Novel Materials for High Efficiency Direct Methanol Fuel Cells

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Arkema Inc.

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Project ID# FC-063

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Overview

Timeline
- Start: May 1st, 2010
- End: June 30th, 2013
- Percent Complete: 56% (as of March 1st, 2012)

Barriers
- Durability
- Cost
- Performance

Budget
- Total Project Funding: $3,355 K
  - DOE Share: $2,488 K
  - Cost Share: $ 867 K
- Funding Received in FY10: $1,278 K
- Funding Received in FY11: $100 K
- Planned Funding for FY12: $700 K

Organization
- Project Lead
  - Arkema Inc.
- Partners (Subcontractors)
  - QuantumSphere Inc. (QSI)
  - Illinois Institute of Technology (IIT)

ARKEMA

Project Organization

David Mountz & Wensheng He - PIs
Project Lead

PEM Development and testing
MEA diagnostics and durability

Subcontractor

Catalyst development
MEA production and testing

Vijay Ramani - PI
Subcontractor

Development of composite membranes and characterization/diagnostics of MEAs

Relevance

- Project Objectives
  - Develop ultra-thin membranes having low methanol crossover, high conductivity, durability, and low cost.
  - Develop cathode catalysts that can operate with considerably reduced platinum loading and improved methanol tolerance.
  - Combine the catalyst and membrane into an MEA having a performance of at least 150 mW/cm^2 at 0.4 V and a cost of less than $0.80/W for the membrane and cathode catalyst.
- Targets

Characteristic	Industry Benchmark	Project Target	Current Status
Methanol Permeability (cm^2/s)	$1x3 \cdot 10^{-6}$	$5x10^{-8}$	$\leq 1x10^{-7}$
Areal resistance (Ωcm^2), 70 ºC	0.12	0.08	0.08
Catalyst Specific Power (mW/mg PGM)†	25	$\geq$ 50	115
Cathode PGM Loading (mg/cm^2)	2.5	$\leq$ 2	~1.3
Power Density (mW/cm^2) @0.4V*	90	150	120
MEA Lifetime (hours)*	> 3,000	5,000	In process

†RDE - 0.45 V & 70 ºC. *Conditions - 1M methanol at 60ÁC

Approach/Project Structure

Task 1 – Membrane Development

Barriers Addressed: Performance & Cost
- PVDF/Polyelectrolyte blend technology
- Composite Membranes
- Started May 2010 - 58% completed

Task 3 – MEA Development

Barriers Addressed: Performance & Durability
- Develop MEAs containing materials from Tasks 1 &2 and perform diagnostics
- Started mid 2011 - 50% completed

Task 2 – Cathode Catalyst Development

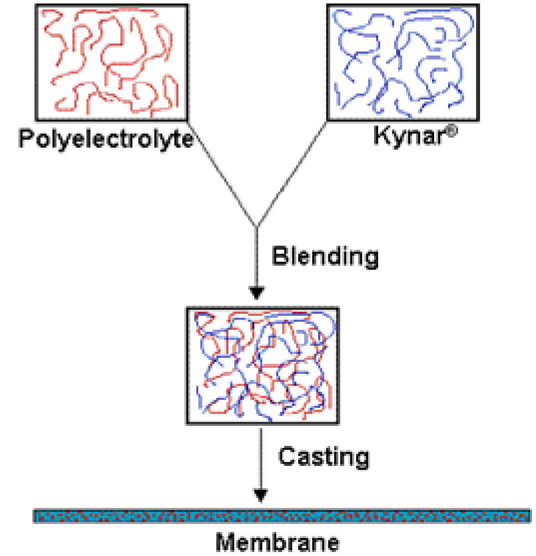
Barriers Addressed: Performance & Cost
- Pd-based co-catalysts
- 100% completed

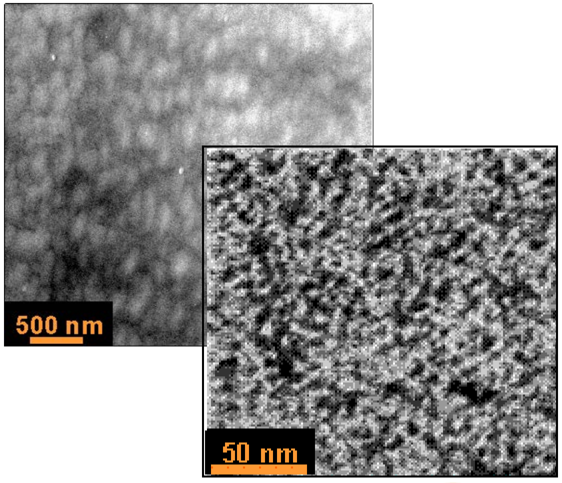
Task 4 – Durability Testing

Barriers Addressed: Durability
- Testing of MEAs from Task 3
- Includes constant current testing and post mortem analysis.
- Started Jan 2012 - 11% completed

Membrane Development

- Polymer Blend
  - Kynar® PVDF
    - Chemical and electrochemical stability
    - Mechanical strength
    - Excellent barrier against methanol
  - Polyelectrolyte
    - H^+ conduction and water uptake
- Flexible Blending Process
  - PVDF can be compatibilized with a number of polyelectrolytes
    - Latest generation taken to a pilot scale is M43, which is a baseline for this project
- Property Control
  - Morphology: 10-100s of nm domains
  - PVDF matrix optimization
  - Tailor the polyelectrolyte composition to minimize methanol permeation
  - Acidic inorganic additives





Technical Approach:

DMFC Cathode Catalyst Development

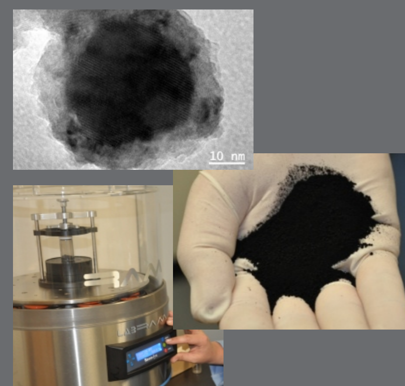
Utilize Pd-based nanoscale catalysts with Pt/C to:

- Increase mW/mg_{PGM} by suppressing methanol oxidation.
- Reduce Pt content → decrease $/W.

SYNTHESIS

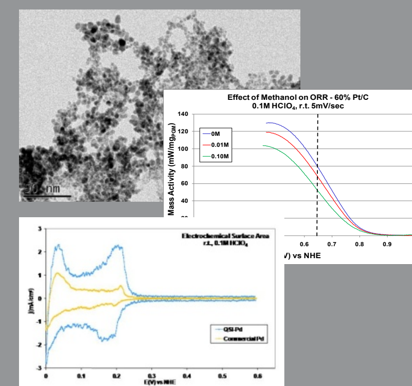
Gas-phase condensation (GPC) synthesis of unsupported Pd-based metal nanoparticles

DESIGN



Integration of Pt/C, alloys, core-shell structure, other co-catalysts, and processing methods

SCREENING



TEM, XRD, BET, TGA. CV and RDE w, w/o CH_3OH. Down-select based on activity, cost, durability

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Approach/ Project Milestones

	Milestones & Go/No-Go Decisions for 2011 and 2012	Date	Progress
Completed	Milestone (Task 1 - Membrane) Generation 1 membrane: areal resistance $\leq$ 0.080 Ωcm^2 and a methanol perm. coeff. $\leq 1x10^{-7}$ cm^2/s.	Jun 2011	Two families of membrane chemistry met the milestone requirements.
	Milestone (Task 2 - Catalyst) 50 mW/mg_{PGM} RDE specific power in presence of 0.1M CH_3OH (0.45V, 70^oC, 50% Pt reduction).	Jun 2011	Three Pd-based catalysts met the milestone requirements.
	Go/No-Go Decision (Task 3 – MEA Development) MEA performance of 120 mW/cm^2 @ 0.4V (60ÁC, 1M methanol).	Jan 2012	Achieved with Arkema membrane using either a commercial GDE or a lab-made cathode with commercial Pt catalyst.
	Deliverable (Task 3 MEA Development) MEA w/ 50% Pt reduction and catalyst specific power $\geq$ 50 mW/mg PGM.	Feb 2012	Met with the membrane/lab-made cathode that passed through the Go/No-Go decision.
Upcoming	Deliverable (Task 3 MEA Development) MEA performance of 150 mW/cm2 @ 0.4 V (60ÁC, 1M methanol).	Sep 2012	120 mW/cm^2 achieved thus far.
	Deliverable (Task 1 Membrane) Generation 2 membrane: areal resistance $\leq$ 0.080 Ωcm^2 and a perm. coeff. $\leq 5x10^{-8}$ cm^2/s.	Dec 2012	Membranes currently have 0.08Ωcm^2 resistance and a perm. coeff icient between $1x10^{-7}$ cm^2/s and $8x10^{-8}$ cm^2/s.

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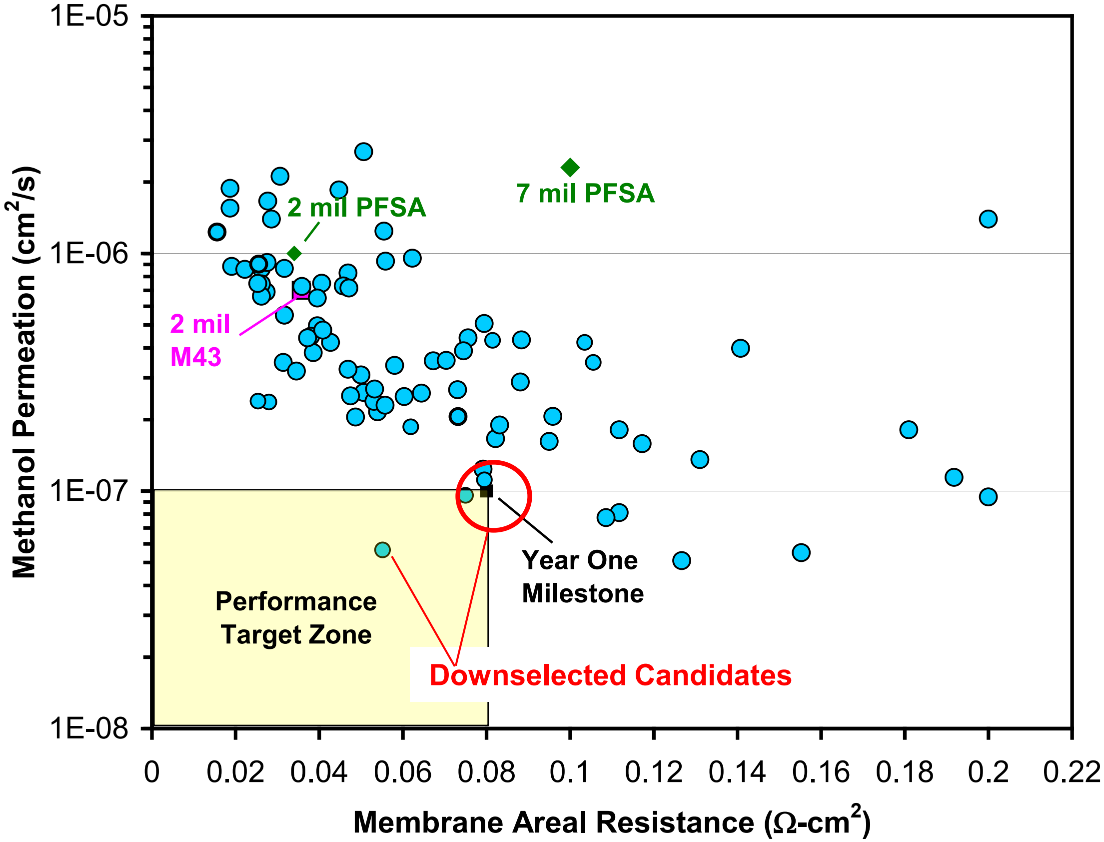
Technical Progress on Task#1:

Membrane Screening – Milestone #1



Key variables affecting performance:

- Polyelectrolyte loading, polarity, and acid content.
- Type and amount of crosslinking agent.

- Testing → PVDF grade, polyelectrolytes, crosslinking agents, and loading of components. Typical sample thickness is 1.1–1.5 mils.
- Two compositions were identified that met milestone requirements. Thickness range is 0.6-0.9 mils.
  - Another composition was downselected that didn't quite meet the milestone requirements, but still gave promising performance.

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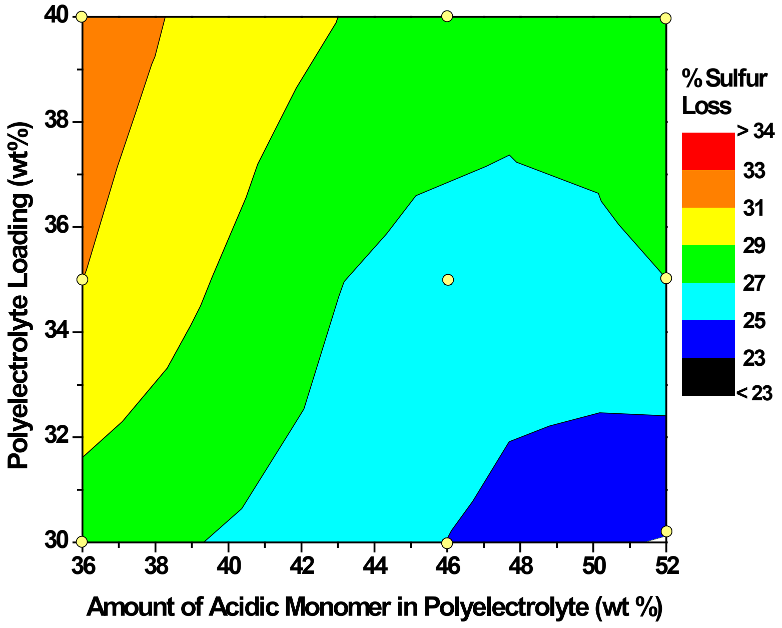
Technical Progress on Task#1:

Arkema Membrane Development – Current Status

- Downselected membranes were scaled up and supplied for MEA development.
- New polyelectrolyte generation is being developed for better performance membranes to meet the next deliverable (and potentially lower cost).
  - Polyelectrolytes show elevated leaching levels in the membranes compared to previous generations (earlier generations show 1-2% under same test).

Initial results from a short term durability test that shows the amount of sulfur removed from the membrane.



- Changing the method of crosslinking and molecular weight are being explored to address the sulfur loss.

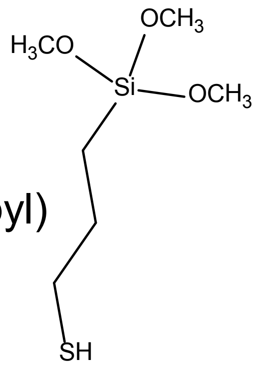
ARKEMA

Technical Progress on Task#1:

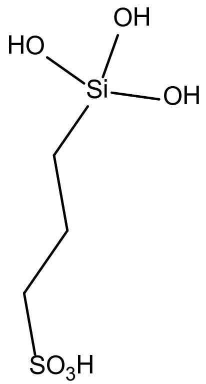
Membrane Development - IIT

- Work on incorporating sulfonated silica particles into a baseline M43 formulation was stopped in second half of 2011.
  - Particle agglomeration and settling was observed during the membrane casting that negatively affected membrane properties.

- In-situ sol-gel chemistry was pursued to address the issues encountered with using the sulfonated silica as an additive.
  - The first system studied was tetraethyl orthosilicate and (3-mercaptopropyl) trimethoxysilane (MPTMS). Composites were formed by adding the precursors to M43 membranes.



    Proton conductivity suffered from the use of hydrogen peroxide used to oxidize the mercaptan groups to sulfonic acid (polyelectrolyte degradation). Work was stopped.



  - 3-trihydroxysilyl-1-propane sulfonic acid (TPS) has been used more recently.

    The precursor rapidly condensed on the surface of the membrane, creating a non-uniform distribution of inorganic phase. More success was obtained when the precursor was added to the membrane solution, which was then cast into composite membrane.

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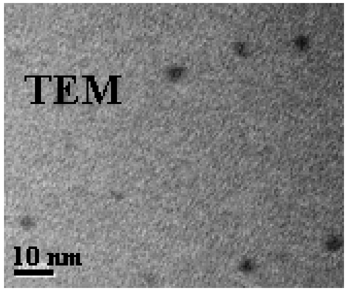
Technical Progress on Task#1:

Composite Membranes Prepared with TPS

- Preliminary results show the composites have particle size ≤ 5 nm. The TPS is dispersed at a moderate level in the membranes.



- Selectivity for the composites is not consistent due to the TPS uniformity. Further testing is in progress.

Membrane	Conductivity @70°C (mS/cm^{-1})	Permeability @ RT (x10^{-7} cm^{2}s^{-1})	Selectivity (x10^{-7} mS*s*cm^{-3})
Pristine Arkema Polymer	130 ± 5	7.5 ± 0.3	17
Arkema Polymer + 5wt% TPS	115 ± 7	6.1 ± 0.2	19
Arkema Polymer + 10wt% TPS	94 ± 6	7.4 ± 0.4	13
Arkema Polymer + 15wt% TPS	80 ± 11	3.5 ± 0.3	23
Arkema Polymer + 20wt% TPS	69 ± 4	5.6 ± 0.3	12

Technical Progress on Task#2:

Summary of Catalyst Activities

- Developed two metal alloy catalysts that show > 75 mW/mg PGM specific power in 0.1M MeOH.

Voltage (v. NHE)	Specific Power Calculated From RDE Testing (mW/mg PGM)			
	Pt/C only	Pt/C + Pd	Pt/C + PdNi	Pt/C + PdMn
0.8	5.2	3.9	6.1	6.2
0.75	16	21	25	28
0.65	**51**	**93**	**78**	**95**
0.55	88	115	116	129

- Synthesized 50g of nano-Pd catalyst and ~5g of each of the metal alloy catalyst for MEA development work.

- Initiated investigation of electrode fabrication techniques for MEA development.

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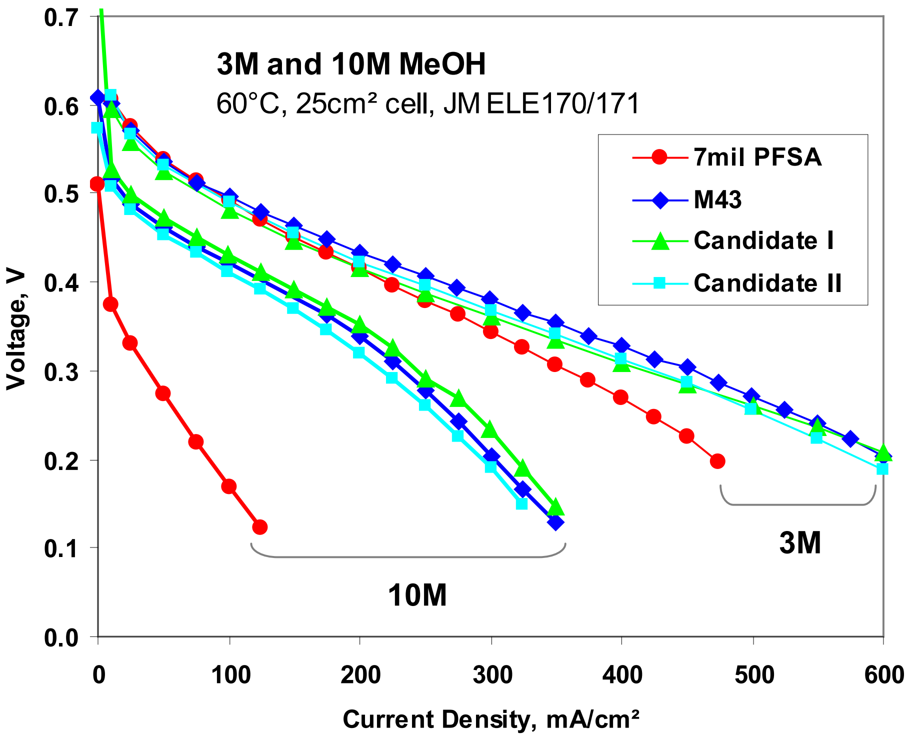
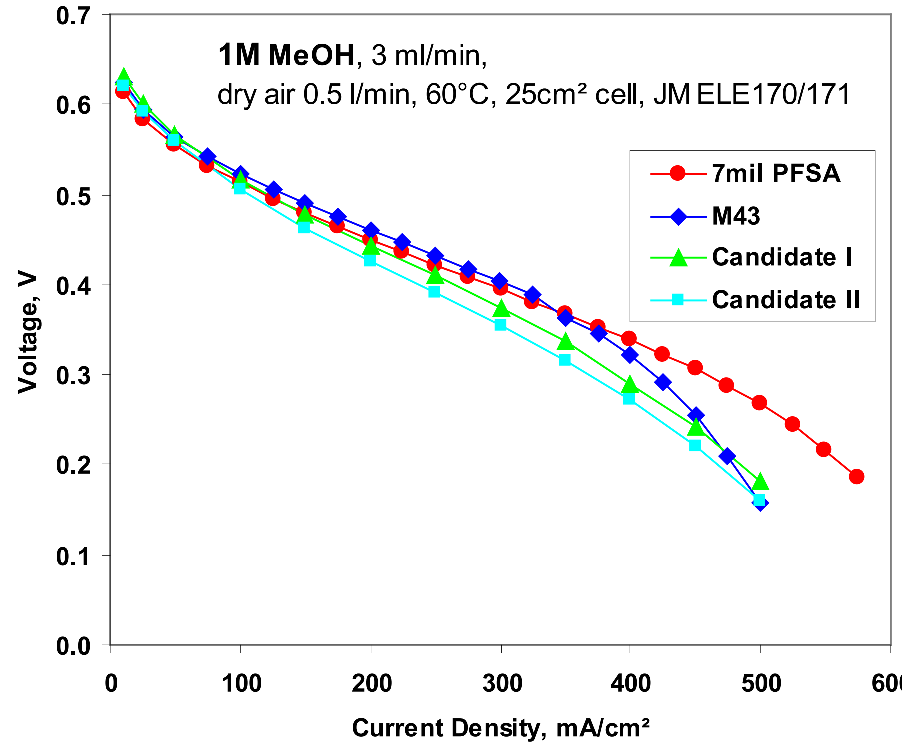
DMFC Performance of Downselected Membrane Candidates

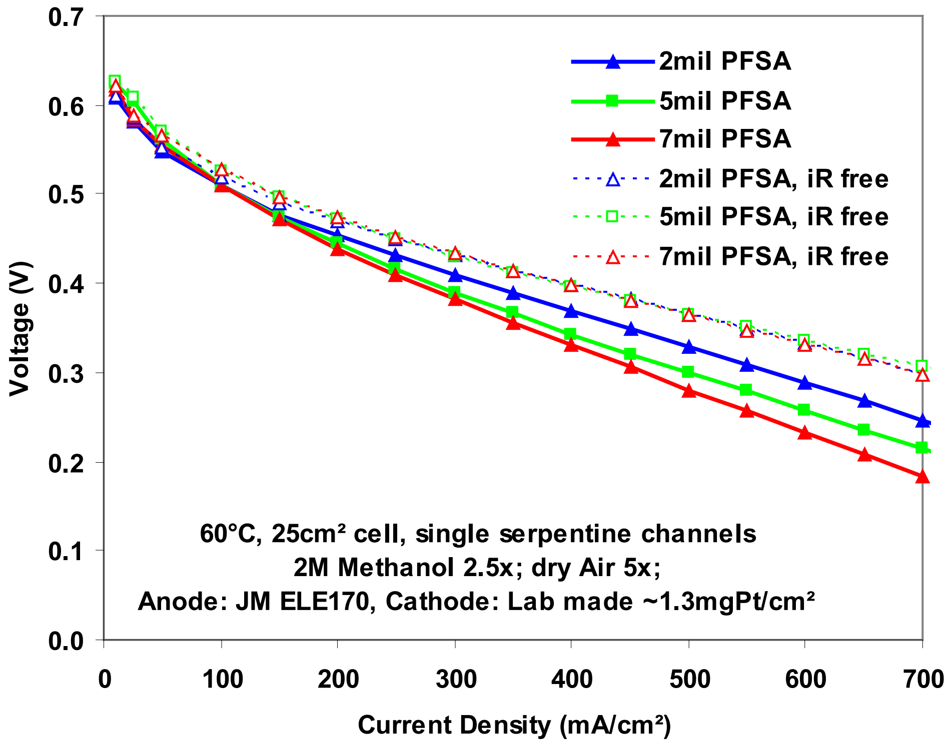




- All of the Arkema membranes outperform 7mil PFSA membrane in both 3M and 10M methanol tests, especially in 10M (some data shown last year).
- Less than expected performance from membranes downselected from milestone work at all methanol concentrations.

Technical Progress on Task#3:

Areal Resistance vs. Methanol Crossover



- Areal resistance has a larger effect than methanol crossover at methanol concentrations $\leq$ 3M in PFSA and Arkema membranes.
  - Trend explains why the downselected membranes have lower performance than M43, which has the highest conductivity of the Arkema membranes.
  - Modeling/MEA diagnostics of this effect have been initiated (collaboration with IIT).
- Less methanol crossover is still highly desired for high fuel utilization.

Membrane	Areal Resistance mOhm-cm²	Methanol crossover flux mA/cm²	Performance V@0.3A/cm²
2mil PFSA	75	330	0.41
5mil PFSA	134	246	0.39
7mil PFSA	168	186	0.38

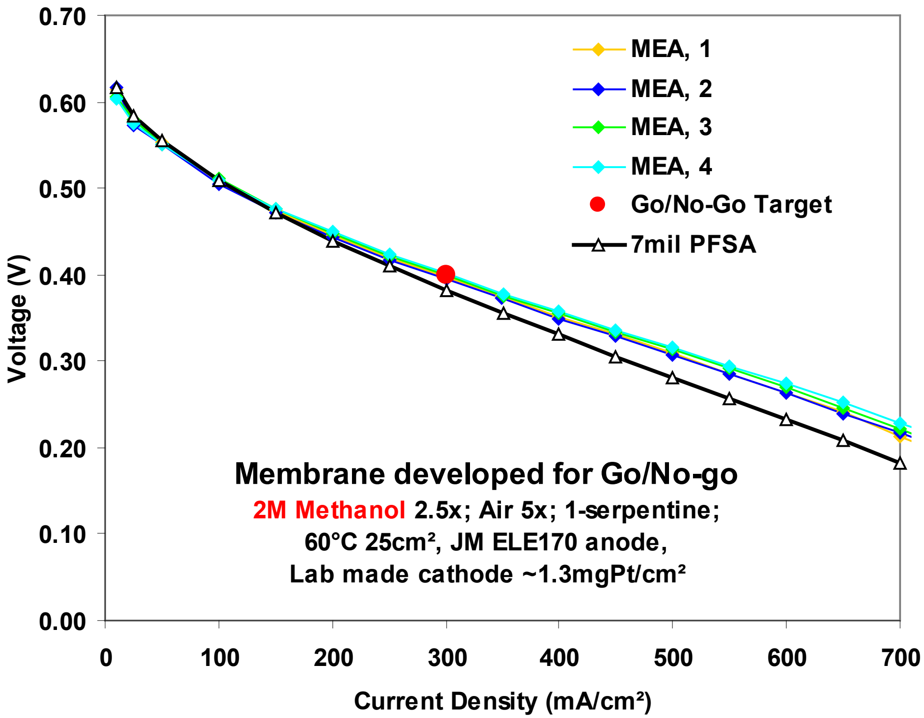
Go/No-Go Work: MEA Development

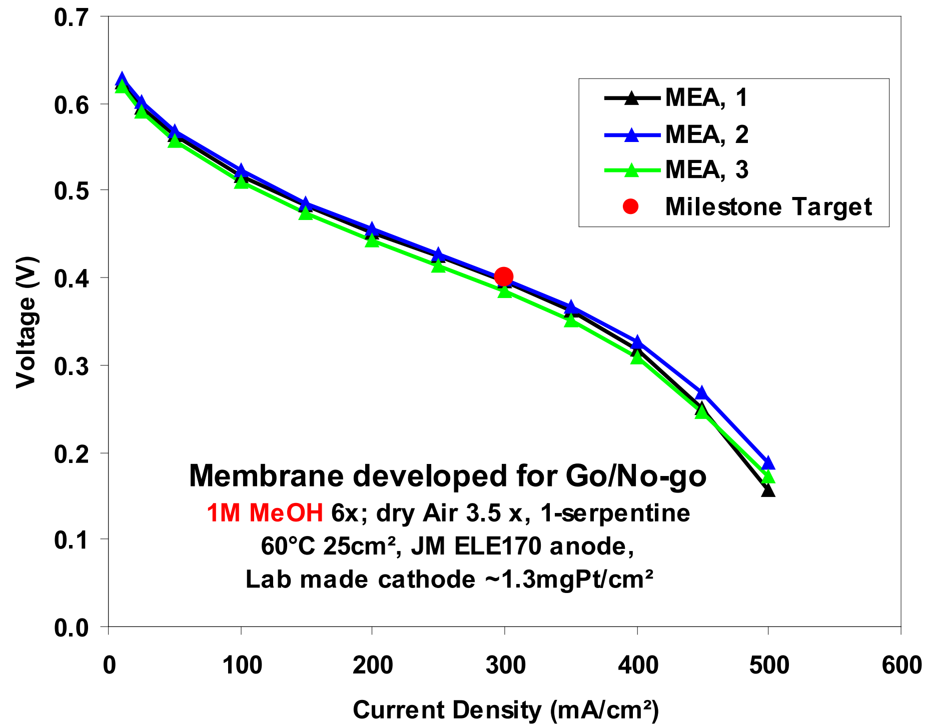
- Two-step Approach:
  - Step 1: Develop a cathode preparation process using Pt/C.
    - Understand preparation factors controlling performance.
    - Match the performance of state-of-the-art JM cathode.
  - Step 2: Develop cathode with QSI co-catalysts.
    - Improve methanol tolerance.
    - Reduce cathode cost.

- Results:
  - Step 1 was completed and the Go/No-Go target was achieved with main catalyst (JM Pt/C) only and with low PGM loadings.
  - Step 2: Performance decreased when Pd co-catalysts were added.

Technical Progress on Task#3:

Arkema MEA Performance: Go/No-Go Target



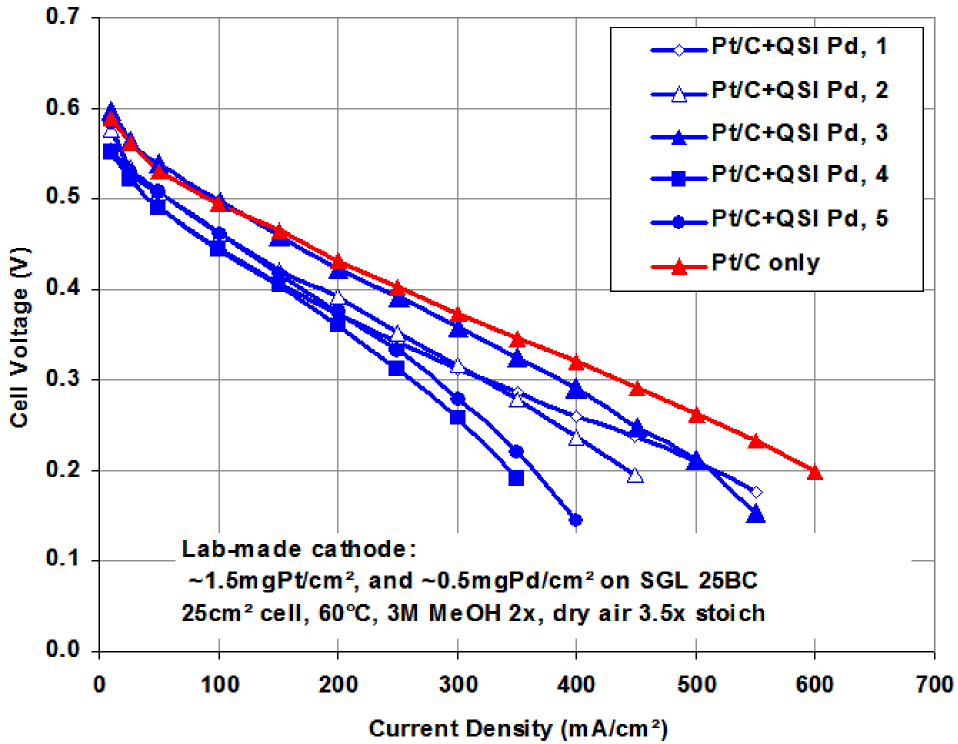


Go/No-Go target achieved with Arkema MEA in 1-2M methanol.

- Obtained with a membrane with slightly more polyelectrolyte than the membranes downselected from the milestone.
- Cathode made at Arkema with Hispec™ 9100 Pt/C catalyst, ~1.3mgPt/cm² loading.
- Cathode flow field changed from a triple- to single-serpentine pattern to improve mass transport & water removal.

Technical Progress on Task#3:

Membrane Performance with Pd-Based Co-catalysts



- Lower performance observed with all three Pd-based co-catalysts.
  - Pd catalysts showed a propensity to agglomerate.
  - RDE results did not correlate with MEA performance and could not be reproduced.
- Work stopped on the Pd catalyst development in the project.

Summary

- Membrane and catalyst compositions were developed that meet year one milestone requirements.
  - Efforts are underway to address the sulfur loss observed with the membrane generation currently under development.
- Composite membranes were successfully prepared with a sulfonic acid containing precursor and show improved selectivity compared to the previous composites.
- 120mW/cm^2 (Go/No-Go target) was achieved with an Arkema membrane and a commercial GDE or a lab-made GDE with commercial Pt catalyst in 1-2M methanol.
  - MEAs with Pt and Pd co-catalysts produce lower performance, presumably due to agglomeration.
  - Membranes with lower areal resistance were needed to to achieve the target.

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Future Work

- Membrane Development (Task 1)
  - Continue membrane development work to achieve target properties for the Q4/2012 deliverable (factors include areal resistance, methanol permeation and cost).
  - Modify the crosslinking and possibly the monomers used in the new polyelectrolyte generation to reduce sulfur loss.
  - Composite membranes: continue evaluating TPS as an additive, as well as explore new additives to enhance selectivity (rare-earth triflate).

- MEA Development (Task 3)
  - Continue development of MEAs and diagnostics with Arkema membrane to meet upcoming deliverable on MEA performance in Q3/2012 (150 mW/cm^2 @0.4V).
  - Factors to investigate include: alternative commercial Pt/C catalysts, increasing catalyst layer porosity/hydrophobicity and understanding the role of methanol crossover in performance.

- MEA Testing and Durability (Task 4)
  - Continue baselines studies and testing of MEAs from Task 3.

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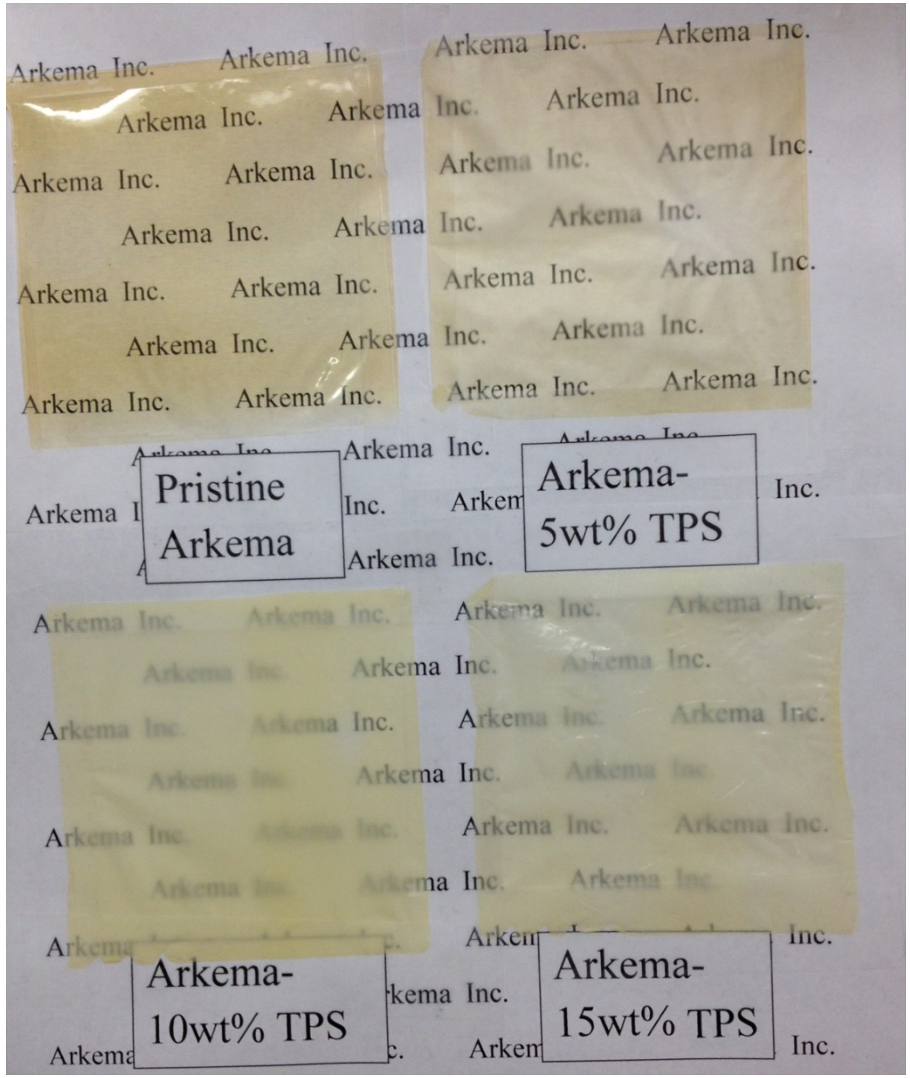
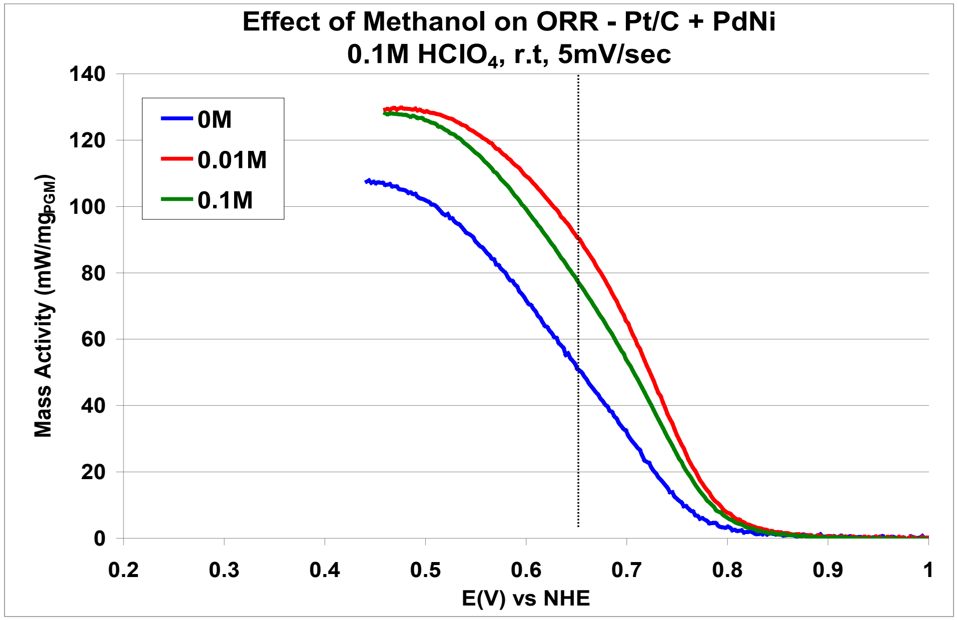
Technical Back-Up Slides

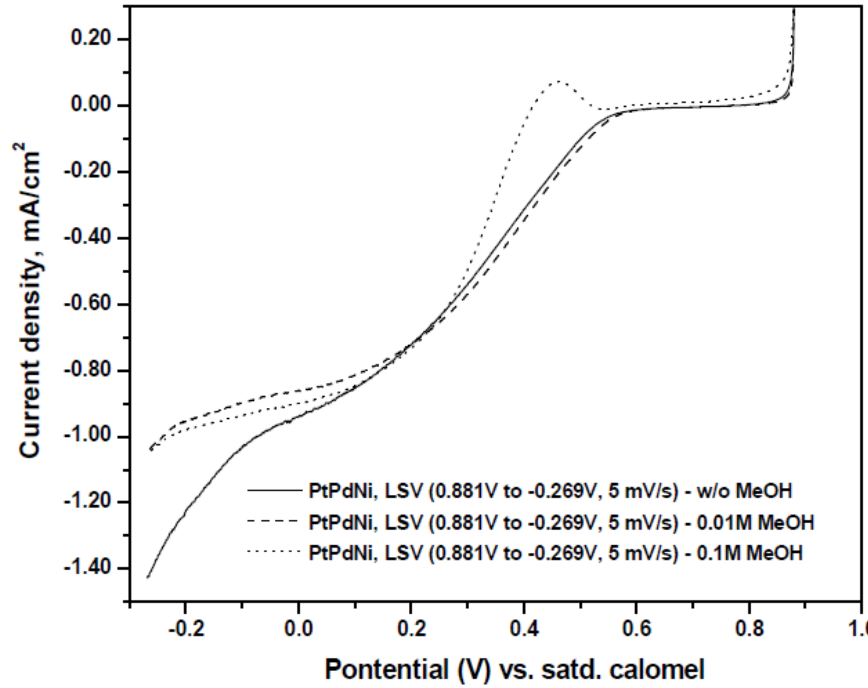
Composite Membranes With Different TPS Loadings



RDE Test Results on PdNi Catalyst



QSI results on Pt/C + PdNi

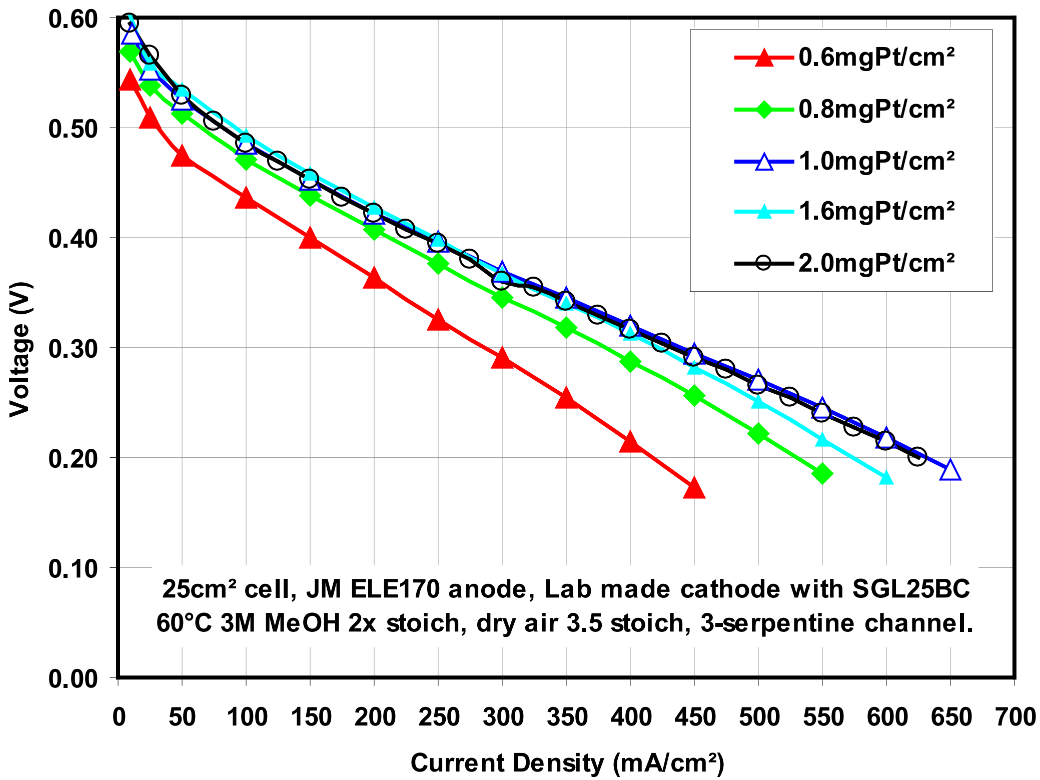


IIT results on Pt/C + PdNi

- RDE screening test results did not correlate to MEA results.
  - RDE test conditions may not simulate actual cathode in MEA testing.
- Discrepancies between RDE results at QSI and IIT.
  - QSI RDE results showed significantly better performance with methanol than no methanol case for Pt/C+PdNi catalyst. While IIT results showed same or reduced performance when adding methanol.

Effect of Pt loading – M43 Baseline

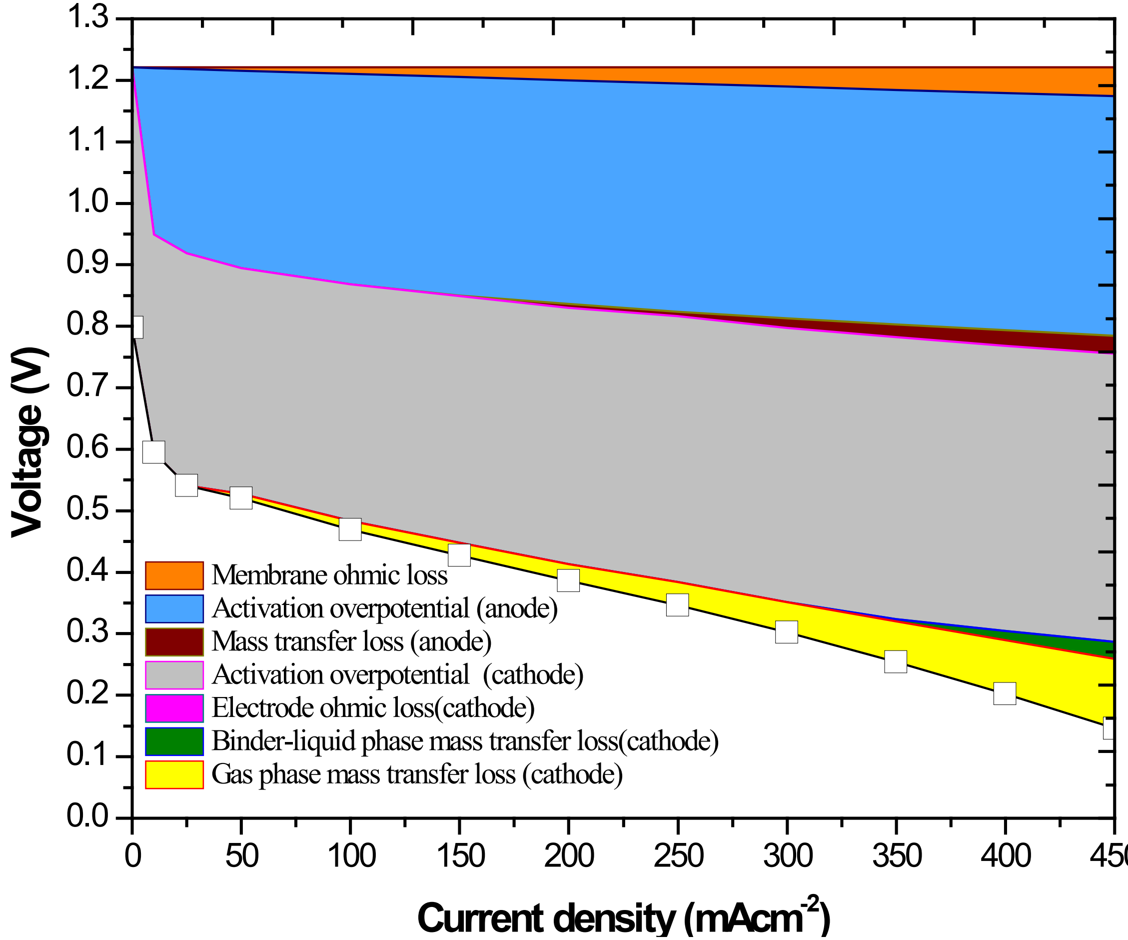
Relevant to Deliverable #3: MEA w/ 50% Pt reduction and catalyst specific power ≥ 50 mW/mg PGM.



- Performance is unchanged for cathode loadings from 1 to 2mgPt/cm².
- Cathode loadings ≤ 0.8mgPt/cm² lead to reduced performance.
- Similar trends for both Arkema and PFSA membranes.

MEA Diagnostics (IIT)

- Polarization curve analysis technique based on Williams et al demonstrated by IIT.
  - Enables detailed breakdown of all the major contributions in MEA performance losses.
  - Used to trouble-shoot the performance issues of lab-made cathodes at IIT.
- Incorporating the effect of methanol crossover was not included in this analysis, but is planned for future work.



Unoptimized lab-made cathodes showed higher gas-phase mass transfer losses (yellow) than commercial electrodes.

M. V. Williams, H. R. Kunz and J. M. Fenton, *J. Electrochem. Soc.*, 2005, 152, A635-A644.