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High Throughput Low-Cost Technologies for the Manufacturing of PEMs with Reduced In-plane Swelling

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Monday June 17th, 2013

Hydrogen + Fuel Cells 2013 Vancouver June 16-19, 2013
Power, Transportation & Energy Storage
An Industry on the Move

National Research Council Canada
Conseil national de recherches Canada

Canada

• *Acknowledgments*

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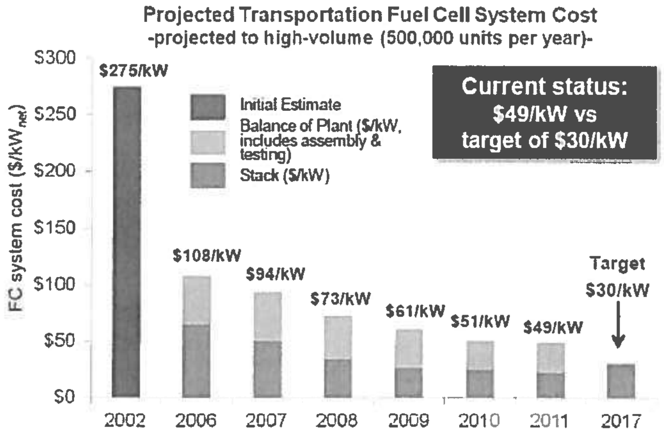
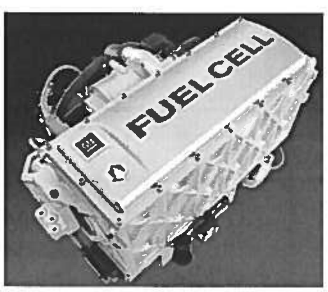
• Global Context



Source: US DOE FY 2013 Budget Request Rollout
February 14, 2012

- **Transportation is responsible of 27% of GHGs Emissions**
- **Electrification of transportation is a solution**
- **Cost reduction required!**

• PEMFC Cost Estimate



At low and intermediate APR, the PEM based electrolyte is still one of the more costly stack components and one needing to be reduced in cost to achieve a cost competitive fuel cell system

Cost estimate for automotive PEMFC stack as a function of annual production rate

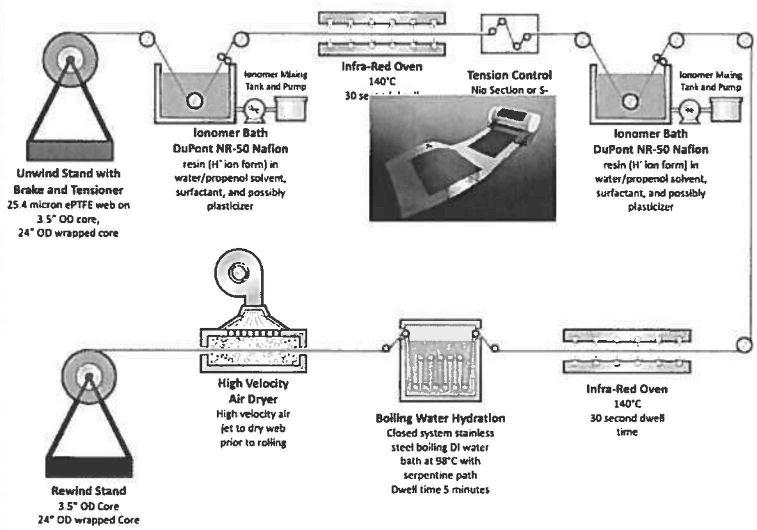
Annual Production Rate	1,000	30,000	80,000	130,000	500,000
System Net Electric Power (Output)	80	80	80	80	80
System Gross Electric Power (Output)	87.91	87.91	87.91	87.91	87.91
Bipolar Plates (Stamped)	$1,684.28	$434.15	$439.95	$433.03	$429.07
MEAs					
Membranes	$5,184.51	$908.84	$562.23	$438.23	$230.78
Catalyst Ink & Application (NSTF)	$1,252.28	$700.37	$695.57	$698.62	$694.83
GDLs	$2,140.33	$1,111.35	$691.53	$537.04	$242.57
M & E Hot Pressing	$72.09	$9.98	$8.23	$8.36	$8.16
M & E Cutting & Slitting	$56.94	$4.42	$3.29	$3.02	$2.82
MEA Frame/Gaskets	$469.80	$319.59	$311.95	$308.29	$301.42
Coolant Gaskets (Laser Welding)	$185.48	$26.48	$29.43	$27.39	$25.54
End Gaskets (Screen Printing)	$149.48	$5.08	$1.97	$1.25	$0.54
End Plates	$87.43	$33.55	$28.91	$26.21	$19.86
Current Collectors	$16.79	$7.18	$5.99	$5.54	$5.07
Compression Bands	$10.00	$8.00	$6.00	$5.50	$5.00
Stack Housing	$61.44	$7.54	$6.44	$5.87	$5.16
Stack Assembly	$76.12	$40.69	$34.95	$33.62	$32.06
Stack Conditioning	$170.88	$53.87	$47.18	$41.38	$28.06
Total Stack Cost	$11,617.87	$3,671.08	$2,873.61	$2,573.36	$2,030.92
Total Stack Cost ($/kW$_{net}$)	$145.22	$45.89	$35.92	$32.17	$25.39
Total Stack Cost ($/kW$_{gross}$)	$132.16	$41.76	$32.69	$29.27	$23.10

"Mass Production Cost Estimation for Direct H2 EM Fuel Cell Systems for Automotive Applications: 2010 Update," September 30, 2010; B.D. James, J.A. Kalinoski, K.N. Baum;

• PEM Manufacturing Process

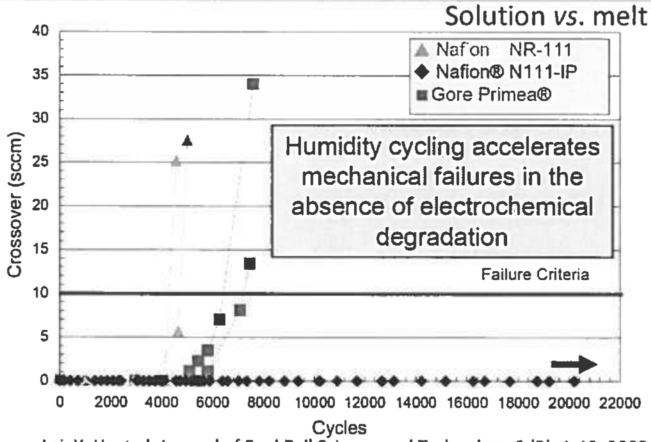
Gore-Select ® membrane fabrication process

- Gore-Select® SOTA electrolyte is based on Nafion® cast on a porous expanded e-PTFE substrate.
- The processing cost to manufacture the PEM remains a major and dominant cost element.
- A cost-competitive process with a reduced number of steps while maintaining the mechanical properties and the performance and durability of Gore® membranes still required.



• PEM Manufacturing Process

Solution *vs.* melt processing



Lai, Y.-H. et al. Journal of Fuel Cell Science and Technology 6 (2), 1-13, 2009.

- Different processing technologies may dramatically change the performance.
- Melt-extruded PEMs have improved mechanical durability compared to solution cast analogs.

MEA	Process for membrane manufacturing	Cycles to failure w/o load	Cycles to failure at a load of 0.1 A/cm²
DuPont™ Nafion® (NR-111)	Solution-cast (25 mm)	4000-4500	800-1000
Gore™ Primea	Reinforced solution-cast (25 mm)	6000-7000	1300
Ion Power™ Nafion® (N111-IP)	**Melt-extruded** (25 mm)	**20000+**	**1800**

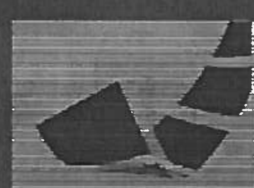
• Objectives

- Our collaborations and industrial projects are focused on paths with the most remaining opportunities and highest impact on cost, performance and durability.

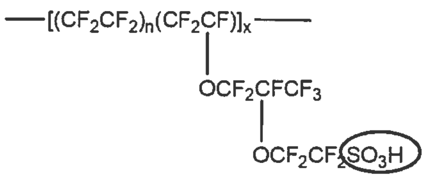
- One of our group focus is the development of advanced polymeric electrolytes with:
  1- higher performance and durability through components design and morphology control
  2- reduced cost through methods of manufacturing; thinner robust membranes, high throughput methods of manufacturing

• Project Objectives

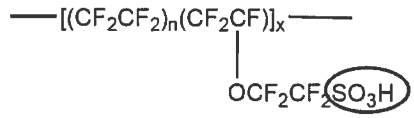
Develop a unique, high-volume manufacturing processes that produces low-cost, durable proton exchange membranes and membrane-electrode-assemblies, capable of meeting the demands of high volume production and durability requirements for automotive applications.



• Objectives



Structure of LSC PFSA



Structure of SSC PFSA

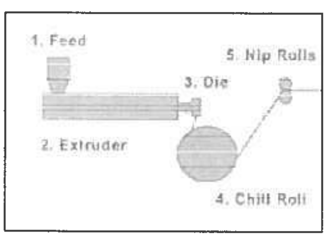
Polyelectrolyte membranes based on PFSA block copolymers are still the state-of-the-art polyelectrolytes in PEMFC

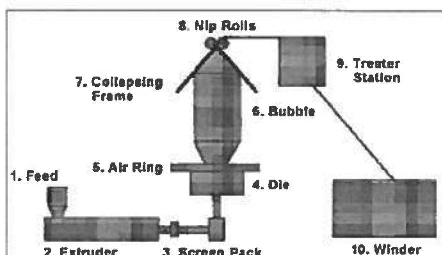
We proposed in this project:

- Investigate melt-processing technologies for thin polyelectrolytes manufacturing and assess their impact on the morphology and properties
- By the use of melt-processing technologies, we were also expecting to improve the durability and reduce manufacturing cost (easily scalable fabrication process for mass production)
- Increase low RH operation (hydrophilic inorganic fillers)

• Manufacturing Process

Melt-extruded thin polyelectrolytes : melt-casting vs. melt-blowing





PFSA: R-1000-CS from Ion-Power in the SO_2F form (EW=1000)
Post hydrolysis for conversion to the SO_3H form

Melt-blown film generally has a better balance of mechanical properties than melt-cast films because it is drawn in both the transverse and machine directions.

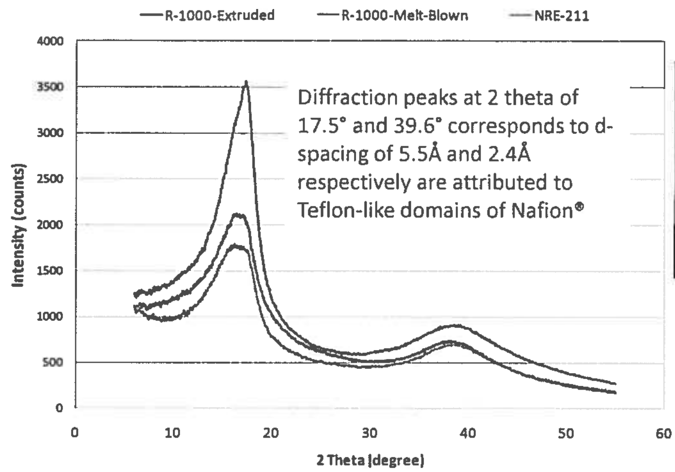
- Melt-blowing process allows a better thickness control (minimize waste)

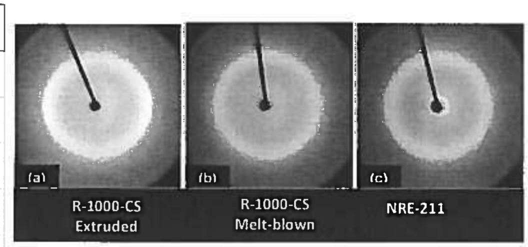
Pilot-scale for thin films polyelectrolytes multilayer melt-blowing process

• Characterization: XRD

(patent application USSN 61/577,138)

XRD Transmission mode on solution-cast extruded and melt-blown membranes





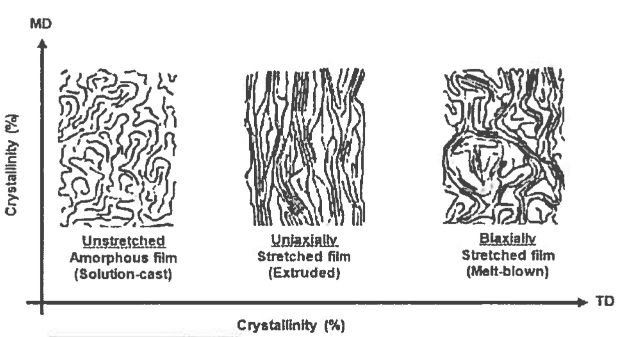
Anisotropic pattern due to the higher orientation generated from the stretching in the machine direction during the cast-extrusion process to achieve the required thickness

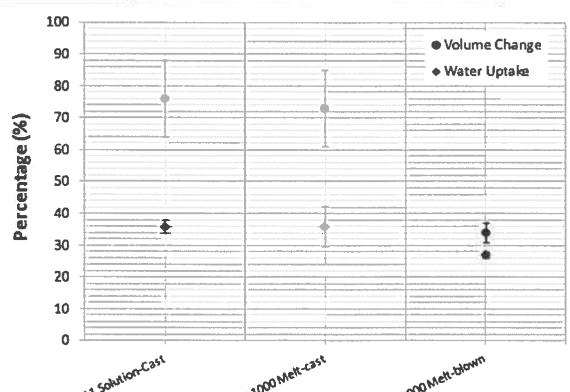
• Characterization: EIS, WU, VC

Melt-extruded thin polyelectrolytes : melt-casting vs. melt-blowing

Sample	IEC (mmol/g)	Conductivity (mS/cm)			Water Uptake (%)	Volume Change (%)
		RT, 100%RH	80°C, 50%RH	80°C, 30%RH		
NR-211	0.91	68.7	23.3	6.04	36.00	76.00
R-1000CS melt-cast	0.92	72.8	27.2	1.96	36.00	73.00
R-1000CS melt-blown	0.87	82.3	34.5	6.67	25.86	35.12

Schematic representation of crystallinity evolution with processing

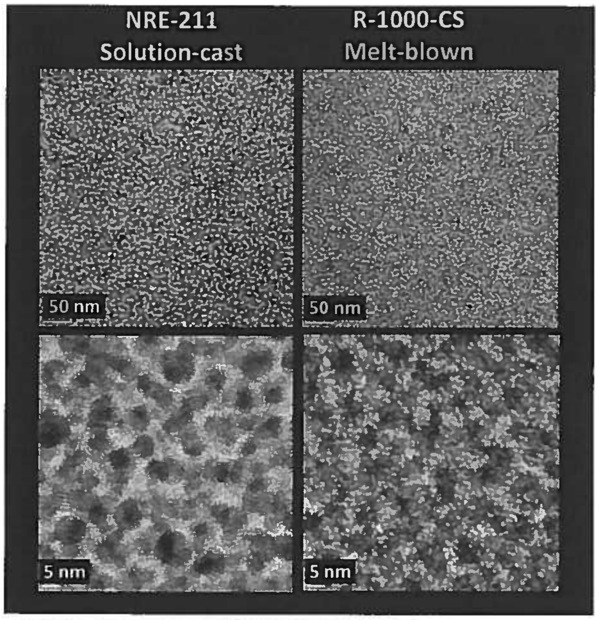


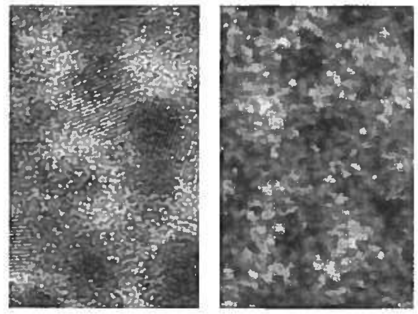


(patent application USSN 61/577,138)

• *Morphology revealed by TEM*

TEM on microtomed and Lead Acetate stained membranes



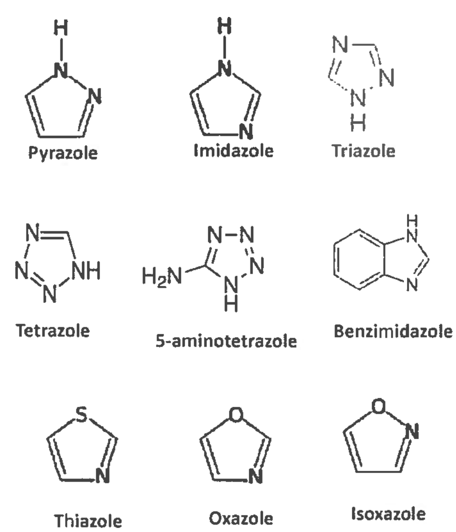


- Solution-cast membrane: ordered ionic domains agglomerated in spheres ranging from 3 to 10 nm diameter
- Melt-extruded membrane: smaller domains (4 to 6 nm), improved dispersion and connectivity . Higher density. Smaller water channels.

• *Bi-functional Additives*

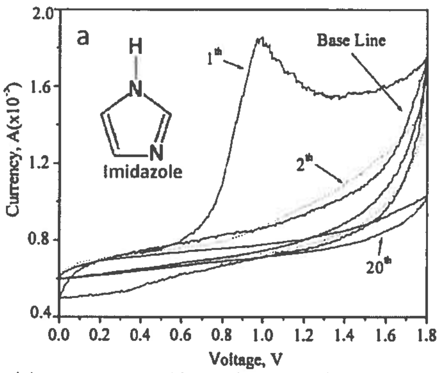
Azoles: bi-functional additives

- Extensively studied as proton carriers in anhydrous PEM especially nitrogen based
- Antifungal function and <u>radical scavengers</u>
- Bi-functional additives:
  - Protection of functional groups (SO_3H)
  - rheology modifiers (Plasticizers)

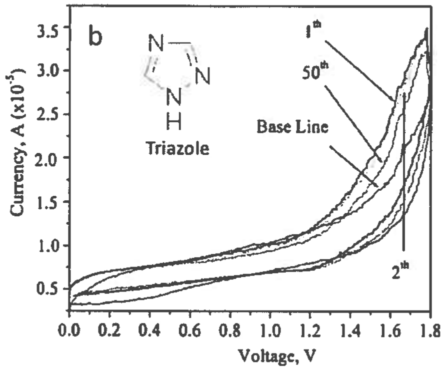


• Bi-functional Additives

Li et al. Chem. Mater. 2005, 17, 5884-5886



(a) Large irreversible oxidation peak near +1.0V (vs Ag/Ag+) in the voltammogram for imidazole. Oxidation products of imidazole are absorbed on the surface Pt electrode and block the surface active sites.

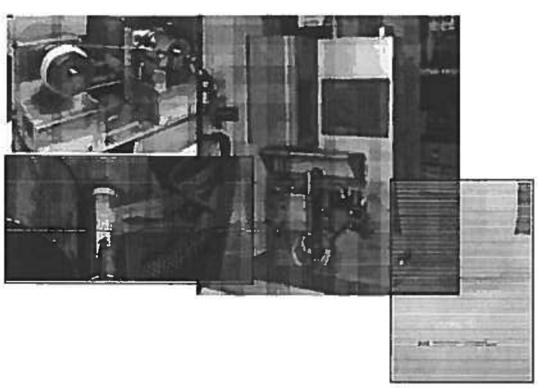


(b) No redox peaks observable for triazole in a wider potential range, 0 to +1.8V (vs Ag/Ag+), and no obvious change took place in the subsequent 50 cycles.

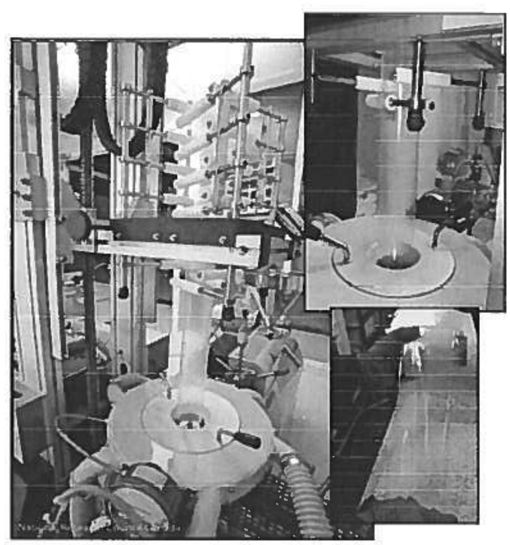
- Imidazole appears to be inadequate for fuel cell applications, largely due to the high electronic density of the Im ring and also due to the diffusion and absorption on the surface of the catalyst
- Azoles with lower electronic density are electrochemically stable for fuel cell applications and effectively promotes proton conductivity of materials and under anhydrous conditions

• Lab-scale and Pilot-scale Manufacturing

Lab-Scale melt-casting and Pilot-scale multilayer melt-blowing line
for thin films polyelectrolytes prototyping

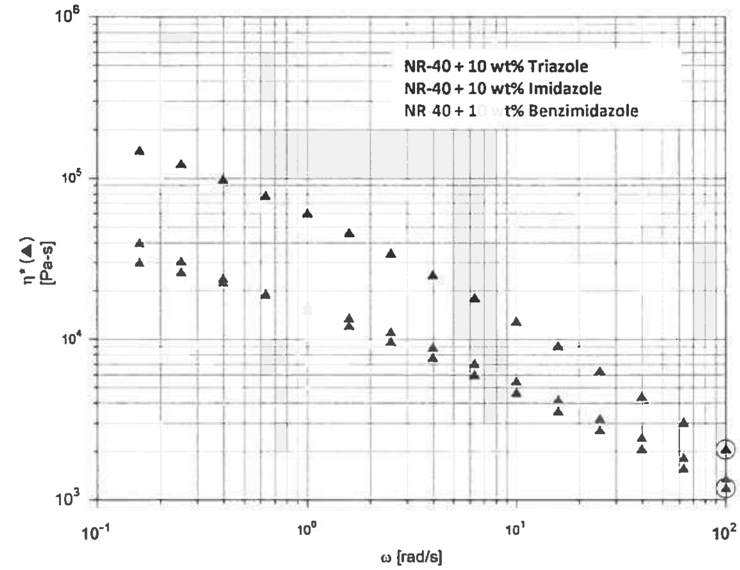


PFSA ionomer: Nafion® NR-40 from Ion-Power in the SO_3H form (EW=1000)
Processing temperature: 260°C



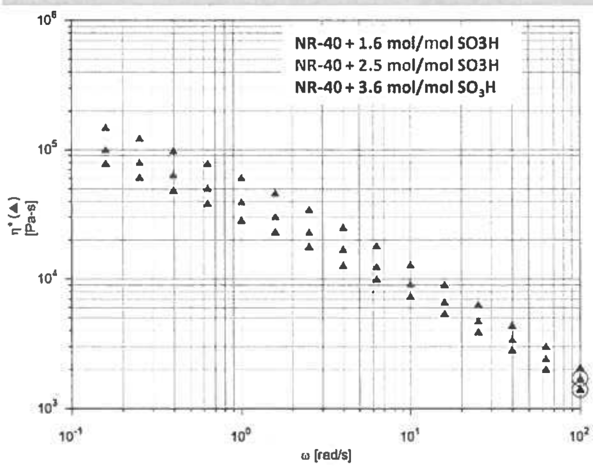
US Provisional patent 61/767.849

• Advanced polyelectrolytes for PEMFC

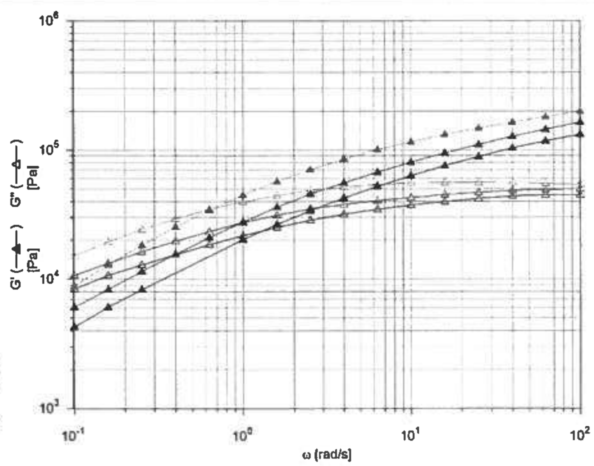


Comparison of viscoelastic dynamic modulus (η*) obtained from frequency sweep tests on Nafion®NR-40 at 260°C with different additives

• Characterization: Rheology (ARES)



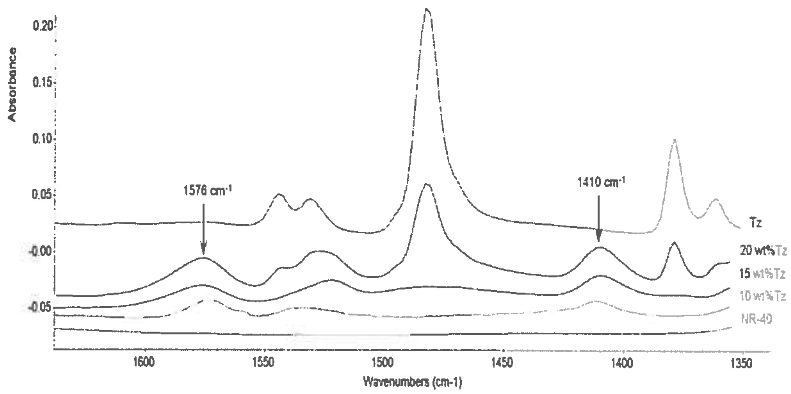
Comparison of viscoelastic dynamic modulus (η*) obtained from frequency sweep tests on NR-40 at 260°C with different additive molar ratios



Comparison of viscoelastic Viscoelastic dynamic storage modulus (G') and loss modulus (G'') obtained from frequency sweep tests on NR-40at 260°C with different additive molar ratios

• Characterization: FTIR-ATR Analysis

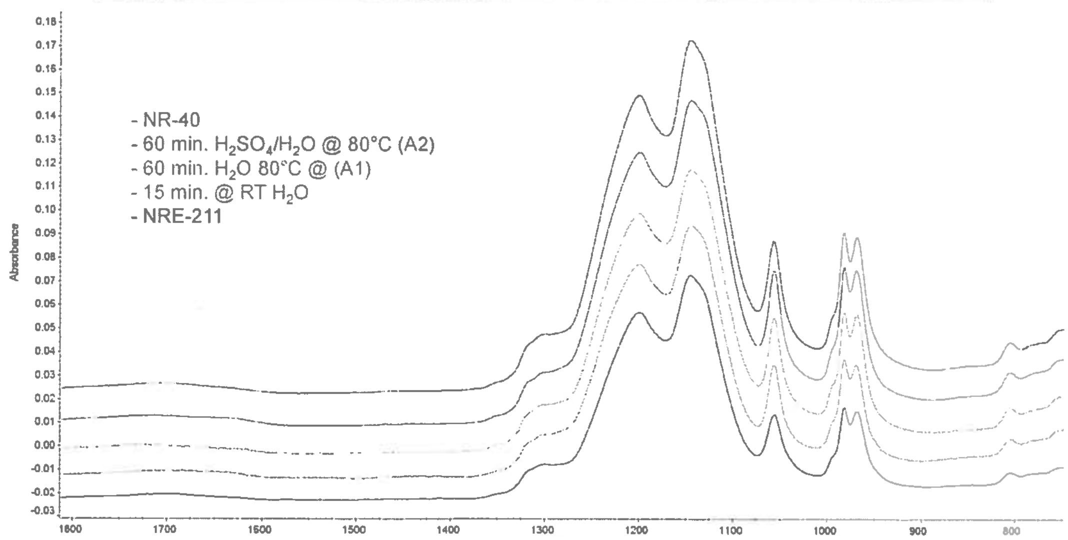
ATR-FTIR spectra recorded for NR-40, triazole and triazole-based PEMs



- Absorption bands at 1576 and 1410 cm^{-1} may be associated to the protonation of the heterocycle of azole as it is speculated that the protons in the Nafion-Tz blend structure are strongly interconnected between SO_3^- and Tz. (Ref. J. Electrochem. Soc. 154(4), A290, 2007)

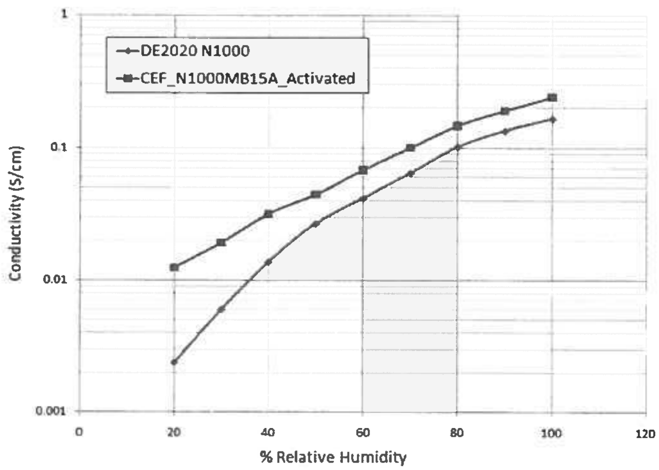
• Characterization: FTIR-ATR Analysis

ATR-FTIR spectra for NR-40 based PEMs with different activation protocols, compared with NRE-211



• *Characterization: Conductivity (EIS)*

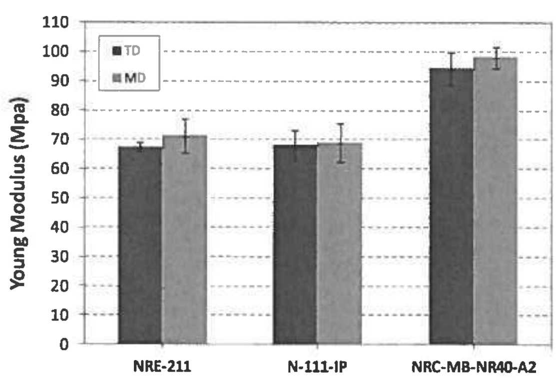
Conductivity as a function of RH and mechanical durability performed by collaborators at GM Electrochemical Energy Research Lab

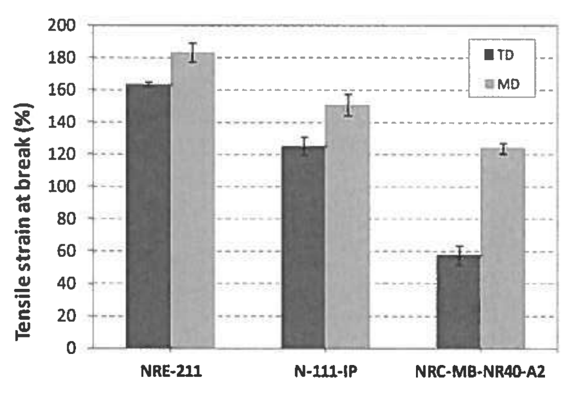


- Mechanical durability protocol: RH cycling from 0 to 150% at 80C
- > 20000 cycles greater than the 6000 cycles lifetime of cast Nafion® reference sample.

• Characterization: Mechanical Properties

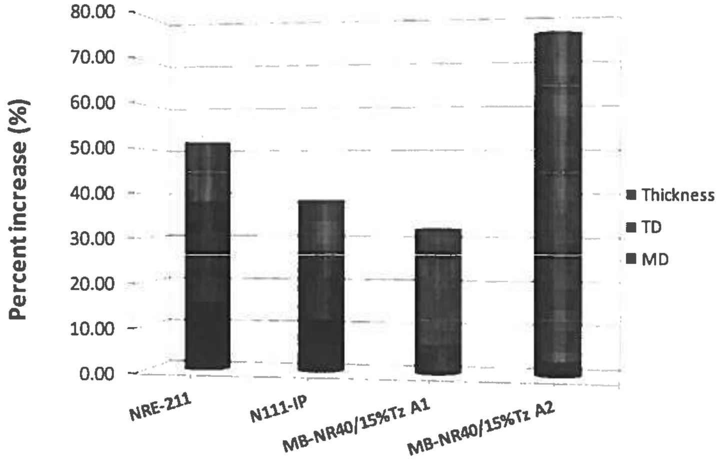
Micro-tensile properties of membranes activated with protocol A2 compared to commercial references





• Characterization: Dimensional stability

Dry/wet changes in thickness and linear expansion in the machine direction (MD) and transverse direction (TD)



These polyelectrolytes swell preferentially in the thickness direction, with little in-plane swelling differing from all commercially available materials!

• Dimensional stability

Pestrak et al. Journal of fuel cell Sci. Tech. 2010, Master Degree thesis Virginia Tech 2010
Gittleman et al. Polymer Electrolyte Fuel Cell Degradation. Elsevier Chap 2. 2012

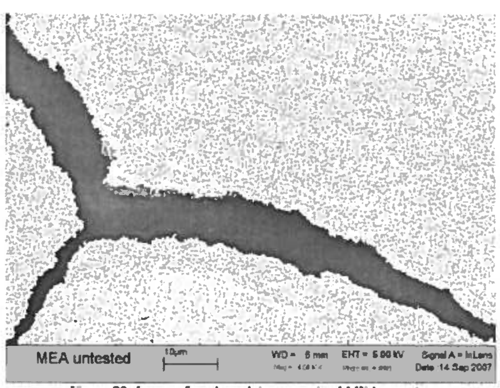


Figure 22: Image of mud crack in as-received MEA sample.

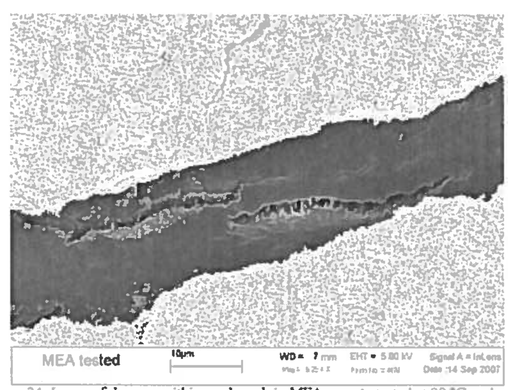
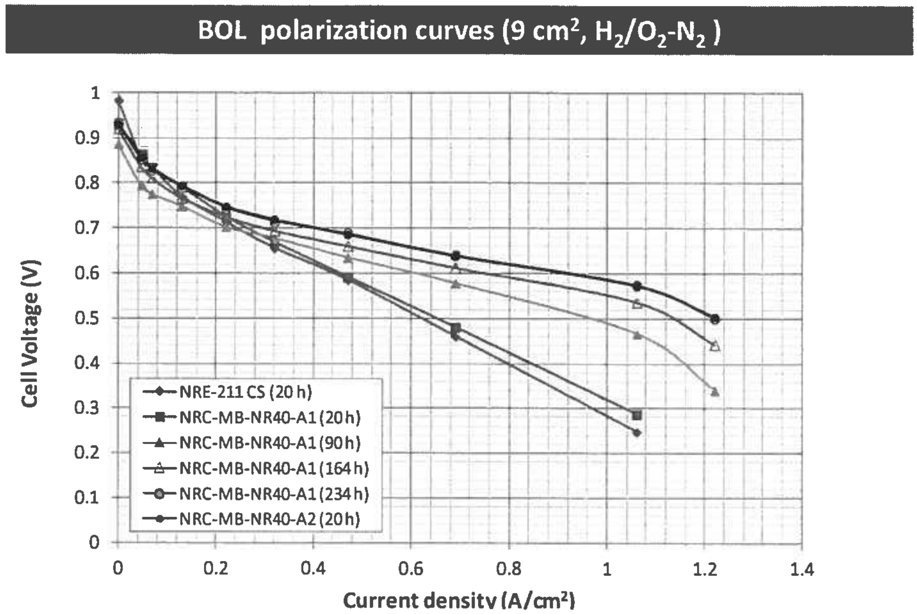


Figure 24: Image of damage within mud crack in MEA sample tested at 90 °C under 20-20 s cycling.

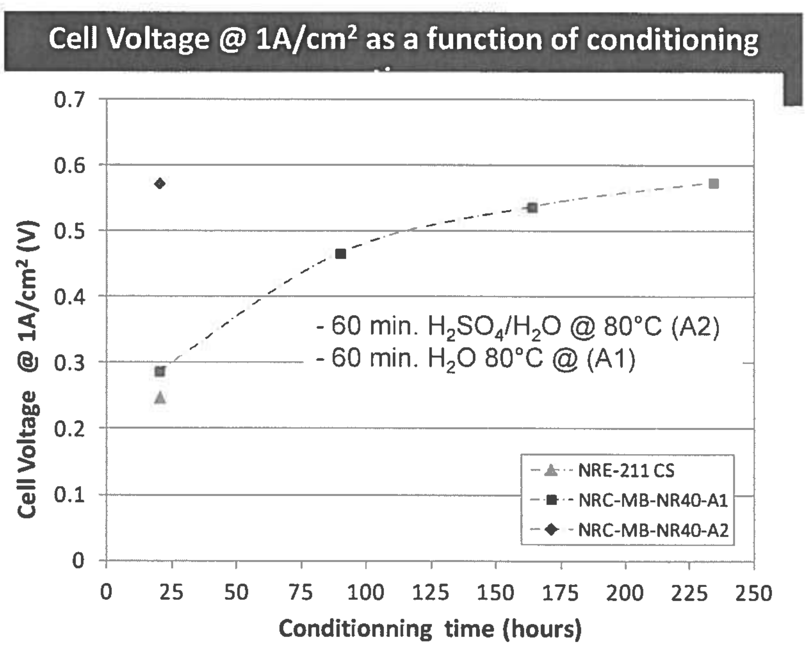
- Polyelectrolyte membranes dimensional stability is critical for PEMFC durability (5000 hours lifetime required for commercial use)
- Reduced volume change during hydration dehydration cycles, may prevent cracks in the catalytic layer and membrane and MEA failure

• Characterization: Polarization FC testing

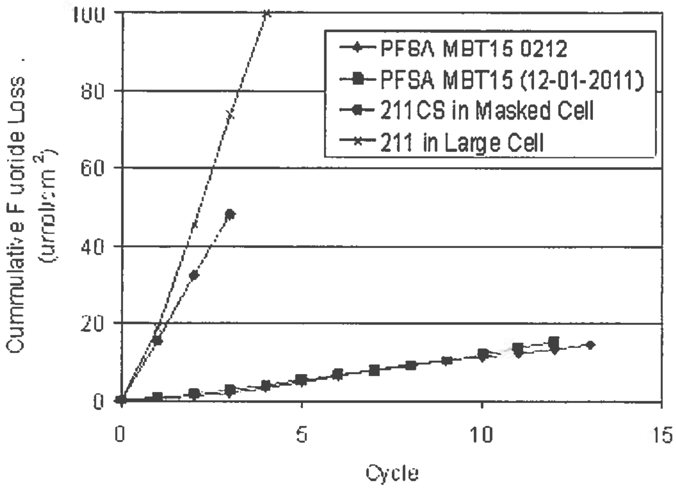


Results provided by Ballard Power Systems

• Characterization: Polarization FC testing



• Characterization: Cumulative Fluoride Loss (OCV AST)



CFL from the cyclic OCV AST on 5 cells stack with Nafion® 211 references and acid extruded PFSA membranes of this project.

Results provided by Ballard Power Systems

- Outstanding chemical durability
- Cumulative fluoride loss was more than one order of magnitude lower than Nafion® 211 reference

CFL = 160 mmol/cm^2 after 120 hours (9.6 cycles) for the stack with Nafion® 211 baseline

CFL = 5 mmol/cm^2 after 162.5 hours (13 cycles) for the five cell stack with the new PEM technology

• Conclusions

1. The use of melt processing technologies allows the identification of opportunities for significant performance and durability improvement , and cost reduction of PFSA based polyelectrolytes for PEMFC

2. Azoles have been used successfully as bi-functional additives providing robust PEMs with reduced in-plane swelling and durability that meets automotive requirements

• *Acknowledgments*

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CNRC·NRC

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Clean Energy Fund Program

Natural Resources Canada

Program for Energy Research and Development

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