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Jamie A. Shetzline
Clemson University

Saheed Bukola
Clemson University

Stephen E. Creager
Clemson University, screage@clemson.edu

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**A CONVENIENT MINIATURE TEST PLATFORM FOR POLYELECTROLYTE MEMBRANE FUEL-CELL
RESEARCH**

Jamie A. Shetzline, Saheed Bukola and Stephen E. Creager*

Department of Chemistry, Clemson University, Clemson SC 29634 USA

* corresponding author. E-mail: screage@clemson.edu. Phone: 864-656-4995

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Abstract

A simple and convenient small-scale fuel-cell test platform was created from a commercial compression fitting and graphite rod current collectors and used to conduct diagnostic tests on disk-shaped membrane-electrode assemblies (MEAs) fabricated from Nafion membranes and Nafion-impregnated platinum-on-carbon-cloth anodes and cathodes. A key advantage of this test platform is that it requires very little material, perhaps just a few milligrams, to conduct a fuel-cell test on a supported catalyst. Electrochemically-active surface area (ECSA) values for supported platinum on carbon-cloth electrodes were obtained by *in-situ* (in the fuel cell) and *ex-situ* (in liquid electrolyte) cyclic voltammetry on similarly-prepared electrodes, and values obtained by these methods were compared with each other to estimate the fraction of platinum catalyst contacted by the Nafion ionomer in the fuel-cell cathode. Polarization curves were acquired under controlled-potential conditions using slow-scan cyclic and sampled-current voltammetry and potential-step amperometry methods with conventional electroanalytical instrumentation. Tests performed using this platform are complementary to rotating disk electrode (RDE) voltammetry tests which also allow for catalyst testing on small amounts of material, albeit in the presence of liquid electrolyte, and are commonly used for initial screening of new fuel-cell catalysts. They are also complementary to conventional fuel-cell testing that is commonly performed on MEAs having active areas more than 100 times larger than that in the present cells.

1. Introduction

Research on new materials for polyelectrolyte-membrane (PEM) fuel cells and water electrolysis cells has been very active in recent decades and has resulted in significant advances in understanding of both materials properties and device behavior.[1-7] The most critical materials in a PEM fuel cell are the ionomer membrane, the anode and cathode catalyst layers and the gas diffusion layers, and each of these materials is subjected to its own characteristic testing as part of research and development activities aimed at creating improved devices. New ionomer materials and proton-exchange membranes are often characterized with respect to ionic conductivity, water uptake, mechanical properties and other properties as a function of temperature and humidity, which is helpful in understanding how these materials will behave in a membrane-electrode assembly (MEA).[8-12] New supported catalysts are often combined with ionomer and characterized with respect to electrochemical surface area (ECSA) and catalytic activity using rotating disk electrode (RDE) methods, with catalyst layers coated on carbon electrodes and immersed in an aqueous acid electrolyte.[4, 13] The ionomer serves principally as a binder in such an experiment since proton transfer to and from catalyst particles occurs principally via the aqueous acid electrolyte. RDE methods are quite powerful for studying electrocatalytic reactions, e.g. the electrochemical oxygen reduction reaction (ORR), and they are widely used for early-stage testing on relatively small amounts of new catalytic materials. RDE methods are also somewhat lacking for diagnostic testing because they do not address the activity of catalysts in the absence of free electrolyte. In particular, issues relating to mixed electron / proton conduction and mass transfer in electrodes, including effects from electrode flooding, are not addressed in RDE testing. These issues may be studied in

conventional fuel-cell testing which typically utilizes a membrane-electrode assembly (MEA) or catalyst-coated membrane (CCM) in a test fixture that provides humidified gases to the MEA / CCM with the cell connected to a computer-controlled load that may be used to acquire polarization curves and conduct diagnostic tests. This type of testing usually uses electrodes having active areas of at least several cm^2 , attached to membranes having areas of at least several tens of cm^2 . It is quite easy for a single test performed using a MEA / CCM of this size to consume the majority of the available membrane or catalyst material in the early stages of new material research. In such a situation, there is no possibility of replicate measurements or testing with systematic adjustment of experimental variables. A need exists for a PEM fuel cell diagnostic testing platform that uses very small amounts of material in electrodes that may be fabricated in a reproducible way and studied in small-scale cells in the absence of free electrolyte, under conditions closer than those from RDE to the conditions that will exist in an operating fuel cell. It is desirable that this diagnostic testing be performed using instrumentation and methods that are commonly available in laboratories where general electrochemical research is performed.

We present here a miniature PEM fuel cell test platform that may be used to conduct tests on catalyst layers containing just a few tens of micrograms of supported catalyst over an area less than 0.1 cm^2 , associated with a polyelectrolyte membrane having a total area of just a few square centimeters, using widely available electroanalytical chemistry instrumentation and methods. Membrane-electrode assemblies for this test platform are fabricated using 1.27 cm (0.5-inch) diameter PEM disks onto which carbon cloth disk electrodes are attached by hot pressing. A single 10x10 cm square of ionomer membrane and a similar amount of catalyst

material would easily provide enough material to fabricate more than fifty MEAs for this test platform. The motivation for creating this test platform is to enable small-scale testing of new electrode materials, as is done by RDE, in a manner that excludes effects from liquid electrolyte and includes the effects of ionomer contact with the catalyst and with the PEM on the overall electrode activity. Miniature PEM fuel cells have been previously fabricated and studied, often with the aim of preparing small power sources, e.g. for portable electronics.[14-32] Most such cells were prepared using microfabrication and/or MEMS techniques, often with the PEM and/or MEA deeply integrated into the device, so they tend not to be very useful for repeated measurements or for systematic diagnostic testing. Even for these cells, a “miniature” cell often has an electrode area greater than 1 cm^2 which is still large when compared with typical electroanalytical tests such as RDE voltammetry which often use disk electrodes with diameters below 0.5 cm.

We demonstrate the utility of the miniature test platform by presenting results from two types of diagnostic testing on the cathode of a small-scale MEA. In the first test, *in-situ* (in the MEA) and *ex-situ* (in aqueous acid liquid electrolyte) cyclic voltammograms of the same supported platinum catalyst are compared, focusing on hydrogen adsorption / desorption and carbon monoxide oxidation peaks to assess electrochemically active surface area (ECSA). By comparing *in-situ* and *ex-situ* voltammograms, an estimate may be made of the fraction of supported catalyst in contact with ionomer in the MEA. It is important in such a test that the electrodes tested be as similar to each other as possible, to avoid being misled by differences associated with electrode preparation. A valid comparison was easy to achieve with the small electrodes used in this miniature test platform because electrodes of nearly identical size and

preparation could be mounted on both a PEM for *in-situ* voltammetry, and on a solid carbon electrode for *ex-situ* voltammetry. In the second test, steady-state polarization curves were acquired using slow-scan linear sweep voltammetry to exercise control over the cell potential under approximately steady-state conditions. Currents from polarization curves are compared with current-time curves acquired at fixed values of applied potential in a series of potential steps. This latter comparison is helpful when identifying and investigating causes of non-steady-state behavior in cells, which can easily occur but is often difficult to identify from conventional polarization-curve testing alone. Miniature test-cell behavior was also compared with behavior of an MEA of conventional size, e.g. polyelectrolyte membrane approximately $8 \times 8 \text{ cm}^2$ with electrodes approximately $2.5 \times 2.5 \text{ cm}^2$, tested in a commercial fuel-cell test apparatus, to establish that small-scale testing is relevant to the behavior in larger cells. Advantages of the miniature cell configuration for early-stage basic research focused on new materials for fuel-cells and electrolysis cells are presented and discussed.

2. Material and Methods

2.1 Cell design and fabrication

The test cell was designed to accept a disk-shaped MEA having a diameter of 1.27 cm (0.5 inch) and was fabricated using simple tools and common materials purchased from commercial sources. Figure 1 shows the cell construction and assembly; further detail is provided in the supplementary materials. The cell body is a commercial straight union compression fitting made from perfluoroalkoxyalkane (PFA) fluoropolymer material and purchased from US Plastic

Corp (Item # 65039). Prior to use the interior passage of the fitting was machined so that it had the same inner diameter (ID) over its full length. Current collectors were fabricated from 0.95 cm (3/8 inch) diameter fine extruded graphite rods purchased from The Graphite Store (Part # NC001320). Each rod was approximately 5 cm long and had a 0.32 cm (1/8 inch) diameter hole drilled in the center for gas entry, with several small grooves carved in the sides for gas exit. The graphite current collectors were held inside sleeves made from poly(tetrafluoroethylene)

(PTFE) that fit snugly in the cell body. Butyl rubber O-rings were used between the MEA and the PTFE sleeve to ensure a gas-tight seal.

2.2 MEA fabrication.

Membrane electrode assemblies were fabricated from Nafion® PEM disks (Nafion®- 212) and platinum-coated carbon cloth electrodes. The Nafion®-212 membrane was cut to form disks (area = 1.27 cm^2) using an arch punch, and carbon cloth electrodes were similarly cut into

Figure 2. Membrane-electrode assemblies prepared for use in miniature PEM fuel cell. Left shows cathode side, diameter = 0.24 cm ($3/32 \text{ inch}$). Right shows anode side, diameter = 0.79 cm ($5/16 \text{ inch}$). Both electrodes are attached to a Nafion®-212 disk, diameter = 1.27 cm (0.5 inch).

disks using hollow metal punches. For most experiments, the anode was a 0.79 cm ($5/16 \text{ inch}$) diameter disk (area = 0.49 cm^2) and the cathode was a 0.24 cm ($3/32 \text{ inch}$) diameter disk (area = 0.045 cm^2). The larger area and higher Pt loading on the anode (see below) were used to avoid edge effects and to help ensure that minimal polarization occurred at the anode. Diagnostic testing was thus focused on the cathode.

Cathodes were prepared from a commercial catalyst-coated carbon cloth electrode (Fuel Cell Store, part number 1610002) consisting of a standard PTFE-treated woven carbon cloth gas diffusion layer (GDL, thickness = 410 micrometers) with a microporous layer (MPL) onto which a 0.3 mg cm^{-2} loading of platinum, consisting of 40% platinum on Vulcan carbon, was loaded on the MPL side. After cutting this electrode sheet to form a cathode disk, a $1 \text{ }\mu\text{L}$ volume of 5 wt.% Nafion® solution was delivered onto the catalyst-coated side of the cathode disk and allowed to dry prior to the electrode being used to make an MEA. The anode was formed from a similar commercial catalyst-coated carbon cloth electrode (Fuel Cell Store, part number 1610008) for which the catalyst coating on the MPL side consisted of a 4 mg cm^{-2} loading of platinum black. Anode disks were cut as described above and were treated with a $7 \text{ }\mu\text{L}$ volume of 5 wt. % Nafion® solution prior to use.

MEA fabrication for this cell consisted of making a stack of anode, PEM and cathode, with the catalyst-coated MPL sides facing the PEM, and then hot-pressing the assembly for five minutes at $140 \text{ }^{\circ}\text{C}$ with 100 lbf pound-force (approximately 445 Newtons) applied using a Carver hot press. This treatment left the two electrodes laminated onto the Nafion layer, as shown in Figure 2.

2.3 Cell assembly.

A **1.27 cm (0.5 inch)** diameter flat-faced stainless steel (SS) rod was used to aid in cell assembly for the miniature PEM fuel cell test fixture. The MEA was placed cathode-side down against the SS rod which was then positioned at the middle of the PFA cell body. A butyl rubber gasket (O-ring) was placed on top of the anode side of the MEA, then a PTFE sleeve was placed

on top of the gasket and pressed down firmly against the MEA. A nickel foam gas diffuser element (250 g m^{-2} , 0.06 cm thick, 3/8 in. diameter disk) was then placed inside the PTFE sleeve, then the graphite rod current collector was inserted into the PTFE sleeve on top of the nickel foam. The anode side of the cell was then sealed by tightening the PFA compression fitting, and the flat-faced SS rod was removed. A similar procedure was followed to assemble the cathode side of the cell, with one additional step. Prior to inserting the nickel foam gas diffuser element, a carbon paper disk (AvCarb P50T, 3/8 in. diameter) was placed on top of the cathode so that it was between the cathode and the nickel foam gas diffuser element. After full assembly, the two current collector graphite rods were gently pushed together and the other side of the PFA fitting was tightened to hold both current collectors in place against the MEA. A thermocouple was then affixed to the outside of the cell body and the cell was wrapped with heat tape for cell temperature control.

2.4 In-situ voltammetry

In-situ electrochemical surface area (ECSA) determination of the supported platinum in the MEA cathodes was performed using a CH Instruments 1140 B potentiostat in two-electrode mode, with the cathode serving as the working electrode and the anode as both the counter electrode and a pseudo-reference electrode. The measurements were made at a cell temperature of 30 °C. Gases were provided to the cell through a short length of 1/8 in OD PFA tubing after bubbling through humidifier bottles held at fixed temperature. ECSA was determined using the hydrogen adsorption/desorption (HAD) method, and also the electrochemical oxidation of CO (CO stripping) method. For HAD measurements the cathode was fed humidified (100% relative humidity, RH) argon gas at 30 °C and the anode was fed 100

% RH hydrogen gas at 30 °C, both at a flow rate of approximately 20 cc per minute. The cell was also held at 30 °C and was broken in using a cyclic sweep at 0.5 V s⁻¹ between 0 and 0.8 V until a stable voltammogram was established. The ECSA determination was made from a voltammetry scan between 0 and 0.8 V in the anodic direction at 50 mV s⁻¹ to oxidize adsorbed hydrogen. Integration of the HAD portion of the voltammograms was used to estimate the ECSA by dividing the HAD charge by the accepted value of 210 microcoulombs cm⁻²_{Pt} for HAD on platinum in accordance with the literature[33]. The baseline due to capacitive current from double layer charging was extrapolated from 0.4 to 0.6 V for all scans to form the baseline for subtraction to obtain the charge due to just the hydrogen oxidative desorption electrode reaction.

For ECSA determination by the CO stripping method, the argon flow to the cathode was briefly interrupted and replaced with a CO gas flow for approximately 10 seconds, then excess CO was removed by again purging with argon gas at a high flow rate for 5 min. A CV scan between 0.0 and 1.1 V was then collected at 50 mV s⁻¹ and the integrated charge from CO oxidation was used to obtain the platinum ECSA by dividing the charge by the accepted value of 420 microcoulombs cm⁻²_{Pt} for oxidation of adsorbed carbon monoxide on platinum[34], and by the platinum mass.

2.5 Ex-situ voltammetry

Ex-situ ECSA determination for the supported Pt in the carbon cloth disk electrodes was performed by cyclic voltammetry in aqueous 0.5 M H₂SO₄ solution. Carbon cloth disk electrodes were cut exactly as described in section 2.2 and were subsequently mounted onto

the surface of a glassy carbon rotating disk electrode (Pine Instruments). A 1 microliter volume of Nafion solution was applied and allowed to dry to bind the carbon cloth disk to the glassy carbon surface prior to use in *ex-situ* voltammetry experiments.

2.6 Polarization curve testing.

Polarization curves were acquired at oxygen-dosed cathodes with the CH Instruments 1140 B potentiostat under controlled-potential conditions using a simple slow-scan linear sweep voltammogram (LSV) over a potential range from 1.0 V to 0.3 V vs the hydrogen-dosed anode at a scan rate of 1 mV s^{-1} . Prior to acquiring a polarization curve, a break-in cycle was performed whereby the applied potential was pulsed between 1.0 and 0.5 V with a 1 s pulse time, for 10 s. This cycling was repeated until the pulse response was stabilized (approximately one hour). Unless otherwise indicated, all measurements were made at a cell temperature of 30°C , with gases passed through humidifier bottles held at 30°C to create humidification levels of approximately 100% RH. Gas flow rates were held at 20 cc per minute unless otherwise indicated.

2.7 Multi-potential-step testing.

Complementary information to polarization curve data was obtained from multi-potential-step measurements in which current was monitored as a function of time as the cathode potential was held for twenty seconds at each of a series of different fixed values, starting at +1.0 V and adjusting in -0.05 V increments from 1.0 V to 0.3 V vs the hydrogen-dosed anode. From the resulting current-time traces it is easy to see whether the currents are varying with time, and if they are, over what potential ranges such variation is observed. This information is

helpful in tracking down sources of non-steady-state behavior, for example due to current-dependent electrode flooding, that might be present in a particular cell.

2.8 Larger-scale MEA fabrication and testing

For the purpose of comparison, tests were also conducted using similar materials in a larger test cell using a larger MEA, following protocols that are commonly used for PEM fuel-cell MEA fabrication and testing. These tests utilized a Scribner model 850C compact fuel cell test station for which the MEA was fabricated from a Nafion 212 membrane of approximate area 56 cm^2 ($7.5\text{ cm} \times 7.5\text{ cm}$) and electrodes having an active area of 6.25 cm^2 ($2.5\text{ cm} \times 2.5\text{ cm}$). The MEA was prepared following a procedure similar to that described in section 2.2 above, adapted for larger sizes. For each of the larger electrodes a $139\text{ }\mu\text{L}$ volume of 5 wt. % Nafion® solution was applied to the active electrode surface and allowed to dry prior to the electrode being hot pressed into the MEA. The decision to use $139\text{ }\mu\text{L}$ of Nafion solution was arrived at by noting that the area ratio for the larger cell to the smaller cell, e.g. 6.25 cm^2 vs. 0.045 cm^2 , is approximately 139:1. Nafion-treated electrodes were hot pressed onto a Nafion®-212 membrane for 5 min at $140\text{ }^\circ\text{C}$ with 400 lbf pound-force (approximately 1180 N) applied using a Carver hot press, in a manner similar to that used for the smaller electrodes. Polarization curves for the larger MEAs were acquired using the Scribner model 850C system with FUELCELL software. Anode gas feed was 0.1 SLM of humidified hydrogen, and cathode gas feed was 0.1 SLM of humidified oxygen. Cell temperature was $30\text{ }^\circ\text{C}$ with humidifier bottle temperatures also at $30\text{ }^\circ\text{C}$ resulting in near 100% RH for gases. These conditions are chosen to be similar to those used with the miniature test cell. MEA break-in was conducted at a constant cell potential of approximately 0.53 V for approximately 4 h prior to polarization testing. *In-situ* cyclic

voltammograms were acquired for the larger MEAs using the same CHI model 1140B potentiostat that was used for the smaller MEAs, with the Scribner test station used only to control cell temperature and gas flow and humidity. During *in-situ* voltammogram acquisition the gas flow at the cathode was changed to be humidified nitrogen gas, at 100% RH, and flow rates at both electrodes were reduced to 0.05 SLM.

3. Results

3.1 *In-situ* voltammetry.

Figure 3 shows *in-situ* voltammograms for a carbon-cloth-based cathode prepared as described in sections 2.2 - 2.4. The HAD voltammogram (left) shows the expected features between 0.05 and 0.4 V (potential applied to cathode vs. anode) for electrochemical hydrogen adsorption / desorption on platinum, superimposed on a capacitive background for the carbon

support. ECSA is determined by extrapolation of the double-layer charging current from the region between 0.4 and 0.6 V back to 0.05 V and integrating the charge for oxidation of adsorbed hydrogen on a positive-going potential sweep. That charge is then normalized by the usual value of 210 μC per cm² for oxidation of adsorbed hydrogen on platinum,[33] and by the mass of platinum in this cathode which is obtained from the electrode area of 0.045 cm² and

the reported platinum loading of $0.3 \text{ mg Pt cm}^{-2}$. Values for ECSA for three independently prepared electrodes are presented in Table 1; the average ECSA value from the three determinations is $38.5 \pm 1.0 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$, with the uncertainty being the standard deviation for the set of three measured values.

Table 1. Electrochemical surface area (ECSA) determinations for three MEA cathodes by *in-situ* cyclic voltammetry in the miniature PEM fuel cell test fixture

MEA number	ECSA from H adsorption / desorption, $\text{m}^2 \text{ g}_{\text{Pt}}^{-1}$	ECSA from CO stripping, $\text{m}^2 \text{ g}_{\text{Pt}}^{-1}$
MEA 1	37.3	59.1
MEA 2	39.0	59.2
MEA 3	39.1	59.5
Average	38.5 ± 1.0	59.3 ± 0.3

Figure 3 right shows another voltammogram for the same MEA, this time reflecting oxidation of adsorbed carbon monoxide. The initial scan in the negative direction shows an absence of HAD peaks, as expected for a Pt surface that is poisoned by CO, and the positive-going scan shows a large oxidative peak for CO oxidation, which upon integration and normalization by Pt mass and the factor of $420 \text{ } \mu\text{C per cm}^2$ for oxidation of adsorbed CO on platinum[34] gives an average ECSA value for three electrodes of $59.3 \pm 0.3 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$, again with the uncertainty as a standard deviation for the set of three measured values. The larger ECSA value from adsorbed CO oxidation is in agreement with prior work that has used both approaches to measure ECSA, and is thought to reflect some difficulty with drawing an

appropriate baseline to account for potential-dependent capacitive charging when integrating HAD peaks compared with the CO oxidation peaks.[35, 36] Also, variations in the surface coverage of adsorbed hydrogen and CO with electrolyte, including the presence / absence of Nafion, have been reported and could be responsible for some of our observed variance in ECSA values from HAD and CO oxidation.[37]

3.2 Ex-situ voltammetry.

Figure 4 shows *ex-situ* voltammograms for a carbon-cloth-based electrode prepared as described in section 2.5 and immersed in an aqueous sulfuric acid solution. This electrode is nearly identical to that from Figure 3; the major difference is that for the experiment in Figure 4

Figure 4. *Ex-situ* cyclic voltammetry of a carbon cloth disk electrode, similar to that shown in Figure 3, except that the electrode was mounted onto a glassy carbon disk electrode and studied at lab ambient temperature (approximately 23 °C) while immersed in aqueous 0.5 M H₂SO₄ solution. Left, hydrogen adsorption / desorption voltammetry, ECSA = 74.1 m² g_{Pt}⁻¹. Right, CO stripping voltammetry, ECSA = 87.3 m² g_{Pt}⁻¹. In both cases the solution was purged with argon gas prior to initiation of scan. Potentials are applied vs. a reversible hydrogen electrode at a scan rate of 50 mV s⁻¹.

the electrode is in electrical contact with a glassy carbon electrode and is immersed in a liquid electrolyte. It is instructive to compare the voltammograms in Figure 4 with those in Figure 3, because those in Figure 4 reflect contributions from all the Pt in contact with the liquid electrolyte, whereas those in Figure 3 reflect only the platinum in contact with the Nafion polymer electrolyte. The platinum ECSA values obtained from Figure 4 are approximately $74 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$ from the HAD method and $87 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$ from the CO stripping method. Both these values are significantly higher than the values obtained for MEA cathodes for which Nafion ionomer was the only electrolyte that could make contact with the Pt catalyst particles. From the ratio of ECSA values from *ex-situ* and *in-situ* measurements, we estimate that our relatively simple method for impregnating platinized carbon cloth electrodes with Nafion polymer electrolyte has resulted in between 50 and 70 percent of the Pt surface area being electrochemically accessible. This finding does not suggest a fundamental limitation on the amount of platinum that may be made accessible when using a Nafion electrolyte in the electrodes, and it is known that refinement of the techniques for integrating polymer electrolyte with electrodes can yield electrodes in which nearly all of the platinum is electrochemically accessible in the absence of liquid electrolyte. Rather, the significance of the results presented here is that they demonstrate a convenient way of studying platinum accessibility using small amounts of material in small electrodes for which it is relatively easy to ensure that the electrode material being studied in the *in-situ* and *ex-situ* voltammetry experiments is the same. Similar measurements could prove highly useful in research seeking to develop and evaluate new catalyst materials, and new ways of integrating catalyst and polymer electrolyte in electrodes.

3.3 Polarization curve testing.

Figure 5. Overlay of three polarization curves acquired for three independently-prepared MEAs in the miniature fuel-cell test fixture, using slow-scan cyclic voltammetry (1 mV s^{-1}) over a potential range from 1.0 V and 0.3 V applied to the oxygen-bathed cathode vs the hydrogen-bathed anode.

Polarization curves were acquired for cells with humidified hydrogen and oxygen feeds on the anode and cathode respectively, with potentiostatic control of the cell potential using an instrument designed principally for conventional electroanalytical measurements. Figure 5 shows an overlay of three polarization curves acquired for three independently prepared MEAs (the same three MEAs for which ECSA data are presented in Table 1) and studied sequentially in the same cell. The figure shows minor variations among the individual polarization curves but in general the curves are in excellent agreement, showing the expected shape for a hydrogen-oxygen PEM fuel cell. Current densities near 2 A cm^{-2} are observed at cell potentials near 0.3 V which was the lowest cell potential tested. Figure 6 presents one of these polarization curves

Figure 6. Overlay of a polarization curve (black, left axis) and a corresponding power density curve (red, right axis) for one of the MEAs from Figure 5. Peak power of approximately 0.7 W cm^{-2} was achieved at a current density near 1.5 A cm^{-2} at a cell potential of approximately 0.45 along with a power density curve that shows a peak power of 0.7 W cm^{-2} at a cell potential near

0.5 V. The performance metrics of these cells are good, particularly for the relatively low cathode platinum loading of $0.3 \text{ mg Pt cm}^{-2}$, but they are not quite current state-of-the-art, which is to be expected for a cell using un-optimized commercial catalysts at a relatively low cell temperature of 30°C . The achievement of superior catalyst and fuel-cell performance is always desired but it is not the main objective of this work. Rather, the objective of this work is to demonstrate diagnostic testing on MEAs and cells that required quite small amounts of material, including both catalyst and membrane, to conduct a complete fuel-cell test in the

absence of any liquid electrolyte. The results from Figures 4-6 show that this objective has been achieved.

It is useful to compare results obtained with the miniature test cell with results on an MEA fabricated using identical materials but in larger size, and tested in a larger test fixture. Figure 7 presents a polarization curve for a larger MEA, fabricated and tested as described in Section 2.8. The polarization curves showing in Figures 6 and 7 are similar to each other, with the

principal difference being found in the high-current region where currents are particularly strongly sensitive to details associated with gas transport, including flow-field dynamics. A key difference between the two cells is that the gas flow field in the miniature cell consists only of

the nickel foam gas diffuser element, whereas the flow field in the larger cell is of the traditional serpentine style in the graphite block current collector. The slightly lower currents in the high-current region of the polarization curve for the larger-area cell could reflect some concentration polarization for gases associated with the serpentine flow field. An *in-situ* voltammogram for this cell (shown in Supplemental Materials) in the hydrogen adsorption / desorption region showed the platinum ECSA for this cathode to be approximately $34 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$ which is approximately 10 percent lower than the value obtained for the smaller MEA. This difference could reflect some difficulty associated with drawing a proper baseline for the HAD ECSA determination, or to some difference in the penetration of Nafion into the electrodes for the larger vs. small cell. Further work to definitively identify causes for this discrepancy in ECSA values and also in the current densities over the full range of cell potentials would require studies on multiple larger-scale MEAs fabricated by nominally identical procedures to obtain statistically-significant results, and is beyond the scope of the present work.

3.4 Multi-potential-step testing.

Figure 8 presents a final data slide showing current-time traces for the three MEAs from Table 1. The experiment involves application of a staircase waveform to the cell, with the applied potential at the cathode initially held at 1.0 V vs. the anode. After twenty seconds the potential is adjusted by -0.05 V to 0.95 V, which is held for a further twenty seconds. This process is repeated until an applied potential of 0.30 V is reached. The Figure shows the variation of current with time for each potential step. The significance of these data is that they provide dynamical information on how current varies with time in different regions along the polarization curve. A polarization curve does not by itself contain any dynamical information;

Figure 8. Overlay of three current-time curves acquired for an applied potential program consisting of a series of potential steps of duration 20 seconds each, applied to the oxygen-bathed cathode between 1.0 V and 0.3 V vs the hydrogen-bathed anode. The applied potential was adjusted by 50 mV for each step.

one typically assumes that the current is passed at steady-state, and tests of this assumption are made by sequential acquisition of polarization curves, which should ideally result in the same curve being obtained in sequential experiments. In fact, this is often not the case, and many changes to the catalyst layer, for example from electrode flooding or drying, or from catalyst poisoning, are possible that could cause non-steady-state behavior. There have even been reports of bi-stability in fuel-cell output associated with cycles of electrode flooding and drying, which give rise to increased and decreased current, or to fluctuations in cell potential at

constant current.[38-40] The data in Figure 8 show that, for the present cells, the approximation that currents are steady state on a twenty-second timescale holds well for currents up to 80 mA.

4. Discussion.

The use of small electrodes and small cells offers some significant advantages relative to conventional fuel-cell testing for which the smallest cells that are regularly tested still have an active area of 5 cm^2 , over 100 times higher than the active cathode area for the cells in the present work. An obvious advantage of using small amounts of material is that fuel-cell testing can be conducted using newly created materials that may be available only in limited quantities. This issue is not very important when using commercial materials such as Nafion membranes and platinized carbon cloth electrodes but it could become quite important in new membrane and catalyst research, where a need often exists to screen materials, often multiple materials, that may be available in small amounts from new synthesis research.

Another advantage of using small amounts of material is that it can allow experiment replication to be more commonly included in testing protocols on new fuel-cell materials. Conventional testing with even the relatively small 5 cm^2 cells can require up to a gram of catalyst material (depending upon how the catalyst is used) and close to 100 cm^2 of ionomer membrane to make just one useable MEA. It is often the case that just one or two tests use up all of the material from an early-stage synthesis effort. New batches of material can be synthesized but there is then some uncertainty regarding how similar two material batches may be, which introduces doubt into the measurements when making comparisons. The ability to run many tests including replicates and controls with relatively small amounts of catalyst or ionomer material could provide important advantages in early-stage fuel-cell research.

Yet another advantage of the present cell configuration is that it should minimize losses associated with gas transport. Gases are delivered in larger-scale fuel cells via flow fields, often of a serpentine style, that present gases to the catalyst layer in patches, with some areas directly exposed to the gas flow stream and others positioned directly underneath the spots where the current collector / bipolar plate makes contact with the catalyst layer. The use of gas diffusion layers between the current collector / bipolar plate and the catalyst layer helps to mitigate problems with uneven gas transport but even so, to achieve even a simple understanding of mass-transfer effects in such a case one must consider the significant spatial variation of mass-transfer rate and current density that can be caused by spatial non-uniformity in the electrode contacts and gas flow. Spatial variations in current density are also possible due to gas depletion and differences in water content of gases at different locations along a flow channel. These effects could in fact be responsible for the lower current densities for the larger MEA (Figure 7) compared with the smaller MEA (Figure 6). Mass-transfer effects associated with flow fields are very important when seeking to maximize power-source performance but they can be quite frustrating when attempting to use fuel-cell test measurements diagnostically, to screen new materials and to learn about fundamental catalyst layer properties in the absence of mass transfer / concentration polarization effects. Due to the very small size of the active electrode region in the present cell configuration, gas transport rates should be quite high and show much less variation with spatial position compared with cells having a complex flow field. These high gas transport rates and the lack of spatial variation in current density are significant advantages when using these cells for diagnostic or material evaluation purposes.

A final advantage offered by the present cell configuration lies in the relatively small currents that are passed. For example, the current density of 2 A cm^{-2} reported in Figures 5 and 6 corresponds to an absolute current of just 90 mA, which is easily achieved using conventional instrumentation without worry about ohmic losses outside of the cell, for example in the leads and contacts. A similar current density in a 5 cm^2 cell would correspond to passage of 10 amperes of current, which in most cases would require the use of specialized instrumentation optimized for high currents, and could also produce heat that could affect the cell temperature. The fact that the present cells allow for a complete fuel-cell test with conventional instrumentation and without need for active cooling could enable useful fuel-cell testing to be done by more laboratories, using research infrastructure that is already present.

5. Conclusion

In summary, a miniature PEM fuel-cell test platform is described and used to perform diagnostic testing of fuel-cell membrane-electrode assemblies that were fabricated using small amounts of material, having active areas less than 0.1 cm^2 , with electroanalytical instrumentation and methods that are commonly available in most laboratories where electrochemistry research is pursued. Testing is performed in the absence of liquid electrolyte which reveals effects associated with transport processes, e.g. ion, electron and mass transport, within the electrode layers. Testing performed using this platform is complementary to RDE-based testing which focusses on electrocatalytic activity but does not provide information on transport processes in electrodes.

6. Acknowledgment

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**A CONVENIENT MINIATURE TEST PLATFORM FOR POLYELECTROLYTE MEMBRANE FUEL-CELL
RESEARCH**

Jamie A. Shetzline, Saheed Bukola and Stephen E. Creager*

Department of Chemistry, Clemson University, Clemson SC 29634 USA

* corresponding author. E-mail: screage@clemson.edu. Phone: 864-656-4995

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Abstract

A simple and convenient small-scale fuel-cell test platform was created from a commercial compression fitting and graphite rod current collectors and used to conduct diagnostic tests on disk-shaped membrane-electrode assemblies (MEAs) fabricated from Nafion membranes and Nafion-impregnated platinum-on-carbon-cloth anodes and cathodes. A key advantage of this test platform is that it requires very little material, perhaps just a few milligrams, to conduct a fuel-cell test on a supported catalyst. Electrochemically-active surface area (ECSA) values for supported platinum on carbon-cloth electrodes were obtained by *in-situ* (in the fuel cell) and *ex-situ* (in liquid electrolyte) cyclic voltammetry on similarly-prepared electrodes, and values obtained by these methods were compared with each other to estimate the fraction of platinum catalyst contacted by the Nafion ionomer in the fuel-cell cathode. Polarization curves were acquired under controlled-potential conditions using slow-scan cyclic and sampled-current voltammetry and potential-step amperometry methods with conventional electroanalytical instrumentation. Tests performed using this platform are complementary to rotating disk electrode (RDE) voltammetry tests which also allow for catalyst testing on small amounts of material, albeit in the presence of liquid electrolyte, and are commonly used for initial screening of new fuel-cell catalysts. They are also complementary to conventional fuel-cell testing that is commonly performed on MEAs having active areas more than 100 times larger than that in the present cells.

1. Introduction

Research on new materials for polyelectrolyte-membrane (PEM) fuel cells and water electrolysis cells has been very active in recent decades and has resulted in significant advances in understanding of both materials properties and device behavior.[1-7] The most critical materials in a PEM fuel cell are the ionomer membrane, the anode and cathode catalyst layers and the gas diffusion layers, and each of these materials is subjected to its own characteristic testing as part of research and development activities aimed at creating improved devices. New ionomer materials and proton-exchange membranes are often characterized with respect to ionic conductivity, water uptake, mechanical properties and other properties as a function of temperature and humidity, which is helpful in understanding how these materials will behave in a membrane-electrode assembly (MEA).[8-12] New supported catalysts are often combined with ionomer and characterized with respect to electrochemical surface area (ECSA) and catalytic activity using rotating disk electrode (RDE) methods, with catalyst layers coated on carbon electrodes and immersed in an aqueous acid electrolyte.[4, 13] The ionomer serves principally as a binder in such an experiment since proton transfer to and from catalyst particles occurs principally via the aqueous acid electrolyte. RDE methods are quite powerful for studying electrocatalytic reactions, e.g. the electrochemical oxygen reduction reaction (ORR), and they are widely used for early-stage testing on relatively small amounts of new catalytic materials. RDE methods are also somewhat lacking for diagnostic testing because they do not address the activity of catalysts in the absence of free electrolyte. In particular, issues relating to mixed electron / proton conduction and mass transfer in electrodes, including effects from electrode flooding, are not addressed in RDE testing. These issues may be studied in

conventional fuel-cell testing which typically utilizes a membrane-electrode assembly (MEA) or catalyst-coated membrane (CCM) in a test fixture that provides humidified gases to the MEA / CCM with the cell connected to a computer-controlled load that may be used to acquire polarization curves and conduct diagnostic tests. This type of testing usually uses electrodes having active areas of at least several cm^2 , attached to membranes having areas of at least several tens of cm^2 . It is quite easy for a single test performed using a MEA / CCM of this size to consume the majority of the available membrane or catalyst material in the early stages of new material research. In such a situation, there is no possibility of replicate measurements or testing with systematic adjustment of experimental variables. A need exists for a PEM fuel cell diagnostic testing platform that uses very small amounts of material in electrodes that may be fabricated in a reproducible way and studied in small-scale cells in the absence of free electrolyte, under conditions closer than those from RDE to the conditions that will exist in an operating fuel cell. It is desirable that this diagnostic testing be performed using instrumentation and methods that are commonly available in laboratories where general electrochemical research is performed.

We present here a miniature PEM fuel cell test platform that may be used to conduct tests on catalyst layers containing just a few tens of micrograms of supported catalyst over an area less than 0.1 cm^2 , associated with a polyelectrolyte membrane having a total area of just a few square centimeters, using widely available electroanalytical chemistry instrumentation and methods. Membrane-electrode assemblies for this test platform are fabricated using 1.27 cm (0.5-inch) diameter PEM disks onto which carbon cloth disk electrodes are attached by hot pressing. A single 10x10 cm square of ionomer membrane and a similar amount of catalyst

material would easily provide enough material to fabricate more than fifty MEAs for this test platform. The motivation for creating this test platform is to enable small-scale testing of new electrode materials, as is done by RDE, in a manner that excludes effects from liquid electrolyte and includes the effects of ionomer contact with the catalyst and with the PEM on the overall electrode activity. Miniature PEM fuel cells have been previously fabricated and studied, often with the aim of preparing small power sources, e.g. for portable electronics.[14-32] Most such cells were prepared using microfabrication and/or MEMS techniques, often with the PEM and/or MEA deeply integrated into the device, so they tend not to be very useful for repeated measurements or for systematic diagnostic testing. Even for these cells, a “miniature” cell often has an electrode area greater than 1 cm^2 which is still large when compared with typical electroanalytical tests such as RDE voltammetry which often use disk electrodes with diameters below 0.5 cm.

We demonstrate the utility of the miniature test platform by presenting results from two types of diagnostic testing on the cathode of a small-scale MEA. In the first test, *in-situ* (in the MEA) and *ex-situ* (in aqueous acid liquid electrolyte) cyclic voltammograms of the same supported platinum catalyst are compared, focusing on hydrogen adsorption / desorption and carbon monoxide oxidation peaks to assess electrochemically active surface area (ECSA). By comparing *in-situ* and *ex-situ* voltammograms, an estimate may be made of the fraction of supported catalyst in contact with ionomer in the MEA. It is important in such a test that the electrodes tested be as similar to each other as possible, to avoid being misled by differences associated with electrode preparation. A valid comparison was easy to achieve with the small electrodes used in this miniature test platform because electrodes of nearly identical size and

preparation could be mounted on both a PEM for *in-situ* voltammetry, and on a solid carbon electrode for *ex-situ* voltammetry. In the second test, steady-state polarization curves were acquired using slow-scan linear sweep voltammetry to exercise control over the cell potential under approximately steady-state conditions. Currents from polarization curves are compared with current-time curves acquired at fixed values of applied potential in a series of potential steps. This latter comparison is helpful when identifying and investigating causes of non-steady-state behavior in cells, which can easily occur but is often difficult to identify from conventional polarization-curve testing alone. Miniature test-cell behavior was also compared with behavior of an MEA of conventional size, e.g. polyelectrolyte membrane approximately $8 \times 8 \text{ cm}^2$ with electrodes approximately $2.5 \times 2.5 \text{ cm}^2$, tested in a commercial fuel-cell test apparatus, to establish that small-scale testing is relevant to the behavior in larger cells. Advantages of the miniature cell configuration for early-stage basic research focused on new materials for fuel-cells and electrolysis cells are presented and discussed.

2. Material and Methods

2.1 Cell design and fabrication

The test cell was designed to accept a disk-shaped MEA having a diameter of 1.27 cm (0.5 inch) and was fabricated using simple tools and common materials purchased from commercial sources. Figure 1 shows the cell construction and assembly; further detail is provided in the supplementary materials. The cell body is a commercial straight union compression fitting made from perfluoroalkoxyalkane (PFA) fluoropolymer material and purchased from US Plastic

Corp (Item # 65039). Prior to use the interior passage of the fitting was machined so that it had the same inner diameter (ID) over its full length. Current collectors were fabricated from 0.95 cm (3/8 inch) diameter fine extruded graphite rods purchased from The Graphite Store (Part # NC001320). Each rod was approximately 5 cm long and had a 0.32 cm (1/8 inch) diameter hole drilled in the center for gas entry, with several small grooves carved in the sides for gas exit. The graphite current collectors were held inside sleeves made from poly(tetrafluoroethylene)

(PTFE) that fit snugly in the cell body. Butyl rubber O-rings were used between the MEA and the PTFE sleeve to ensure a gas-tight seal.

2.2 MEA fabrication.

Membrane electrode assemblies were fabricated from Nafion® PEM disks (Nafion®- 212) and platinum-coated carbon cloth electrodes. The Nafion®-212 membrane was cut to form disks (area = 1.27 cm^2) using an arch punch, and carbon cloth electrodes were similarly cut into

Figure 2. Membrane-electrode assemblies prepared for use in miniature PEM fuel cell. Left shows cathode side, diameter = 0.24 cm (3/32 inch). Right shows anode side, diameter = 0.79 cm (5/16 inch). Both electrodes are attached to a Nafion®-212 disk, diameter = 1.27 cm (0.5 inch).

disks using hollow metal punches. For most experiments, the anode was a 0.79 cm (5/16 inch) diameter disk (area = 0.49 cm^2) and the cathode was a 0.24 cm (3/32 inch) diameter disk (area = 0.045 cm^2). The larger area and higher Pt loading on the anode (see below) were used to avoid edge effects and to help ensure that minimal polarization occurred at the anode. Diagnostic testing was thus focused on the cathode.

Cathodes were prepared from a commercial catalyst-coated carbon cloth electrode (Fuel Cell Store, part number 1610002) consisting of a standard PTFE-treated woven carbon cloth gas diffusion layer (GDL, thickness = 410 micrometers) with a microporous layer (MPL) onto which a 0.3 mg cm^{-2} loading of platinum, consisting of 40% platinum on Vulcan carbon, was loaded on the MPL side. After cutting this electrode sheet to form a cathode disk, a $1 \text{ }\mu\text{L}$ volume of 5 wt.% Nafion® solution was delivered onto the catalyst-coated side of the cathode disk and allowed to dry prior to the electrode being used to make an MEA. The anode was formed from a similar commercial catalyst-coated carbon cloth electrode (Fuel Cell Store, part number 1610008) for which the catalyst coating on the MPL side consisted of a 4 mg cm^{-2} loading of platinum black. Anode disks were cut as described above and were treated with a $7 \text{ }\mu\text{L}$ volume of 5 wt. % Nafion® solution prior to use.

MEA fabrication for this cell consisted of making a stack of anode, PEM and cathode, with the catalyst-coated MPL sides facing the PEM, and then hot-pressing the assembly for five minutes at $140 \text{ }^{\circ}\text{C}$ with 100 lbf pound-force (approximately 445 Newtons) applied using a Carver hot press. This treatment left the two electrodes laminated onto the Nafion layer, as shown in Figure 2.

2.3 Cell assembly.

A 1.27 cm (0.5 inch) diameter flat-faced stainless steel (SS) rod was used to aid in cell assembly for the miniature PEM fuel cell test fixture. The MEA was placed cathode-side down against the SS rod which was then positioned at the middle of the PFA cell body. A butyl rubber gasket (O-ring) was placed on top of the anode side of the MEA, then a PTFE sleeve was placed

on top of the gasket and pressed down firmly against the MEA. A nickel foam gas diffuser element (250 g m^{-2} , 0.06 cm thick, 3/8 in. diameter disk) was then placed inside the PTFE sleeve, then the graphite rod current collector was inserted into the PTFE sleeve on top of the nickel foam. The anode side of the cell was then sealed by tightening the PFA compression fitting, and the flat-faced SS rod was removed. A similar procedure was followed to assemble the cathode side of the cell, with one additional step. Prior to inserting the nickel foam gas diffuser element, a carbon paper disk (AvCarb P50T, 3/8 in. diameter) was placed on top of the cathode so that it was between the cathode and the nickel foam gas diffuser element. After full assembly, the two current collector graphite rods were gently pushed together and the other side of the PFA fitting was tightened to hold both current collectors in place against the MEA. A thermocouple was then affixed to the outside of the cell body and the cell was wrapped with heat tape for cell temperature control.

2.4 In-situ voltammetry

In-situ electrochemical surface area (ECSA) determination of the supported platinum in the MEA cathodes was performed using a CH Instruments 1140 B potentiostat in two-electrode mode, with the cathode serving as the working electrode and the anode as both the counter electrode and a pseudo-reference electrode. The measurements were made at a cell temperature of 30 °C. Gases were provided to the cell through a short length of 1/8 in OD PFA tubing after bubbling through humidifier bottles held at fixed temperature. ECSA was determined using the hydrogen adsorption/desorption (HAD) method, and also the electrochemical oxidation of CO (CO stripping) method. For HAD measurements the cathode was fed humidified (100% relative humidity, RH) argon gas at 30 °C and the anode was fed 100

% RH hydrogen gas at 30 °C, both at a flow rate of approximately 20 cc per minute. The cell was also held at 30 °C and was broken in using a cyclic sweep at 0.5 V s⁻¹ between 0 and 0.8 V until a stable voltammogram was established. The ECSA determination was made from a voltammetry scan between 0 and 0.8 V in the anodic direction at 50 mV s⁻¹ to oxidize adsorbed hydrogen. Integration of the HAD portion of the voltammograms was used to estimate the ECSA by dividing the HAD charge by the accepted value of 210 microcoulombs cm⁻²_{Pt} for HAD on platinum in accordance with the literature[33]. The baseline due to capacitive current from double layer charging was extrapolated from 0.4 to 0.6 V for all scans to form the baseline for subtraction to obtain the charge due to just the hydrogen oxidative desorption electrode reaction.

For ECSA determination by the CO stripping method, the argon flow to the cathode was briefly interrupted and replaced with a CO gas flow for approximately 10 seconds, then excess CO was removed by again purging with argon gas at a high flow rate for 5 min. A CV scan between 0.0 and 1.1 V was then collected at 50 mV s⁻¹ and the integrated charge from CO oxidation was used to obtain the platinum ECSA by dividing the charge by the accepted value of 420 microcoulombs cm⁻²_{Pt} for oxidation of adsorbed carbon monoxide on platinum[34], and by the platinum mass.

2.5 Ex-situ voltammetry

Ex-situ ECSA determination for the supported Pt in the carbon cloth disk electrodes was performed by cyclic voltammetry in aqueous 0.5 M H₂SO₄ solution. Carbon cloth disk electrodes were cut exactly as described in section 2.2 and were subsequently mounted onto

the surface of a glassy carbon rotating disk electrode (Pine Instruments). A 1 microliter volume of Nafion solution was applied and allowed to dry to bind the carbon cloth disk to the glassy carbon surface prior to use in *ex-situ* voltammetry experiments.

2.6 Polarization curve testing.

Polarization curves were acquired at oxygen-dosed cathodes with the CH Instruments 1140 B potentiostat under controlled-potential conditions using a simple slow-scan linear sweep voltammogram (LSV) over a potential range from 1.0 V to 0.3 V vs the hydrogen-dosed anode at a scan rate of 1 mV s^{-1} . Prior to acquiring a polarization curve, a break-in cycle was performed whereby the applied potential was pulsed between 1.0 and 0.5 V with a 1 s pulse time, for 10 s. This cycling was repeated until the pulse response was stabilized (approximately one hour). Unless otherwise indicated, all measurements were made at a cell temperature of 30°C , with gases passed through humidifier bottles held at 30°C to create humidification levels of approximately 100% RH. Gas flow rates were held at 20 cc per minute unless otherwise indicated.

2.7 Multi-potential-step testing.

Complementary information to polarization curve data was obtained from multi-potential-step measurements in which current was monitored as a function of time as the cathode potential was held for twenty seconds at each of a series of different fixed values, starting at +1.0 V and adjusting in -0.05 V increments from 1.0 V to 0.3 V vs the hydrogen-dosed anode. From the resulting current-time traces it is easy to see whether the currents are varying with time, and if they are, over what potential ranges such variation is observed. This information is

helpful in tracking down sources of non-steady-state behavior, for example due to current-dependent electrode flooding, that might be present in a particular cell.

2.8 Larger-scale MEA fabrication and testing

For the purpose of comparison, tests were also conducted using similar materials in a larger test cell using a larger MEA, following protocols that are commonly used for PEM fuel-cell MEA fabrication and testing. These tests utilized a Scribner model 850C compact fuel cell test station for which the MEA was fabricated from a Nafion 212 membrane of approximate area 56 cm^2 ($7.5\text{ cm} \times 7.5\text{ cm}$) and electrodes having an active area of 6.25 cm^2 ($2.5\text{ cm} \times 2.5\text{ cm}$). The MEA was prepared following a procedure similar to that described in section 2.2 above, adapted for larger sizes. For each of the larger electrodes a $139\text{ }\mu\text{L}$ volume of 5 wt. % Nafion® solution was applied to the active electrode surface and allowed to dry prior to the electrode being hot pressed into the MEA. The decision to use $139\text{ }\mu\text{L}$ of Nafion solution was arrived at by noting that the area ratio for the larger cell to the smaller cell, e.g. 6.25 cm^2 vs. 0.045 cm^2 , is approximately 139:1. Nafion-treated electrodes were hot pressed onto a Nafion®-212 membrane for 5 min at $140\text{ }^\circ\text{C}$ with 400 lbf pound-force (approximately 1180 N) applied using a Carver hot press, in a manner similar to that used for the smaller electrodes. Polarization curves for the larger MEAs were acquired using the Scribner model 850C system with FUELCELL software. Anode gas feed was 0.1 SLM of humidified hydrogen, and cathode gas feed was 0.1 SLM of humidified oxygen. Cell temperature was $30\text{ }^\circ\text{C}$ with humidifier bottle temperatures also at $30\text{ }^\circ\text{C}$ resulting in near 100% RH for gases. These conditions are chosen to be similar to those used with the miniature test cell. MEA break-in was conducted at a constant cell potential of approximately 0.53 V for approximately 4 h prior to polarization testing. *In-situ* cyclic

voltammograms were acquired for the larger MEAs using the same CHI model 1140B potentiostat that was used for the smaller MEAs, with the Scribner test station used only to control cell temperature and gas flow and humidity. During *in-situ* voltammogram acquisition the gas flow at the cathode was changed to be humidified nitrogen gas, at 100% RH, and flow rates at both electrodes were reduced to 0.05 SLM.

3. Results

3.1 *In-situ* voltammetry.

Figure 3 shows *in-situ* voltammograms for a carbon-cloth-based cathode prepared as described in sections 2.2 - 2.4. The HAD voltammogram (left) shows the expected features between 0.05 and 0.4 V (potential applied to cathode vs. anode) for electrochemical hydrogen adsorption / desorption on platinum, superimposed on a capacitive background for the carbon

support. ECSA is determined by extrapolation of the double-layer charging current from the region between 0.4 and 0.6 V back to 0.05 V and integrating the charge for oxidation of adsorbed hydrogen on a positive-going potential sweep. That charge is then normalized by the usual value of 210 μC per cm² for oxidation of adsorbed hydrogen on platinum,[33] and by the mass of platinum in this cathode which is obtained from the electrode area of 0.045 cm² and

the reported platinum loading of $0.3 \text{ mg Pt cm}^{-2}$. Values for ECSA for three independently prepared electrodes are presented in Table 1; the average ECSA value from the three determinations is $38.5 \pm 1.0 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$, with the uncertainty being the standard deviation for the set of three measured values.

Table 1. Electrochemical surface area (ECSA) determinations for three MEA cathodes by *in-situ* cyclic voltammetry in the miniature PEM fuel cell test fixture

MEA number	ECSA from H adsorption / desorption, $\text{m}^2 \text{ g}_{\text{Pt}}^{-1}$	ECSA from CO stripping, $\text{m}^2 \text{ g}_{\text{Pt}}^{-1}$
MEA 1	37.3	59.1
MEA 2	39.0	59.2
MEA 3	39.1	59.5
Average	38.5 ± 1.0	59.3 ± 0.3

Figure 3 right shows another voltammogram for the same MEA, this time reflecting oxidation of adsorbed carbon monoxide. The initial scan in the negative direction shows an absence of HAD peaks, as expected for a Pt surface that is poisoned by CO, and the positive-going scan shows a large oxidative peak for CO oxidation, which upon integration and normalization by Pt mass and the factor of $420 \text{ } \mu\text{C per cm}^2$ for oxidation of adsorbed CO on platinum[34] gives an average ECSA value for three electrodes of $59.3 \pm 0.3 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$, again with the uncertainty as a standard deviation for the set of three measured values. The larger ECSA value from adsorbed CO oxidation is in agreement with prior work that has used both approaches to measure ECSA, and is thought to reflect some difficulty with drawing an

appropriate baseline to account for potential-dependent capacitive charging when integrating HAD peaks compared with the CO oxidation peaks.[35, 36] Also, variations in the surface coverage of adsorbed hydrogen and CO with electrolyte, including the presence / absence of Nafion, have been reported and could be responsible for some of our observed variance in ECSA values from HAD and CO oxidation.[37]

3.2 Ex-situ voltammetry.

Figure 4 shows *ex-situ* voltammograms for a carbon-cloth-based electrode prepared as described in section 2.5 and immersed in an aqueous sulfuric acid solution. This electrode is nearly identical to that from Figure 3; the major difference is that for the experiment in Figure 4

Figure 4. *Ex-situ* cyclic voltammetry of a carbon cloth disk electrode, similar to that shown in Figure 3, except that the electrode was mounted onto a glassy carbon disk electrode and studied at lab ambient temperature (approximately 23 °C) while immersed in aqueous 0.5 M H₂SO₄ solution. Left, hydrogen adsorption / desorption voltammetry, ECSA = 74.1 m² g_{Pt}⁻¹. Right, CO stripping voltammetry, ECSA = 87.3 m² g_{Pt}⁻¹. In both cases the solution was purged with argon gas prior to initiation of scan. Potentials are applied vs. a reversible hydrogen electrode at a scan rate of 50 mV s⁻¹.

the electrode is in electrical contact with a glassy carbon electrode and is immersed in a liquid electrolyte. It is instructive to compare the voltammograms in Figure 4 with those in Figure 3, because those in Figure 4 reflect contributions from all the Pt in contact with the liquid electrolyte, whereas those in Figure 3 reflect only the platinum in contact with the Nafion polymer electrolyte. The platinum ECSA values obtained from Figure 4 are approximately $74 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$ from the HAD method and $87 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$ from the CO stripping method. Both these values are significantly higher than the values obtained for MEA cathodes for which Nafion ionomer was the only electrolyte that could make contact with the Pt catalyst particles. From the ratio of ECSA values from *ex-situ* and *in-situ* measurements, we estimate that our relatively simple method for impregnating platinized carbon cloth electrodes with Nafion polymer electrolyte has resulted in between 50 and 70 percent of the Pt surface area being electrochemically accessible. This finding does not suggest a fundamental limitation on the amount of platinum that may be made accessible when using a Nafion electrolyte in the electrodes, and it is known that refinement of the techniques for integrating polymer electrolyte with electrodes can yield electrodes in which nearly all of the platinum is electrochemically accessible in the absence of liquid electrolyte. Rather, the significance of the results presented here is that they demonstrate a convenient way of studying platinum accessibility using small amounts of material in small electrodes for which it is relatively easy to ensure that the electrode material being studied in the *in-situ* and *ex-situ* voltammetry experiments is the same. Similar measurements could prove highly useful in research seeking to develop and evaluate new catalyst materials, and new ways of integrating catalyst and polymer electrolyte in electrodes.

3.3 Polarization curve testing.

Figure 5. Overlay of three polarization curves acquired for three independently-prepared MEAs in the miniature fuel-cell test fixture, using slow-scan cyclic voltammetry (1 mV s^{-1}) over a potential range from 1.0 V and 0.3 V applied to the oxygen-bathed cathode vs the hydrogen-bathed anode.

Polarization curves were acquired for cells with humidified hydrogen and oxygen feeds on the anode and cathode respectively, with potentiostatic control of the cell potential using an instrument designed principally for conventional electroanalytical measurements. Figure 5 shows an overlay of three polarization curves acquired for three independently prepared MEAs (the same three MEAs for which ECSA data are presented in Table 1) and studied sequentially in the same cell. The figure shows minor variations among the individual polarization curves but in general the curves are in excellent agreement, showing the expected shape for a hydrogen-oxygen PEM fuel cell. Current densities near 2 A cm^{-2} are observed at cell potentials near 0.3 V which was the lowest cell potential tested. Figure 6 presents one of these polarization curves

Figure 6. Overlay of a polarization curve (black, left axis) and a corresponding power density curve (red, right axis) for one of the MEAs from Figure 5. Peak power of approximately 0.7 W cm^{-2} was achieved at a current density near 1.5 A cm^{-2} at a cell potential of approximately 0.45 along with a power density curve that shows a peak power of 0.7 W cm^{-2} at a cell potential near

0.5 V. The performance metrics of these cells are good, particularly for the relatively low cathode platinum loading of $0.3 \text{ mg Pt cm}^{-2}$, but they are not quite current state-of-the-art, which is to be expected for a cell using un-optimized commercial catalysts at a relatively low cell temperature of 30°C . The achievement of superior catalyst and fuel-cell performance is always desired but it is not the main objective of this work. Rather, the objective of this work is to demonstrate diagnostic testing on MEAs and cells that required quite small amounts of material, including both catalyst and membrane, to conduct a complete fuel-cell test in the

absence of any liquid electrolyte. The results from Figures 4-6 show that this objective has been achieved.

It is useful to compare results obtained with the miniature test cell with results on an MEA fabricated using identical materials but in larger size, and tested in a larger test fixture. Figure 7 presents a polarization curve for a larger MEA, fabricated and tested as described in Section 2.8. The polarization curves showing in Figures 6 and 7 are similar to each other, with the

principal difference being found in the high-current region where currents are particularly strongly sensitive to details associated with gas transport, including flow-field dynamics. A key difference between the two cells is that the gas flow field in the miniature cell consists only of

the nickel foam gas diffuser element, whereas the flow field in the larger cell is of the traditional serpentine style in the graphite block current collector. The slightly lower currents in the high-current region of the polarization curve for the larger-area cell could reflect some concentration polarization for gases associated with the serpentine flow field. An *in-situ* voltammogram for this cell (shown in Supplemental Materials) in the hydrogen adsorption / desorption region showed the platinum ECSA for this cathode to be approximately $34 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$ which is approximately 10 percent lower than the value obtained for the smaller MEA. This difference could reflect some difficulty associated with drawing a proper baseline for the HAD ECSA determination, or to some difference in the penetration of Nafion into the electrodes for the larger vs. small cell. Further work to definitively identify causes for this discrepancy in ECSA values and also in the current densities over the full range of cell potentials would require studies on multiple larger-scale MEAs fabricated by nominally identical procedures to obtain statistically-significant results, and is beyond the scope of the present work.

3.4 Multi-potential-step testing.

Figure 8 presents a final data slide showing current-time traces for the three MEAs from Table 1. The experiment involves application of a staircase waveform to the cell, with the applied potential at the cathode initially held at 1.0 V vs. the anode. After twenty seconds the potential is adjusted by -0.05 V to 0.95 V, which is held for a further twenty seconds. This process is repeated until an applied potential of 0.30 V is reached. The Figure shows the variation of current with time for each potential step. The significance of these data is that they provide dynamical information on how current varies with time in different regions along the polarization curve. A polarization curve does not by itself contain any dynamical information;

Figure 8. Overlay of three current-time curves acquired for an applied potential program consisting of a series of potential steps of duration 20 seconds each, applied to the oxygen-bathed cathode between 1.0 V and 0.3 V vs the hydrogen-bathed anode. The applied potential was adjusted by 50 mV for each step.

one typically assumes that the current is passed at steady-state, and tests of this assumption are made by sequential acquisition of polarization curves, which should ideally result in the same curve being obtained in sequential experiments. In fact, this is often not the case, and many changes to the catalyst layer, for example from electrode flooding or drying, or from catalyst poisoning, are possible that could cause non-steady-state behavior. There have even been reports of bi-stability in fuel-cell output associated with cycles of electrode flooding and drying, which give rise to increased and decreased current, or to fluctuations in cell potential at

constant current.[38-40] The data in Figure 8 show that, for the present cells, the approximation that currents are steady state on a twenty-second timescale holds well for currents up to 80 mA.

4. Discussion.

The use of small electrodes and small cells offers some significant advantages relative to conventional fuel-cell testing for which the smallest cells that are regularly tested still have an active area of 5 cm^2 , over 100 times higher than the active cathode area for the cells in the present work. An obvious advantage of using small amounts of material is that fuel-cell testing can be conducted using newly created materials that may be available only in limited quantities. This issue is not very important when using commercial materials such as Nafion membranes and platinized carbon cloth electrodes but it could become quite important in new membrane and catalyst research, where a need often exists to screen materials, often multiple materials, that may be available in small amounts from new synthesis research.

Another advantage of using small amounts of material is that it can allow experiment replication to be more commonly included in testing protocols on new fuel-cell materials. Conventional testing with even the relatively small 5 cm^2 cells can require up to a gram of catalyst material (depending upon how the catalyst is used) and close to 100 cm^2 of ionomer membrane to make just one useable MEA. It is often the case that just one or two tests use up all of the material from an early-stage synthesis effort. New batches of material can be synthesized but there is then some uncertainty regarding how similar two material batches may be, which introduces doubt into the measurements when making comparisons. The ability to run many tests including replicates and controls with relatively small amounts of catalyst or ionomer material could provide important advantages in early-stage fuel-cell research.

Yet another advantage of the present cell configuration is that it should minimize losses associated with gas transport. Gases are delivered in larger-scale fuel cells via flow fields, often of a serpentine style, that present gases to the catalyst layer in patches, with some areas directly exposed to the gas flow stream and others positioned directly underneath the spots where the current collector / bipolar plate makes contact with the catalyst layer. The use of gas diffusion layers between the current collector / bipolar plate and the catalyst layer helps to mitigate problems with uneven gas transport but even so, to achieve even a simple understanding of mass-transfer effects in such a case one must consider the significant spatial variation of mass-transfer rate and current density that can be caused by spatial non-uniformity in the electrode contacts and gas flow. Spatial variations in current density are also possible due to gas depletion and differences in water content of gases at different locations along a flow channel. These effects could in fact be responsible for the lower current densities for the larger MEA (Figure 7) compared with the smaller MEA (Figure 6). Mass-transfer effects associated with flow fields are very important when seeking to maximize power-source performance but they can be quite frustrating when attempting to use fuel-cell test measurements diagnostically, to screen new materials and to learn about fundamental catalyst layer properties in the absence of mass transfer / concentration polarization effects. Due to the very small size of the active electrode region in the present cell configuration, gas transport rates should be quite high and show much less variation with spatial position compared with cells having a complex flow field. These high gas transport rates and the lack of spatial variation in current density are significant advantages when using these cells for diagnostic or material evaluation purposes.

A final advantage offered by the present cell configuration lies in the relatively small currents that are passed. For example, the current density of 2 A cm^{-2} reported in Figures 5 and 6 corresponds to an absolute current of just 90 mA, which is easily achieved using conventional instrumentation without worry about ohmic losses outside of the cell, for example in the leads and contacts. A similar current density in a 5 cm^2 cell would correspond to passage of 10 amperes of current, which in most cases would require the use of specialized instrumentation optimized for high currents, and could also produce heat that could affect the cell temperature. The fact that the present cells allow for a complete fuel-cell test with conventional instrumentation and without need for active cooling could enable useful fuel-cell testing to be done by more laboratories, using research infrastructure that is already present.

5. Conclusion

In summary, a miniature PEM fuel-cell test platform is described and used to perform diagnostic testing of fuel-cell membrane-electrode assemblies that were fabricated using small amounts of material, having active areas less than 0.1 cm^2 , with electroanalytical instrumentation and methods that are commonly available in most laboratories where electrochemistry research is pursued. Testing is performed in the absence of liquid electrolyte which reveals effects associated with transport processes, e.g. ion, electron and mass transport, within the electrode layers. Testing performed using this platform is complementary to RDE-based testing which focusses on electrocatalytic activity but does not provide information on transport processes in electrodes.

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