Development of High Performance Fuel Cell Membranes for the Automotive Industry

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Development of High Performance Fuel Cell Membranes for the Automotive Industry

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National Research Council Canada Conseil national de recherches Canada

Canada

NRC·CNRC
Automotive

Outline

- Introduction of NRC-IMI: expertise and technological platforms
- Development of solid polymer electrolytes for:
  - hydrogen fuel cells
  - lithium batteries
- Conclusions
- Acknowledgments

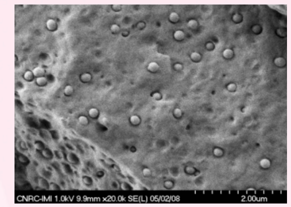
Overview of NRC-IMI:
Mission

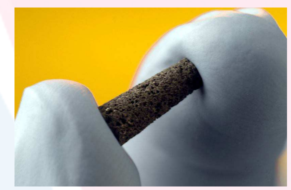
NRC-IMI's mission is to help Canadian industry to address the challenges of a sustainable economy and to develop solutions for national priorities by:

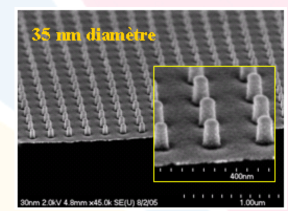
- Providing an advanced materials and manufacturing RTD capacity to key industries and to regional communities;

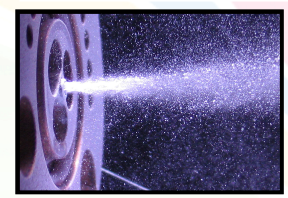
- Engaging industrial, academic and international partners in the commercialization of technology to strengthen Canada's innovation system;

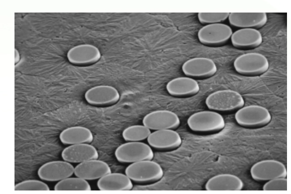
- Performing RTD research and technology anticipating threats and opportunities for national priorities.











Development of Fuel Cell Membranes at NRC-IMI

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Use of melt-processing technologies

- Cost reduction
- Easily scalable fabrication process for mass production
- Improved PEMs mechanical durability

New polyelectrolyte materials

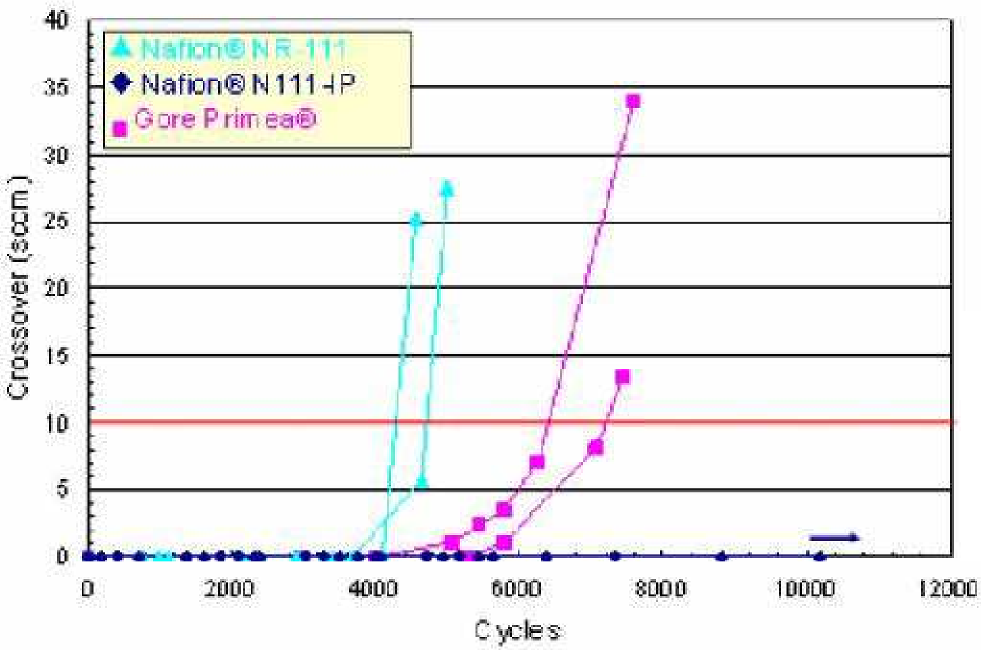
- Design of new materials through synthesis or melt-blending
- Enhanced performance at high T and/or reduced RH
- Improved dimensional and chemical stability
- Reduced permeability

Incorporation of nanofillers

- Increase the number of protonic carriers
- Increase operation temperature (grafting of high temperature proton carriers)
- Decrease water dependence
- Improve mechanical and chemical stability

Durability of Extruded Membranes

T. Greszler, GM Fuel Cell Activities, September 2006



Crossover leak as a function of number of humidity cycles during inert RH cycling of NR-111 (▲), N111-IP (◆), and Gore™ Primea® (■) PFSA membranes. The N111-IP tests were stopped before any crossover was measured. Line at 10 sccm indicates test failure criteria.

Homogeneous membranes:

- Nafion® NR-111 (Dupont), 25µm, solution-cast.
- Nafion® N-111-IP (IonPower), 25µm, extruded.

Composite membranes:

- Gore Primea® (Gore), 25µm, solution-cast.

MEA	Cycles to Failure w/o load	Cycles to Failure @ 0.1 A/cm^2
DuPont™ Nafion® (NR-111)	**4000-4500**	**800-1000**
Ion Power™ Nafion® (N111-IP)	**20000+**	**1800**
Gore™ Primea	**6000-7000**	**1300**

- Different fabrication processes change dramatically the electrolyte performance.
- Melt-processing generates morphologies that confer higher reinforcement and improved mechanical durability.

Fuel Cell Membranes: NRC-IMI's Technology

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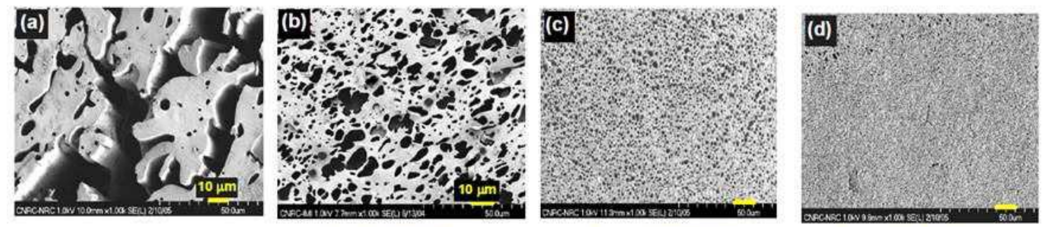


5 wt. %MAM 5 wt. %SBM5050 5 wt. %SBM2080

Morphology control achieved via melt-processing.

- Use of hydrocarbon-based PEMs is extremely cost effective.
- Melt-processing technologies are low-cost, easily-scalable manufacturing processes.

Polymer Morphology Control

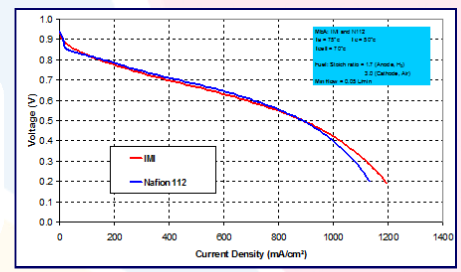
Performance

Mechanical Durability

Chemical Durability

Cost

Polymer blending provides a route to reduce volume swell, increase elasticity while maintaining fuel cell performance in hydrated conditions.



Courtesy of NRC-IFCI

Incorporation of additives is easily facilitated through melt blending.

- Extruded membranes show improved mechanical durability compared to cast membranes.
- Polymer blending provides reinforcement.

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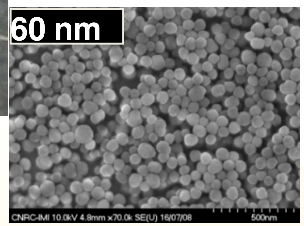
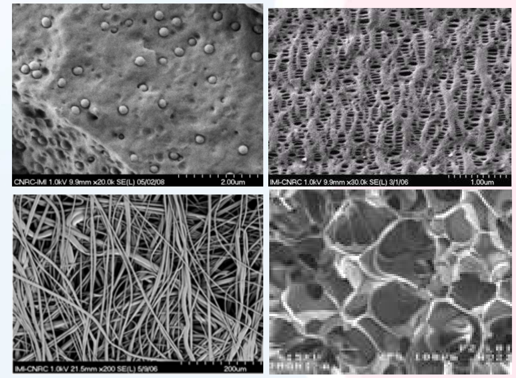
Expertise and Capabilities





Material Processing using Melt-Technologies

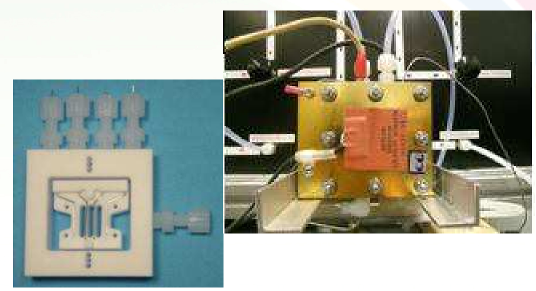
Polymer and Particle Synthesis

Material Characterisation

NRC-IMI

Failure Analysis and Mitigation Strategies

Performance & Durability Testing



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Expertise and Capabilities:
Processing Scale-up

5-layer blown film line
- 12.5 mm extruders (100-500g)
- 20 mm “pancake” die (layer flat 200 mm)
- ABCBA layer structure
- State-of-the-art air ring

5-layer cast film line
- 12.5 mm extruders (100-500g)
- 100 and 150 mm flat die
- ABCBA layer structure
- On-line characterization

Bench-top Extrusion [5 to 10g]

Micro-processing [100 to 500 g]

Pilot Scale [kg]

5-layer blown film line

100 mm die (layflat 850 mm)

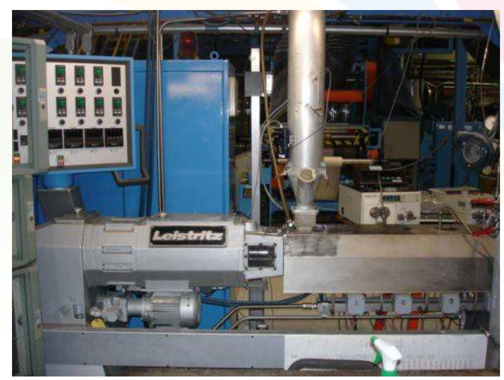
ABCDE layer structure

Monolayer blown film line

50 mm die, single layer

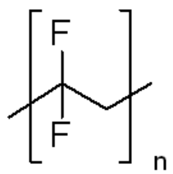
Twin-screw compounders

Leistritz 34 mm and W&P 30mm

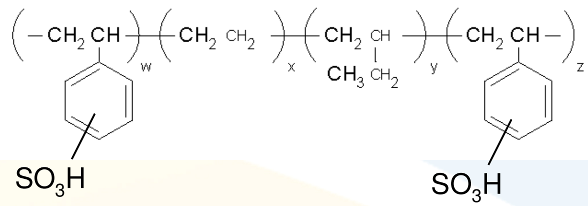


DSM micro-compounder (5cc) twin-screw
- Formulation development
- Preliminary investigations

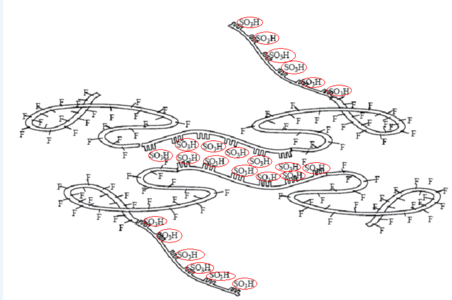
Semi-Fluorinated PEM from Polymer Blends



Polyvinylidene fluoride (PVDF)



Sulfonated Poly (styrene-(ethylene-butylene)-styrene) triblock copolymer (SEBS)

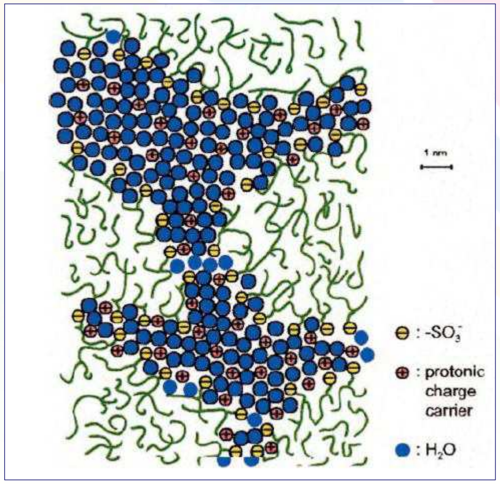


Reinforced Polymer Electrolyte Membrane

$$-(CF_2\text{-}CF_2)_n\text{-}CF\text{-}CF_2\text{-}$$
$$O\text{-}(CF_2\text{-}CF\text{-}O)_m\text{-}CF_2\text{-}CF_2\text{-}SO_3H$$
$$CF_3$$

Chemical Structure of Nafion©

Grot, W., Du Pont de Nemours and Company, U.S. 3718627, (1968)



Structure of Hydrated Nafion© Membrane

Paddison et al. Annu. Rev. Mater. Res. 33 (2003) 289

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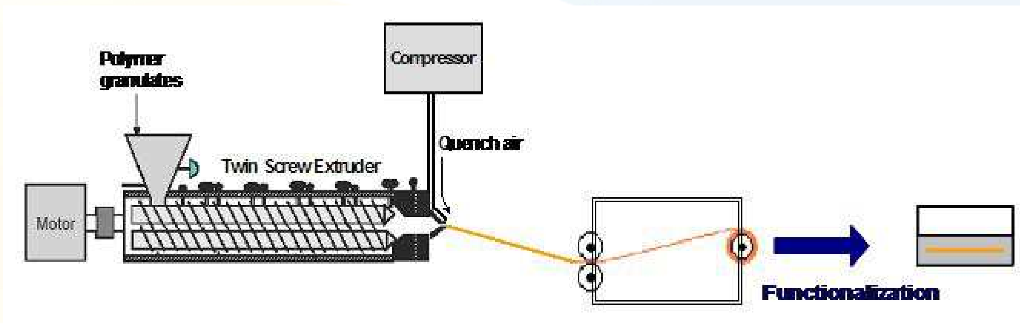
Semi-Fluorinated PEM from Polymer Blends

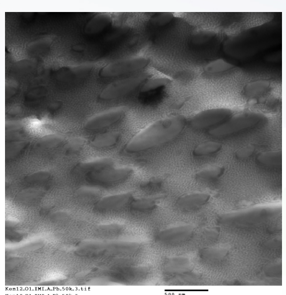
Processing:

- Large scale twin screw extrusion for blend SEBS/PVDF/compatibilizer blends preparation
- Twin screw extrusion – melt cast for membranes forming (down to 30 microns)

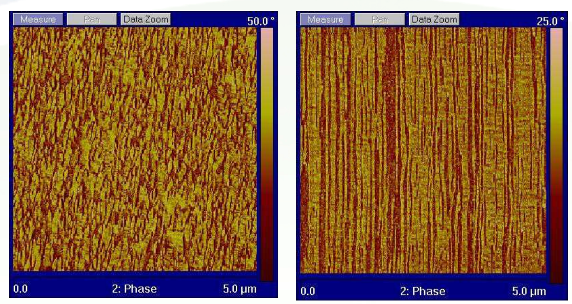


- Post-functionalization with $ClSO_3H$ in DCE
- Time and $ClSO_3H$ concentration to control the sulfonation degree

Pictures of the membrane before and after sulfonation



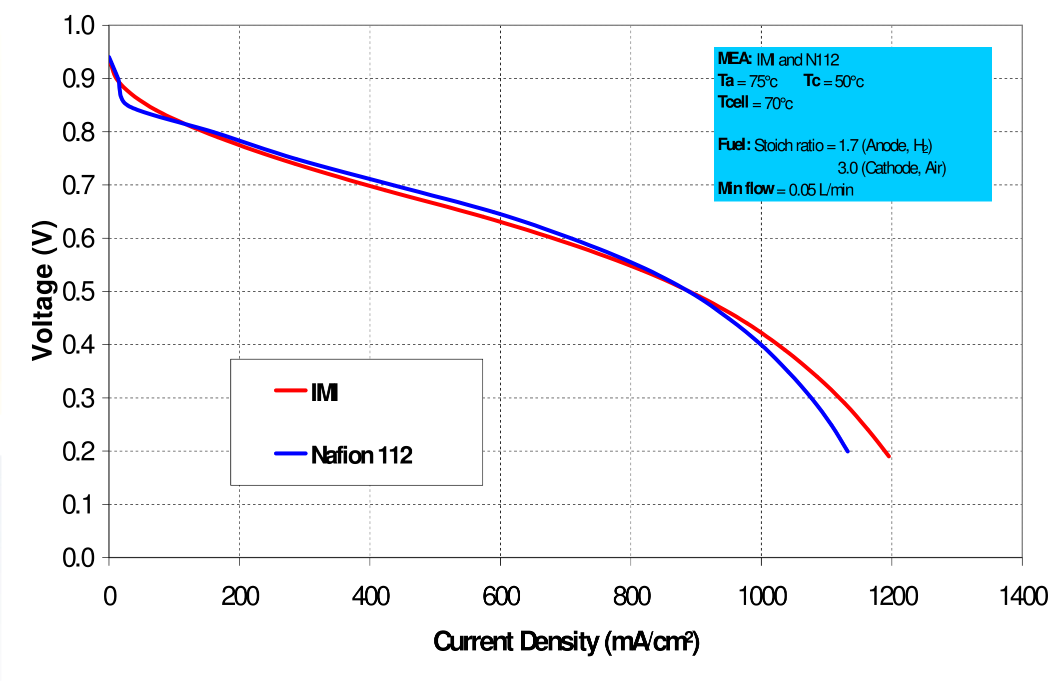
TEM image of a PVDF/SEBS membrane prepared by melt-extrusion



AFM on co-continuous semi fluorinated PEM prepared by melt-processing. Clear phase is the hydrophobic polymer (reinforcement). Dark phase is the hydrophilic polymer. (Right image: MD, left: TD)

Semi-Fluorinated PEM from Polymer Blends

I-V curve for ~50μm thick membrane (Courtesy of NRC-IFCI)

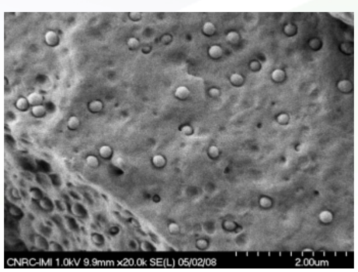


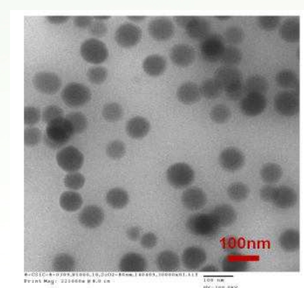
- CCM for MEA preparation; air for I-V curve measurements.
- BOL fuel cell performance close to that of Nafion 112.
- PEMs obtained by melt-processing technologies are robust and show very high mechanical properties and an outstanding hydrolytic stability (6000 hydration-dehydration cycles) with a hydrocarbon based ionomer.

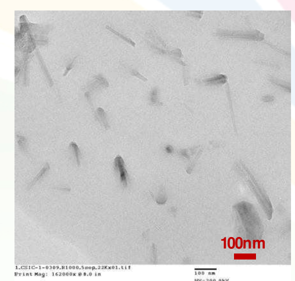
Nanocomposite PEMs

- Use of melt-processing technologies:
  - easily scalable process for mass production
  - cost reduction
  - improved performance compared to solvent cast membranes (durability, humidity cycling)

- Incorporation of inorganic nanofillers
  - good dispersion in the molten polymer
  - improve thermal stability, dimensional stability, fuel crossover
  - clay nanoparticles
  - silica nanoparticles







TEM images on nanocomposite melt-extruded PEMs (top with sepiolite; left: with silica nanoparticles).

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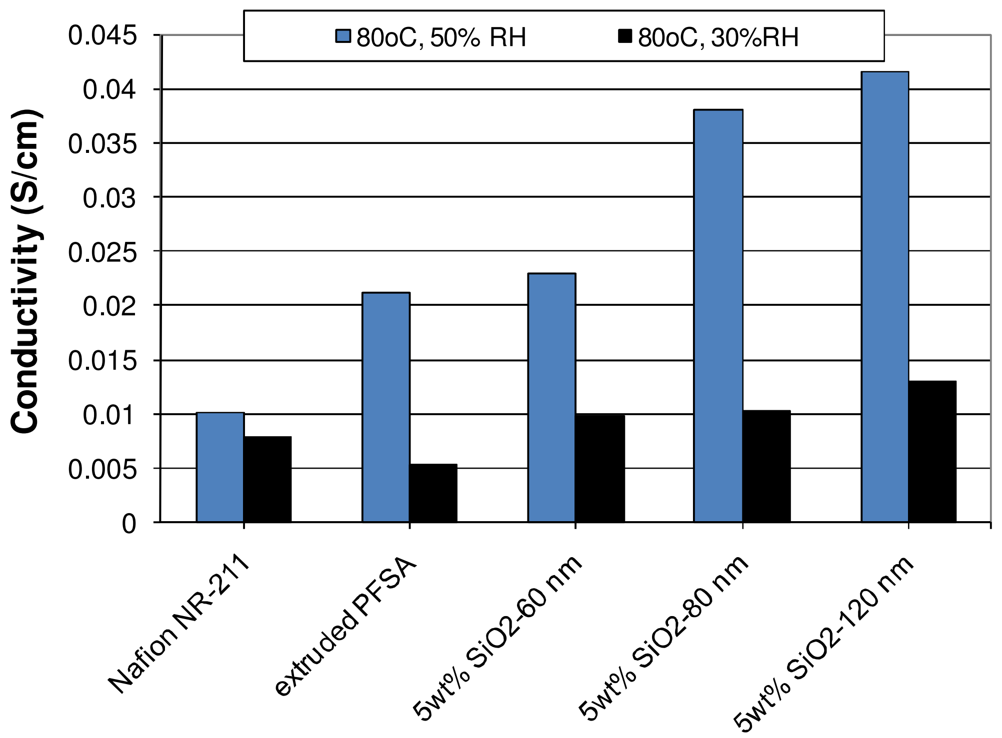
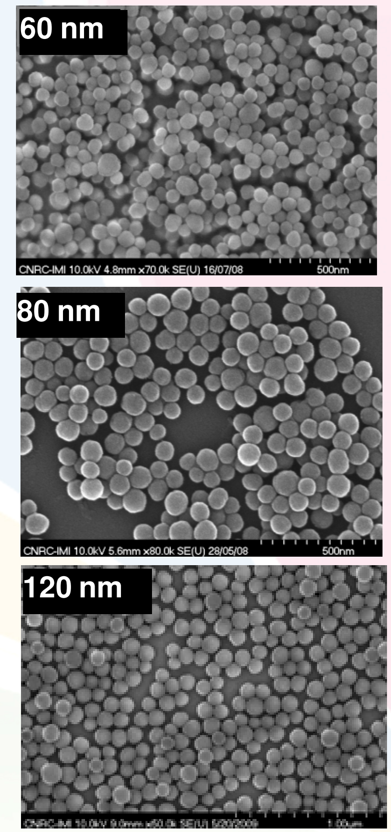
Nanocomposite PEMs:
Conductivity at Low RH

<u>Proton conductivity measured at T=80°C at 30 and 50%RH for 5wt% composite PEMs containing silica nanoparticles</u>





- Conductivity of composite PEMs is higher than Nafion at 80° C and low RH.
- Higher dimensional stability; volume change reduced by 35%.

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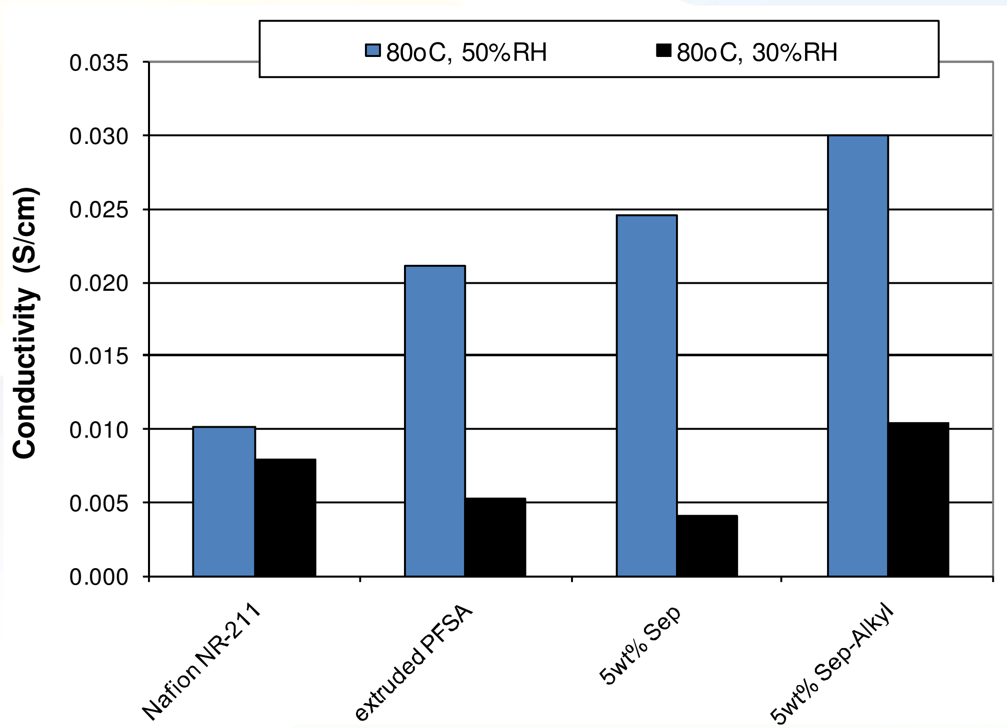
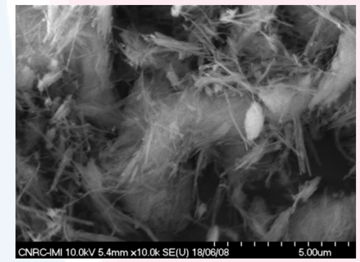
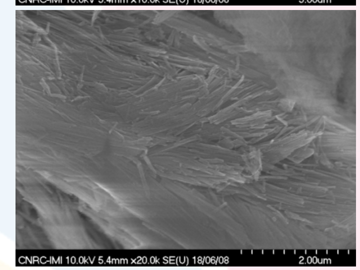
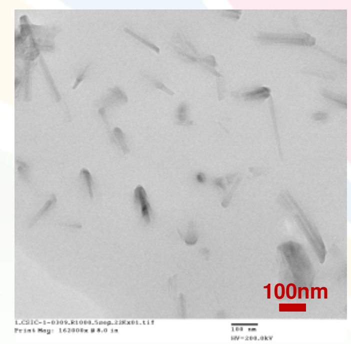
Nanocomposite PEMs:
Conductivity at Low RH

Proton conductivity measured at T=80°C at 30 and 50%RH for 5wt% composite PEMs containing functionalized clays









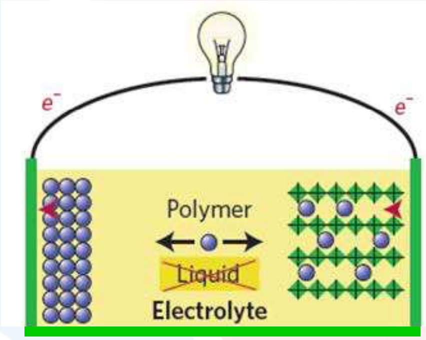
- Conductivity of composite PEMs is higher than Nafion at 80° C and low RH.
- Higher dimensional stability; volume change reduced by xx%.

Solid Polymer Electrolytes for Li Batteries

Current activities focus on the development of electrolyte components to improve performance and enhance safety of all solid Li-batteries:

Technology limitations:

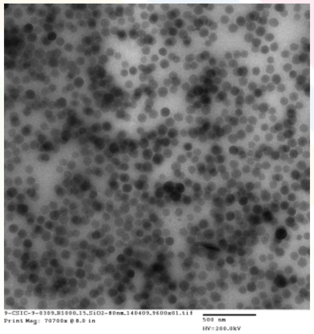
- Liquid or polymer gel electrolytes:
  - flammability issues
  - low mechanical and dimensional stability
- Solid electrolytes:
  - low conductivity at room temperature
  - battery operation: 70-90° C
  - costs related to heating system



Basic structure of an all solid state lithium battery

NRC-IMI's approaches:

- Design of innovative multi-components solid electrolytes
- Incorporating components with different functionalities:
  - conductivity enhancers
  - safety additives
- Use of well-established expertise in polyelectrolytes design and melt-processing technologies (industrially scalable processes)



25 micron thick melt-extruded nanocomposite polyelectrolyte (NRC-IMI)

Solid Polymer Electrolytes for Li Batteries

Different routes to advanced solid polyelectrolytes for Li-batteries

Multicomponent electrolyte systems

New lithium conducting polymers and copolymers

Additives:
Overcharge protection
(Redox shuttles, shutdown additives)

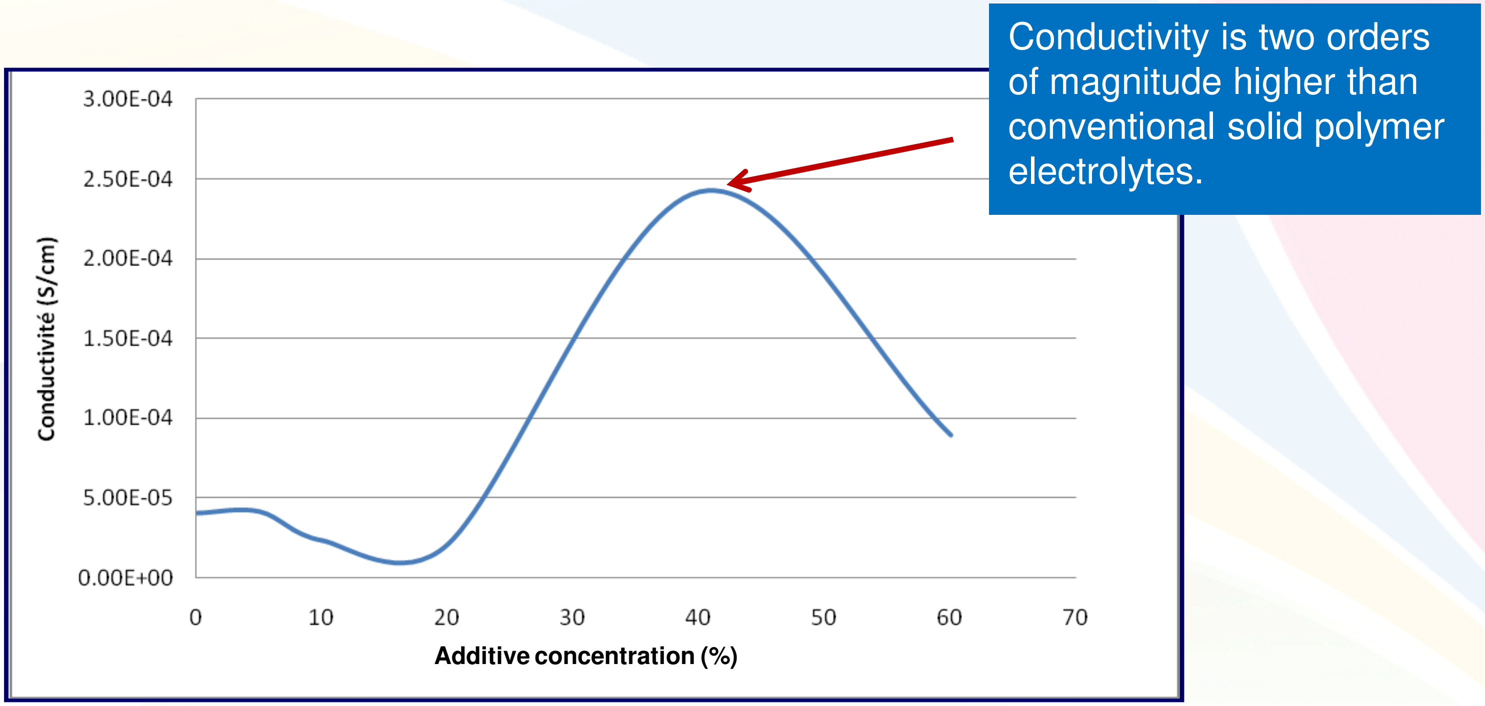
Additives:
Flame retardants

Additives:
Limit crystallinity
(polymer blend and nanofillers)

Additives:
Conductivity enhancers

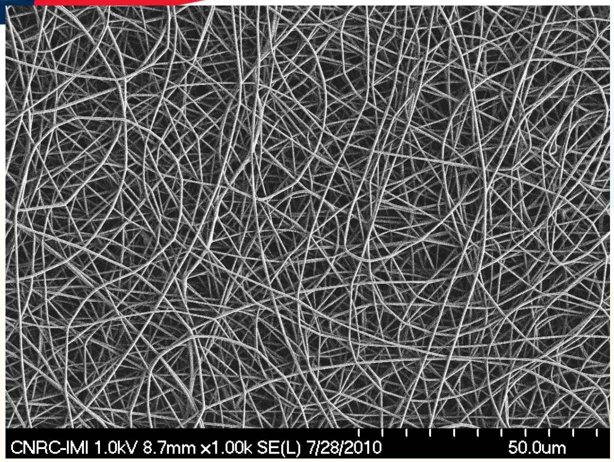
Solid Polymer Electrolytes for Li Batteries

Conductivity <u>at room temperature</u> for a thermoplastic-based solid electrolyte prepared by melt-extrusion at NRC-IMI.

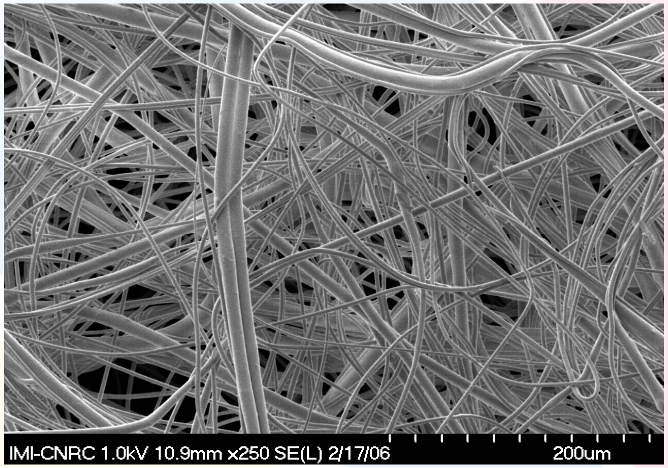


- Conductivity sufficient for operation of battery systems at room temperature.

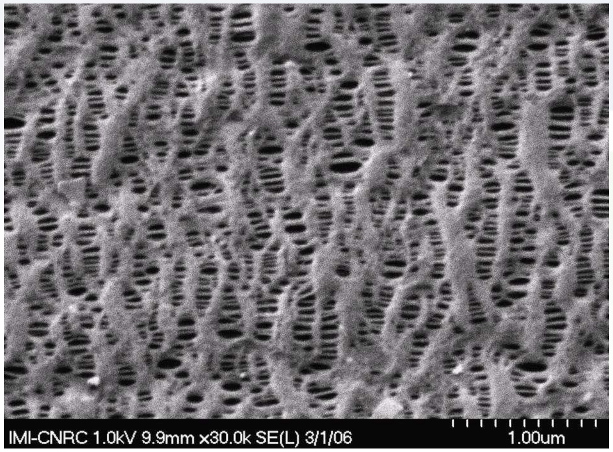
Separator Technologies



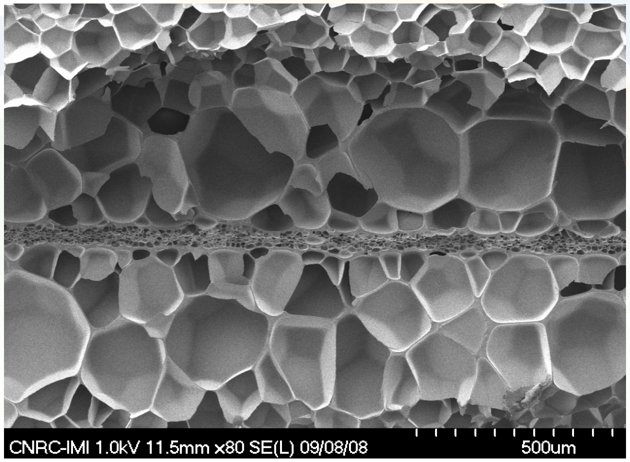
Electrospun nanofibers



Melt-blown microfibers



Porous membranes



Polymer foams

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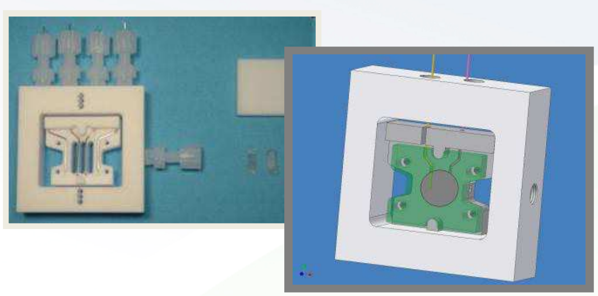
Equipment and Capabilities

VMP3 multi-channel potentiostat
1260 Solartron impedance analyzer

Mbraun LabMaster glove box with
H_2O/O_2 analyzer



In-Plane and through-plane cells for
conductivity measurements

Energy Storage Devices Anhydrous Facility

In operation… Spring 2011!

Business Opportunities

- NRC-IMI is ready to partner with developers, integrators and end-users to better understand and help exploit advanced polymer-based technologies for the production of energy storage devices.
- The R&D resources at NRC-IMI are accessible to industries as well as research laboratories that wish to conduct collaborative projects with an integrated approach in order to benefit from technical support, or to carry out feasibility studies in the development of a process.

- Visit us: NRC Automotive Office, Booth #13 (Wednesday, September 15th)

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NRC-IMI's Functional Polymer Systems Group

Thank you for your attention!


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