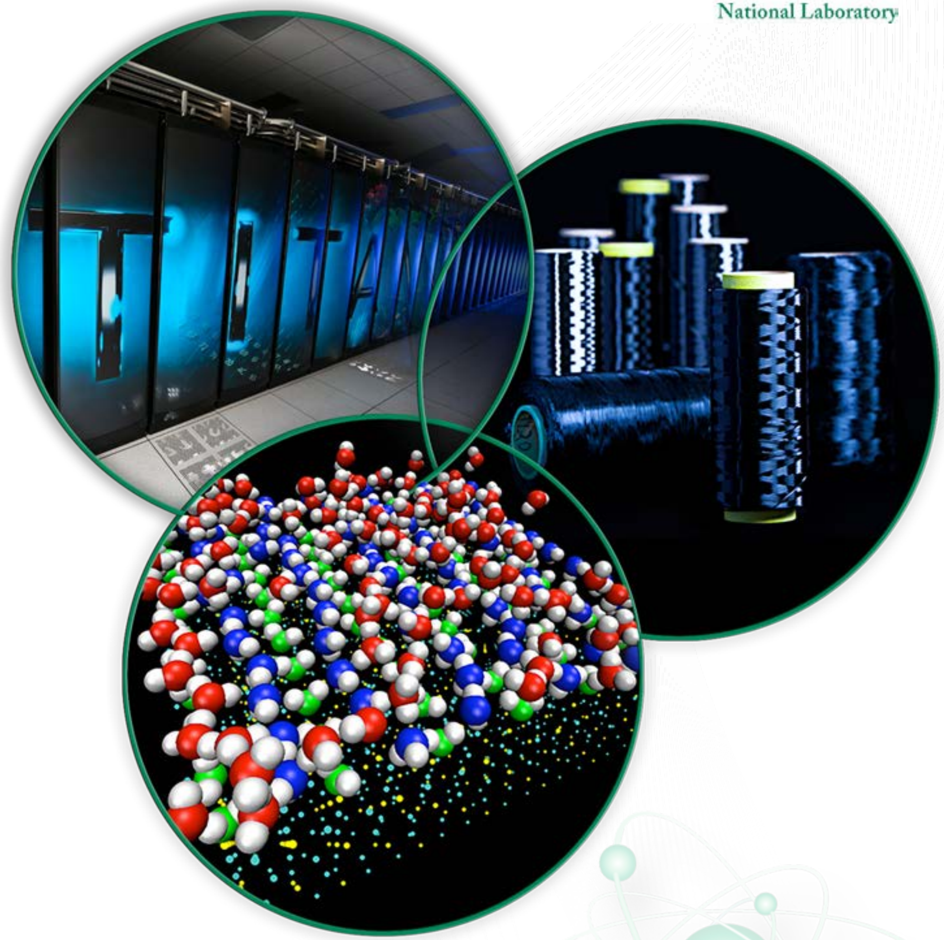
High Conductivity Durable Anion Conducting Membranes



<u>Tom Zawodzinski,</u> Jimmy Mays, Todd Toops, David Wood, Jianlin Li
Oak Ridge National Laboratory

June 8, 2015

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Project ID FC122

Overview

Timeline

- Project Start: 10/1/14
- Project End: 9/30/15
- Percent Complete: 50%

Barriers

- Barrier Addressed
  - **By 2020, reduce FC cost to $35/kWh.**

Budget

- Total project funding
  - $500k
- $500k in FY15

Partners

- Project Lead: ORNL
- Interactions/Collaborations (discussion only)
  - National Laboratories: NREL, LANL
  - Industry: Eastman Business Park

Relevance & Objectives

Fuel Cell Technologies Office

- Main Objective: The goal of this project is the development of highly conducting, durable AEMs and their demonstration in AFCs.
- To address this goal, we leverage experience in preparing AEMs for zinc-air batteries (ZABs) with high conductivity (**greater than 100 mS/cm and up to ~500 mS/cm at room temperature**), new findings regarding the durability of these membranes and how degradation pathways can be controlled, and ORNL capabilities for developing and coating electrodes.
- Developed high throughput synthesis approach to allow assessment, screening of polymers

- Relevance to Barriers and Targets
  - AFCs offer the possibility of removing PMs from the cell.

Project Milestones

Task Schedule

Task #	Project Milestones	Type	Task Completion Date				Progress Notes
			Original Planned	Revised Planned	Actual	Percent Complete	
1	Cross-linked loaded membrane (CLAM) with high conductivity of >100 mS/cm2 at RH=50%.	Milestone	12/31/14			70%	**MET**
2	AEM with conductivity > 60 mS/cm2.	Milestone	1/31/15			50%	**MET**
3	First MEA with CLAM films; testing in fuel cell with ASR less than 0.1 ohm-cm2 and no cathode precious metal.	Deliverable	3/31/15			25%	**MET**
4	Report on relationship between AEM fuel-cell durability and accelerated testing protocols	Milestone	6/30/15			5%	Not started.
5	First new AEM-based MEA; testing in fuel cell with ASR less than 0.1 ohm-cm2 and no cathode precious metal.	Milestone	9/30/15			0%	Not started.

Project Approach

'CLAM' Membrane

- **Problems:**
  - AEMs have low to modest conductivity.
  - AEM active groups tend to be less stable than
  - Polymer synthesis and membrane formation is slow and erratic at the bench scale.
  - AFC development lags
- **Overall technical approach and strategy:**

1. Use pre-formed polymer backbones to enable rapid evaluation of different functionalities.
2. Control local environment of cation to foster high OH^- conduction and high durability.
3. Control membrane swelling and mechanical properties using cross-linking and/or blending..
4. Durability testing protocol included.
5. Prepare and test CCMs.
6. Approach to scale-up, both polymer and membranes, directly integrated into approach, with follow-on commercial partners identified.
7. Dual-pronged approach using two different types of active polymers.

Approach – Polymers by design-'High-throughput' Polymer Preparation using a series of building blocks

Building Blocks (some can have multiple purposes):

1. 'Proto'-functionalized **backbone** allowing large batch synthesis, facile reactions to add functions
2. **Cationic moieties**
3. **Additives** to control local environment to promote conduction and durability
4. **Cross-linking agents** to control swelling
5. **Blending polymers** for improved mechanical properties

Approach allows rapid variation of polymer chemistry for rapid assessment of hypotheses.

Approach – Two-pronged Membrane Synthesis

Cross-linked, Loaded Anion-conducting Membranes (CLAMs)

Membrane Preparation:

- Using building blocks to provide some functionality, medium for KOH/H_2O uptake, dimensional stability; KOH left in.
- Multiple 'generations' prepared
  - Gen 0:
  - Gen 1:
  - Gen 2: cross-linking
  - Gen 3: blends
- Major effort on processing materials into films

Conventional AEMs (AEMs)

Membrane Preparation:

- Using building blocks to provide all functionality, medium for H_2O uptake, dimensional stability
- Pure anion conductor (no KOH)
- Multiple 'generations' prepared
  - Gen 0:
  - Gen 1:
  - Gen 2: cross-linking
  - Gen 3: blends
- Less effort on processing materials into films

Durability Testing:

- Tested by soaking at $60^{o}C$ in concentrated KOH;
- Analyze conductivity, breakdown products

Technical Accomplishments – Executive Summary (FY15 Q1-2)

- High-throughput, Polymers by Design approach implemented for two distinct families of materials.
- CLAMs prepared that meet targets for conductivity (>100 mS) at lowered RH (50%). (**Milestone met.)**
- AEMs prepared that meet conductivity targets of >60mS. (**Milestone met.)**
- A CLAM-based MEA (>200 micron thick membrane) has been shown to have an ASR of ~0.09 ohm-cm^2, achieving better than the target (~0.1 ohm-cm^2.) (**Milestone met.)**
- **Seeking IP protection on our ideas**

Technical Accomplishments –Polymer Synthesis High Throughput, High Diversity Approach

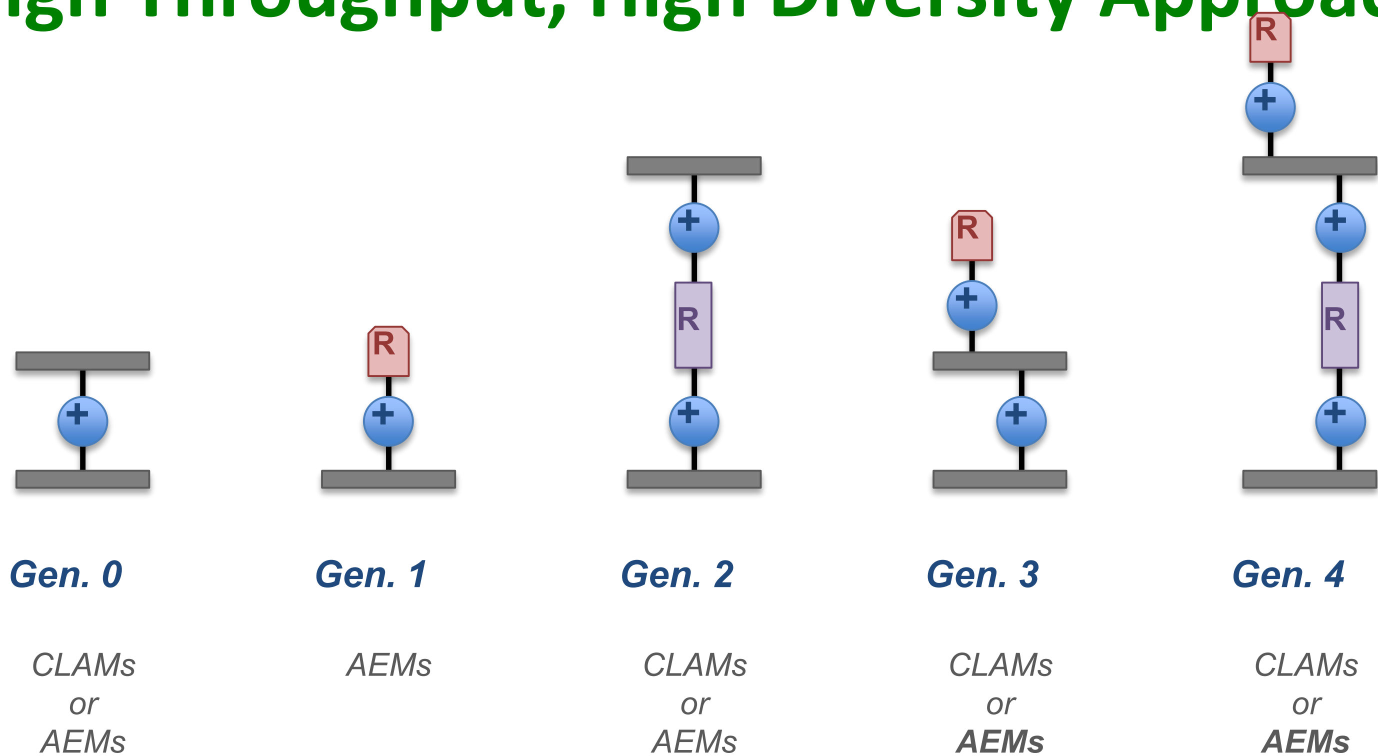


Illustration of generic building blocks: R = cross-linker (purple, large rectangle) or additive (red, small rectangle)

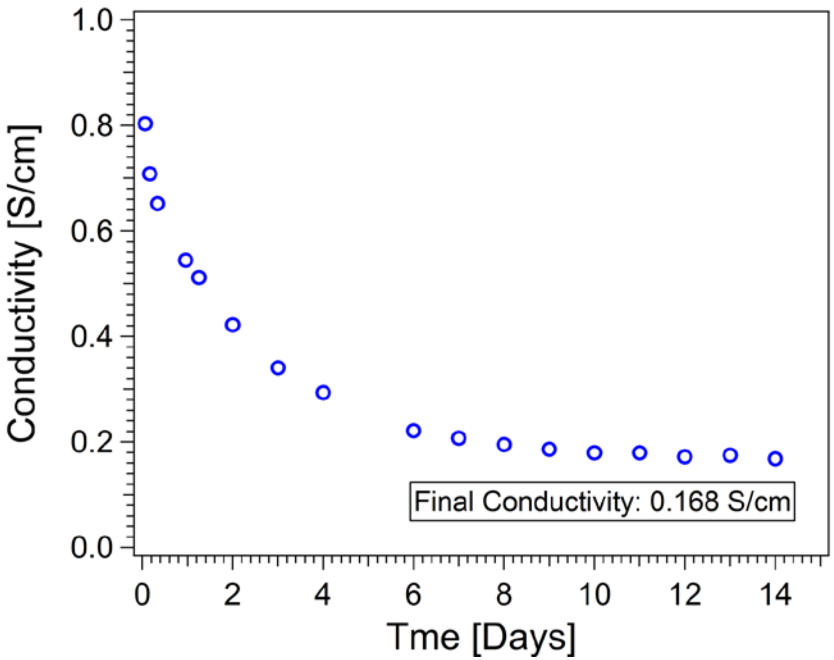
Families of both CLAMs and AEMs have been prepared.
Over 40 distinct compositions studied.

Technical Accomplishments – CLAMs meet Conductivity Targets

Table 1: Effect of Cation, additives on Membrane Properties, Gen 3 CLAMs

Building Block	Additive	Cond. [S/cm]	Durability [Days]	IEC [mmol/g]
1	A1	0.41	> 60	0.16
2	A1	0.39	13	0.37
3	A1	0.10	> 60	0.86
4	A1a	0.32	> 60	0.85
4	A1b	0.30	> 60	0.88
4	A1c	0.30	> 60	0.80
1	A1a	0.39	> 60	1.80
1	A1b	0.32	> 60	0.91
1	A1c	0.41	> 60	1.18

Technical Accomplishments – CLAMs meet Conductivity Targets



Milestone: conductivity greater than 100 mS/cm at 50% RH

Plot showing CLAM conductivity when exposed to 50% RH
Decrease reflects slow dehydration to new condition.

Another milestone met: CCM ASR ~ 0.09 ohm-cm^2 (300 micron thick membrane)

Technical Accomplishments – AEMs meet Conductivity Targets

- AEM synthesis used a new multiblock polymer backbone as 'proto'
- Blocks include:
  - Functionalizable block (for addition of cation etc.)
  - Elastomeric block for mechanical properties
  - Block to control swelling
- Another example of 'polymers by design'

Milestone: conductivity greater than 60 mS/cm at 50% RH achieved

Collaborations

- NB: In general, we are at an early stage and are not yet ready for or requiring collaboration

- Partners
  - University of Tennessee-Knoxville: Zawodzinski, Mays joint appointment at ORNL

- Collaborative Activities
  - Participated in discussion of targets for AEMs/AFCs for next MYPP
  - Working with industry, non-profit partners to enable scale-up of syntheses, film formation, CCMs etc

Future Work

- Develop CCM preparation, including tailoring polymers for mechanical properties
- Continue AEM development using high-throughput polymer by design approach to explore
  - ***Milestone: less than 0.1 ohm-cm^2 with AEM***
- Cell testing
  - Electrocatalyst development
  - Electrode structure development with coating process
  - Extensive in situ diagnostics of cell performance
  - Modeling
- Refine Durability testing
  - Increase level of detail to reveal degradation mechanisms
  - ***Milestone: report on findings***

Summary

- **Objective:** Develop advanced membranes for AFCs.
- **Approach:** Prepare polymers using 'building block' approach
  - High throughput from a backbone polymer with a reactive group
  - Explore cation chemistry as well as effects of cross-linking and other additives to achieve high conductivity and high durability
- **Technical:** Two different paths are being explored. Excellent conductivity and apparently good durability have been achieved with 'CLAM' chemistry. Acceptable (target) conductivity has been achieved with AEM chemistry. MEAs have been prepared and reach ASR targets.
- All FY15-16 milestones are on schedule.
- **Collaborators:** Univ. Tennessee-Knoxville
- **Commercialization:** Patent applications in development.

Acknowledgements

- U.S. DOE EERE-FCTO

- Shane Foister
- Asa Roy, Ramez Elgammal, Chris Bruneau, Mary McBride
- Jimmy Mays, Kostas Mischronis
- David Wood III, Jianlin Li
- Todd Toops

Information Dissemination and Commercialization

- **Patenting in progress**