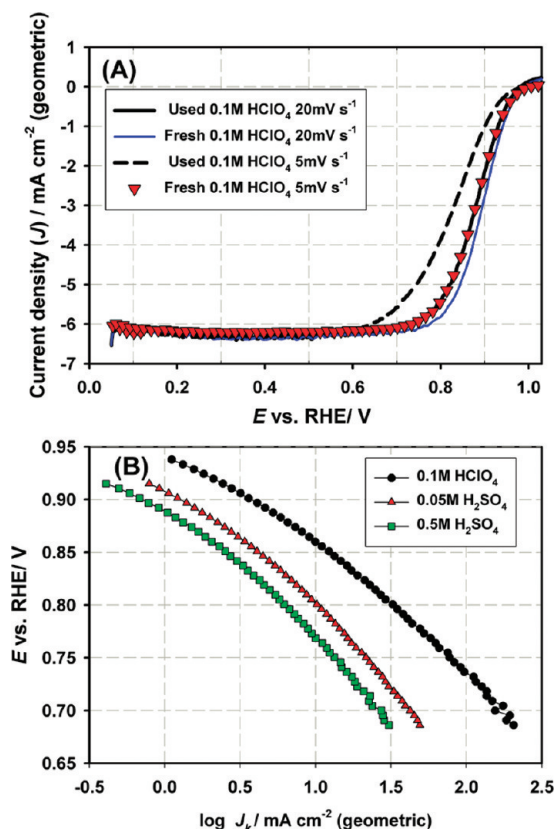


Figure 5. (A) ORR polarization curves for the film shown in Figure 2c recorded during the anodic sweep (0.05 V → 1.03 V versus RHE) in previously used 0.1 M HClO₄ electrolyte at 20 mV s⁻¹ (black line) and 5 mV s⁻¹ (dashed black line) and fresh 0.1 M HClO₄ electrolyte at 20 mV s⁻¹ (blue line) and 5 mV s⁻¹ (red triangles). (B) *E* versus log |*J_k*|, or Tafel plots (obtained using eq 3), measured for a good film in fresh 0.1 M HClO₄, 0.05 M H₂SO₄, and 0.5 M H₂SO₄ at 20 mV s⁻¹. Electrode rotation rate = 1600 rpm; O₂ saturated electrolytes; 30 °C; Pt loading = 20 μg_{Pt} cm⁻².

Table 1. A 20% Pt/Vulcan carbon standard should have a *I_m* of ~0.20 A mg_{Pt}⁻¹ at 20 mV s⁻¹ and a *I_s* of 300 μA cm_{Pt}⁻². The *I_m* and *I_s* values reported in Table 1 demonstrate the importance of having a good film when evaluating the activity of a catalyst. The *I_m* of the good film is ~55% higher than that of the bad film for polarization curves measured at both 20 mV s⁻¹ and 5 mV s⁻¹. Likewise, the *I_s* of the good film is ~40% higher than that of the bad film.

We also report the ORR results for the same 20% Pt/Vulcan carbon catalyst, but with a Pt loading of 14.3 μg_{Pt} cm⁻² both at 30 °C and 60 °C. The *I_m* and *I_s* obtained for a Pt loading of 14.3 μg_{Pt} cm⁻² matches the data obtained for the Pt loading of 20 μg_{Pt} cm⁻². The *I_m* and *I_s* values obtained at 60 °C are comparable to those measured at 30 °C and match well with values reported by Gasteiger et al.¹

CATALYTIC ACTIVITY VERSUS IMPURITIES IN ELECTROLYTE AND ELECTROLYTE CHOICE

The cleanliness and choice of the electrolyte play a dominant role in the catalyst activity evaluation procedures. As noted earlier, best results are obtained with a clean or fresh electrolyte comprising a non-adsorbing anion (e.g., ClO₄⁻).⁴ The impact of the electrolyte on ORR performance is illustrated in this section. Figure 5A compares the ORR polarization curves for the good

film shown in Figure 2c recorded during the anodic sweep (0.05 V → 1.03 V) in “used” and fresh 0.1 M HClO₄ electrolyte at 20 mV s⁻¹ and 5 mV s⁻¹. The fresh electrolyte is directly from the stock solution. The used electrolyte was in service over a two day period for the evaluation of Pt/Vulcan carbon catalyst for the ORR and was purged with UHP argon and O₂ over the two-day period.

The impact of electrolyte cleanliness is seen in the mixed kinetic-diffusion controlled region of Figure 5A, especially at the lower scan rate of 5 mV s⁻¹. The polarization curves recorded in the used electrolyte have the lowest activity towards the ORR in measurements made at both 5 mV s⁻¹ and 20 mV s⁻¹. The *E*_{1/2} of the curve measured in the fresh electrolyte (0.90 V) is shifted 10 mV more positive than that of the used electrolyte (*E*_{1/2} = 0.89 V) at 20 mV s⁻¹. The ORR polarization curve measured at 5 mV s⁻¹ in the fresh electrolyte exactly overlays the ORR polarization curve measured at 20 mV s⁻¹ in the used electrolyte. The effect of the used electrolyte on the ORR is more pronounced for the polarization curve recorded at 5 mV s⁻¹. Its *E*_{1/2} is shifted 90 mV more negative than that of the fresh electrolyte. Further, the current densities measured in the mixed kinetic-diffusion controlled region are much higher for the curves measured in the fresh electrolyte than the used electrolyte at both scan rates. The limiting current density plateau is not affected by the presence of impurities in the electrolyte. The *I_m* values calculated from the polarization curves measured in the fresh electrolyte are ~30% higher than those calculated from polarization curves measured in the used electrolyte at 20 mV s⁻¹ and ~60% higher at 5 mV s⁻¹ scan rate. The same trend is clearly visible when comparing the *I_s*.

The *E* vs. log |*J_k*| curves, or Tafel plots (obtained using Equation 3), for a good film at 20 mV s⁻¹ and a rotation speed of 1600 rpm in fresh 0.1 M HClO₄, 0.05 M H₂SO₄, and 0.5 M H₂SO₄ are compared in Figure 5B. The catalytic activity is strongly dependent on the choice of the working electrolyte in the order 0.1 M HClO₄ > 0.05 M H₂SO₄ > 0.5 M H₂SO₄. The *I_m* measured in the 0.1 M HClO₄ electrolyte is 80% higher than in the 0.5 M H₂SO₄, as reported in Table 1.

CONCLUSION

This tutorial describes the experimental details for accurate measurements of the electrochemical surface area and mass- and area-specific activities of O₂ reduction electrocatalysts. Critical factors for obtaining correct data are glassware cleanliness, electrode film quality, and electrolyte choice and purity. We find that the Pt mass-specific activity of a good film is ~55% higher than that of a bad film for polarization curves measured at both 20 mV s⁻¹ and 5 mV s⁻¹; similarly, a good film can give as much as ~40% higher area-specific activity than a bad film. The Pt mass-specific activities calculated from experiments in a clean, fresh electrolyte are typically ~30–60% higher than those in used electrolyte. The catalytic activity is strongly dependent on the choice of the working electrolyte in the order 0.1 M HClO₄ > 0.05 M H₂SO₄ > 0.5 M H₂SO₄. The Pt mass-specific activity measured in 0.1 M HClO₄ is 80% higher than in 0.5 M H₂SO₄. Once researchers can replicate the measurement of Pt/carbon standard activity in their laboratories, they can effectively benchmark the activity of newly developed catalysts.

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REFERENCES

- (1) Gasteiger, H. A.; Kocha, S. S.; Sompalli, B.; Wagner, F. T. *Appl. Catal., B* **2005**, *56*, 9–35.
- (2) Mayrhofer, K. J. J.; Strmcnik, D.; Blizanac, B. B.; Stamenkovic, V.; Arenz, M.; Markovic, N. M. *Electrochim. Acta* **2008**, *53*, 3181–3188.

- (3) Damaskin, B. B. *Laboratory course in electrochemistry*; Vysshaya shkola: Moscow, 1991.
- (4) Markovic, N.; Gasteiger, H.; Ross, P. N. *J. Electrochem. Soc.* **1997**, *144*, 1591–1597.
- (5) Paulus, U. A.; Schmidt, T. J.; Gasteiger, H. A.; Behm, R. J. *J. Electroanal. Chem.* **2001**, *495*, 134–145.
- (6) Schmidt, T. J.; Gasteiger, H. A. In *Handbook of Fuel Cells - Fundamentals, Technology and Applications*; Vielstich, W., Gasteiger, H. A., Lamm, A., Eds.; Wiley, 2003; Vol. 2, p 316.
- (7) Higuchi, E.; Uchida, H.; Watanabe, M. *J. Electroanal. Chem.* **2005**, *583*, 69–76.
- (8) Gojkovic, S. L.; Zecevic, S. K.; Savinell, R. F. *J. Electrochem. Soc.* **1998**, *145*, 3713–3720.
- (9) Gloaguen, F.; Convert, P.; Gamburzev, S.; Velez, O. A.; Srinivasan, S. *Electrochim. Acta* **1998**, *43*, 3767–3772.
- (10) Gloaguen, F.; Andolfatto, F.; Durand, R.; Ozil, P. *J. Appl. Electrochem.* **1994**, *24*, 863–869.
- (11) Watanabe, M.; Igarashi, H.; Yosioka, K. *Electrochim. Acta* **1995**, *40*, 329–334.
- (12) Zecevic, S. K.; Wainright, J. S.; Litt, M. H.; Gojkovic, S. L.; Savinell, R. F. *J. Electrochem. Soc.* **1997**, *144*, 2973–2982.
- (13) Takahashi, I.; Kocha, S. S. *J. Power Sources* **2010**, *95*, 6312–6322.
- (14) Deegan, R. D.; Bakajin, O.; Dupont, T. F.; Huber, G.; Nagel, S. R.; Witten, T. A. *Nature* **1997**, *389*, 827–829.
- (15) Deegan, R. D.; Bakajin, O.; Dupont, T. F.; Huber, G.; Nagel, S. R.; Witten, T. A. *Phys. Rev. E* **2000**, *62*, 756–765.
- (16) Stamenkovic, V.; Markovic, N. M.; Ross, P. N. *J. Electroanal. Chem.* **2001**, *500*, 44–51.
- (17) Baturina, O. A.; Gould, B. D.; Garsany, Y.; Swider-Lyons, K. E. *Electrochim. Acta* **2010**, DOI: 10.1016/j.electacta.2010.06.004.
- (18) Biegler, T.; Rand, D. A. J.; Woods, R. *J. Electroanal. Chem.* **1971**, *29*, 269–277.
- (19) Ralph, T. R.; Hards, G. A.; Keating, J. E.; Campbell, S. A.; Wilkinson, D. P.; Davis, M.; St-Pierre, J.; Johnson, M. C. *J. Electrochem. Soc.* **1997**, *144*, 3845–3857.

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