Non-PGM Target Update

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Joint CWG/DWG Meeting, Golden, CO, December 18th, 2013 - Agenda

10:30 am	**Welcome & introductions**
10:40 am	Relevance of RDE measurements of catalyst activity and durability to performance in an MEA and aqueous electrolyte alternatives to RDE - Rachel O'Malley (Johnson Matthey Fuel Cells, U.K.)
11:10 am	Experience from DOE-EERE-FCTO Projects regarding relevance of RDE measurements to MEA performance - Project PIs or designated project representatives
12:30 pm	**Working lunch:** RDE Activity and Durability Protocols for PGM catalysts - Debbie Myers (ANL) and Piotr Zelenay (LANL), discussion leaders
1:30 pm	Quantitative diagnostic tools presently available and their limitations; discussion of the information and tools needed for modeling at the macro-, micro-, molecular scales - David Harvey (Ballard), discussion leader
2:30 pm	Electrode morphology and carbon support changes during catalyst and electrode durability tests - Rod Borup (LANL), presenter & discussion leader
3:05 pm	**Break** (snack and beverages)
3:15 pm	RDE and MEA Protocols for non-PGM catalyst activity and durability evaluation - Piotr Zelenay, discussion leader
4:00 pm	Summary of February, 2013 DWG Meeting Results; Discussion of additional R&D needs related to PEMFC durability and catalysis - Donna Ho, Debbie Myers, Cassidy Houchins, and Working Group Co-chairs
4:30 pm	**Adjourn**

Points for Discussion of Non-PGM ORR Catalyst Targets

Originally discussed at CWG meeting in Arlington, VA on May 15th, 2013; updated before the combined CWG-DWG meeting in Golden, CO on December 18th, 2013:

- Areal current density the only measure of catalyst performance
- Areal current density specified at more than one point (voltage) to address both the catalyst activity (efficiency) and electrode-design (power) requirements, e.g. 0.85 V or 0.90 V (increase relative to the present reference voltage value) and 0.60 V, respectively.

  Example *(operation on O_2, 2017 target)**:** 100 mA cm^{-2} at 0.85 V and 1.0 A cm^{-2} at 0.60 V (measured)*
- Targets not tied to any specific catalyst loading, electrode thickness, etc.
- Volumetric activity no longer part of the metrics
- No *iR* correction
- No Tafel extrapolation to the reference potential (voltage)
- Fuel cell performance targets on O_2 (1.0 bar O_2) and air (0.2 bar O_2?)
- Realistic fuel cell operating conditions: humidification, stoich, etc.
- Durability targets consistent with those for Pt-based ORR catalysts
- Potential/voltage cycling in air rather than nitrogen
- No RDE target; a screening tool only

Comments on Targets

- The long-term non-PGM catalyst performance targets should be derived from the overall system targets that would allow a non-PGM fuel cell system to be competitive with an IC engine system, similar to how the Pt system targets were derived. The over-arching system targets that need to be met are **cost**, **efficiency**, and **durability**. A secondary target is **heat rejection** at rated power. (ANL)
- Given that for current Pt systems catalyst cost is ~ ½ the stack cost, if we had a zero cost catalyst we could have twice as much of all the other components and have a system with the same cost as the Pt system, i.e. the power density of a system with a "free" catalyst would need to be at a minimum ½ that of a Pt system. Assuming then that we meet the cost targets at the Pt system performance targets, and that the ratio of costs remains similar, this then implies the following loading independent target for non-PGM MEA performance at rated power (1000 mW/cm^2)/2: **500 mW/cm^2**. (ANL)
- The efficiency should match the Pt system efficiency. For the Pt system we have used an estimate of peak efficiency rather than determine efficiency at the most common point in the drive cycle. We have assumed to date that this is at ¼ power, and for Pt catalysts have used 0.80 V or 64% efficiency point. Therefore, the target for non-PGM performance should be 64% efficiency at ¼ power = 64% efficient at 125 mW/cm^2. This implies: **156 mA/cm^2 at 0.80 V**. (ANL)
- Durability needs to be the same as for a PGM system, *i.e.* loss of catalytic activity of **< 40%**, to meet end-of-life performance requirements after **5000 hrs**. (ANL)

Comments on Targets

- **Volumetric activity target should be eliminated entirely** and replaced by two design points: one at **0.80 V** and one at **0.60 V**. Those two design points should be for well-defined MEA test conditions, including membrane thickness. **No iR correction**. (UNM)

- Maintain 'volumetric activity target' but instead of using extrapolation to estimate activity at 0.80 V set for a measured activity target of **11 A/cm^3 at 0.90 V**, ***iR*-corrected**. (Equivalent to 300 A/cm^3 at 0.80 V assuming 70 mV/dec Tafel slope.) Consistent criteria between PGM and non-PGM will enable ready comparison. In addition, measurements at low current density will mitigate device variation, such as ohmic resistances. (GM)

- **Keep 0.80 V as a design point**, do not prematurely exclude new formulations and research groups. The practical design point of 0.60 V will assure appropriate physical morphology, "ink integration" and MEA design. Agrees with the expressed needs of three automotive manufacturers in Japan, claiming primary interest in the performance between 0.75 V and 0.55 V. (UNM)

- Strongly recommend testing under **fully humidified pure O_2 at higher stoich** (*e.g.*, **9.5**) in order to understand kinetics and local oxygen transport. Conditions recommended in the December CWG meeting (lower O_2 stoich or use of air) are inappropriate. (GM)

- **No target for RDE measurements**. (GM)

- Do we have/need 2017 **targets on air**? (Ballard)

- The non-PGM system needs to meet the **heat rejection requirement** of **$Q/\Delta Ti < 1.45$**. (ANL)

Summary of Targets Responses

- Areal current density the only measure of catalyst performance – **agreement**
- Areal current density specified at more than one point (voltage) to address both the catalyst activity (efficiency) and electrode-design (power) requirements, e.g. 0.85 V or 0.90 V (increase relative to the present reference voltage value) and 0.60 V, respectively.

  – **agreement** on two-point approach (with one exception when maintaining volumetric activity is preferred); **disagreement** on the value of higher voltage
- Targets not tied to any specific catalyst loading, electrode thickness, etc. – **agreement**
- Volumetric activity no longer part of the metrics – **disagreement**
- No *iR* correction – **disagreement**
- No Tafel extrapolation to the reference potential (voltage) – **agreement**
- Fuel cell performance targets on O_2 (1.0 bar O_2) and air (0.2 bar O_2?) – **no clear preference**
- Realistic fuel cell operating conditions: humidification, stoich, etc. – **agreement** on most, **disagreement** on stoich
- Durability targets consistent with those for Pt-based ORR catalysts – **agreement**
- Potential/voltage cycling in air rather than nitrogen – **no clear preference**
- No RDE target; a screening tool only – **agreement**

Proposed Non-PGM ORR Catalyst Activity Protocol (LANL & UNM): Fuel Cell

- **Test conditions:**
  - 25 or 50 cm^2; smaller cell, *e.g.*, 5 cm^2 allowed though not recommended
  - 80°C
  - O_2 and air, stoich 3.0
- **OCV measurement** at O_2 and air, stoich 3.0
- **Fuel cell polarization plots:**
  - O_2 and air, stoich 3.0
  - Current density (mA cm^{-2}) measured at two voltages: 0.90 V or 0.85 V and 0.60 V
  - As recorded data reported with HFR (Ω cm^2) provided at both voltages

Proposed Non-PGM ORR Durability Protocol: Fuel Cell

- **Test conditions:**
  - 25 or 50 cm^2; smaller cell, *e.g.*, 5 cm^2 allowed though not recommended
  - 80°C
  - N_2 and air (stoich 3.0)
  - Ionomer content and deposition method optimized for particular catalyst
- **Cycling:**
  - between 0.2 V and 1.1 V
  - 50 mV s^{-1}
  - 500, 1000, 5000, 10000, 30000 cycles
- **Reporting:**
  - OCV
  - Polarization plots (steady-state; up & down)
  - Current density (mA cm^{-2}) measured at two voltages: 0.90 or 0.85 V and 0.60 V
  - As recorded data reported with HFR (Ω cm^2) provided

Comments on Fuel Cell (MEA) Testing

- **Pressure** and **RH** should be defined and included. (IRD)
- Humidity? 60% and 100% **RH**. (Ballard)
- Spell out operating conditions – **RH**, **stoich** (maybe RH 50%, cathode stoich of ~ **2.5-3.0**). (LANL).
- Why such a **high stoichiometry**? A value of **1.8** or **2.0** would be more realistic and consistent with the desire to obtain data closer to application operation conditions. This comment also applies to the proposed durability protocol. (HNEI)
- What's the purpose of **cycling between 0.2-1.1 V**? Why not **0.2-1.0 V** (*i.e.* OCV)? In order to simulate high potentials for startup/shutdown one needs ~ 1.4-1.5 V. (LANL)
- Upper potential limit of 1.1 V may be too low. Since we are targeting automotive applications where startup/shutdown is such an important factor, it may be useful to set a higher UPL (*e.g.*, **1.3 V**) as an **additional target** for direct comparison with PGM catalysts. (Ballard)
- **Cycling between 0.2-1.1 V**: How to handle in case we are testing a promising catalyst but OCV is ~ 0.9 V? (IRD)
- Fuel cell testing: **Leave off** or **not state 5 cm^2**.(LANL)
- Recommend **reporting** current density at 0.70 V on H_2/O_2 and 0.60 V on H_2/air. (GM)
- Testing should be done under the **same conditions as specified for Pt MEA testing**. (ANL)

Comments on Fuel Cell (MEA) Testing

- **MEA test parameters.** (GM)

Electrode thickness	> 100 μm
Temperature	80°C
Data acquisition	4 min/point (average and report the last min)
Pressure (anode/cathode)	150 $kPa_{abs,out}$
Relative humidity	100%
Stoich	2.0/9.5

Note: *iR-correction is encouraged for H_2/O_2 measurements; no correction for H_2/air.*

Proposed Non-PGM ORR Activity & Durability Protocol: RDE

- **Test conditions:**
  - 0.2 mg cm^{-2}; 0.1 mg cm^{-2}; 0.6 mg/cm^{-2} (activity & durability)
  - 25°C, 0.1 M H_2SO_4
  - O_2 in activity testing; N_2 and O_2 in activity and durability testing;
  - Ionomer content and deposition method optimized for particular catalyst
  - 900 rpm
- **Cycling:**
  - between 0.2 V and 1.1 V vs. RHE
  - 50 mV s^{-1}
  - 0, 500, 1000, 5000 cycles
- **Reporting:**
  - OCP (at galvanostatic zero current)
  - Steady-state polarization plots – constant potential, 25 mV increments, from OCP down (constant-current plots also allowed)
  - Report change in $E_{1/2}$ (V) and change in OCP (V)

Comments on Electrochemical (RDE) Testing

- Mention **RRDE** to emphasize the need to assess peroxide levels. **Peroxide yield** should be reported. (HNEI)
- Report RDE results in both acid and **alkaline electrolyte**, *i.e.*, H_2SO_4 and KOH. (IRD)
- Should **perchloric acid** be considered instead of sulfuric acid to facilitate comparisons with Pt-based catalysts? (HNEI).
- Upper potential limit of 1.1 V may be too low. Since we are targeting automotive applications where startup/shutdown is such an important factor, it may be useful to set a higher UPL (*e.g.*, **1.3 V**) as an **additional target** for direct comparison with PGM catalysts. (Ballard)
- It is important to test catalysts with **different loadings** to evaluate possible impact on 2- or 4-electron transfer and the impact of oxygen diffusion within catalyst layers. (Ballard)
- For consistency with Pt/C research, use a rotation rate of **1600 rpm** and **0.1 M $HClO_4$** in RDE work. If H_2SO_4 is used the activity of NPMC will appear artificially higher than it truly is when compared to Pt/C. (Ballard)

Comments on Electrochemical (RDE) Testing

- **Test parameters** for activity measurements in RDE. (GM)

	Linear Sweep Voltammetery (LSV)
Electrolyte	0.1 M $HClO_4$ or 0.05 M H_2SO_4
RDE disk	GC
Counter electrode	Pt gauze/Au gauze/Graphite & frit-isolated
Reference electrode	RHE
Working electrode	Saturated O_2
Temperature	25^{o}C
Voltage Range	0.05 - 1.00 V
Scan Rate	5 mV/s
Scan Direction	Anodic (0.05→1.0 V)
# of Scans	Average of 3 scans per electrode; 3 electrodes per catalyst
Analysis	Kinetic current @ 0.90V (no background or ohmic correction)

Notes: *(1) LSV might not be appropriate with thick and high electrocapacitive non-PGM electrode. In this case steady-state measurement may be more appropriate. (2) In order to appropriately measure kinetic current on thin film, one must do a loading/thickness study to determine the film diffusion resistance prior to reporting the activity value.*

Summary

- Responses generally dependent on whether non-PGM catalysts are viewed as:

  (a) subject of continuing materials development and engineering effort

  or

  (b) relatively mature technology that should match Pt in real-life systems

- **Targets:** **(1)** majority favoring elimination of the volumetric activity target and its replacement it with current density targets at two voltage values; agreeing on the lower voltage (0.60 V), disagreeing on the higher voltage (from 0.80 V to 0.90 V); **(2)** majority favoring durability targets to be as those for Pt; disagreeing on the range of cycling; **(3)** no support for RDE performance targets; **(4)** no specific values proposed for areal current-density targets

- **Fuel cell (MEA) testing:** **(1)** cathode stoichiometry and cycling range the most controversial points; **(2)** RH to be specified (100% most popular)

- **Electrochemical testing:** **(1)** cycling range the most controversial point; **(2)** H_2O_2 should be reported; **(3)** various electrolytes proposed (issue unlikely to become controversial)