Comparison of High-Throughput Electrochemical Methods for Testing Direct Methanol Fuel Cell Anode Electrocatalysts

Benny C. Chan, a Renxuan Liu, b Krishnakumar Jambunathan, a,b Hong Zhang c Guoying Chen, a,b Thomas E. Mallouk, a,z and Eugene S. Smotkin c,d, **

a Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, USA
b NuVant Systems, Incorporated, Chicago, Illinois 60616, USA
c Division of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616, USA
d Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana 46556, USA

The screening and testing of fuel cell electrocatalysts often involves comparisons under conditions that do not closely match their use in membrane electrode assemblies. We compared the activities of several commercial and homemade Pt and PtRu catalysts for electrochemical methanol oxidation by four different techniques: disk electrode linear sweep voltammetry in aqueous methanol/sulfuric acid solutions, optical fluorescence detection in aqueous methanol solutions containing a fluorescent acid-base indicator, steady-state voltammetry in a 25 electrode array fuel cell with a large common counter electrode, and steady-state voltammetry in a conventional direct methanol fuel cell. The fluorescence detection method, which is a high-throughput technique developed for large arrays of electrocatalysts, can distinguish active from inactive catalysts, but it does not accurately rank active catalysts. Both the disk electrode and array fuel cell methods gave a reliable ranking of the catalysts studied. The best agreement occurred between the array fuel cell and single electrode fuel cell catalyst ranking. A wide range of catalytic activities was found for PtRu catalysts of the same nominal composition that were prepared by different methods.

© 2005 The Electrochemical Society. [DOI: 10.1149/1.1857772] All rights reserved.

The efficiency of a fuel cell can be, in principle, much higher than that of a combustion engine by converting chemical energy directly into electrical energy. While hydrogen fuel cells are efficient and may become a major source of energy within the next few decades, fuel cells are not yet practical for most purposes. For large-scale power applications, fuel cells must compete with commodity power sources such as fossil fuels. The barrier to commercialization is high for commodity power, particularly since the infrastructure to consume process because the activity of a catalyst depends not only on its composition but also on the manner in which it is prepared. Because the best synthetic methods are specific to certain compositions, the correlation between composition and process parameters cannot be ignored. Thus, there is a large combined parameter space that should be explored when varying catalyst composition. In addition, the testing of catalysts in fuel cells introduces some uncertainty because of cell-to-cell variability in counter electrodes, membranes, and fabrication processes. To accelerate this process, parallel screening methods have been developed for the discovery and high-throughput testing of fuel cell catalysts, 10,12-15

One of these high-throughput methods is optical screening. 10,16,17 In methanol electro-oxidation (Reaction 1), six protons are generated per molecule of methanol. Protons can be detected by a fluorescent acid-base indicator, 3-pyridin-2-yl-(4,5,6)triazolo[1,5-α] pyridine (TPt, Ni 3 1 complex, \( pK_a = 1.5 \)). 18 See Scheme 1. The electrode array is a catalyst composition map, in which all the catalyst spots are shorted together into a single working electrode. As the potential of the array is varied, there is a drop in local pH near the most active catalyst spots, causing fluorescence by the dye.

Optical screening data have not always correlated well with fuel cell testing of new catalysts. The screening conditions do not match fuel cell conditions closely. The electrolyte in the optical screening is a liquid, and the experiment is done at ambient temperature, whereas the fuel cell uses a polymer electrolyte membrane at significantly higher temperature. Catalysts usually require a conditioning period in the fuel cell, and often this step is not done in the
optical screening cell. The data are not recorded as a conventional current-voltage curve, but as the onset of potential of fluorescence.

To match the conditions of a fuel cell more closely, a high-throughput screening cell has been developed by Liu and Smotkin. The test cell is a fuel cell with 25 individually addressable working electrodes and a large common counter electrode. Each electrode is hot-pressed on Nafion to make a conventional membrane electrode assembly (MEA) structure. The catalysts are conditioned and are tested in parallel to obtain polarization curves. As noted, the method of synthesis is important when comparing catalysts. When catalysts are prepared in situ, tested in parallel to obtain polarization curves.

With NaHSO₃ and then oxidatively decomposing with H₂O₂. A better strategy is to use a co-catalysts. When catalysts are prepared in situ, tested in parallel to obtain polarization curves. As noted, the method of synthesis is important when comparing catalysts. When catalysts are prepared in situ, tested in parallel to obtain polarization curves.

Testing methods is needed. Thus, a comparison of the reliability of different catalyst screening method may be less useful than a more reliable but slower methods are known to produce very active, high surface area PtRu assembly. The catalysts are conditioned and are

known in these cases, where catalyst synthesis is the slow step, the highest-throughput testing methods are used. The Adams method PtRu, one Watanabe method PtRu, and one Catalytic was synthesized by the literature method involving making a Pt-oxide colloid by reducing H₂PtCl₆ with a platinum counter and a reference standard hydrogen electrode (SHE). The working electrode rotation (array potential) initially was +250 mV vs SHE. The potential was increased in 10 mV increments and allowed to stand at each potential for 10 min. The solution above the catalyst spots was monitored by eye for fluorescence. The potential was increased until all catalysts generated visible fluorescence.

Disk electrode testing of electrocatalysts.—Catalysts inks were prepared by stirring overnight 0.1 g of catalyst with 100 μL of water and 265 μL of Nafion solution (Aldrich) (15 wt % Nafion on a catalyst basis). The ink was pipetted (3 μL) on a polished glassy carbon rotating disk electrode (RDE) (radius 0.15 cm). Catalyst masses varied from 0.2 to 0.4 mg, although within a given data set of four duplicate electrodes the variation was smaller, typically 30%.
The electrode was dried in a 60°C oven for 30 min and allowed to cool to room temperature in a desiccator. The electrode was weighed to obtain the catalyst weight. The RDE was placed into a Pine Instruments rotator and connected to an electrochemical workstation (BioAnalytical Systems 100B). The reference electrode was a saturated calomel electrode (SCE). The SCE was isolated from the test solution using a Luggin capillary filled with 0.5 M sulfuric acid. One aliquot of the catalysts was tested in 50 mL of a solution of 0.5 M methanol in 0.5 M sulfuric acid. The solution was saturated with bubbling argon and capped with plastic wrap and was also stirred magnetically using a Teflon-coated stirbar. The rotation rates of the RDE tested were 0, 600, 1000, and 2000 rpm. After initial tests were done to determine the independence of current on rotation rate, all subsequent scans were done without rotation. Four replicate polarization curves were obtained from each catalyst. The potential sweep rate was 1 mV/s. The temperature of the solution was held at 25 or 60°C by a temperature controller, which heated the cell with heating tape.

Array fuel cell MEA preparation.—Anode and cathode catalyst inks were prepared by dispersing the catalysts in a solubilized Nafion solution (Aldrich) as described by Wilson. The solubilized Nafion encased the catalyst particles and facilitated contact of the catalyst particles with the 7 mil thick membrane electrolyte, Nafion 117. After extensive stirring, the ink was applied to one side of the gas diffusion layer (GDL) and dried in an oven. The GDL was then pressed against the polymer membrane during fuel cell assembly. Alternatively, the catalysts could be decal-transferred to the Nafion layer.

Carbon fiber paper (Toray paper, E-TEK, TGP-H-060) was used for the array GDL system. Toray paper was cut to size (4 × 4 in.) for the counter/reference electrode. Pt black (Johnson-Matthey, stock 12755, lot J27J16) ink was applied to this side of the GDL.
The array side of the MEA was prepared with four duplicate samples for each of six catalyst samples. Four catalyzed GDLs were prepared for each catalyst by coating a square of GDL material and positioned randomized so that there was no knowledge of expected catalytic activity. The set of catalysts used contained two highly active commercial catalysts (Johnson-Matthey PtRu, 50:50 nominal composition). In principle, these catalysts should have the same activities, but in practice, some variation between lots can occur. The set also included a poor catalyst (Pt) and several experimental PtRu catalysts of nominal 50:50 atomic ratio and variable activity.

**Characterization of electrocatalysts.**—Catalysts were characterized using powder X-ray diffraction (XRD) and Brunauer, Emmett, and Teller method (BET) surface area measurements. A Philips X’Pert MPD diffractometer was used for the XRD patterns. Data were obtained using step scans in 0.04 steps from 10 to 118 degrees 2 0. Lattice parameters and particle sizes were calculated using Rietveld profile refinement (GSAS and EXPGUI). The BET surface area was measured by using nitrogen adsorption on a Micromeritics ASAP 2000 instrument.

**Results and Discussion**

Six unsupported Pt and PtRu catalysts were tested with the identification randomized so that there was no knowledge (in all experiments except LSV, which was performed last) of expected catalytic activity. The set of catalysts used contained two highly active commercial catalysts (Johnson-Matthey PtRu, 50:50 nominal composition). In principle, these catalysts should have the same activities, but in practice, some variation between lots can occur. The set also included a poor catalyst (Pt) and several experimental PtRu catalysts of nominal 50:50 atomic ratio and variable activity.

**Optical screening.**—The onset potentials (Table I) show the rankings of these catalysts by the optical screening method. Johnson-Matthey PtRu lot L108I03 was difficult to distinguish from the Adams PtRu with only a 5 mV difference in fluorescence onset. The Johnson-Matthey PtRu lot A11L18 and the Watanabe method PtRu catalyst method could not be differentiated, at 290 mV. The Johnson-Matthey PtRu fluoresced at 320 mV, but with very slight fluorescence. For the final sample, the Watanabe method with borohydride reduction, fluorescence began at 350 mV.

Although the differences in onset potential were slight when different catalysts were compared, multiple spots of the same catalyst gave very reproducible results. For each catalyst, 20 individual spots were tested simultaneously. In all cases, except for the Adams method PtRu and the borohydride Watanabe method PtRu, the onset of fluorescence for all 20 spots occurred at the same potential. For the Adams and modified Watanabe PtRu catalysts, two spots did not fluorescence at the same onset potential. For the modified Watanabe PtRu, these two spots completely delaminated from the surface and did not fluoresce. For the Adams method catalyst, the onset of fluorescence for two spots was 350 mV higher. The catalyst had partially delaminated from the Toray carbon paper. With a lower effective loading, these two catalyst spots required higher overpotentials to generate enough protons for PTFE fluorescence to become visible. For all six catalysts, at least 90% of the spots had the same fluorescence onset potential.
Disk electrode LSV.—In LSV, the current generated by each catalyst at a given potential can be used to rank its activity, provided that mass-transfer effects can be eliminated. Normally, the mass-transfer limited current is kept high by rotating the electrode. The mass-transfer limited current is known from the Levich equation and can be compared to the observed current. If the observed current is less than a few percent of $i_l$, it is assumed to be kinetically limited. If the observed current is higher, then it is necessary to correct for mass-transfer effects.

Changing the rotation rate in preliminary experiments did not significantly alter the shape of the $i$-$V$ curves or increase the current. This suggested that the mass-transfer limited current with stirring/bubbling alone (at zero rotation rate) was high relative to the kinetic current for the catalysts and loadings used. To calibrate the mass-transfer limited current under these conditions, a series of RDE experiments were performed using 5 mM aqueous $\text{Ru(NH}_3)_6\text{Cl}_6^{3+}$, which is a fast, reversible one-electron redox couple. These experiments gave clear mass-transfer limited plateau currents at potentials negative of $\sim 0.40 \text{ V vs. SCE}$, from which it could be determined that the effective rotation rate with stirring/bubbling was ca. 75 rpm. Under these conditions, the mass-transfer limited current was 0.45 mA. Because the methanol electro-oxidation experiments were done using 0.5 M methanol ($n = 6$), the mass-transfer limited current should be approximately 600 times higher, i.e., 270 mA. The observed currents (Fig. 1 and 2) are in the range of a few milliamperes, consistent with the idea that methanol electro-oxidation is kinetically limited. Thus, rotation was not used for subsequent measurements.

Increasing concentrations of methanol in the solution to 6 M had little effect on the current or the shape of the $i$-$V$ curve in LSV (Fig. 2). This is consistent with previous observations that at low overpotentials the reaction kinetics are approximately zero order in methanol concentration.

The six catalysts were tested in quadruplicate, and the averaged $I$-$V$ curves are shown in Fig. 3. In this and in the other voltammetric methods studied, catalysts may be ranked by comparing the current at any potential. However, the most relevant potential range is that in which DMFC anodes are actually used (300-400 mV vs. normal hydrogen electrode). At 25°C, there was very little current in this potential range at the disk electrodes, and some catalysts (e.g., Adams and Watanabe PtRu) could not be differentiated. The catalysts were better differentiated at slightly higher potentials, and were ranked at 425 mV. The Adams catalyst and the Watanabe catalyst gave about half the current of the two commercial PtRu catalysts (0.87 and 0.59 mA/mg).

By increasing the temperature, the activity of the catalysts was increased, and the current onset occurred at lower potentials. At
60°C (Fig. 4), the catalysts were differentiated at 350 mV (Table I). The ranking of catalyst activity was similar to that obtained at 25°C, but this ranking could be made with greater confidence because of higher current density in the potential region of interest (300-400 mV). The difference in temperature changes the adsorption properties of the catalysts. At room temperature, platinum is the only species able to adsorb methanol. The –OH adsorbs on the Ru and cannot be displaced by methanol. Thus, Pt is the only site where methanol oxidation can occur. As the temperature rises, methanol can adsorb on ruthenium, and the oxidation of methanol can occur on both Pt and Ru.²⁷

Array and single cell fuel cell testing.—Array fuel cell testing was also used to rank the activity of the six catalysts (Fig. 5). The anode was an array of 25 electrodes that were individually addressed. The six catalysts were tested as four replicates of each. The current onset occurred at sufficiently low potential that the catalysts could have been ranked at 300 mV, but for comparison with the disk electrode results, the catalysts were ranked at 350 mV (Table I). The two Johnson-Matthey PtRu catalysts ranked the same as the Adams catalyst within one standard deviation. The Watanabe catalyst was ~20 mA lower in activity compared to the commercial PtRu catalysts. The borohydride Watanabe had the lowest activity of the PtRu catalysts.

The LSV, optical screening, and high-throughput fuel cell results were compared to single cell fuel cell testing, which is the most widely accepted method to test catalysts under “real” conditions (Fig. 6). The rankings of the catalysts at ~0.35 V were similar to that of the high-throughput fuel cell testing and disk electrode testing (Table I). Again, the two Johnson-Matthey PtRu catalysts had the highest activity. The Adams and Watanabe catalysts were about half as active as the commercial catalysts. The Johnson-Matthey Pt and the borohydride Watanabe had the lowest activity of the six catalysts.

Recently, Reetz et al.²⁰ described a method for synthesizing Pt-based catalysts via an aqueous colloidal oxide method. The colloidal oxides were reduced using hydrogen, a mild reducing agent, to yield alloy catalysts. We synthesized unsupported Pt₅₀Ru₅₀ catalysts by using this method and compared their performance in methanol solutions with Johnson-Matthey Pt/Ru and Adams Pt/Ru catalysts using RDE, the array fuel cell, and a single fuel cell. Figure 7 shows
the array fuel cell cate samples of each of the six catalysts. It is also important to note were obtained in a single experiment, which evaluated four repli-

technique, and 24 individual experiments were needed to obtain the data shown in Fig. 4. The array fuel cell data shown in Fig. 5

even though it is instrumentally simpler, disk voltammetry is a serial technique. Although larger differences in

onset potential are found for poorer catalysts, then it should be studied further by another electro-

ing results were the most difficult to correlate with the fuel cell testing. The optical screening method has two levels of activity, high and low. However, within the “high” range, catalysts are differenti-
ated by onset potential differences of only a few millivolts. Thus, if an unknown catalyst has an onset potential close to that of a known good catalyst, then it should be studied further by another electro-

chemical technique. Although larger differences in onset potential were found for poorer catalysts (e.g., Pt and Watanabe borohydride PtRu), the ranking of these catalysts did not match the single cell

Catalyst

Comparison of electrochemical techniques.—The optical screening results were the most difficult to correlate with the fuel cell testing. The optical screening method has two levels of activity, high

and low. However, within the “high” range, catalysts are differentiated by onset potential differences of only a few millivolts. Thus, if an unknown catalyst has an onset potential close to that of a known good catalyst, then it should be studied further by another electrochemical technique. Although larger differences in onset potential were found for poorer catalysts (e.g., Pt and Watanabe borohydride PtRu), the ranking of these catalysts did not match the single cell results.

The disk electrode and array fuel cell ranking of catalysts both correlated well with the single cell fuel cell ranking. There was a closer correspondence between the three methods for data collected at 60°C: at 25°C, the currents observed by LSV are small and base-

deline current differences become significant, particularly at low over-
potential. It is interesting that the 60°C disk electrode data provide a reliable ranking of catalysts, because the catalyst/aqueous electrolyte interface is chemically different from the catalyst/Nafion interface in the fuel cell experiments. This difference is reflected in the low current, e.g., ~2 mA/mg for the two best PtRu catalysts. For the same catalysts, the mass-normalized currents were substantially higher and were comparable to each other in the array fuel cell (~25 mA/mg) and single cell DMFC (~20 mA/mg) experiments. Although it is instrumentally simpler, disk voltammetry is a serial technique, and 24 individual experiments were needed to obtain the data shown in Fig. 4. The array fuel cell data shown in Fig. 5 were obtained in a single experiment, which evaluated four repli-

cates of each of the six catalysts. It is also important to note that catalyst activities can be differentiated at lower overpotential in the array fuel cell (Fig. 5) than in the disk electrode experiments (Fig. 3 and 4).

**Table II. Physical characterization data for DMFC anode catalysts.**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Lattice parameter (Å)</th>
<th>Particle size (nm)</th>
<th>Surface area (±5 m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Johnson-Matthey</td>
<td>3.9200 ± 0.0001</td>
<td>10.4 ± 0.1</td>
<td>30</td>
</tr>
<tr>
<td>(JM) PtLot C15L25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>JM PtRu Lot L10803</td>
<td>3.880 ± 0.001</td>
<td>5.0 ± 0.2</td>
<td>65</td>
</tr>
<tr>
<td>JM PtRu Lot A1IL18</td>
<td>3.881 ± 0.001</td>
<td>4.0 ± 0.1</td>
<td>62</td>
</tr>
<tr>
<td>Adams method</td>
<td>3.8867 ± 0.0009</td>
<td>4.1 ± 0.1</td>
<td>42</td>
</tr>
<tr>
<td>Watanabe</td>
<td>3.8943 ± 0.0006</td>
<td>5.7 ± 0.1</td>
<td>64</td>
</tr>
<tr>
<td>Watanabe borohydride</td>
<td>3.8847 ± 0.0006</td>
<td>5.6 ± 0.1</td>
<td>27</td>
</tr>
<tr>
<td>Reetz method</td>
<td>3.8822 ± 0.0006</td>
<td>2.0 ± 0.1</td>
<td>102</td>
</tr>
</tbody>
</table>

**Figure 7.** Array fuel cell polarization curves obtained at 60°C in 0.5 M methanol solution comparing Johnson-Matthey Pt/Ru catalyst with home-

made catalysts prepared by the Reetz and Adams methods.

**Figure 8.** Powder XRD patterns of DMFC anode catalysts.
catalysts. In this case, the use of a stronger reducing agent leads to rapid and simultaneous reduction of both Pt and Ru.

Conclusions

Four electrochemical techniques for ranking the activities of DMFC anode electrocatalysts were compared. The most reliable rankings were obtained by disk electrode LSV and by high-throughput array fuel cell testing at 60°C. These methods had the best correlation with the single cell fuel cell testing. The array fuel cell offers rapid testing of catalysts under actual fuel cell conditions and eliminates some of the variables (such as counter electrode variations) that would be encountered when performing replicate runs with single cell fuel cells. The optical screening method was effective in ranking at two different levels, high activity and low activity. Thus, it is possible to use the optical screening method in survey experiments that compare relatively large numbers of catalysts, but it is advisable to follow up those experiments with a more precise testing method.

Acknowledgments

This work was supported by the Army Research Laboratory Collaborative Technology Alliance in Power and Energy, Cooperative Agreement no. DAAD19-01-2-0010, and by NuVant Systems, Inc.

The Pennsylvania State University assisted in meeting the publication costs of this article.

References