VII.D.4 Corrosion Protection of Metallic Bipolar Plates for Fuel Cells

John A. Turner (Primary Contact) and Heli Wang
National Renewable Energy Laboratory (NREL)
1617 Cole Blvd.
Golden, CO 80401
Phone: (303) 275-4270; Fax: (303) 275-3033; E-mail: john_turner@nrel.gov

Collaborating Coauthor: Michael P. Brady
Oak Ridge National Laboratory (ORNL)
P.O. Box 2008
Oak Ridge, TN 37831

DOE Technology Development Manager: Nancy Garland
Phone: (202) 586-5673; Fax: (202) 586-9811; E-mail: Nancy.Garland@ee.doe.gov

Start Date: 2004
Projected End Date: Project continuation and direction determined annually by DOE

Objectives

- Identify metallic bipolar plate materials and coatings that are low in cost, lightweight, corrosion resistant, gas impermeable, and amenable to mass manufacturing.
- Assemble corrosion systems for operation in a simulated proton exchange membrane fuel cell (PEMFC) environment and for the 100°–200°C range using polyphosphoric acid for material evaluation in this environment.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells & Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- A. Durability
- B. Costs

Technical Targets

This project is directed toward the DOE technical targets for bipolar plates of \$6/kW, weight of 1 kg/kW, corrosion rate of <1 $\mu A/cm^2$, and interfacial contact resistance of <10 $m\Omega\text{-}cm^2$ by 2010. Specific DOE bipolar plate targets for hydrogen (H_2) permeation rate, electrical conductivity, flexural strength, and flexibility have also been set, most of which are more relevant to graphite and composite bipolar plates than metallic bipolar plates.

To meet the cost and weight goals, the allowable alloy cost is estimated to be no greater than \$5–\$10/lb, with plate thickness of the order of 0.1 mm. Preliminary short-term corrosion tests in an aggressive simulated PEMFC environment and contact resistance tests suggest that protective nitride layers can be formed on iron-chromium (Fe-Cr) base alloys that can potentially be made in the \$5–\$10/lb range (not including nitridation and stamping costs). Long-term durability of these nitrided alloys remains to be demonstrated. The following table lists the status of some bare and nitrided alloys.

	Interfacial Contact Resistance (ICR)@140 N/cm^2 (newton/square centimeter), m$\Omega \cdot$cm^2	Current at –0.1 V, H$_2$ Purge, µA/cm^2	Current at 0.6 V, Air Purge, µA/cm^2	Cost, $/kW
349™	110	-4.5~-2.0	0.5~0.8	1.7
AISI446	190	-2.0~-1.0	0.3~1.0	1.9
2205	130	-0.5~+0.5	0.3~1.2	1.3
Nitrided AISI446	6.0	-1.7~-0.2	0.7~1.5	N/A
Modified AISI446	4.8	-9.0~-0.2	1.5~4.5	N/A
Target 2010	10 m$\Omega \cdot$cm^2	<1 µA/cm^2	<1 µA/cm^2	$6/kW

Note: Cost data were based on the base price of cold rolled coil from Allegheny Ludlum: $2.66/lb for 349™, $3.00/lb for AISI446, and $1.98/lb for 2205. By assuming 6 cells/kW for a PEMFC, that the dimensions of a bipolar plate are 24 cm × 24 cm × 0.010 cm (which gives a 400-cm^2 utilization surface area in a 0.1-mm-thick sheet), and a density of 8 g/cm^3, a single plate should weigh 50 g and 6 plates would be 300 g (<1 kg/kW).

Approach

- Gain understanding of the relationship between alloy composition and bipolar plate performance.

- Evaluate nitrided alloys in PEMFC environments, determine best alloy compositions(s) for PEMFC bipolar plate application, optimize nitride formation, and evaluate the level of protection achieved by corrosion and fuel cell testing.

- Evaluate new alloys and possible coating materials and methods.

Accomplishments

- We made significant gains in understanding and improving the nitrided surface formed on low-cost Fe-Cr base alloys, with short-term corrosion and contact resistance measurements indicating behavior equal to that of the nitrided 50:50 nickel: chromium (Ni-50Cr).

- Nitriding conditions were shifted to match the industrial applications, and excellent results were obtained for nitrided stainless steels in corrosion and interfacial contact resistant tests.

- Conducting fluorine-doped tin oxide (SnO$_2$:F) coatings on low-cost stainless steels were shown to reduce the corrosion rate significantly, providing promising results.

- We have established the high-temperature corrosion assembly and identified specific parameters for high-temperature testing.

- We tested bare stainless steels and industrial graphite bipolar plate materials in 170°C phosphoric acid (H$_3$PO$_4$) and established a baseline.

Future Directions

- Continue NREL/ORNL collaboration on alloy development and nitridation, complete optimization of nitrided surface on Fe-Cr base alloys, and provide guidance for further improvement.

- Investigate new alloy compositions and coatings and modify coating parameters for improved performance.

- Select candidate austenitic- or ferritic-based stainless steels and complete optimization of the baseline alloy composition range to provide a basis for scale-up activities.

- Investigate bare alloys, coated steels, and nitrided alloys in a high-temperature simulated phosphoric acid fuel cell (PAFC) environment.

- Carry out further NREL/industrial collaborations.

Introduction

The bipolar plate is one of the most important components in PEMFCs. Thin metallic bipolar plates, especially those made of specialty stainless steels, offer the potential for mechanical strength, gas permeability, reduced weight/volume, significantly lower cost, and better performance compared to machined graphite bipolar plates, offering a pathway toward high-speed, high-volume manufacturing. In PEMFC environments, a passive film naturally protects stainless steels. Although this passive film protects the steel from further corrosion, it also leads to high surface electrical resistance, degrading the performance of the fuel cell. If the surface layer could be made conducting, it would not only protect the underlying metal plate from corrosion, but would also provide a conducting pathway for the flow of current.

Approach

For this work, we are applying our expertise in stainless steel alloys and corrosion testing, in collaboration with ORNL, to evaluate nitride metal samples. Our approach has already led to the filing of a joint patent application for the nitridation of AISI446. We will continue our survey of current commercially available alloys to determine the best combination of alloy composition and additives. The combination must yield acceptable corrosion resistance and excellent surface contact resistance. The advantage of our approach is that if the coating develops pinholes or is damaged during manufacturing, the underlying material will passivate and not have a significant impact on stack performance. We will then suggest new alloys for additional coating experiments. We will continue to characterize conducting oxides as coatings. NREL has considerable experience in conductive oxides and their high-speed application through our work in photovoltaics. Because we are not interested in the optical transparency for this application, we can focus on optimizing these materials for high conductivity and corrosion resistance.

Our work on high-temperature membranes has led to inquires from industry about the performance of metals in the temperature range of 100°–200°C. With some modifications, our system is capable of operating in this temperature range, so we have made the necessary changes to allow operation at higher temperatures and have begun the characterization of the stainless steels. In addition, we will test the nitrided steels in this environment. We have initiated a study of graphite material in this environment to set a baseline.

Results

Work in fiscal year (FY) 2005 was divided into three areas: (1) identification of alloy compositions/nitridation conditions that lead to protective Cr-nitride formation on Fe-(20-30)Cr based stainless steels; (2) characterization of the SnO_2:F coating on different stainless steels and their performance in PEMFC environments; and (3) initiation of a study of the behavior of the bare and nitrided stainless steels in a high-temperature (170°C) H_3PO_4 environment. Our work on nitrided and coated alloys is targeted at meeting DOE goals; testing in the high-temperature H_3PO_4 environment is designed to answer industrial inquiries.

It has been shown that AISI446 generates a complex layer of an oxygen-nitrogen mixture with chromium and iron after thermal nitridation for 2 hr at 1100°C in pure nitrogen gas (N_2). This kind of layer also showed excellent corrosion resistance and low internal contact resistance (ICR) in PEMFC environments. This already led to a joint ORNL-NREL record of invention. From the points of view of economic and industrial feasibility, the same steel was nitrided at a lower temperature and in a mixed atmosphere of N_2-4H_2, which is more amenable to industrial scale-up than pure N_2 for nitriding. Similar low ICR values have been obtained with such steel.

To identify the influence of alloying elements, we selected AL29-4C® steel, a superferritic steel with a simpler composition of Fe-29Cr-4Mo base, to be nitrided. AL29-4C® steel coupons were thermally nitrided at 800°–900°C in mixed N_2-4H_2. When nitrided in N_2-4H_2 at this temperature, the ICRs are very close to the values with nitrided AISI446 (Figure 1). ICR values for AL29-4C® nitrided at 1100°C in pure N_2 are shown for comparison. They are even lower than those for the AISI446 nitrided under the same conditions (Figure 1).
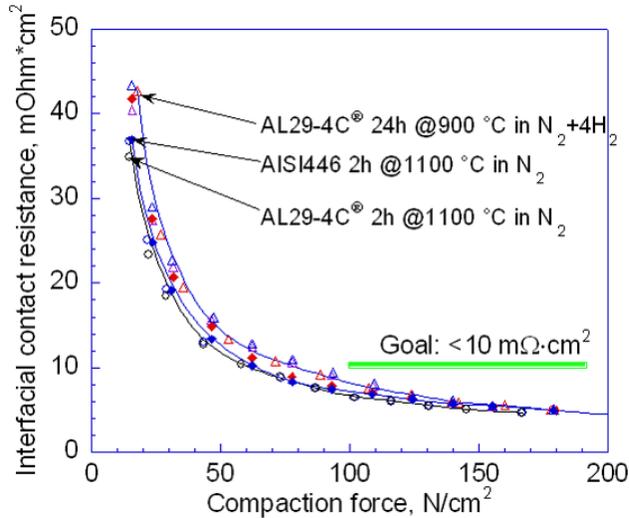
Figure 1. Low ICR of AL29-4C® alloy is obtained either at lower temperatures with longer processing times or at higher temperatures with shorter processing times. ICR for AISI446 nitrided for 2 hr at 1100°C in pure N_2 is shown for comparison. Note the gas used at the lower temperature.

Dynamic polarization curves for the nitrided AL29-4C® steel in 1 mole (M) sulfuric acid (H_2SO_4) + 2 ppm F⁻ at 70°C with different purging gases are almost identical, suggesting that the purging gases have little effect. When the nitrided alloy is potentiostatically polarized at –0.1 V, the current stabilizes at –3.0 µA/cm² at the end of the test. Cathodic current (minus) means that the surface is cathodically protected and the anodic dissolution of the electrode is eliminated. When the nitrided alloy sample is polarized at 0.6 V in the solution purged with air, the current is very stable at a very low level of close to zero (Figure 2). The stable current is approximately 0.3–0.5 µA/cm², in agreement with the dynamic polarization.

The ICR of the nitrided alloy in PEMFC environments increases after 7.5 hr of polarization (Figure 3), although it is still below the targeted 20 mΩ·cm² (2 times the goal of 10 as both faces of the coupon were measured). Only 1.2–1.3 ppm dissolved Fe are found in tested solutions by means of inductively coupled plasma (ICP) spectroscopy. This low level of dissolution indicates the excellent corrosion resistance of the nitrided alloy in PEMFC environments.
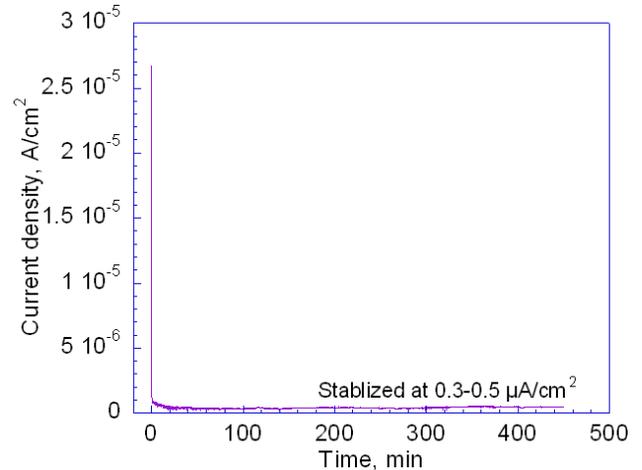

Figure 2. Anodic behavior of nitrided AL29-4C® alloy at 0.6 V in 1 M H_2SO_4 + 2 ppm F⁻ at 70°C purged with air. Nitridation was carried out at 900°C in N_2-$4H_2$.
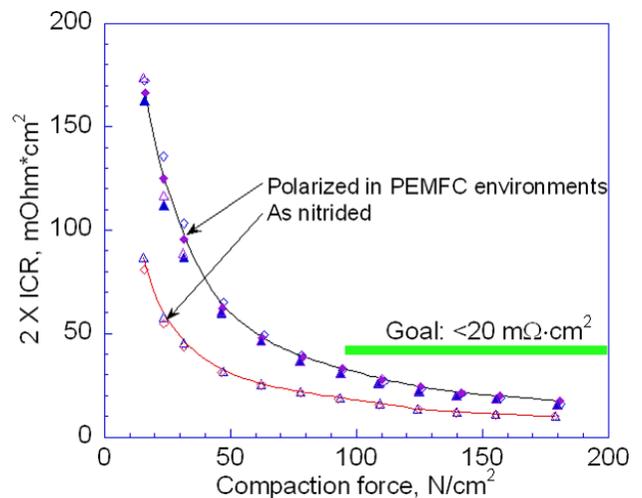

Figure 3. Influence of polarization on the ICR of AL29-4C® alloy nitrided for 24 hr at 900°C in N_2-$4H_2$. Note that 2 times ICR is used.

When coated with SnO_2:F, the substrate steel has a significant influence on the polarization curve. This certainly has implications for other coating schemes and alloys. Dynamic polarization measurements indicated that all of the coated steels have lower passivating currents than the bare ones in the hydrogen-gas-purged solution. Coated austenitic stainless steels (316L, 317L, and 349™) have higher passivating currents than the bare ones in air-purged

solution. Coated AISI441 and AISI446 also have lower passivating currents than the bare ones in the air-purged solution, and coated AISI444 has a higher passivating current than the bare one in the same condition.

In PEMFC environments, all the coated steels showed lower currents than the bare steels, indicating the beneficial effect of the coating. Coated AISI446 seems the best among all the coated steels with a very stable cathodic current of -1 to -3.5 $\mu A/cm^2$ in the PEMFC anode environment (Figure 4) and a stable current of 0 to 1.0 $\mu A/cm^2$ in the PEMFC cathode environment during the entire test period. Coated 317L and AISI444 showed promising lower currents in the PEMFC environments (Figure 4). The ICP analysis in Table 1 gives a better view about the dissolved metal ions. On the other hand, ICR values increase somehow compared with the bare steels. We believe that the air-formed oxide film on the surface of the steels may need to be modified to have better conductivity.

We tested graphite composite as a baseline because this material has been used as a bipolar plate
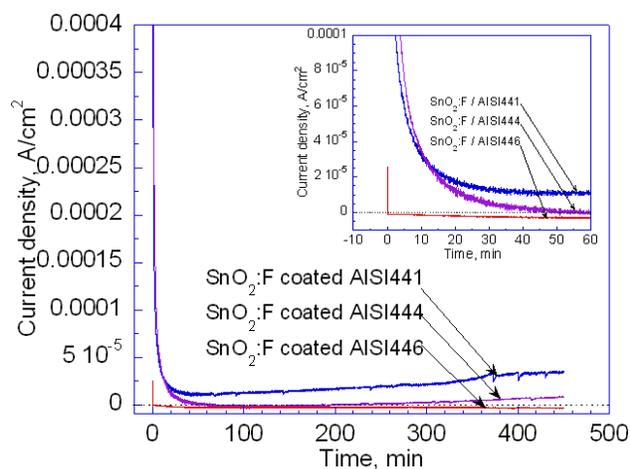

Figure 4. Transient currents of SnO_2:F-coated ferrite stainless steels at -0.1 V in 1 M H_2SO_4 + 2 ppm F^- at 70°C purged with hydrogen gas. The inset shows the transient currents in the first hour of the test.

in phosphoric acid fuel cells (PAFCs). Graphite composite coupons from PlugPower had low ICRs, 14–16 $m\Omega \cdot cm^2$ in the range of 100–200 N/cm^2, when pressure-tested at NREL. When polarized in

Table 1. Concentrations of Fe, Cr, and Ni Ions after Polarization in PEMFC Environments for 7.5 hr*

Material	PEMFC Anode Environment, ppm			PEMFC Cathode Environment, ppm		
	Fe	Cr	Ni	Fe	Cr	Ni
316L	21.18	4.60	2.49	9.02	1.94	1.41
317L	3.98	0.65	0.39	1.29	-	-
349™	1.70	0.12	-	1.47	-	-
SnO_2/316L	10.83	1.97	1.38	1.12	0.10	0.11
SnO_2/317L	4.03	0.69	0.56	0.87	-	-
SnO_2/349™	1.27	-	-	1.07	-	-
AISI441	622.9	135.7	1.07	462.8	101.2	0.95
AISI444	141.5	37.86	0.30	328.3	67.97	0.94
AISI446	1.46	-	-	0.99	-	-
SnO_2/441	24.15	4.51	-	330.3	68.72	0.60
SnO_2/444	12.70	2.09	-	64.42	13.73	0.22
SnO_2/446	1.24	-	-	0.98	-	-

*Analyzed by means of ICP with an average of 3 samples
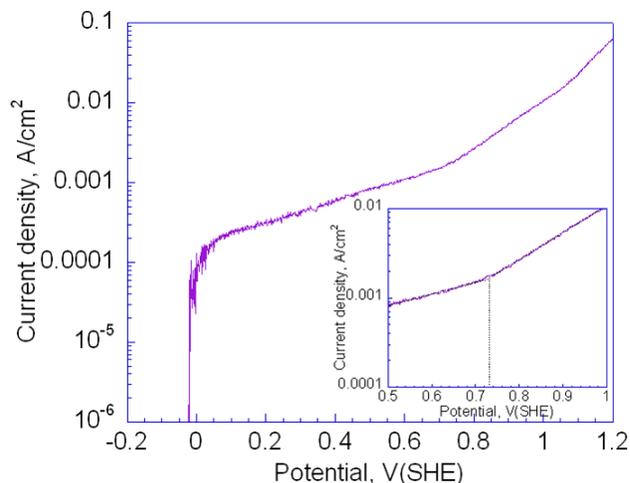(-) = not detected

Figure 5. Polarization curve for PlugPower's graphite in 98% H_3PO_4 at 170°C. The electrolyte was purged with pressured air during the test. The sample was stabilized at open circuit potential, followed by an anodic potential scan with a rate of 1 mV/sec. The inset shows the detail of the two Tafel regions.

Figure 6. Potentiostatic polarization of 316L steel in H_3PO_4 at 170°C purged either with hydrogen gas or air. The inset shows the current decay during the first 20 minutes of polarization.

98% H_3PO_4 at 170°C, two slopes were noticed (Figure 5). In electrolyte purged with air, the turning point was seen at approximately 0.73 V, suggesting that the highest potential could be utilized with a lower dissolution mechanism. Potentiostatic polarization at 0.1 V with a hydrogen gas purge indicates that current increases with polarization time, reaching 1.35 mA/cm^2 after 3 hr. Polarization at 0.7 V with an air purge showed an increase of current, followed by a stable current at 5.20 mA/cm^2. The higher current at the cathode side is the dominant part of the dissolution of the plate material.

We also investigated the behavior of three austenite stainless steels in this high-temperature environment. Passivation occurs for all the steels tested, regardless of the type of purging gas. The passivating peak currents, however, are on the order of tens of mA/cm^2, significantly higher than those in simulated PEMFC environments. Moreover, passivation current (the lowest current in the passivation region) is on the order of mA/cm^2. Both indicate the aggressive corrosive environment of the polyphosphoric acid at high temperature. Figure 6 shows the potentiostatic polarization of bare 316L steel in 98% H_3PO_4 at 170×C. In both air purge and hydrogen gas purge cases, current has a sharp decay
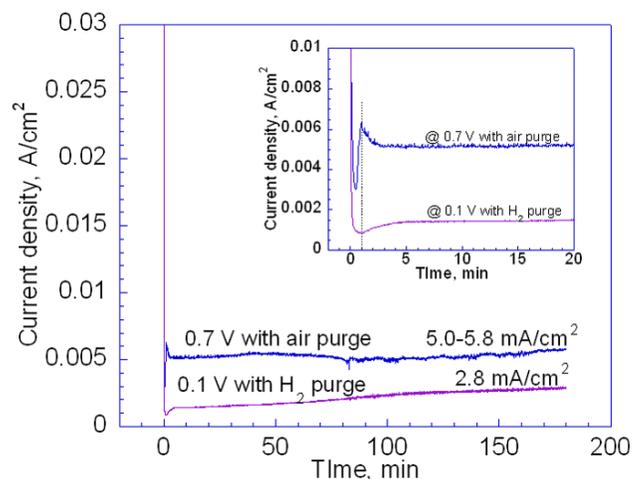
as soon as the potential is applied, followed by a recovery of the current. When the steel was polarized at 0.1 V in a hydrogen-gas-purged electrolyte, the current recovered gradually, then stabilized at 2.8 mA/cm^2 at the end of the test. When polarized at 0.7 V in an air-purged electrolyte, however, there is a secondary current peak at approximately 1 min polarization, followed by a reasonably stable current of 5.0–5.8 mA/cm^2. The reason for the peak is not clear at this time. The currents in both cases are comparable to those with graphite composites in the same environment. Lower currents registered with 904L steel in the same condition, at 1.15 and 1.30 mA/cm^2, respectively, possibly resulting from the higher alloying content (especially the Cr content).

Conclusions

• Nitrided stainless steels showed low interfacial contact resistance and excellent corrosion resistance in aggressive PEMFC environments. Nitrided AISI446 and Al29-4C® meet the DOE surface resistance goal and almost meet the corrosion rate goal. The total cost is not available because the test was conducted at the laboratory scale. Further research is needed to determine the best alloy composition(s) for PEMFC bipolar plate application and to optimize nitride formation.

- The conductive SnO_2:F coating is beneficial to the application of stainless steels for PEMFC bipolar plates. The coating significantly reduced the dissolution rate of the steels. Good corrosion resistance was obtained with coated 317L and AISI444. Improvement in the deposition parameters and procedures is needed to achieve lower contact resistance.

- High-temperature H_3PO_4 is very corrosive, with order of mA/cm^2 current obtained for both graphite composites and polarized austenite stainless steels. The cathode environment (0.7 V with air purge) is more corrosive than the anode one (0.1 V with hydrogen gas purge) for the materials tested. Work in this field is just beginning, and more evaluations are necessary.

Special Recognitions & Awards/Patents Issued

1. Brady, M. P., Wang, H., and Turner, J. A. (2005). Surface Modified Stainless Steels for PEM Fuel Cell Bipolar Plates. U.S. Patent Disclosure, February.

FY 2005 Publications/Presentations

1. Wang, H., Brady, M. P., Teeter, G., and Turner, J. A. (2004). Thermally nitrided stainless steels for polymer electrolyte membrane fuel cell bipolar plates. Part 1: Model Ni-50Cr and austenitic 349TM alloys. *J. Power Sources* 138, 86. Wang, H., Brady, M. P., More, K. L., Meyer H. M. III, and Turner, J. A. (2004). Thermally nitrided stainless steels for polymer electrolyte membrane fuel cell bipolar plates. Part 2: Beneficial modification of passive layer on AISI446. *J. Power Sources* 138, 79.

2. Brady, M. P., Tortorelli, P. F., Wang, H., Yang, B., Wilson, M., Garzon, F., Turner, J. A., and Buchanan, R. A. (2004). Thermally Nitrided Metallic Bipolar Plates for PEM Fuel Cells. Poster presented at the Fuel Cell Seminar, San Antonio, TX, October.

3. Wang, H., Teeter, G., and Turner, J. A. (2005). Investigation of a duplex stainless steel as polymer electrolyte membrane fuel cell bipolar plate material. *J. Electrochem. Soc.* 152, B99.

4. Turner, J. A. (2005). Hydrogen Fuel Cells. Presented to a group from the Federal Energy Management Program, Golden, CO, February.

5. Turner, J. A. (2005). Fuel Cell Technology and the Sustainable Hydrogen Economy. Presented at the University of Las Vegas, Las Vegas, NV, February.

6. Turner, J. A. (2005). Fuel Cell Technology and the Sustainable Hydrogen Economy. Presented at Augsburg College, Minneapolis, MN, April.

7. Wang, H., and Turner, J. A. SnO_2:F coated ferritic stainless steels for PEM fuel cell bipolar plates, submitted for publication in *J. Power Sources*.

8. Brady, M. P., Yang, B., Tortorelli, P. F., More, K. L., Wang, H., and Turner, J. A. Thermally Nitrided Metallic Bipolar Plates for Proton Exchange Membrane Fuel Cells. Invited presentation for the Materials for the Hydrogen Economy Symposium at the Materials Science & Technology 2005 Meeting, Pittsburgh, PA, September.