



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

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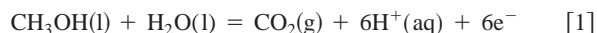
The screening and testing of fuel cell electrocatalysts often involves comparisons under conditions that do not closely match their use in membrane electrode assemblies. We compared the activities of several commercial and homemade Pt and PtRu catalysts for electrochemical methanol oxidation by four 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 rankings. A wide range of catalytic activities was found for PtRu catalysts of the same nominal composition that were prepared by different methods.

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Manuscript submitted May 18, 2004; revised manuscript received August 21, 2004. Available electronically January 28, 2005.

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.¹ 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 distribute hydrogen, a gaseous fuel, has not been developed. However, liquid fuels are already easily distributed. For premium power applications in particular, *e.g.*, power packs for electronics, uninterrupted power sources, and mobile/portable applications, fuel cells that utilize liquid fuels can represent an attractive alternative to batteries and other conventional power sources.

Direct methanol fuel cells (DMFCs) based on polymer electrolyte membranes are a leading candidate for the use of liquid fuels. A practical DMFC requires superior electrocatalysts for the anode half-cell reaction

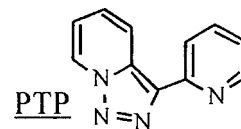


Aqueous methanol undergoes a six-electron oxidation at the anode to produce protons and carbon dioxide.² At the cathode, oxygen and protons are reduced to water.³ DMFCs could in principle achieve 1.2 V at open circuit, but the voltage is degraded by slow electrode kinetics at the anode and cathode and by methanol crossover from the anode to the cathode side of the cell.

The best-known anode electrocatalysts for DMFCs are PtRu alloys.⁴ Combinations of Pt and other metals, including PtSn,⁵ PtW,⁶ PtPd,⁷ ternary alloys of PtRuOs,⁸ and quaternary alloys containing PtRuWSn⁹ and PtRuOsIr¹⁰ have also been studied for methanol oxidation. While some of these more complex compositions compare favorably with PtRu when both are prepared as low surface area catalysts (*e.g.*, by the borohydride reduction method),¹¹ so far there are no high surface area catalysts that have higher activity than high surface area PtRu. There remains a strong practical incentive to find better catalysts than PtRu, because of the high mass loading of precious metals currently needed in DMFCs.

The discovery of new fuel cell electrocatalysts is a time-consuming 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 compare electrocatalysts for a particular half-cell reaction, a sufficiently large number of experiments must be done to average out these variations. 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-*a*]pyridine (PTP, Ni²⁺ complex, p*K*_a = 1.5).¹⁸ See Scheme 1. The electrode array is a catalyst composition map, in which all the cata-



Scheme 1.

lyst 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

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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.¹⁴ 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* in large arrays, for example, by pipetting reagents on porous electrodes or by co-evaporating metals on planar electrodes, relatively low surface area materials are produced, and the testing ranks poor catalysts. These rankings may have little meaning when the “discovered” compositions are prepared in bulk form as high surface area catalysts and compared to good commercial catalysts. A better strategy is to use a high surface area synthetic method that is scalable to end use if good catalysts are discovered. Unfortunately, these methods are not easily adapted to array synthesis. For example, the Watanabe¹⁹ and Reetz²⁰ methods are known to produce very active, high surface area PtRu catalysts, but both require fairly large solvent volumes, long reaction times, and physical separation of the solid catalyst. In these cases, where catalyst synthesis is the slow step, the highest-throughput screening method may be less useful than a more reliable but slower method. Thus, a comparison of the reliability of different catalyst testing methods is needed.

In this paper, we compare the optical screening method, linear sweep voltammetry (LSV) of disk electrodes, and array fuel cell testing with single cell fuel cell testing of DMFC anode catalysts. Six catalysts were examined, two Johnson-Matthey PtRu catalysts of nominal 50:50 atomic composition, one Johnson-Matthey Pt catalyst, one Adams method PtRu, one Watanabe method PtRu, and one modified Watanabe method PtRu. The identification of the catalysts was randomized and unknown during testing by the optical and fuel cell methods, but was known for follow-up studies using LSV of disk electrodes.

Experimental

High surface area catalysts were synthesized by literature methods. The Adams method is a molten salt flux procedure.²¹ Metal salts, H_2PtCl_6 (Alfa Aesar, 1.685 g, 3.375 mmol) and RuCl_3 (Alfa Aesar, 0.832 g, 3.375 mmol), were dissolved in 250 mL deionized (DI) water. NaNO_3 (30 g, 100 times molar excess) was then dissolved in the solution. After stirring for 0.5 h, the mixture was dried at 50°C overnight and ground thoroughly. The mixture was then loaded into an alumina crucible, and the fusion reaction carried out at 500°C for 3 h. A solid melt with a dark brown layer at the bottom and a white salt layer at the top was obtained. The melt was filtered and washed thoroughly with DI water to remove soluble nitrates, nitrites, and chlorides. The dark solid was then suspended in water and reduced by bubbling H_2 at room temperature for 24 h (flow rate 35 mL/min). Black particles precipitated from the solution during the reduction process. After filtering through a 0.1 μm nylon filter and thorough washing with DI water, the isolated catalyst was dried in an oven at 50°C for 12 h.

Catalysts were also prepared by the Watanabe method.¹⁹ The method involves making a Pt-oxide colloid by reducing H_2PtCl_6 with NaHSO_3 and then oxidatively decomposing with H_2O_2 . A RuCl_3 solution was added along with NaOH solution to form the Ru-oxide colloid. The solution was then bubbled with hydrogen at room temperature to reduce the oxides. A modified Watanabe method was also tested, in which the final hydrogen reduction step was replaced by sodium borohydride reduction.

Catalysts were also synthesized by a colloidal surfactant method developed by Reetz *et al.*²⁰ Stoichiometric amounts of catalyst precursors PtCl_4 and RuCl_3 (Alfa Aesar, Ward Hill, MA) were mixed with a surfactant (dodecyltrimethyl (3-sulfopropyl) ammonium hydroxide, Aldrich, Milwaukee, WI) under basic conditions (sodium

carbonate, Aldrich, Milwaukee, WI) in DI water and heated at 80°C for about 20 h to yield a dark colloidal solution containing mixed metal oxides. The solution was then reduced chemically by H_2 at room temperature. This was followed by filtration and repeated washing and drying at 60°C to obtain the catalyst powder.

Optical screening of electrocatalysts.—The optical screening solution was prepared in a 1 L volumetric flask as 6 M methanol (Aldrich), 0.5 M NaClO_4 (Alfa Aesar), 30 mM NiClO_4 (Alfa Aesar), and 100 μM PTP in water. The PTP was prepared by the literature method.¹⁸ The pH was adjusted to 3.5 by the addition of perchloric acid. The six electrocatalysts tested were two lots of the same nominal composition, Johnson-Matthey PtRu (lot L108I03 and lot A11L18) and Johnson-Matthey Pt (lot C15L25), Adams method PtRu, Watanabe method PtRu, and Watanabe method PtRu with borohydride reduction. The catalysts were suspended in slurries (0.028 g catalyst/mL DI water). The catalysts (20 spots of each catalyst) were dispensed via manual pipette (10 μL aliquots for a loading of 4 mg/cm^2) on Toray carbon paper using a Plexiglas template (spot diam of 3 mm). The array was dried overnight. The array was placed into the optical screening cell with the PTP screening solution. The cell was connected to a potentiostat (EG&G PAR 363) with a platinum counter and a reference standard hydrogen electrode (SHE). The working electrode (array) potential was initially set to +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.—Catalyst 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).²² 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 reweighed 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 to prevent chloride poisoning of the catalysts.²³ Catalysts were 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.²⁴ 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.²⁴

Carbon fiber paper (Toray paper, E-TEK, TGPH-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.

Table I. Rankings of six catalysts using different electrochemical techniques. Catalysts are listed in rank order of activity in each column.

Optical onset potential (mV)	25°C LSV <i>i</i> (mA/mg) 425 mV	60°C LSV <i>i</i> (mA/mg) 350 mV	Array fuel cell (mA) 350 mV	Single fuel cell −350 mV
PtRu L108I03 265	PtRu L108I03 2.81	PtRu A11L18 2.56	PtRu A11L18 72 mA	PtRu L108I03 0.40 A
Adams 270	PtRu A11L18 2.22	PtRu L108I03 1.56	PtRu L108I03 65 mA	PtRu A11L18 0.35 A
PtRu A11L18 290	Adams 1.44	Watanabe 1.13	Adams 59 mA	Adams 0.25 A
Watanabe 290	Watanabe 1.10	Adams 1.03	Watanabe 46 mA	Watanabe 0.20 A
Pt 320	Pt 0.21	Watanabe BH ₄ [−] 0.14	Watanabe BH ₄ [−] 11 mA	Watanabe BH ₄ [−] 0.04 A
Watanabe BH ₄ [−] 370	Watanabe BH ₄ [−] 0.16	Pt 0.12	Pt 0 mA	Pt 0 A

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 then stamping out 0.375 in diam disks.

The counter/reference electrode was hot-pressed on Nafion 117 (160°C at 1800 lb-force for 5 min). The 25 working electrodes were hot-pressed on the other side of the Nafion sheet (160°C at 1000 lb-force for 5 min). This was a five-layer GDL integrated MEA. Six catalysts, each catalyst occupying four positions distributed randomly on the array and one blank spot, were tested.

Array fuel cell testing.—A NuVant Systems NUV100P high-throughput screening unit was used to test the catalysts. The design of this 25 working electrode instrument has been described in a previous paper.¹⁴ The working and counter/reference electrodes were conditioned by passing humidified hydrogen through both sides of the assembled cell at 60°C overnight. The potential was scanned linearly between 0 and 0.2 V several times. The anode stream was switched to methanol (0.5 M, 10 mL/min), and humidified hydrogen was passed through the counter/reference side. Linear scans between 0 and 0.7 V were done repetitively until steady-state performance was attained. The electrode potentials were stepped from 0 to 0.8 V in 10 mV increments at 5 s intervals. The potential was reset to 0 V at the completion of the scan.

Single cell fuel cell MEA preparation.—Anode and cathode catalyst inks were prepared in the same manner as described for the array fuel cell MEA preparation. The inks were applied on a GDL and hot-pressed on a Nafion 117 membrane. All MEA anodes and cathodes had a catalyst loading of 4 mg/cm². All MEA cathodes were made from Pt black (Johnson-Matthey, stock 12755, lot J27J16).

Fuel cell testing procedure.—A Scribner fuel cell load unit, series 890B, was used for single cell testing. To obtain the anode performance curve, humidified hydrogen was purged through the cathode side, making the cathode a reference dynamic hydrogen electrode (DHE). External power was required to drive the current flow. The load unit could not provide the power, so an unregulated power supply was connected in series to provide current flow in the galvanostatic mode while not affecting the current interruption compensation.

The single cell was conditioned by passing water through both the anode and cathode flow fields for 24 h. Methanol solution was then purged through the anode and humidified hydrogen from a water sparger 25°C above the cell operating temperature through the cathode to obtain full cell anode performance.

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 θ . Lattice parameters and particle sizes were calculated using Rietveld profile refinement (GSAS and EXPGUI).²⁵ 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 catalyst could not be differentiated, at 290 mV. The Johnson-Matthey Pt 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 fluoresce 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 +5 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 PTP fluorescence to become visible. For all six catalysts, at least 90% of the spots had the same fluorescence onset potential.

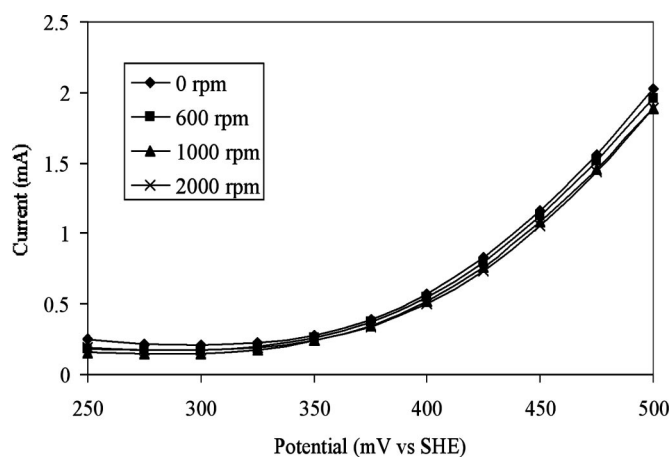


Figure 1. Polarization curves at different rotation rates for disk electrodes in 0.5 M methanol in 0.5 M sulfuric acid at 25°C, using Johnson-Matthey PtRu catalyst lot A11L18.

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 (Fig. 1). 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 $[\text{Ru}(\text{NH}_3)_6]^{3+}$, which is a fast, reversible one-electron redox couple. These experiments gave clear mass-transfer limited plateau currents at potentials negative of -0.40 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 (Table I). The Johnson-Matthey Pt and borohydride Watanabe catalyst had the lowest activity, generating almost no current. The catalysts with the highest activity were the two Johnson-Matthey PtRu catalysts (1.63 and 1.55 mA/mg

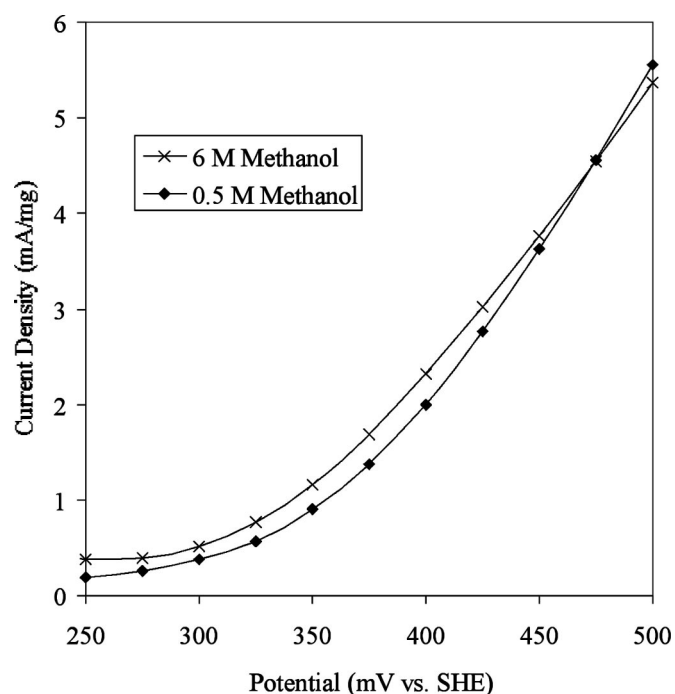


Figure 2. Polarization curves with Johnson-Matthey PtRu catalyst lot A11L18 at 25°C at high and low methanol concentrations.

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.²⁶ At

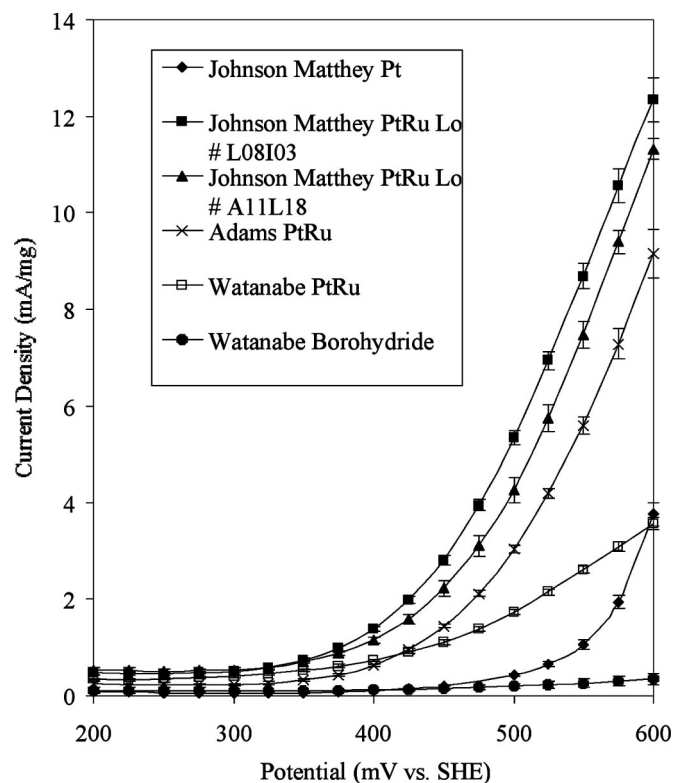


Figure 3. Disk electrode polarization curves obtained at 25°C in 0.5 M H_2SO_4 and 0.5 M methanol, 1 mV/s scan rate.

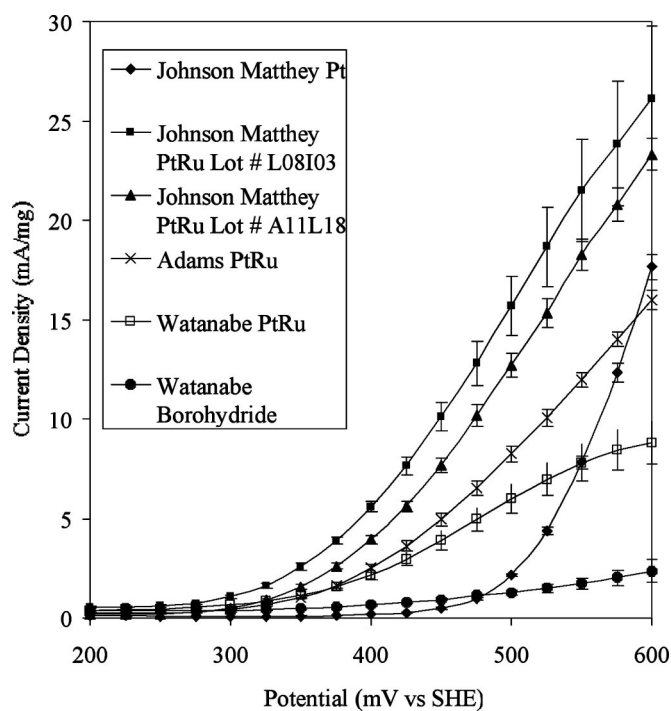


Figure 4. Disk electrode polarization curves obtained at 60°C in 0.5 M H_2SO_4 and 0.5 M methanol, 1 mV/s scan rate.

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 $-\text{OH}$ adsorbs on the Ru and cannot be displaced by methanol. Thus, Pt is the only site where

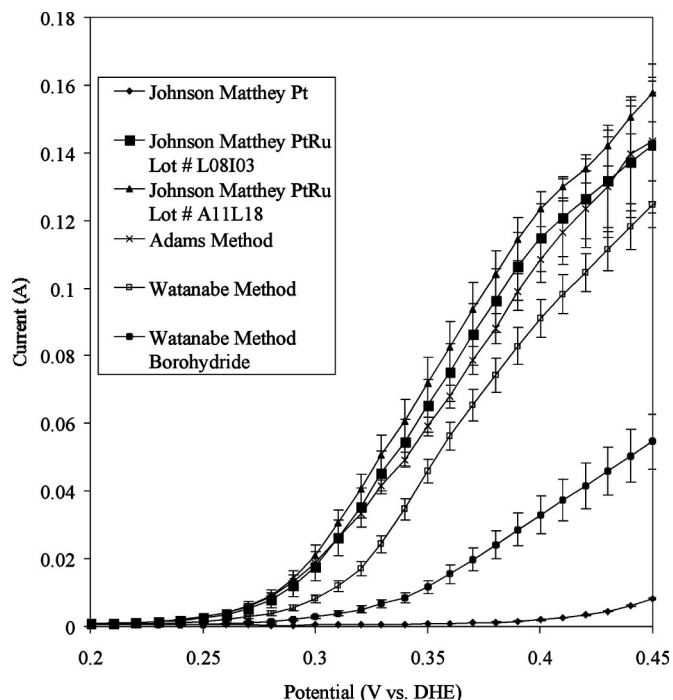


Figure 5. Array fuel cell polarization curves obtained at 60°C.

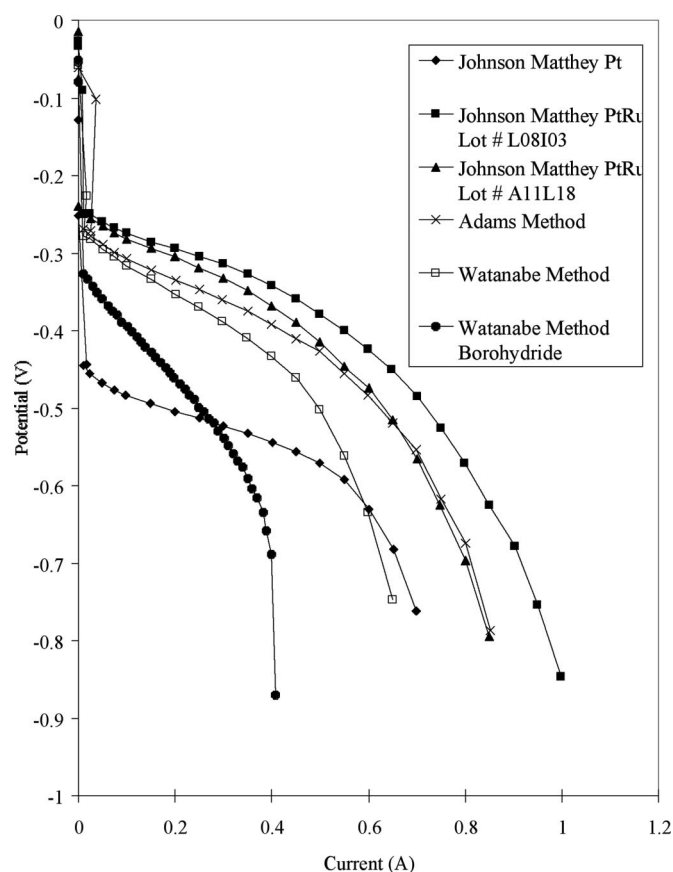


Figure 6. Fuel cell polarization curves of catalysts at 60°C.

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 six 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 $\text{Pt}_{50}\text{Ru}_{50}$ 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

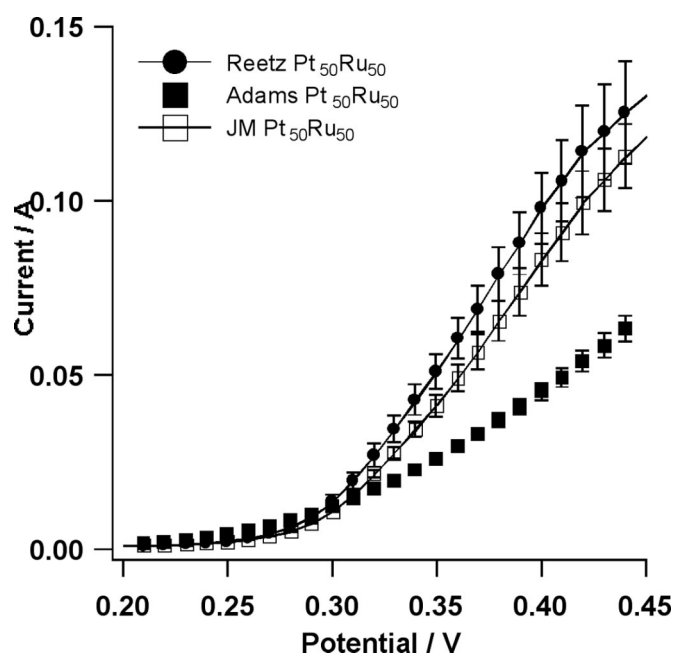


Figure 7. Array fuel cell polarization curves obtained at 60°C in 0.5 M methanol solution comparing Johnson-Matthey Pt/Ru catalyst with home-made catalysts prepared by the Reetz and Adams methods.

the polarization results obtained using the array fuel cell at 60°C. Pt/Ru catalysts synthesized by the Reetz method yield higher methanol oxidation currents compared to both JM Pt/Ru catalysts and the Adams Pt/Ru catalyst. This result reinforces the idea that catalysts of the same composition that are prepared by different methods, in this case by using different reducing agents, have widely differing activity as DMFC anode catalysts.

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 baseline current differences become significant, particularly at low overpotential. 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 replicate samples 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).

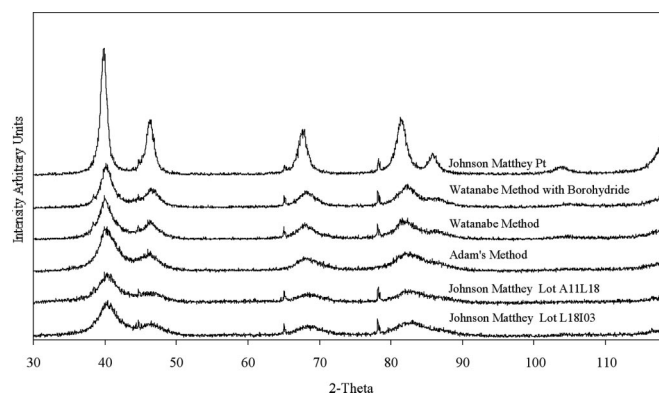


Figure 8. Powder XRD patterns of DMFC anode catalysts.

Characterization of electrocatalysts.—To understand the differences between catalysts of the same nominal compositions, they were analyzed using powder XRD (Fig. 8). The particle sizes and lattice parameters were calculated by using Rietveld profile fitting (Table II). The particle sizes of the PtRu catalysts were similar. If full utilization of methanol is assumed, a higher surface area catalyst should have higher activity. The two Johnson-Matthey PtRu catalysts and the Watanabe catalyst had similar surface areas (~60 m²/g) within the error of the measurement (±5 m²/g). The Adams method catalyst had a slightly lower surface area (42 m²/g) than the Watanabe and Johnson-Matthey PtRu catalysts. However, the activity of the Adams method was on the same order as that of the Watanabe catalyst (64 m²/g). The Watanabe method with borohydride reduction had the lowest surface area and also the lowest activity of all the PtRu catalysts.

In all the PtRu catalysts, ruthenium was partially alloyed with the face-centered cubic Pt phase as seen by the smaller lattice parameter compared to pure Pt. No evidence of an elemental hexagonal close-packed Ru phase was seen in the XRD patterns. The differences in alloying of the PtRu catalysts were small. The two commercial PtRu catalysts alloyed the most, as evidenced by their smaller lattice parameters (3.880 and 3.881 Å). The Watanabe and Adams methods gave less alloying of Ru with lattice parameters of 3.8867 and 3.8943 Å, respectively. The Watanabe method with borohydride had an intermediate lattice parameter of 3.8847 Å. The Watanabe method involves codeposition of Pt and Ru oxides, which may not mix the oxides intimately. In both the Adams and Watanabe method, hydrogen reduction occurs at low temperature, which may result in nucleation of a Pt-rich phase first with some alloying of the Ru. The remaining Ru may exist as well-dispersed adatoms or as an amorphous phase on the surface of the Pt. The slightly greater degree of alloying observed for the Watanabe borohydride catalyst is consistent with previous XRD studies of borohydride preparation of alloy

Table II. Physical characterization data for DMFC anode catalysts.

Catalyst	Lattice parameter (Å)	Particle size (nm)	Surface area (±5 m ² /g)
Johnson-Matthey (JM) Pt Lot C15L25	3.9200 ± 0.0001	10.4 ± 0.1	30
JM PtRu Lot L108I03	3.880 ± 0.001	5.0 ± 0.2	65
JM PtRu Lot A11L18	3.881 ± 0.001	4.0 ± 0.1	62
Adams method	3.8867 ± 0.0009	4.1 ± 0.1	42
Watanabe	3.8943 ± 0.0006	5.7 ± 0.1	64
Watanabe borohydride	3.8847 ± 0.0006	5.6 ± 0.1	27
Reetz method	3.8822 ± 0.0006	2.0 ± 0.1	102

catalysts.¹¹ 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.

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