DOE CELL COMPONENT ACCELERATED STRESS TEST PROTOCOLS FOR PEM FUEL CELLS

(Electrocatalysts, Supports, Membranes, and Membrane Electrode Assemblies)

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Fuel cells, especially for automotive propulsion, must operate over a wide range of operating and cyclic conditions. The desired operating range encompasses temperatures from below the freezing point to well above the boiling point of water, humidity from ambient to saturated, and half-cell potentials from 0 to >1.5 volts. Furthermore, the anode side of the cell may be exposed to hydrogen and air during different parts of the driving and start/stop cycles.

The severity in operating conditions is greatly exacerbated by the transient and cyclic nature of the operating conditions. The cell/stack conditions cycle, sometimes quite rapidly, between high and low voltages, temperatures, humidities, and gas compositions. The cycling results in physical and chemical changes, sometimes with catastrophic results.

This document describes test protocols to assess the performance and durability of fuel cell components intended for automotive propulsion applications. The goal of this testing is to gain a measure of component durability and performance of electrocatalysts and supports, membranes, and membrane electrode assemblies (MEAs) for comparison against 2010 DOE targets contained in **Reference 1**. The resulting data may also help to model the performance of the fuel cell under variable load conditions and the effects of ageing on performance.

These protocols are intended to establish a common approach for determining and projecting the durability of polymer electrolyte membrane (PEM) fuel cell components under simulated automotive drive cycle conditions.

This document is not intended to be comprehensive as there are many issues critical to a vehicular fuel cell (e.g., freeze/thaw cycles) that are not addressed at this time. Additional issues will be addressed in the future. Furthermore, it is recognized that the cycles specified herein have not been fully correlated with data from stacks and systems operated under actual drive cycles. Therefore, additional tests to correlate these results to real world lifetimes is needed, including actual driving, start/stop, and freeze/thaw cycles.

The durability of catalysts can be compromised by platinum (Pt) sintering, particle growth, and dissolution, especially at high electrode potentials; this sintering/dissolution is accelerated under load-cycling. Durability of catalyst supports is another technical barrier for stationary and transportation applications of PEM fuel cells. Corrosion of high-surface area carbon supports poses significant concerns at high electrode potentials and is accelerated during start/stop cycles and during higher temperature operation (>100°C).

Membranes are another critical component of the fuel cell stack and must be durable and tolerate a wide range of operating conditions including low humidity (20 to 100% RH) and high

temperature (-40 to 120°C for transportation applications and >120°C for stationary applications). The low operating temperature and the humidity requirements of current membranes add complexity to the fuel cell system that impacts the system cost and durability. Improved membranes are needed that perform better and are less expensive than the current generation of polymer membranes.

The associated testing protocols and performance metrics are defined in Table 1 for electrocatalysts, Table 2 for catalyst supports, Table 3 for membrane/MEA chemical stability, and Table 4 for membrane/MEA mechanical durability, respectively, as derived from **References 2, 3, and 4**.

The specific conditions and cycles are intended to isolate effects and failure modes and are based on assumed, but widely accepted, mechanisms. For example, the electrocatalyst cycle is different from the support cycle because they suffer from different degradation mechanisms under different conditions. Similarly, membrane/MEA chemical degradation is distinguished from mechanical degradation.

Durability screening at conditions and under cycles different from those presented here-in are acceptable provided that the developer can provide:

- conclusive/convincing evidence that the cycle/conditions do not compromise separation/isolation of degradation mechanisms

- degradation rates extrapolated to the conditions/cycles prescribed here-in

Data to be reported, if applicable, at each point on the polarization curves and during steady-state and variable load operation include, but are not limited to:

- Ambient temperature and pressure
- Cell voltage
- Cell current and current density
- Cell temperature
- Cell resistance, if available (along with test conditions)
- Fuel inlet and outlet temperature
- Fuel flow rate
- Fuel inlet and outlet pressure
- Fuel inlet dew point
- Air inlet and outlet temperature
- Air flow rate
- Air inlet and outlet pressure
- Air inlet dew point
- Fuel and air quality
- Coolant inlet temperature
- Coolant outlet temperature
- Coolant flow rate

Pre-test and post-test characterization of cell and stack components should be performed according to developer's established protocols. At the discretion of the developer, tests should be terminated when hydrogen crossover exceeds safe levels.

References

1. Hydrogen, Fuel Cells & Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan, August 2006 (http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/)
2. Appendix D of DOE Solicitation **DE-PS36-06GO96017**
3. Mathias, M., et al, "Two Fuel Cells in Every Garage?" Interface Vol. 14, No 3, Fall 2005.
4. Mathias, M., et al, "Can Available Membranes and Catalysts Meet Automotive PEFC Requirements?" Presentation at ACS Meeting, Philadelphia, August 2004.

Table 1
Electrocatalyst Cycle and Metrics

Cycle	Step change: 30s at 0.7V and 30s at 0.9 V. Single cell 25 - 50cm^2	
Number	30,000 cycles	
Cycle time	60 s	
Temperature	80°C	
Relative Humidity	Anode/Cathode 100/100%	
Fuel/Oxidant	Hydrogen/N_2	
Pressure	150 kPa absolute	
Metric	**Frequency**	**Target**
Catalytic Activity*	Beginning and End of Life	≤60% loss of initial catalytic activity
Polarization curve from 0 to ≥1.5 A/cm^{2**}	After 0, 1k, 5k, 10k, and 30k cycles	≤30mV loss at 0.8 A/cm^2
ECSA/Cyclic Voltammetry	After 1, 10, 30, 100, 300, 1000, 3000 cycles and every 5000 cycles thereafter	≤40% loss of initial area
*Activity in A/mg @ 150kPa abs backpressure at 900mV iR-corrected on H_2/O_2, 100%RH, 80°C		
** Polarization curve per USFCC "Single Cell Test Protocol" Section A6		

Table 2
Catalyst Support Cycle and Metrics

Cycle	Hold at 1.2 V for 24h; run polarization curve and ECSA; repeat for total 200h. Single cell 25 - 50 cm^2	
Total time	Continuous operation for 200 h	
Diagnostic frequency	24 h	
Temperature	95°C	
Relative Humidity	Anode/Cathode 80/80%	
Fuel/Oxidant	Hydrogen/Nitrogen	
Pressure	150 kPa absolute	
Metric	**Frequency**	**Target**
CO_2 release	On-line	**<10% mass loss**
Catalytic Activity*	Every 24 h	≤60% loss of initial catalytic activity
Polarization curve from 0 to ≥1.5 A/cm^{2**}	Every 24 h	≤30mV loss at 1.5 A/cm^2 or rated power
ECSA/Cyclic Voltammetry	Every 24 h	≤40% loss of initial area
*Activity in A/mg @ 150kPa abs backpressure at 900mV iR-corrected on H_2/O_2, 100%RH, 80°C		
**Polarization curve per USFCC "Single Cell Test Protocol" Section A6		

Table 3
MEA Chemical Stability and Metrics

Test Condition	**Steady state OCV, single cell 25 - 50cm^2**	
Total time	200 h	
Temperature	90°C	
Relative Humidity	Anode/Cathode 30/30%	
Fuel/Oxidant	Hydrogen/Air at stoics of 10/10 at 0.2 A/cm^2 equivalent flow	
Pressure, inlet kPa abs (bara)	Anode 250 (2.5), Cathode 200 (2.0)	
Metric	**Frequency**	**Target**
F^- release or equivalent for non-fluorine membranes	At least every 24 h	No target – for monitoring
Hydrogen Crossover (mA/cm^2)*	Every 24 h	≤20 mA/cm^2
OCV	Continuous	≤20% loss in OCV
High-frequency resistance	Every 24 h at 0.2 A/cm^2	No target – for monitoring
*Crossover current per USFCC "Single Cell Test Protocol" Section A3-2, electrochemical hydrogen crossover method		

Table 4
Membrane Mechanical Cycle and Metrics
(Test using a MEA)

Cycle	**Cycle 0% RH (2 min) to 90°C dewpoint (2 min), single cell 25 - 50cm^2**	
Total time	Until crossover >10 sccm or 20,000 cycles	
Temperature	80°C	
Relative Humidity	Cycle from 0% RH (2 min) to 90°C dewpoint (2 min)	
Fuel/Oxidant	Air/Air at 2 slpm on both sides	
Pressure	Ambient or no back-pressure	
Metric	**Frequency**	**Target**
Crossover*	Every 24 h	≤10 sccm
*Crossover per USFCC "Single Cell Test Protocol" Section A3-1, pressure test method with 3 psig N_2		

Excerpts from: **USFCC Single Cell Test Protocol July 13, 2006**
(http://www.usfcc.com/resources/technicalproducts.html#form**)**

Section A3) Leak Testing

Step one, Pressure Test Method is required. The Electrochemical Hydrogen Crossover Method, Step 2 can be performed in addition to Step 1 for comparison, but is not required.

1) Pressure Test Method: Refer to Leak Check Procedure, Single Cell, USFCC Document Number 04-070 using the pressure settings outlined below,

a) External leaks:

i) Check for sealing leaks using equal 25 psig N_2 on the anode and cathode.

ii) With cell pressurized and gas inlet/exits blocked, a leak is determined when gas pressure drops 1 psi over 10 minutes.

b) Crossover leaks:

i) Check for crossover leaks from anode-to-cathode and cathode-to-anode using 3 psig N_2 on the anode and cathode, respectively (*This point was reworded for clarification.*)

2) Electrochemical Hydrogen Crossover Method:

The testing procedure for hydrogen crossover is based on an electrochemical detection of the molecular hydrogen passing through the membrane. For that purpose, the assembled cell is purged with hydrogen at the anode side and with nitrogen at the cathode side. In this mode, the fuel cell anode serves as reference and counter electrode and the fuel cell cathode acts as the working electrode (three-electrode arrangement). Under these conditions, a voltammogram is recorded. The detected current resulting from the oxidation of molecular hydrogen at the fuel cell cathode is determined.

a) Recommended Equipment:

i) The following equipment is recommended. Equivalent may be used. Record manufacturer, model and settings for actual equipment used.

ii) Princeton Applied Research Potentiostat/Galvanostat, Model 273

b) Assembled Cell Operating Condition:

i) Cell temperature approximately 24°C (room temperature)

ii) Gases at 100% relative humidity

iii) Stoichiometry Hydrogen = 1.5 @ 1 A/cm

iv) (Alternative: 4% Hydrogen/Nitrogen, 500 cc/min)

v) Nitrogen = 30 nl/h

vi) Pressure = 1 bar at sea level.

c) Testing Procedure for Probing the Cathode:

i) Purge the anode with hydrogen and the cathode with nitrogen for at least 30 minutes to equilibrate the cell.

ii) Set the range on the potentiostat to 0.1 to 0.4V and the scan rate to 2.0 mV/s.

iii) Run the scan and wait 10 minutes

iv) Repeat the Sweep Voltammetry.

v) The crossover current is determined from the steady state value at 300 mV. The recorded value is then translated into a hydrogen crossover in terms of ml/min-cm^2.

vi) Repeat the procedure twice to verify the result.

d) Potentiostat settings:

i) Current range: 2 Amps

ii) 1st potential: 100 mV

iii) 2nd potential: 400 mV

iv) Scan speed: 2 mV/s

e) Reference Values

i) The typical acceptable value for hydrogen crossover for Nafion 1135 membrane is 0.014 mL/min-cm^2, which is equivalent to 2 mA/cm^2; see Figure A2 (*not included here*).

Section A6) Polarization Curve Conditions and Load Sequence

a) General Procedure (*repeated polarizations as described in i and v below are not necessary for the purposes of the DOE Accelerated Stress Test protocol.)*

i) Perform Polarization Curve 1 three times. Then perform Polarization Curve 2 three times.

ii) Table A3 specifies the polarization curve load sequence, to be followed in the order presented.

iii) Maintain conditions for each sequence step for 20 minutes.

iv) A wait period of 10 minutes should be observed between polarization curves. During this period, return the gas flow rates to the equivalent of 10 stoich at 10 amps and set the current to 40 amps.

v) Conduct subsequent polarization curves until repeatable results are observed (within 5mV deviation of the previous polarization curve at 40A). Then record the next three polarization curves as reportable data.

Sequence Step	Current Density (mA/cm^2)
0	0 (use flows for Step 1)
1	100
2	200
3	400
4	600
5	800
6	1000
7	1200

Table A3: Round-Robin Polarization Curve Sequence

b) Polarization Curve 1

i) Polarization Curve 1 test conditions are listed below.

Fuel: Hydrogen, 1.2 Stoich, 100 % RH

Oxidant: Air, 2.0 Stoich, 100 % RH

Temperature (C): 80

Pressures (psig): 25

c) Polarization Curve 2

Polarization test conditions are listed below.

Fuel: Hydrogen, 1.2 Stoich, 100 % RH

Oxidant: Air, 2.0 Stoich, 100 % RH

Temperature (C): 60

Pressures (psig): 0 at outlet (~3psig back-pressure at full flow)