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# A convenient miniature test platform for polyelectrolyte membrane fuel-cell research

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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

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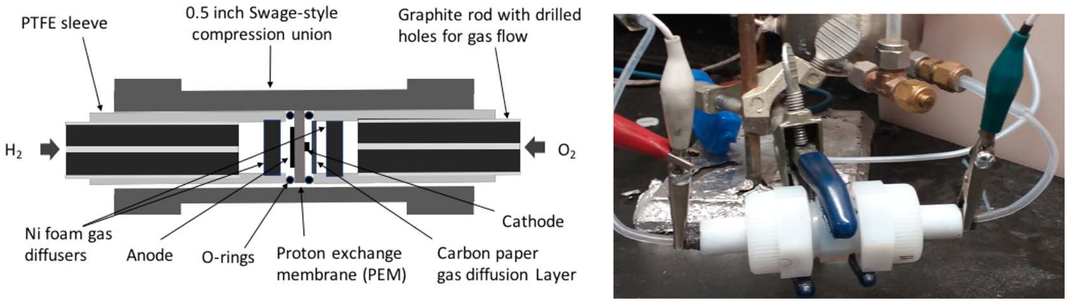

**Fig. 1.** Graphical and pictorial illustrations of the miniature PEM fuel cell test fixture developed for this work. Left, diagram of the assembled parts that make up the test fixture. Right, photograph of the text fixture in use. For clarity, the bottom photograph is shown without the heating tape that normally surrounds the cell when in use to allow for cell temperature control.

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-in.) diameter PEM disks onto which carbon cloth disk electrodes are attached by hot pressing. A single 10 × 10 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 × 8 $cm^2$ with electrodes approximately 2.5 × 2.5 $cm^2$, 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 in.) and was fabricated using simple tools and common materials purchased from commercial sources. Fig. 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 in.) 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 in.) 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 disks using hollow metal punches. For most experiments, the anode was a 0.79 cm (5/16 in.) diameter disk (area = 0.49 $cm^2$) and the cathode was a 0.24 cm (3/32 in.) 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