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Title: Technical Assistance to Developers

Author(s): Rockward, Tommy
Borup, Rodney L.
Garzon, Fernando H.
Mukundan, Rangachary
Spernjak, Dusan

Intended for: Report

Technical Assistance to Developers

R. L. Borup (Primary Contact), T. Rockward, F. Garzon, R. Mukundan, and D. Spernjak
Los Alamos National Laboratory
P.O Box 1663
Los Alamos, NM 87545
Phone: (505) 667-2823
E-mail: borup@lanl.gov

DOE Manager (Headquarters)

HQ: Nancy Garland
Phone: (202) 586-5673
E-mail: nancy.garland@ee.doe.gov

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Project End Date: Project continuation and direction determined annually by DOE

Objectives

- Support technically, as directed by DOE, fuel cell component and system developers
- Assess fuel cell materials and components and give feedback to developers
- Assist the DOE Durability Working Group with the development of various new material durability Testing protocols
- Provide support to the U.S. Council for Automotive Research (USCAR) and the USCAR/DOE Fuel Cell Technology Team
- FY2012 Specific Technical Objectives
    - Evaluate novel MPL materials
    - Develop of startup/ shutdown protocol
    - Test the impact of hydrophobic treatment on graphite bi-polar plates
    - Perform complete diagnostics on metal bi-polar plates for corrosion
    - Participate and lead efforts in the DOE Working Groups

Technical Barriers

This project addresses the following technical barriers from section 3.4.4.2 of the Fuel Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability
(B) Cost
(C) Performance

FY 2012 Accomplishments

- Evaluation of novel MPL materials showing improvements in mass transport and durability after hydrophilic treatment including the addition of C-nanotubes into the MPL.
- Successful completion of startup/ shutdown protocol tests.
- Testing of graphite bi-polar plate hydrophobic treatment showing better performance than an untreated graphite plate at low current densities (i.e. < 500 mA/cm^2).

- Application of several different diagnostics tools to study the titania coated stainless steel bi-polar plates corrosion resistance including fuel cell testing using a drive cycle protocol, AC impedance spectroscopy, and XRF elemental imaging. Participation in the DOE Fuel Cell Technical Team, co-chairing DOE Working Group meetings on Durability and Transport Modeling Working; presenting data and leading discussions on protocol development.

Introduction

This task supports the allowance of technical assistance to fuel-cell component and system developers as directed by the DOE. This task incl*u*des testing of novel materials and participation in the further development and validation of single cell test protocols. This task also covers technical assistance to DOE Working Groups, the U.S. Council for Automotive Research (USCAR) and the USCAR/DOE Driving Research and Innovation for Vehicle efficiency and Energy sustainability (U.S. Drive) Fuel Cell Technology Team. Assistance includes technical validation of new fuel cell materials and methods, single cell fuel cell testing to support the development of targets and test protocols, and regular advisory participation in other working groups and reviews. This assistance is made available to PEM fuel cell developers by request and DOE Approval.

Approach

The LANL fuel cell team has extensive knowledge and in-house analytical capabilities. These capabilities along with the personnel uniquely allow us to conduct thorough diagnostics and confirm results of existing and novel materials. In FY12, several requests were approved by the DOE to be completed under this task. Requests granted were the testing of novel MPL materials, development and testing a new startup/shutdown protocol, investigation of the impact of the hydrophilic treatment of a graphite bipolar plate material, and validation of enhanced corrosion protection of titania coated stainless steel bipolar plate materials. Detailed highlights of these projects will be further discussed below.

Results

In FY12, we completed testing, analysis provided feedback to both the collaborator and our DOE managers in four major component areas. Some selected findings were as follows:

1) Novel MPL materials were evaluated in a 50cm^2 fuel cell operating at 80 ºC, 100% RH, 50% air utilization and 28.4 PSIG back pressure. We tested three different cathode GDLs with varying MPL amounts and different carbon-fiber substrates. In particular, we the GDLs were a standard MPL with carbon/PTFE/binder (25BC), a standard MPL with a hydrophilic treatment (25BL), and a standard MPL with carbon nanotubes (25BN). The findings indicated that GDLs 25BL and 25BN both improved in the mass transport region compared to 25BC, but only 25BN resolved durability issues that surfaced in the others.

2) The startup/shutdown protocol was development in collaboration with Ballard Power and initial test were conducted. A graphical representation of the shut-down/start-up protocol is shown below in figure 1.
3) Below we show pictures of a plain bi-polar plate (left) and a hydrophobic-treated bi-polar plate (right). Water droplet contact angle measurements clearly demonstrated that the treated plate is more hydrophobic. Here we focus on their impact on PEM fuel cell performance when the treated bi-polar plates were used on the cathodes. We used identical tests materials, varying cathode plate types only, to allow for a direct comparison between the plates. An identical test protocol was performed on both plates. The test protocol included a 2 hr break-in period, VIs, and several full impedance spectra at various current densities using 100, 50, and 25% RH. The VIs showed at low currents densities (< 500 mA/cm^2) the hydrophobic plate performs slightly better, while extensive

flooding was observed at the higher currents. In order to further investigate this phenomenon, impedance spectra in the different regions of the VI were probed. At low current densities (< 20 mA/cm^2), the hydrophobic plate keeps the cathode catalyst layer and MEA more hydrated. This results in improvement in HFR and decreased catalyst sheet resistance. Product water keeps the catalyst layer hydrated especially at drier inlet RH operation. At higher current densities (> 1 A/cm^2), the use of a hydrophobic flow field became a detriment since it led to increased mass transport resistance due to less efficient water removal from the cathode catalyst layer and GDL.

4) We conducted a systematic study using several different diagnostics to test coated metal bi-polar plates for enhanced corrosion protection. This task was requested after the observation of small discolorations in the metal bi-polar plates after they were manufactured and coated and fuel cell tested. Initial speculation was that they were due to galvanic corrosion; however, our X-ray elemental mapping results did not indicate materials losses from corrosion. In fact, no significant change in the elemental composition of the titanium oxide coating or the underlying stainless steel was observed.

   The long term corrosion resistance of the treated plates still needs confirmation. Laboratory corrosion tests were developed to further characterize the corrosion resistance of the treated plates. However, the uncertainty of this material after being subjected to an aggressive drive cycle conditions in an actual fuel cell remained. There are currently no accelerated stress tests for corrosion testing bi-polar plates; however an existing DOE drive-cycle was modified and used in this task. The drive cycle called for 30K cycles going from 1A to 60A with a 30 seconds settling time at each current for a total of 500 hours. The fuel cell operates with hydrogen and air fixed flows (669 and 1773 sccm) at 80 ºC and slightly oversaturated humidification conditions and ambient back pressure. We performed beginning-of-tests and end-of-test diagnostics for comparisons, which included digital imaging, XRF elemental mapping of plates and MEA, initial and final VIRs, AC impedance and contact resistance measurements. The VIRs behaved similarly for the metal and graph plates. The digital imaging showed visible discoloration for the metal plates, more significant at the anode outlets. These changes were compared with the neutron imaging of a similar plate tested under similar conditions. The location of liquid water imaged by neutron scattering coincided with the regions of discoloration observed on the metal plates. Elemental mapping at the anode outlet show titanium loss from the outer layer. This is depicted below in Figure 4. Analyses of bi-polar plates (post test) indicates corrosion present on anode plate, typically where large amounts of liquid water was present and minimal corrosion present on cathode plate (but not zero). Analysis of MEAs shows small levels metal contamination of GDL/MEA which correlates to approximately ~ 5% - ~ 14% of the sulfonic acid sites if all of the cations reside inside the membrane; the cationic concentration was also higher where liquid water was present. In addition the contact resistance increased of the cathode plate.

Conclusions and Future Directions

In FY12 LANL

1) Performed characterization on tested metal bipolar plates, and performed in situ testing of metal bipolar and presented these results to DOE and the U.S. Drive Fuel Cell Tech Team.

2) Completed testing of new novel MPL layers with hydrophilic fibers to analyze the changes in mass transport.

3) Interacted with various organizations to discuss the proper protocols for shut-down/start-up in terms of durability testing (with results presented from University of Nancy at the AMR).

4) Measure the performance of novel bipolar plate flow field coatings.

5) Provided support for program interaction with DOE; such as the support for the co-chair of the DOE Fuel Cell Technologies Durability Working Group and the co-chair of the DOE Transport Modeling Working Group.

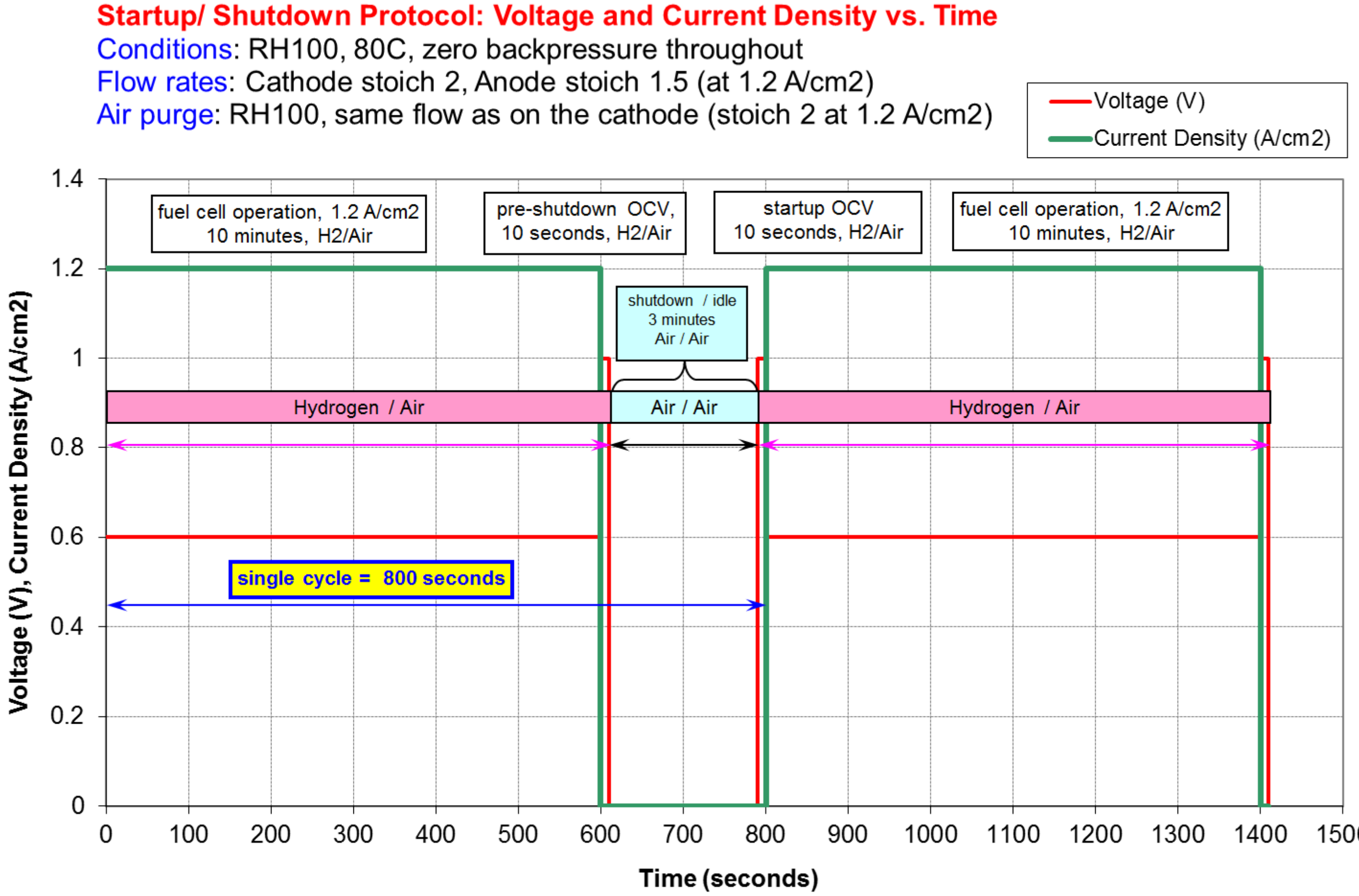
For FY13, we will continue to support fuel cell developers as directed by DOE to provide capabilities that exist at LANL not readily available to many developers.

Acronyms

MPL-Micro Porous Layer
DOE- Department of Energy
MEA-Membrane-Electrode Assembly
PEM- Proton Exchange Membrane
US CAR-United States Council for Automotive Research
DRIVE- Driving Research and Innovation for Vehicle efficiency and Energy
LANL- Los Alamos National Laboratory
XRF- X-Ray Fluorescence
VIR-Voltage-Current-Resistance
GDL-Gas Diffusion Layer

Figure Captions

Figure 1. Test results using newly developed startup/shutdown protocol.
Figure 2. Illustration comparing the contact angles of graphite bipolar plates: Plain vs. Treated.
Figure 3. Polarization curves measurements from a plain vs. treated bipolar plate operating at 100 and 25% RH.
Figure 4. Elemental mapping images of metal bipolar plates taken after completing a DOE drive cycle protocol.



Startup/ Shutdown Protocol: Voltage and Current Density vs. Time
Conditions: RH100, 80C, zero backpressure throughout
Flow rates: Cathode stoich 2, Anode stoich 1.5 (at 1.2 A/cm2)
Air purge: RH100, same flow as on the cathode (stoich 2 at 1.2 A/cm2)
Voltage (V)
Current Density (A/cm2)
fuel cell operation, 1.2 A/cm2 10 minutes, H2/Air
pre-shutdown OCV, 10 seconds, H2/Air
startup OCV 10 seconds, H2/Air
fuel cell operation, 1.2 A/cm2 10 minutes, H2/Air
shutdown / idle 3 minutes Air / Air
Hydrogen / Air
Air / Air
Hydrogen / Air
single cycle = 800 seconds
Voltage (V), Current Density (A/cm2)
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
Time (seconds)

Figure 1

Plain bipolar plate (graphite). **Treated bipolar plate.**

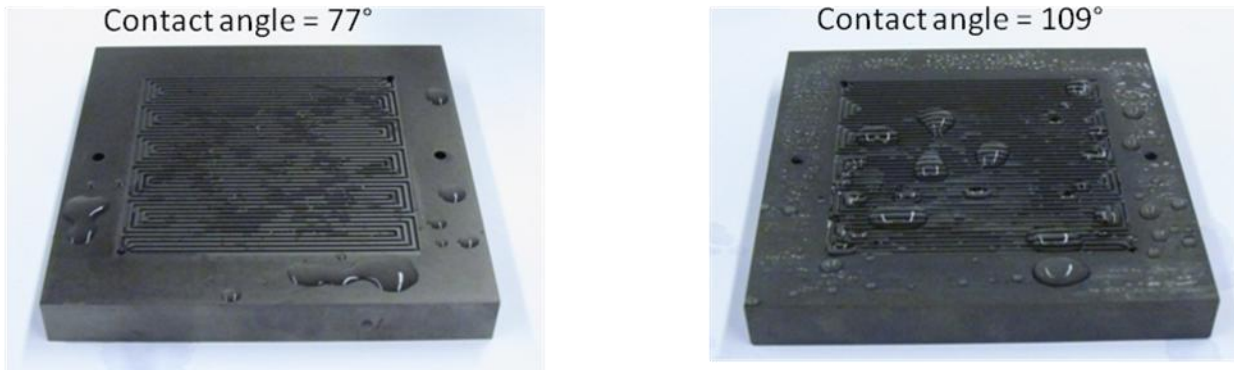


Figure 2

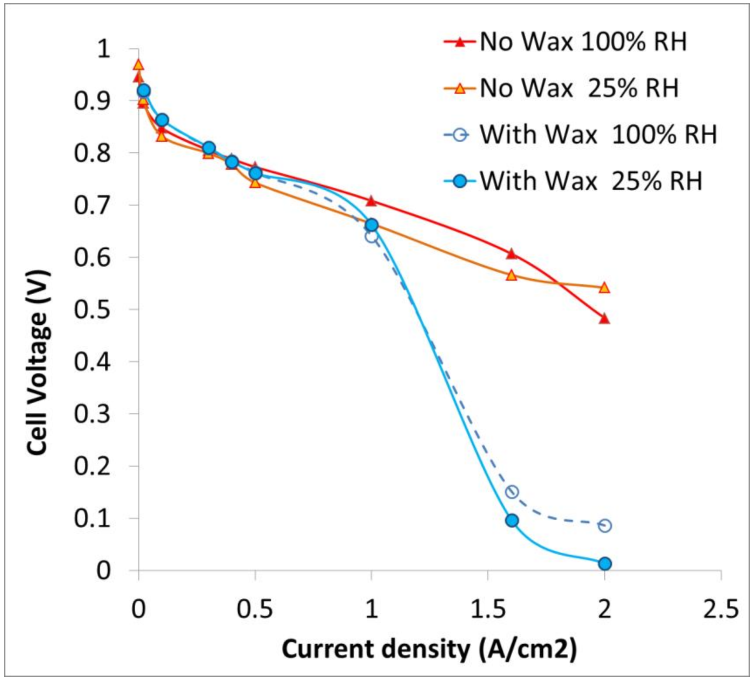

No Wax 100% RH
No Wax 25% RH
With Wax 100% RH
With Wax 25% RH
Cell Voltage (V)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.5
1
1.5
2
2.5
Current density (A/cm2)

Figure 3

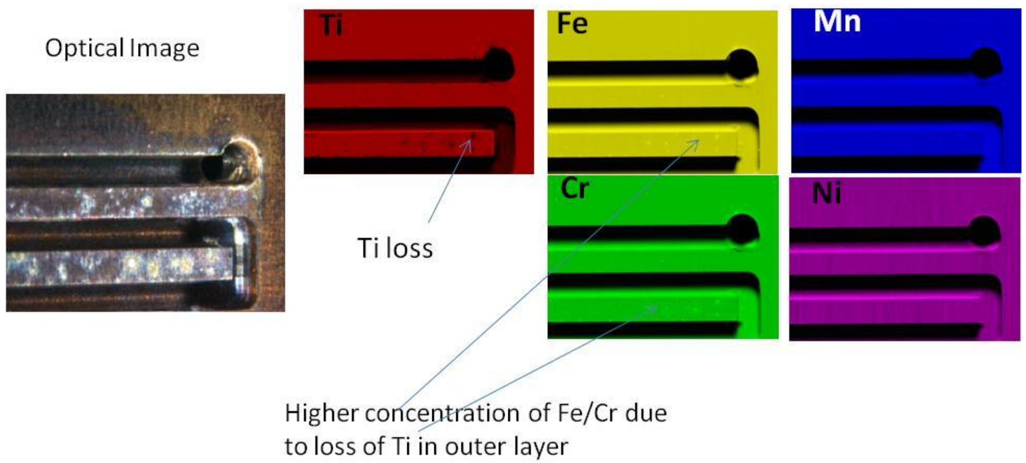

Optical Image
Ti
Fe
Mn
Cr
Ni
Ti loss
Higher concentration of Fe/Cr due to loss of Ti in outer layer

Figure 4