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High Temperature Membrane with Humidification-Independent Cluster Structure

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Overview

Timeline

- Start: June 2006
- End: May 2011
- 80% complete

Barriers

- Low Proton Conductivity at 25-50% Inlet Relative Humidity and 120^{o}C

Budget

- Total project funding
  - DOE share: $1500k
  - Contractor share: $600k
- Funding received in FY09: $300k
- Funding for FY10: $300k

Partners

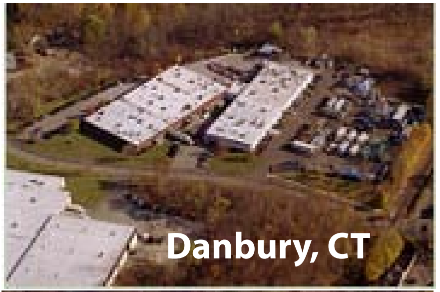
- Polymer Partner
  - Polymer & membrane fab. and characterization
- Additive Partners
  - Additives synthesis and characterization
- Consultants
  - Polymer, additives

Acknowledgements

- DOE: Donna Ho, Terry Payne, Jason Marcinkoski, Amy Manheim, Greg Kleen, Reg Tyler, Tom Benjamin and John Kopasz
- UCF: Jim Fenton, Darlene Slattery & Team (Testing protocols, membrane and MEA evaluation)
- FCE Team: Pinakin Patel, Ray Kopp, Jonathan Malwitz

FCE Overview

- **Leading fuel cell developer for over 40 years**
  - MCFC, SOFC, PAFC and PEM (up to 2.8 MW size products)
  - Over 500 million kWh of clean power produced world-wide (>50 installations)
  - Renewable fuels: over two dozen sites with ADG fuel
  - Ultra-clean technology: CARB-2007 certified: Blanket permit in California
- **Highly innovative approach to fuel cell development**
  - Internal reforming technology (45-50% electrical efficiency)
  - Fuel cell-turbine hybrid system (55-65% electrical eff.)
  - Enabling technologies for hydrogen infrastructure
    - Co-production of renewable H_2 and e^- (60-70% eff. w/o CHP)
    - Solid state hydrogen separation and compression
- **High temp. membrane: leverage existing experience in composite membranes for other fuel cell systems (PAFC, MCFC, SOFC)**



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Relevance

Objectives:

- Develop polymer membranes with improved conductivity at up to 120°C
- Develop membrane additives with high water retention and proton conductivity
- Fabricate composite membranes
- Characterize polymer and composite membranes
- Fabricate MEAs using promising membranes and characterize

Relevance

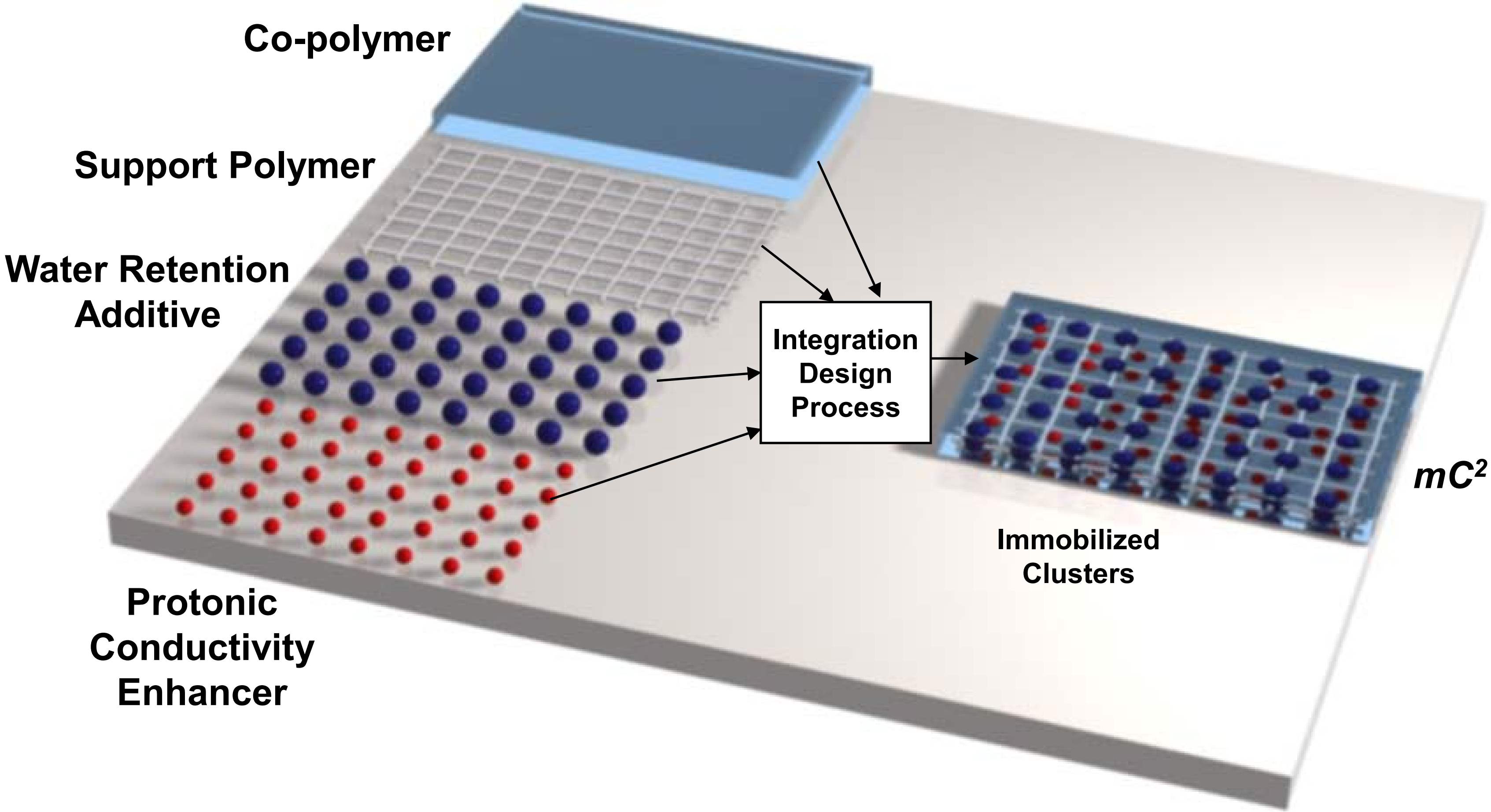
Impact of HTM:

- **Higher conductivity membranes increase power density and efficiency of the fuel cell stack**
- **Operation at low relative humidity (RH) eliminates need for external humidification → simplifies the fuel cell system**
- **Operation at elevated temperatures simplifies thermal management (smaller radiator)**
- **Simpler system increases overall efficiency of fuel cell power plant → contributes to DOE cost goal ≤ \$45/kW$_e$**
- **Reduced weight of automotive fuel cell system leads to higher fuel efficiency**

Approach for the Composite Membrane

Target Parameter	DOE Target (2010)	Approach
Conductivity at: 120 C	100 mS/cm	Multi-component composite structure, lower EW, additives with highly mobile protons
: Room temp.	70 mS/cm	Higher number of functional groups
: -20 C	10 mS/cm	Stabilized nano-additives
Inlet water vapor partial pressure	1.5 kPa	Immobilized cluster structure
Hydrogen and oxygen cross-over at 1 atm	2 mA/cm^2	Stronger membrane structure; functionalized additives
Area specific resistance	0.02 Ωcm^2	Improve bonding capability for MEA
Cost	20 $\$/m^2$	Simplify polymer processing
Durability: - with cycling at >80 C - with cycling at $\leq$80 C	 >2000 hours >5000 hours	Thermo-mechanically compliant bonds, higher glass transition temperature
Survivability	-40 C	Stabilized cluster structure design

Composite Membrane Concept



Multi-Component System with Functionalized Additives

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Milestones

Milestone	FY09 Goal	FY10 Goal	Current Status
Screen Nano-additive Incorporation Options	complete	-	**complete** ✓
Characterize Advanced Membrane	complete	-	**complete** ✓
120°C Conductivity: Go/No-Go	100 mS/cm at 50% RH	-	**86-148 mS/cm** ✓
Provide membrane samples to UCF for MEA Fabrication	-	complete	**complete** ✓
Go/No-Go decision composite membrane	-	in progress	**in progress**
Select low-cost, long life membrane design	-	planned	**planned**
1000 hr stability test	-	planned	**planned**

All FY09 Milestones Met, FY10 in Progress

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Technical Accomplishments

Major Achievements:

- **Resolved 80% of issues observed in additive synthesis**
- **Significantly increased batch size for both additive types**
    - **Proton Conductivity Enhancer from 1 to 25g batch**
    - **Water retaining additive from 2 to 8g batch**
- **Incorporation of Additives into mC^2 at the Nano-scale**
- **All FY09 Program Milestones Met**

Technical Accomplishments

Design of Experiments Leading to Accomplishments since last Review:

- **Three preparations of improved low-EW co-polymer, with increased molecular weight**
- **Development of new solvent system for improved compatibility with di-valent protonic conductivity enhancer**
- **Fabrication and characterization of eight additive batches (water retaining and proton conducting)**
- **Synthesis of over 10 batches of mC^2**
- **Over 15 membrane conductivity tests**

Technical Accomplishments

Improvements in Proton-conducting Additive for mC^2

Parameter	Baseline	Improved	Positive Impact
No. of mobile protons per molecule	one	two	Enhance protonic conductivity
Thermal Stability	~200 C	300+ C	Greater robustness during synthesis of mC^2 and MEA
Processing Cost			
- Batch size	1g	25g	Improve process control for scale-up
- No. of steps	12	7	Lower processing cost
- Precursor	expensiv e	lower cost	Reduced raw material cost

Technical Accomplishments

Additive Synthesis

Issue Observed	Improvement Strategy	Status	Resolved
Instability of water retaining nano-particles: particle size growth from 80 to 1000^{+} nm	Identify triggers for agglomeration	Good stability achieved (eliminated drying step)	√
Chemical stability of water retaining nano-particles	Process changes to avoid the triggers	Particles of 50-80 nm diameter	√
Relatively low proton density in protonic conductivity enhancer	Increase density of mobile protons	Synthesized protonic conductivity enhancer with twice the amount of mobile protons per molecule	In progress
High cost of protonic conductivity enhancer	Identify alternate molecule with simpler synthesis and lower starting material cost	Synthesized additive with ~15x lower material cost and ~6x shorter processing time per mobile proton	√
mC^2 synthesis limited by quantity of protonic conductivity enhancer	Scale-up protonic conductivity enhancer batch size	Increased batch size by 25x	√

Technical Accomplishments

Additive Functionalization

Issue Observed	Improvement Strategy	Status	Resolved
Due to large size of protonic conductivity enhancer molecule, proton density is not increased vs. low-EW polymer	Improvement expected due to higher proton mobility	Awaiting verification via conductivity and cell testing	In progress
Protonic conductivity enhancer adsorbs readily on water retaining additive, but high loadings causes agglomeration and could leach out	Limit loading to monolayer (stronger bonds)	mC^2 synthesis with new batch of functionalized additive in progress	In progress

Technical Accomplishments

mC^2 Fabrication

Issue Observed	Improvement Strategy	Status	Resolved
Additive particles concentrated on top side of cast mC^2 film	Avoid particle shifting during drying step (decrease solvent evaporation rate)	Synthesized dispersion with 3x higher polymer content	√
Chemically changed structure of additives in fully processed mC^2	Identify chemical incompatibility and/or processing mismatch	Modified polymer solvent system for improved compatibility	√
Additive particle concentration in mC^2 lower than expected	Identify leaching mechanism	Eliminated hot acid treatment step from mC^2 processing	√
Unsupported protonic conductivity enhancer leaches out of mC^2 in boiling water	Support protonic conductivity enhancer on water retaining additive	mC^2 synthesis with new batch of functionalized additive in progress	In progress
Ionomer mechanical properties reduced at low EW	Develop alternate polymerization process to increase molecular weight (greater polymer chain entanglement)	Awaiting verification via conductivity and cell testing	In progress

Technical Accomplishments

MEA Fabrication

Issue Observed	Improvement Strategy	Status	Resolved
UCF's standard MEA fabrication requires ion exchange with metal ion – not previously tested with FCE's polymer	Fabricate according to UCF procedure and run cell test	UCF cell test in progress – initial results encouraging	In progress
UCF's standard MEA fabrication requires long hotpressing time (~30 minutes) – could damage polymer in H^+ form	Modify temperature settings to reduce hot pressing time	Successfully hot pressed within 7 minutes; MEA evaluation in progress	In progress
Metal ion exchange may not be reversible for functionalized additive	Modify UCF MEA fabrication procedure to avoid ion exchange	Initial sample fabricated at UCF; testing in progress	In progress

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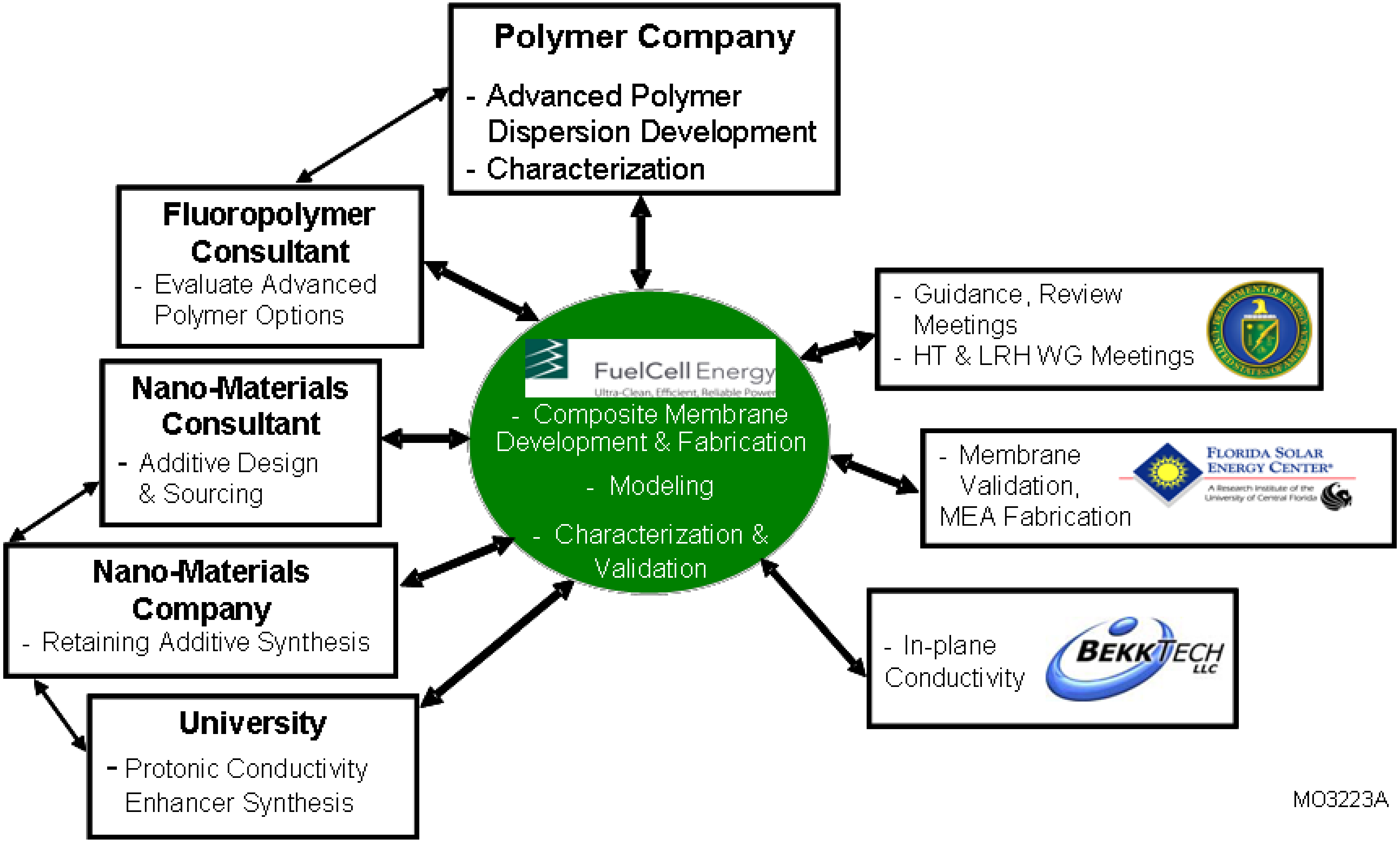
Technical Accomplishments

Development of mC^2 Components and Synthesis Process Improvements

- **Proton Conducting Additive: Synthesized improved additives with greater proton density, greater thermal stability and over 80% reduction in cost.**
- **Water Retention Additive: Identified processing factors leading to chemical instability and physical particle size growth. Improved synthesis process developed and validated.**
- **Additive Functionalization: High level of agglomeration observed. Concentration optimization led to a mono-layer coverage strategy.**
- **mC^2 Fabrication: Identified adverse interactions between the co-polymer and functionalized additives leading to functionality and activity loss. Development of a more robust synthesis process is underway.**
- **MEA from Baseline Membrane: Delivered improved membrane materials to UCF for MEA fabrication and validation.**

Collaborations



Comprehensive Team Integrates Specialized Expertise

Proposed Future Work

- Continue to develop advanced polymer dispersions (increase molecular weight, lower EW)
- Optimize and further simplify integration of additives (integrate at precursor level)
- Develop compatible MEA fabrication process in collaboration with UCF
- Cell testing at 95 and 120°C
- Durability Testing (including 1000^{+} hr stability test)

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Proposed Future Work

Upcoming Key Milestones:

- **Go/No-Go decision for composite membrane (46 month milestone)**
- **Select low-cost, long life membrane design (50 month milestone)**
- **Readiness to meet DOE targets (1000 hr stability test – 52 month milestone)**
- **Membrane/MEA evaluation by DOE (annually)**

Project Summary

- Identified improved water retaining additive processing conditions to provide particle stability during functionalization and mC^2 fabrication
- Identified and synthesized higher proton density and lower cost protonic conductivity enhancer
- Each new or modified additive has required synthesis and steps to incorporate into the mC^2 process
- Working with UCF to resolve MEA fabrication challenges
- Overall, about 50% of the issues identified have been resolved. Work is progressing to resolve the remaining challenges

Project Summary Table

DOE 2010 Technical Targets for Membranes for Transportation Applications				
Performance Parameter	Units	2010 Target	Standard Membrane Nafion NRE-212®	FY09-10 Result
Conductivity at 30°C and 80% RH	mS/cm	70	33	74
Conductivity at 120°C and 50% RH	mS/cm	100	39	86-148

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