Novel Materials for High Efficiency Direct Methanol Fuel Cells

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Arkema Inc.

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Project ID# FC063

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Overview

Timeline

- Start: May 1st, 2010
- End: June 30th, 2013
- Percent Complete: 90%
  (as of February 28th, 2013)

Budget

- Total Project Funding: $3,153k
  - DOE Share: $2,338k
  - Cost Share: $813k
- Funding received in FY12: $650k
- Funding for FY13: $310k

Barriers

- Durability
- Cost
- Performance

Organization

- Project Lead
  - Arkema Inc.
- Subcontractors
  - Illinois Institute of Technology (IIT)
  - IRD Fuel Cells, LLC.

Project Organization and Collaborations

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David Mountz & Wensheng He - PIs
Project Lead

- PEM development and testing.
- MEA development, diagnostics, and durability.

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Vijay Ramani – PI
University Subcontractor

- Development of organic/inorganic membranes.
- MEA characterization and diagnostics.
- Work period ended in November 2012.

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Madeleine Odgaard – PI
Industrial Subcontractor

- MEA development and durability testing using optimized Arkema membranes.
- Short stack testing.
- 5 month contract initiated in Jan 2013.

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Relevance

Project Objectives

1. Develop a membrane technology having low methanol crossover, high conductivity, and increased durability.
2. Develop cathode catalysts that can operate with considerably reduced platinum loading and improved methanol tolerance.
3. Combine the cathode 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 two components.

Current Key Project Targets

Characteristic	Industry Benchmark	Project Target	Current Status	DOE Barriers Addressed
Methanol Permeability (cm^2/s)	$3x10^{-6}$	$1x10^{-7}$	$5x10^{-7}$	Performance, Cost
Areal resistance ($\Omega * cm^2$), 70ºC	0.12 (7mil PFSA)	0.0375	0.030	Performance, Cost
Power Density (mW/cm^2)@0.4V*	90	150	140	Performance, Cost
MEA Lifetime (hours)*	> 3,000	5,000	1,500-3,000	Durability, Cost

***Conditions - 1M methanol at 60 C**

Approach/Project Structure

Task 1 – Membrane Development

Barriers Addressed: Performance & Cost

- PVDF/polyelectrolyte blend technology (Generations 1 and 2).
- Composite membranes based on Gen 1 PVDF/polyelectrolyte blend technology.
- Started May 2010 – about 95% of scheduled work is completed.

Task 2 – Cathode Catalyst Development

Barriers Addressed: Performance & Cost

- Methanol-tolerant Pd-based co-catalysts.
- Work stopped at Go/No-go decision in Jan 2012. Work focused on project objectives 1 and 3 after Jan.

Task 3 – MEA Development

Barriers Addressed: Performance & Durability

- Develop MEAs from materials in Task 1 with commercial catalyst/GDEs and perform diagnostics.
- Started mid 2011 – all scheduled work at Arkema is completed. IRD's work is 85% 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 – Arkema's work is 78% completed. Durability work at IRD just initiated.

Approach/ Project Milestones

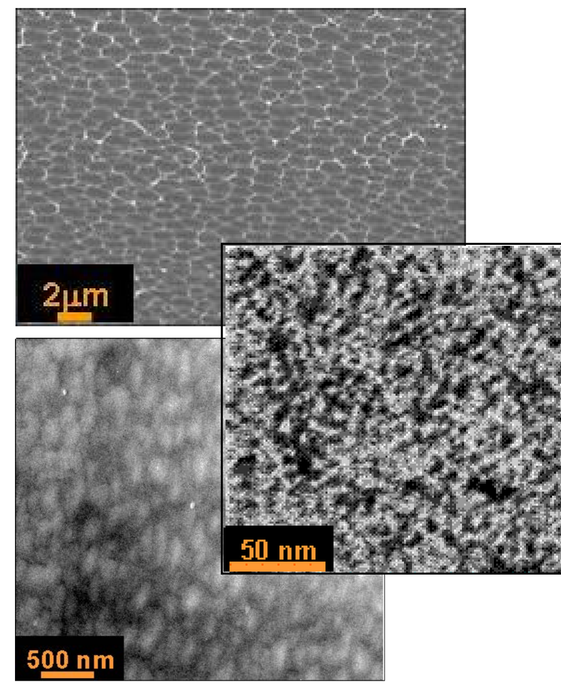
Milestones & Go/No-Go Decisions for 2012 and 2013	Due Date	Progress
Go/No-Go Decision #1 (Task 3 – MEA Development) MEA performance of 120 mW/cm^2 @ 0.4V (60 C, 1M methanol).	Jan 2012	Target achieved with Arkema membrane using either a commercial GDE or a lab-made cathode with commercial Pt catalyst. Cathode catalyst work stopped.
Deliverable #3 (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 Go/No-Go decision #1.
Go/No-Go Decision #2 (Task 1 – Membrane) MEA performance of 135 mW/cm^2 @ 0.4V (60°C, 1 M methanol) using composite membranes.	Sep 2012	Composite membranes showed similar or lower power density compared to the baseline Arkema membrane. Work stopped.
Deliverable #4 (Task 1 – Membrane) Generation 2 membrane: areal resistance $\leq$ 0.0375 $\Omega * cm^2$ and a methanol perm. coeff. $\leq$ $1x10^{-7}$ cm^2/s.	Sep 2012	Generation 1 membrane optimized to have a 0.030$\Omega * cm^2$ AR and a $5x10^{-7} cm^2/s$ methanol perm. coeff. Generation 2 membranes are still showing poor properties due to high solubility in water (leaching).
Deliverable #5 (Task 3 – MEA Development) MEA performance of 150 mW/cm^2 @ 0.4 V (60 C, 1M methanol).	Dec 2012	140 mW/cm^2 was achieved using an optimized Gen 1 membrane and commercially available GDEs.
Deliverable #6 (Task 4 – Durability) MEA with Arkema membrane passes 5,000 h durability testing.	Jun 2013	1,500-3,000 hour MEA durability with Gen 1 membranes and commercial GDEs.

Technical Approach:

Membrane Development

- Polymer Blend
  - Kynar® PVDF $\left[CH_2\text{-}CF_2 \right]$
    - Chemical and electrochemical stability
    - Mechanical strength and excellent methanol barrier
  - Polyelectrolyte
    - H^+ conduction

- Flexible Blending Process
  - PVDF can be compatibilized with >10 polyelectrolytes
  - Easily scalable process: 100s of ft^2 have been produced
- Property Control
  - Morphology: phase separation on the scale of 10-1000s of nm
  - PVDF matrix optimization
  - Tailor polyelectrolyte composition and microstructure (Generation 1 and 2 polyelectrolytes)
  - Acidic inorganic additives



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Technical Progress (Task 1 - Membrane Development):

Arkema Membranes

Polyelectrolyte Generations Investigated in This Grant:

- Generation 1: Crosslinkable, highly sulfonated polyelectrolytes with a random microstructure. Approach was developed in a previous grant and optimized in this grant for DMFCs.
- Generation 2: Polyelectrolytes with controlled microstructures → potential for lower cost (up to half) and different morphologies than Generation 1 materials.

Membrane Development with Generation 1 Polyelectrolytes:

- No polyelectrolyte development; optimized the PVDF: PE ratio and membrane thickness. Work was built on the composition developed for the first Go/No-go decision (Go/No-go#1 criteria = $0.08\Omega*cm^2$ AR & $1x10^{-7}cm^2/s$ methanol perm. coeff.).
- Optimized membrane properties:
  - — Methanol permeation coefficient: $5x10^{-7}cm^2/s$
  - — Areal resistance: $0.030\Omega*cm^2$ (~1.2mil thick)
- Membrane meets the areal resistance for Deliverable #4, but the methanol permeation doesn't meet the target of $1x10^{-7}cm^2/s$ due to limitations with permselectivity.

Generation 2 Polyelectrolyte Development

- Work in the past year focused on resolving the sulfur loss issue reported last year.
- High sulfur loss was traced to polyelectrolyte dissolution (20-35% sulfur loss in initial testing), which was leading to property drift and low conductivity.

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Technical Progress (Task 1 - Membrane Development):

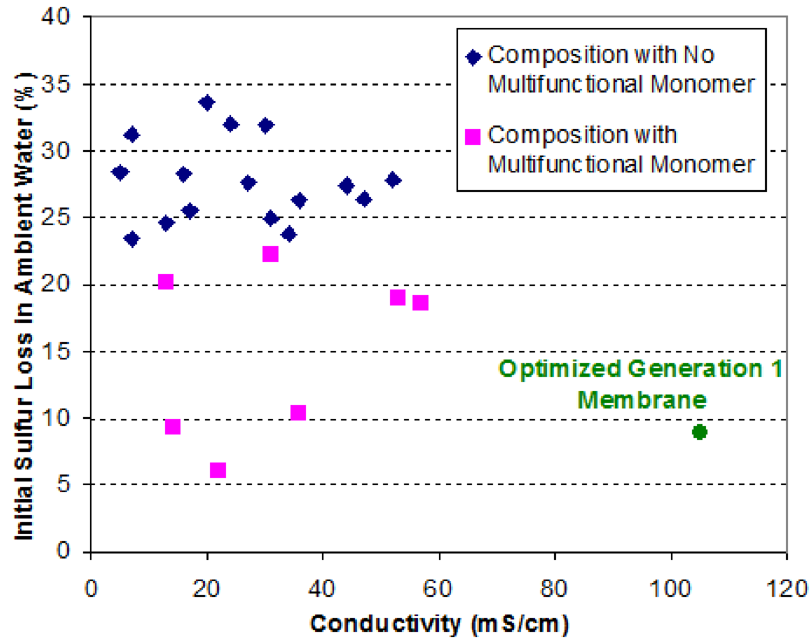
Generation 2 Polyelectrolyte

Reason for the sulfur loss: Generation 2 polyelectrolytes have an IEC of 1.8 - 2.4 meq/g, compared to about 4 meq/g for the Generation 1 polyelectrolyte. Generation 1 polyelectrolytes show superior stability to Generation 2 because they are chemically crosslinked in the PVDF matrix, while the Generation 2 materials are tethered through associations in the hydrophobic blocks in the microstructure. These physical crosslinks are not sufficient to stop the dissolution of the polyelectrolyte, especially in hot water.

Approaches pursued to correct the sulfur loss:

- **Use of crosslinking agents, such as organic peroxides, added to the existing polyelectrolyte.**
  - No functionality was incorporated into the polyelectrolyte specifically to promote the reaction.
  - Some degree of reaction occurred, but sulfur loss wasn't improved without compromising conductivity.

- **Increase the polyelectrolyte molecular weight**
  - MW was increased significantly by adjusting po merization conditions → polyelectrolyte/PVDF solutions gelled and couldn't be processed.
  - Use of a multi-functional monomer in the polymerization was also explored → the sulfur loss was decreased (10-20%). However, conductivity didn't increase appreciably and the solutions were not homogeneous (microgel).
  - Sulfur loss is still unacceptably high level in 80 C water (15-30% loss in a few hours).



- **Use of a crosslinkable monomer incorporated into the polyelectrolyte is currently being explored.**
  - Synthesis was successful, but there are issues with the solubility of the polyelectrolyte in solvent.
  - Alternative solvents and processing methods are being explored.

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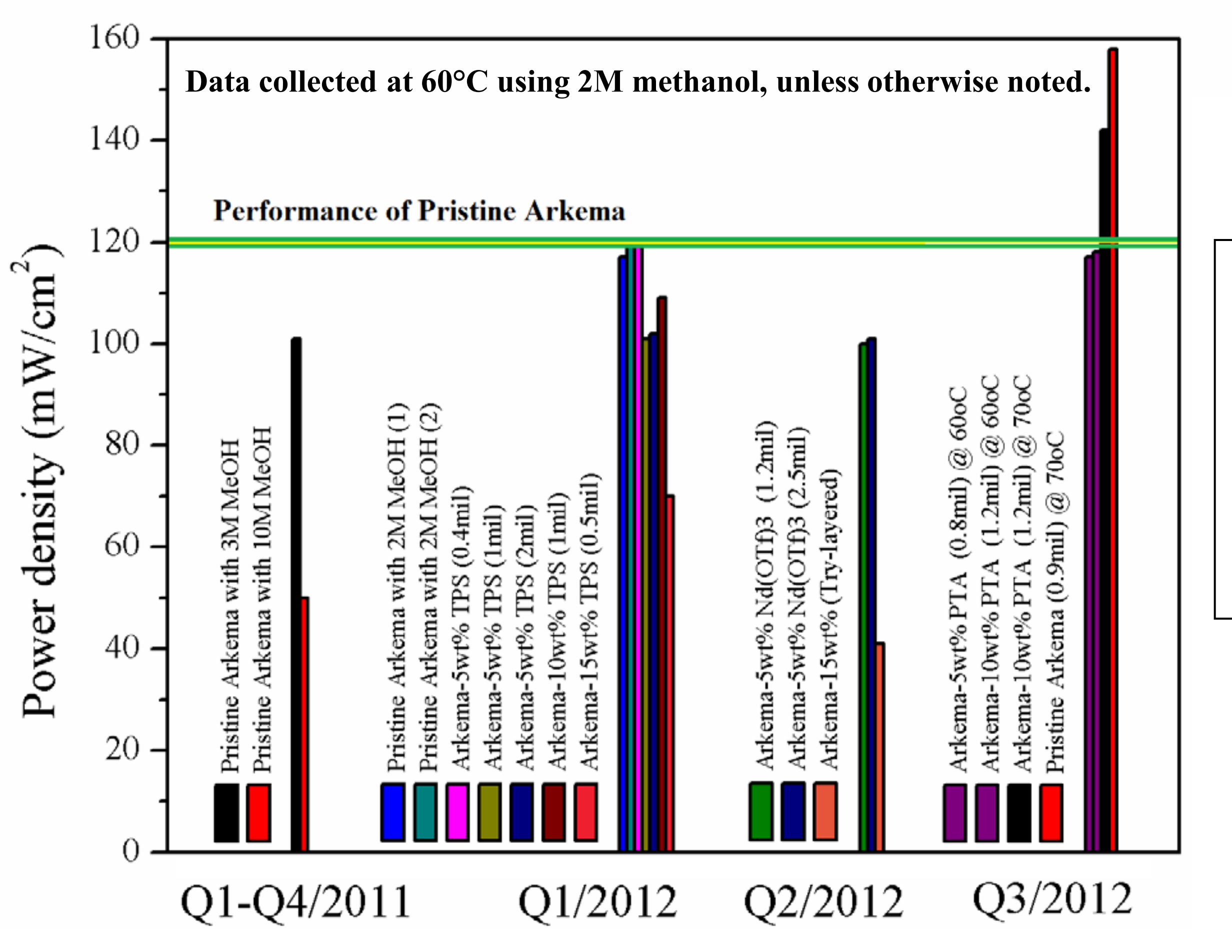
Technical Progress (Task 1 - Membrane Development): Go/No-go Decision #2: IIT Composite Membrane Program



TPS = 3-trihydroxysilyl-1-propane-sulfonic acid
$Nd(OTf)_3$ = neodymium trifluoromethanesulfonate
PTA = phosphotungstic acid
Tri-layered = Three layer laminate composite membrane structure

- A variety of inorganic materials were incorporated inside an early Generation 1 membrane technology.
- Although most of the additives increased selectivity, they typically decreased conductivity → lead to a decrease in MEA performance compared to the baseline Arkema membrane. None of the membranes met the requirements of Go/No-go #2.

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MEA Development and Diagnostics

Approach:

Arkema

- Screen commercially available GDEs to determine the effect of different parameters (e.g. catalyst loading & GDL/MPL construction) on performance.
- MEA diagnostics
  - Understand and quantify the effect of methanol crossover.
  - Analyze failures in the durability test.

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- Screen GDLs, catalyst loading, and ink formulations with an optimized Arkema membrane composition to determine their effect on initial MEA performance.

Progress (Arkema)

- ELE 170/171 showed high mass transport resistance from anode in 1M methanol.
- 2 sets of Johnson Matthey electrodes were tested: ELE 156/157 and ELE 196/197.

Anode/Cathode Series	Anode Catalyst Loading	Cathode Catalyst Loading	Remarks
ELE 170/171	3 mg Pt/cm^2 1.5 mg Ru/cm^2	1.5 mg Pt/cm^2	Standard electrodes used in most of the testing to date
ELE 156/157	2.5 mg Pt/cm^2 1.25 mg Ru/cm^2	1.0 mg Pt/cm^2	Lower catalyst loadings. Same catalyst ink formulation as standard.
ELE 196/197	3 mg Pt/cm^2 1.5 mg Ru/cm^2	1.5 mg Pt/cm^2	GDE designed for hydrocarbon membranes.

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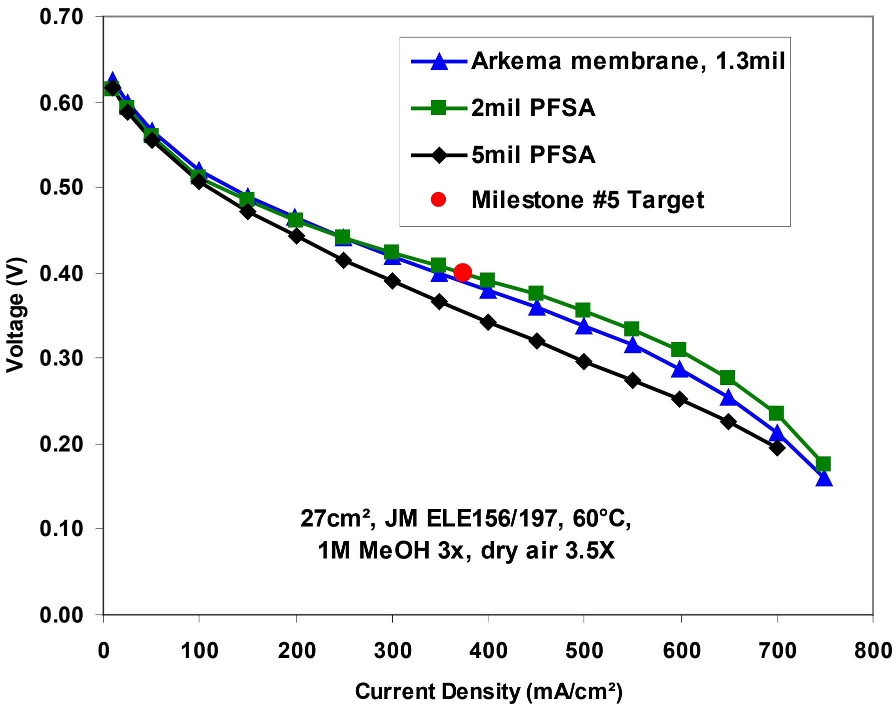
Technical Progress (Task 3 - MEA Development):

Effect of Different Commercial Electrodes

- ELE 156 was similar to ELE 170 in 2M methanol, but showed better 1M methanol performance. ELE 157 was comparable to ELE 171.
  - The ELE 156 performance in 1M methanol is attributed to lower mass transport stemming from the thinner catalyst layer.
- ELE 196 gave the same performance as ELE 170. ELE 197 showed improvement over ELE 171.
  - The improvement is likely attributed to enhanced water management and oxygen transport due to the GDE design.



- A combination of ELE 156 and 197 gave substantially improved performance over the ELE 170/171 electrodes:
  - A 140 mW/cm^2 power density was achieved, which is approaching the milestone #5 metric of 150 mW/cm^2.
  - Both PFSA and Arkema membranes benefit from the electrode combination.

Technical Progress (Task 3 - MEA Development):

IRD MEA Development and Durability Testing

- **Motivation:** There is a need for a better understanding of how the MEA/electrode construction affects the MEA performance and durability with our membranes.

- **MEA Development – screen several parameters to find the optimum MEA performance:**
  - GDL
  - Ink formulation
  - Catalyst loading
    - Cathode (1.25 - 1.5 mg/cm^2 PGM)
    - Anode (1.8 - 4.5 mg/cm^2 PGM)
  - MEA construction – 5 and 7 layer designs

- **Results:**
  - MEA cathode development is completed. The performance is similar to the JM reference GDE.
  - Anode development is not complete. The construction is not optimized for the lower methanol crossover of our membrane.
    - Electrode structure, porosity, hydrophobicity, ionomer/catalyst ratio are being explored.

- **600 hour single cell durability and short stack testing will start in May. Durability testing may be extended if the results are positive.**

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MEA Durability

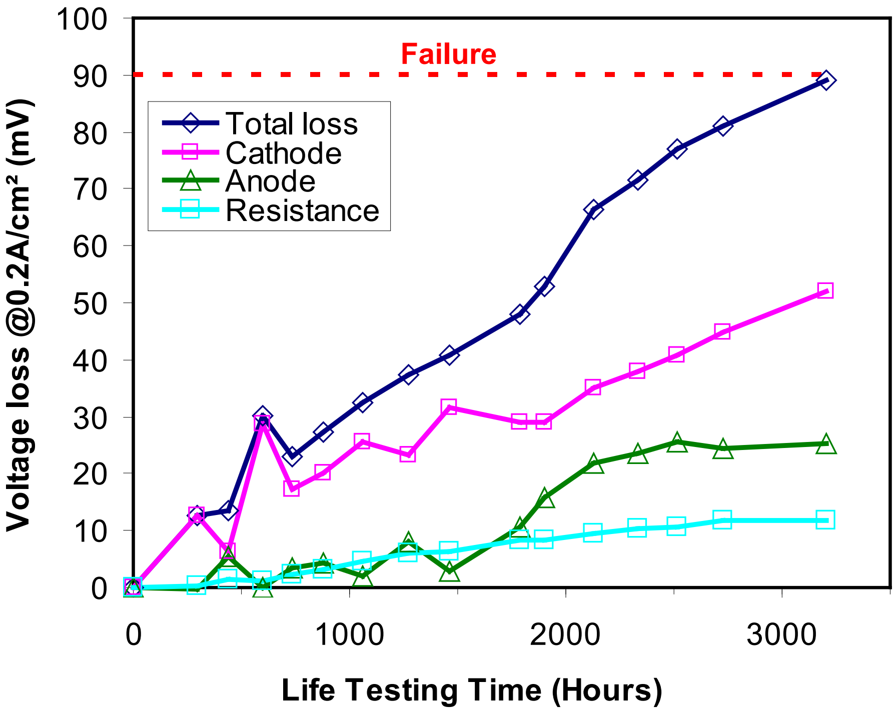
- **Arkema protocol: single cell at constant current 0.2A/cm^2, 60°C, 2M methanol.**
  - Failure criteria: 20% loss in performance.

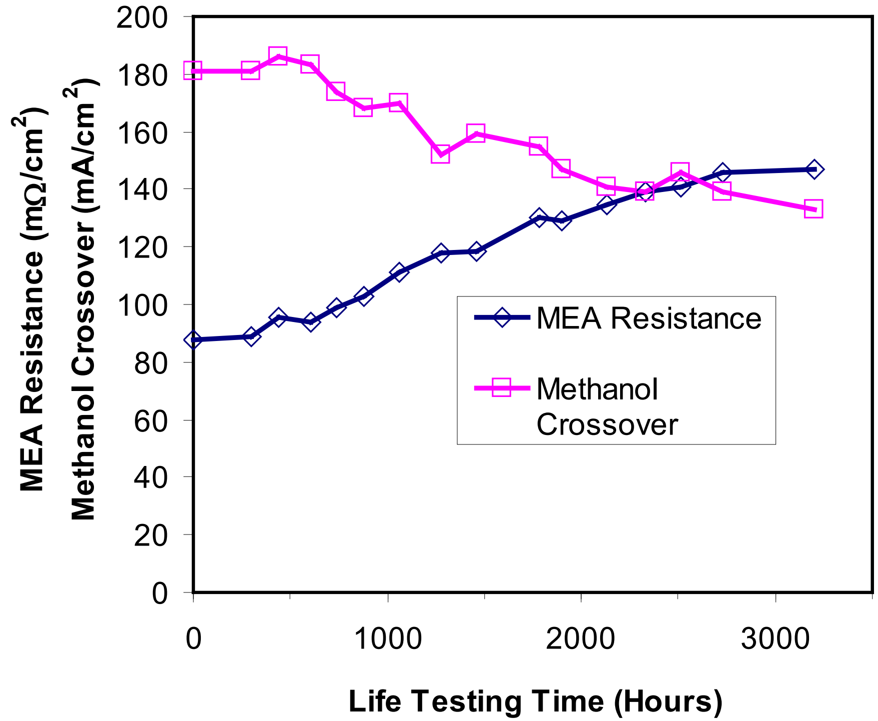
- **Current results:**
  - Arkema membranes: 1,500 - 3,000 hours.
    - The range is primarily due to the polyelectrolyte (PE) loadings used (see below).
  - PFSA membranes: > 4,000 hours.

- **Observed failure modes:**
  - A majority of the MEAs failed due to >20% performance loss.
    - >85% of total loss is from the electrodes.
    - Similar behavior observed with both PFSA and Arkema MEAs.
  - PE Loading Effects:
    - Arkema membranes with lower PE loadings failed earlier due to higher areal and interfacial resistance (1,500-2,000 hours of durability).
    - Excessive PE (>35%) can cause pin-hole/crack failure due to poor mechanical properties (1,500 hours of durability).
    - Optimal PE loading is in 30-35% range. (3,000 hours of durability).

Technical Progress (Task 4 – Durability Testing):
Arkema MEA Performance Decay

1.3 mil Arkema Membrane, JM ELE 170/171
0.2A constant current test, 60°C, 2M methanol



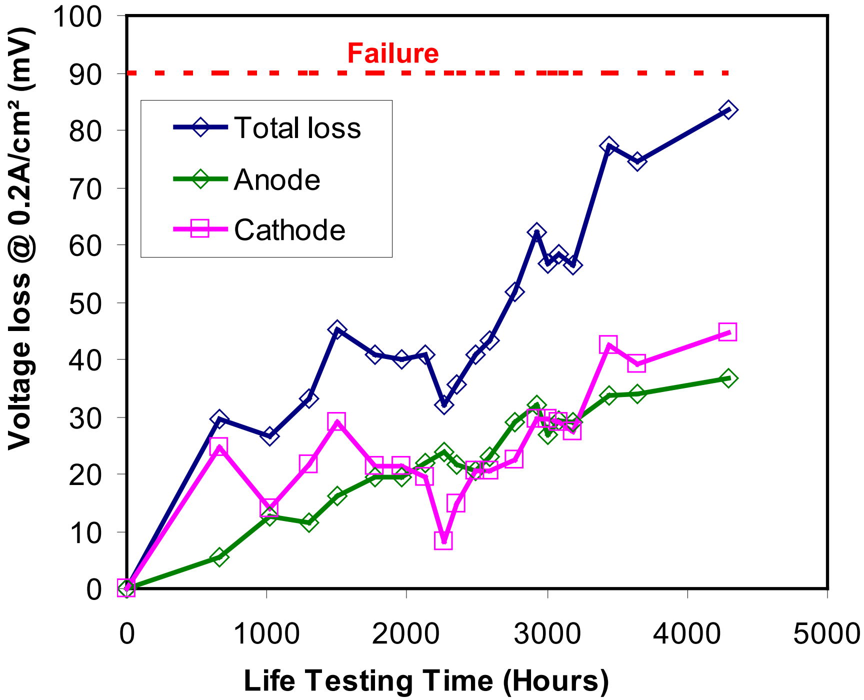


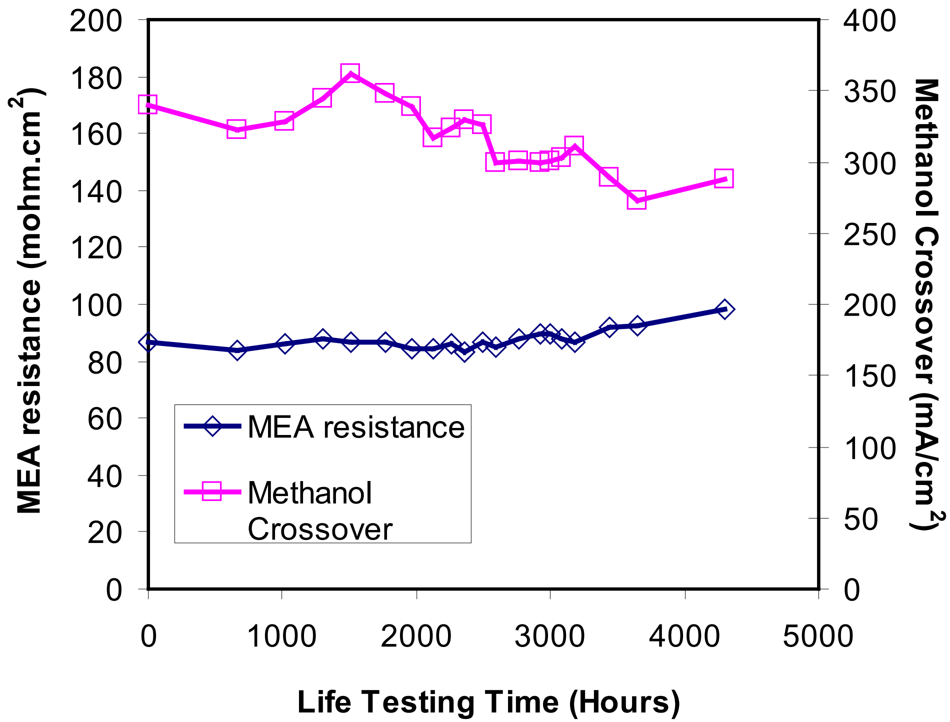
- A majority of performance losses are from the electrodes (>85%).
  - A range of electrode contribution to the losses have been observed. Cathode losses are higher than the anode losses in some MEAs. The electrode losses are equivalent in others.
- Roughly 10% of the total loss stems from an increase in MEA resistance.

Technical Progress (Task 4 – Durability Testing):

PFSA MEA Performance Decay

2mil PFSA Membrane, JM ELE 170/171
0.2A constant current test, 60°C, 2M methanol

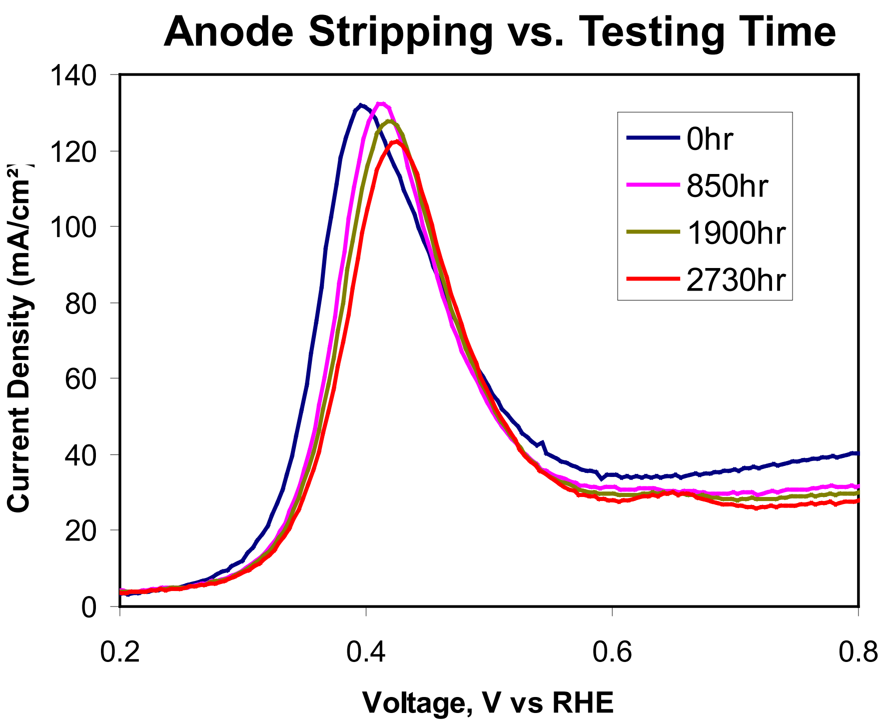


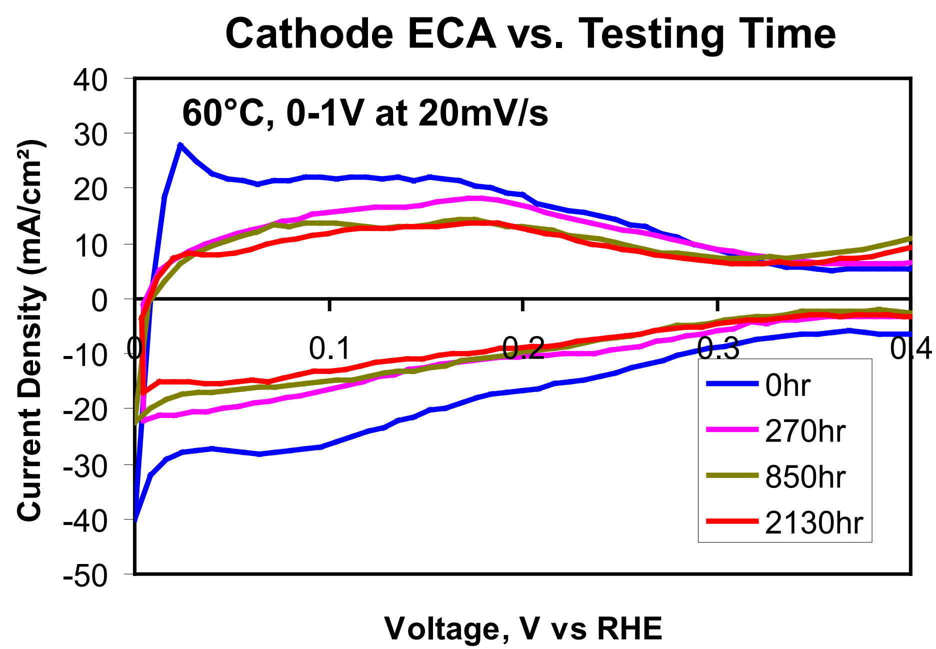


- Performance losses are primarily due to electrodes.
- MEA resistance showed little or no increase over time, compared to the MEA with the Arkema membrane.

Electrode Degradation

1.3 mil Arkema Membrane, JM ELE 170/171





Anode degradation

- Active area ↓
- Catalyst activity ↓
  - Peak shifts to higher V

Cathode degradation

- Significant decrease in active area

Technical Progress (Task 4 – Durability Testing):
Potential Causes for MEA Performance Decay

- Loss of catalytic surface area
  - Similar cathode ECA profiles between Arkema and PFSA MEAs
  - Ru crossover is anticipated to be a minor issue due to the stabilized anode design
  - This is likely not an explanation for the difference between the Arkema and PFSA MEA performance
- Degradation of membrane and membrane/electrode interface
  - Manifested by increasing MEA resistance over time
  - The PFSA MEA showed a significantly lower MEA resistance decay rate
  - Degradation in membrane/electrode interface can lead to additional contributions to the MEA resistance beyond the membrane ohmic losses
    - Poor catalyst utilization induces higher local current density and higher polarization losses
- Increased transport resistance
  - Loss of hydrophobicity in electrode
    - Contact angle on GDL did not show significant difference between PFSA and Arkema based MEA
  - Other sources of transport resistance are being investigated

Summary

- **Membrane Development**
  - Generation 1 membrane compositions were refined to meet the areal resistance requirements of Deliverable #4, but have a higher methanol permeation than the target value.
  - Leaching has been decreased in Generation 2 membranes, but the rates are still unacceptably high.

- **MEA Development**
  - Compared to standard ELE 170/171, the ELE 156 anode and ELE 197 cathode combination with an Arkema membrane shows a significant performance advantage due to improved mass transport.
  - MEA power density is 140mW/cm^2, approaching the target for Deliverable #5 (150mW/cm^2).

- **MEA Durability**
  - Generation 1 Arkema membranes are showing 1,500-3,000 hours of durability, which is short of Deliverable #6 (5,000 hours).
  - Membrane loadings in the range of 30-35% PE have a higher durability.
  - Results have shown that electrode degradation is the major contributor to most PFSA and Arkema MEA failures.
  - The lower durability of the Arkema membrane is likely due to increasing interfacial resistance or transport resistance.

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Future Work

- **MEA Durability**
  - Continue to study the effect of variables in the membrane/electrode:
    - —Generation 1 Membrane: effect of elevated crosslinking level
    - —Electrodes: ELE 156/197
  - Post-mortem analysis of recently failed Arkema and PFSA membranes that passed 3,000 and 4,000 hours, respectively.
  - Review IRD's work on MEA development and initiate short-term durability testing.

- **Membrane Development**
  - Testing of membrane compositions with a crosslinkable monomer into the Generation 2 polyelectrolyte, including short-term durability of promising candidates.

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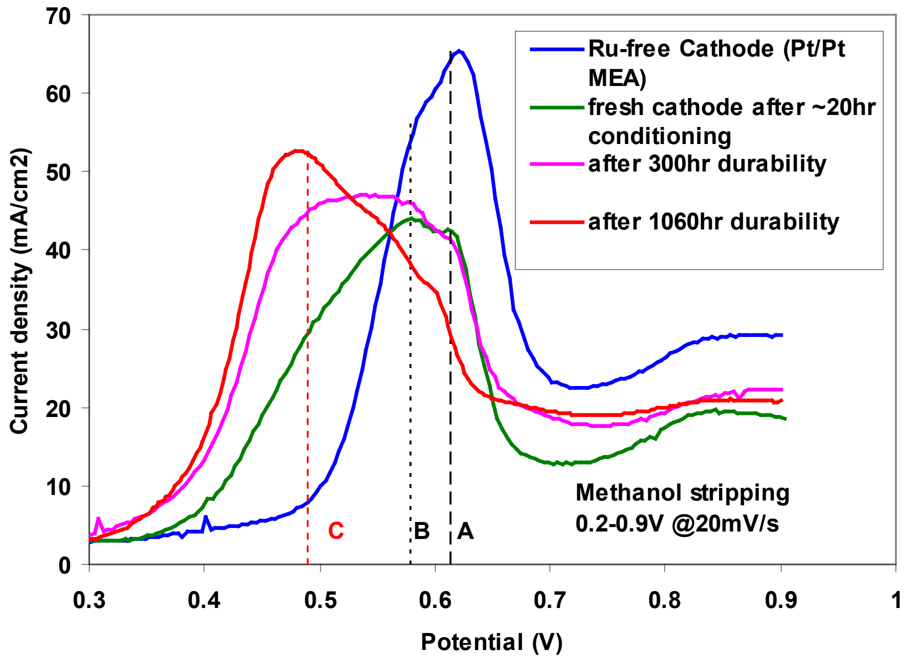
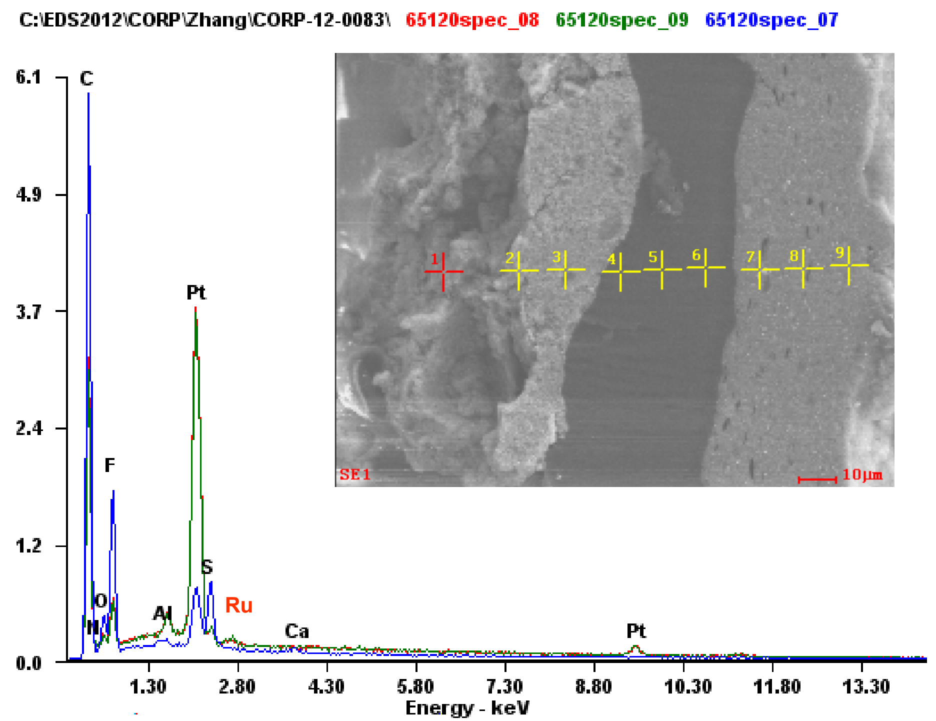
Technical Back-up Slides

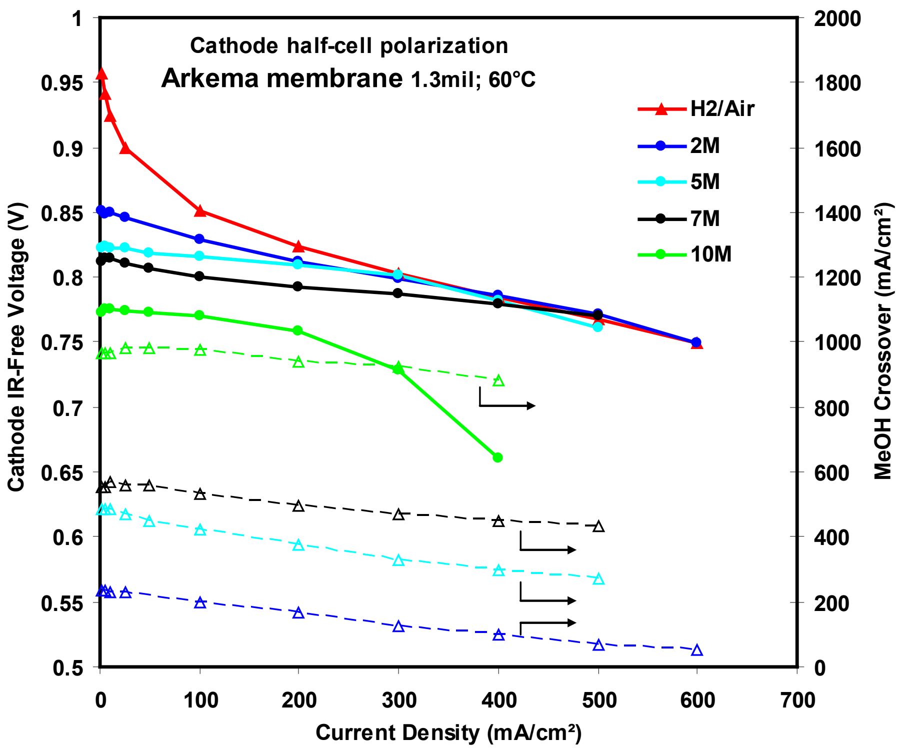
Ruthenium Crossover

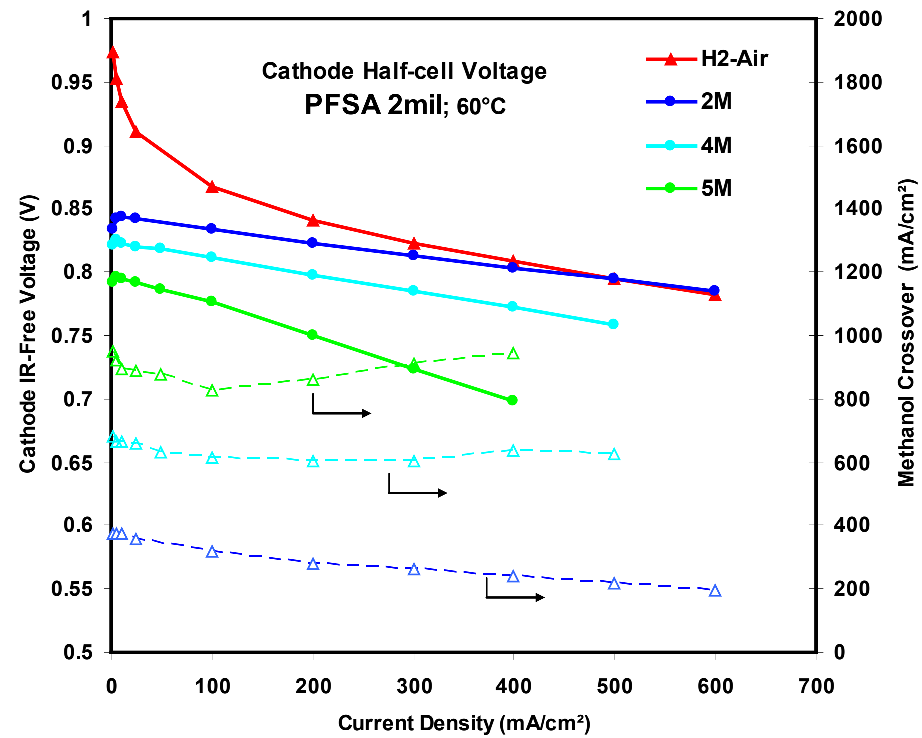




- A significant portion of the observed Ru contamination (peak C) occurred during the 20hr initial MEA conditioning.
- EDS analysis of post mortem MEA showed a low amount of Ru at cathode.
- Overall level of Ru contamination/crossover is anticipated to be low due to the use of JM stabilized anode.

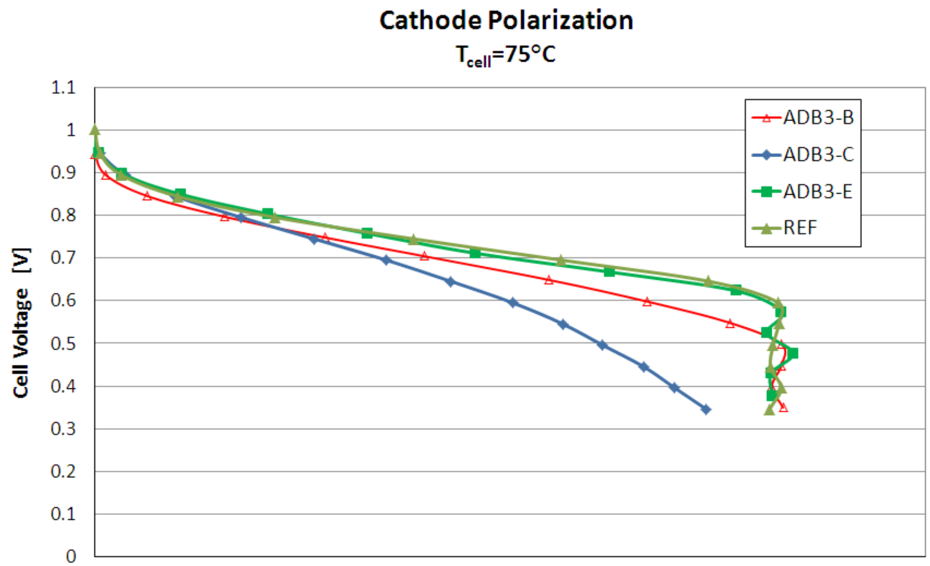
Effect of Methanol Crossover (MCO)

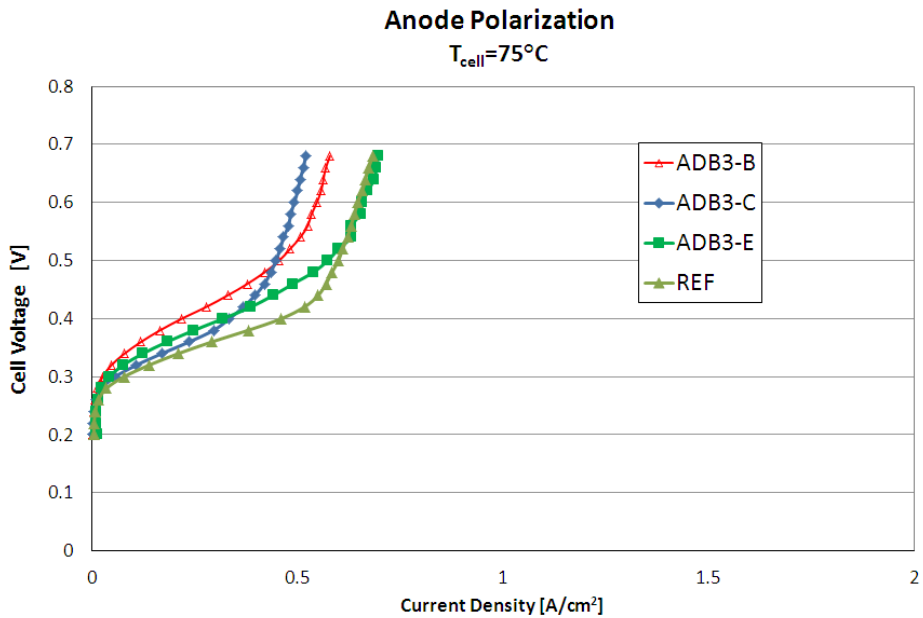




- **At methanol concentrations ≤ 2M, methanol crossover has a minimal impact at high currents.**
- **For the ELE171 cathode, methanol crossover > 400-500mA/cm^2 causes significant performance loss in whole range.**

IRD MEA Development



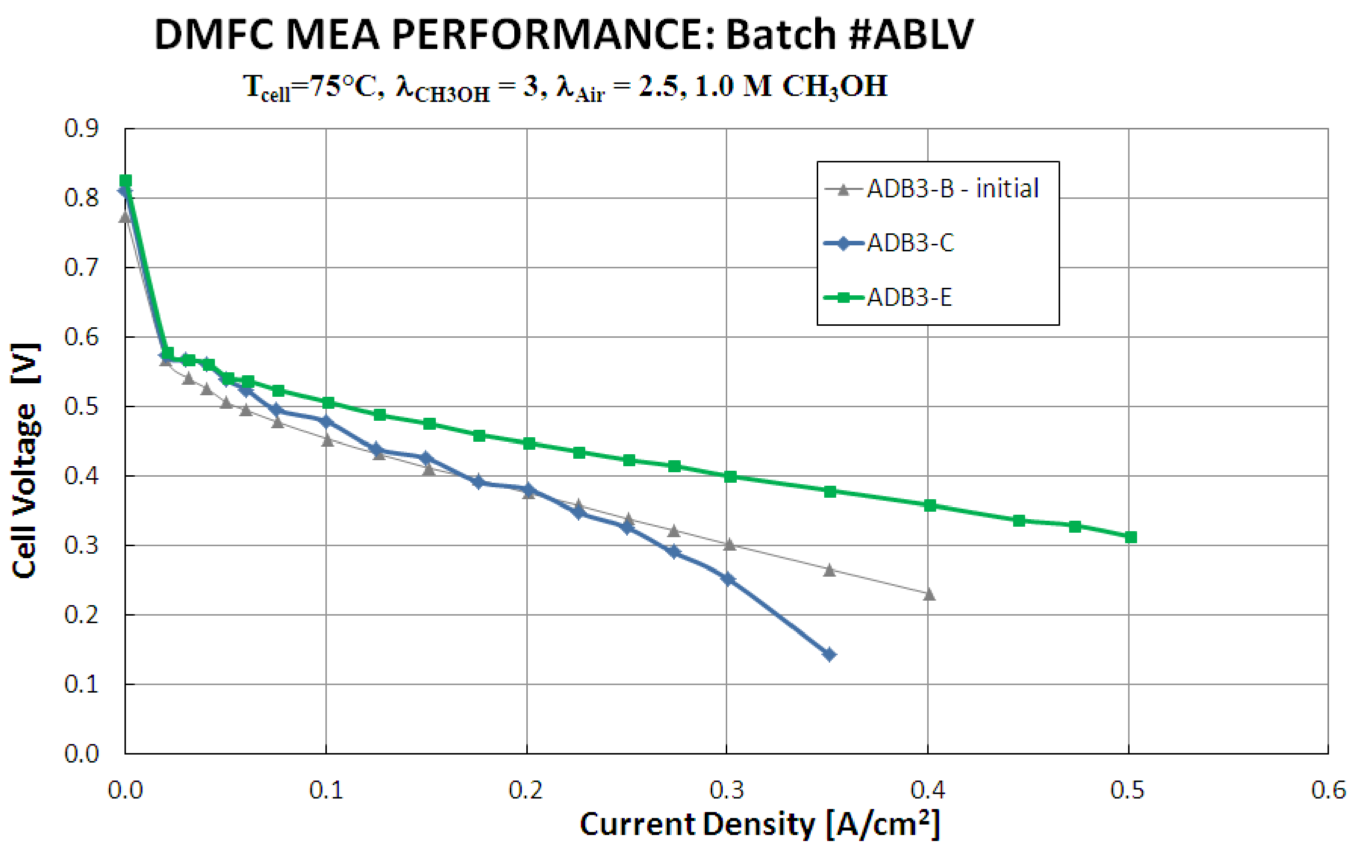


- **Cathode half-cell polarization. One IRD cathode showed similar performance to JM reference.**

- **Anode half-cell polarization. Anode catalyst loading is 1.8mg/cm^2 PGM. IRD anodes showed lower performance than JM reference, partially due to lower catalyst loadings. Anodes are still under development**

The reference uses JM ELE170/171 electrodes, the other three use IRD developmental electrodes.

IRD MEA Development Data Example



- **Three samples contain different GDLs with air permeabilities ranging from 0.35-1.5 $cm^3/(cm^2*s)$.**
  - Permeability ranking is ADB3-E > ADB3-B > ADB3-C
  - The highest permeability gave the best performance.
- **Cathode and anode loadings for all samples are 1.2mg/cm^2 and 1.8mg/cm^2, respectively.**

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