New manufacturing process for cost reduction and durability improvement of proton exchange membrane fuel cells

Mokrini, Asmae; Chenitz, Régis; Vachon, François; Jiang, Ruichun; Gittleman, Craig; Merlo, Luca; Oldani, Cluadio

New Manufacturing Process for Cost Reduction and Durability Improvement of Proton Exchange Membrane Fuel Cells

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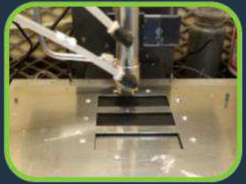
Automotive and Surface Transportation Research Center

Materials for Energy Technologies Team

Automotive and Surface Transportation Research Center - Boucherville

Advanced Polymer electrolytes processing

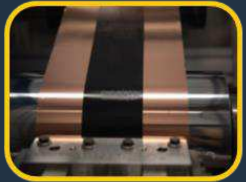


Electrodes architecture

Electrolysis

PEM Fuel cell performance and durability

Anode materials developement-recycling



R2R electrodes manufacturing

Li-ion batteries manufacturing

Battery characterization and cycling

NRC’s PEM Fuel Cell Manufacturing Technology

Project Objective, Funding and Collaborators

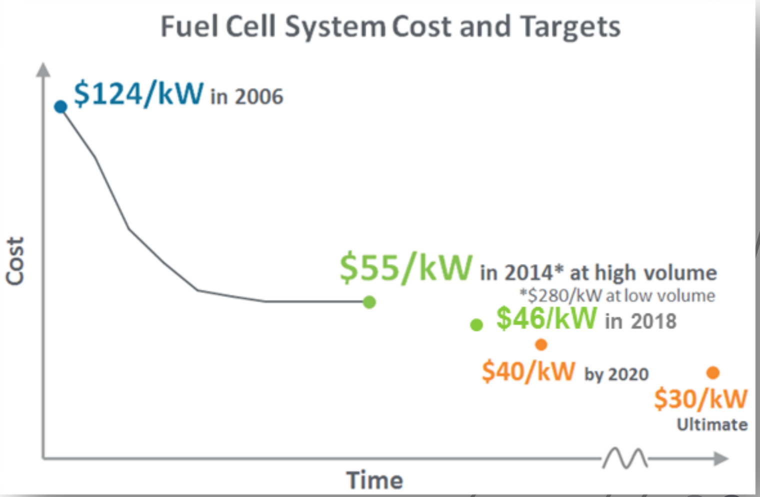
- **The project addresses PEM Fuel Cells Cost and Durability technology barriers**

- The main objective is the development of a breakthrough high-volume manufacturing process for the production of advanced Proton Exchange Membranes (PEM) and Membrane-Electrodes Assemblies (MEA) with improved performance and durability and reduced cost for applications in Fuel Cell electric vehicles (FCEV).

- Funding from NRCan through Energy Innovation Program (EIP) and NRC through Vehicle Propulsion Technologies (VPT) Program. (> 1 M$, over 4 years 2016-2020)
- Attracted interest and support from several collaborators: Solvay, 3M, GM, and NREL.

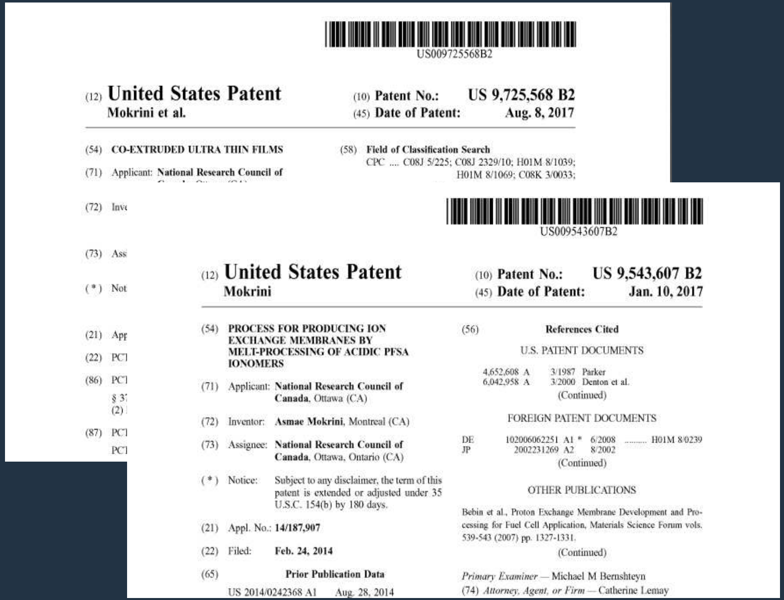
Natural Resources Canada

Energy Innovation Program



DOE. FUEL CELL TECHNOLOGIES OFFICE. 2015 (Updated for 2018)

NRC'S PEM manufacturing technology



US009725568B2

(12) United States Patent
Mokrini et al.

(10) Patent No.: US 9,725,568 B2
(45) Date of Patent: Aug. 8, 2017

(54) CO-EXTRUDED ULTRA THIN FILMS
(71) Applicant: National Research Council of

(58) Field of Classification Search
CPC C08J 5/225; C08J 2329/10; H01M 8/1039; H01M 8/1069; C08K 3/0033;

US009543607B2

(12) United States Patent
Mokrini

(10) Patent No.: US 9,543,607 B2
(45) Date of Patent: Jan. 10, 2017

(54) PROCESS FOR PRODUCING ION EXCHANGE MEMBRANES BY MELT-PROCESSING OF ACIDIC PFSA IONOMERS

(71) Applicant: National Research Council of Canada, Ottawa (CA)

(72) Inventor: Asmae Mokrini, Montreal (CA)

(73) Assignee: National Research Council of Canada, Ottawa, Ontario (CA)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 180 days.

(21) Appl. No.: 14/187,907

(22) Filed: Feb. 24, 2014

(65) Prior Publication Data
US 2014/0242368 A1 Aug. 28, 2014

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(Continued)

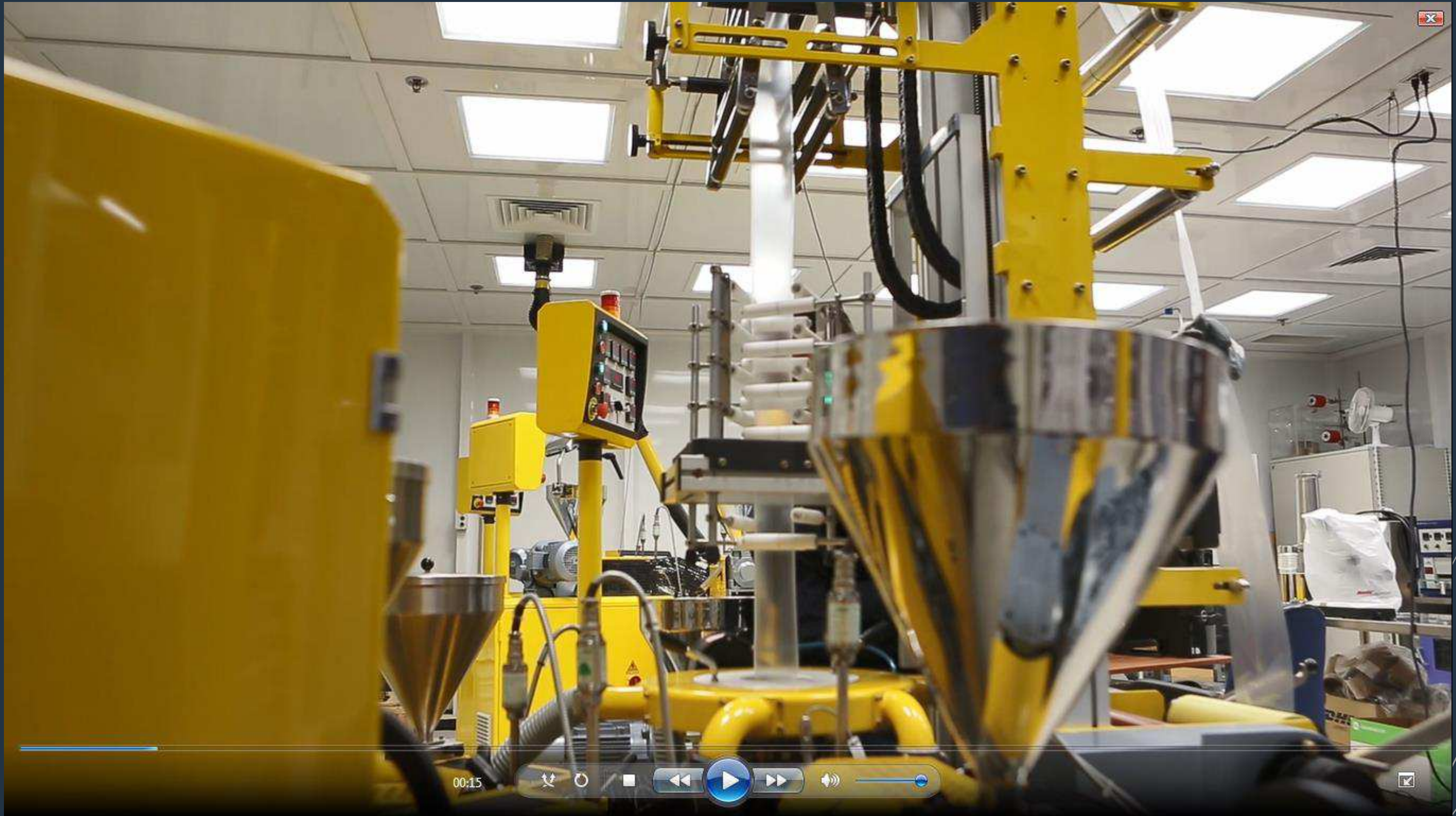
Primary Examiner — Michael M Bernshteyn
(74) *Attorney, Agent, or Firm* — Catherine Lemay

- Proton Exchange Membrane (PEM) is one of the most expensive PEMFC components at low production rates

- The advantages of NRC technology
  - ✓ Reduced production cost
  - ✓ High throughput manufacturing process
  - ✓ Simplified production process
  - ✓ Remove reinforcement (e-PTFE)
  - ✓ Improved durability
  - ✓ Maintain performance

Multilayer Melt-Blowing

The process



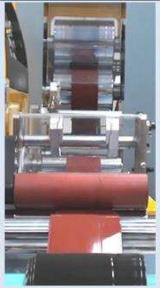
Key R&D Facilities
Polymer processing laboratory

Micro-scale Cast Film Line *DSM-Xplore*
Formulation development
Materials prescreening
Batch volume: 5mL
Screw speed: 1-400 rpm
Film line with three slit dies (width / thickness)
- 35 mm / 0.1, 0.2, 0.4 and 0.6 mm
- 50 mm / 0.1 and 0.2 mm
- 65 mm / 0.1 and 0.2 mm

Lab-Scale 500 g - 5 Kg

SMALL-SCALE CAST FILM LINE - *LABTECH*
3 single screw extruders (12.5mm – l/d=30)
5 layers ABCBA
Two dies: 100 and 150 mm wide
Minimum / maximum thickness: 0.025 / 2 mm
1.5 kg/h for each extruder
Maximum speed: 160 rpm



SMALL-SCALE BLOWN FILM LINE - *LABTECH*
5 single screw extruders (12.5mm – l/d=30)
5 layers
Die diameter: 20 mm – lay flat max: 160 mm
Die gap available: 0.81, 1.2 and 1.5 mm
1.5 kg/h for each extruder




Pilot Scale > 5Kg (MC)- 15 Kg (MB)

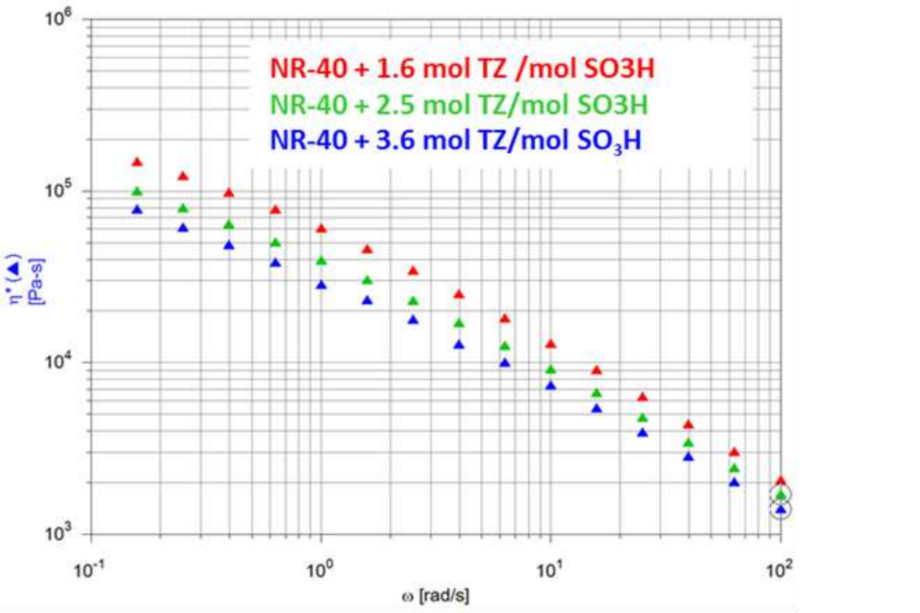
SEMI-INDUSTRIAL CAST FILM LINE – *DAVIS-STANDARD / LABTECH*
Single screw extruder (25.4 mm – l/d=27)
Horizontal and vertical extrusion mode
Two sheet dies:(width / thickness):
- 200 mm / 1.9, 3.2, 4.4 and 7.6 mm
- 350 mm / 1, 2, 3 and 4 mm
Maximum speed: 15 m/min



SEMI-INDUSTRIAL BLOWN FILM LINE – *BRAMPTON ENGINEERING*
5 single screw extruders
5 layers; ABCDE: 38, 32, 38, 32 and 32 mm
Die diameter: 100 mm – lay flat max: 865 mm
Blow-up ratio 4.5 : 1
Maximum speed: 100 m/min




Bi-functional additive
Rheology



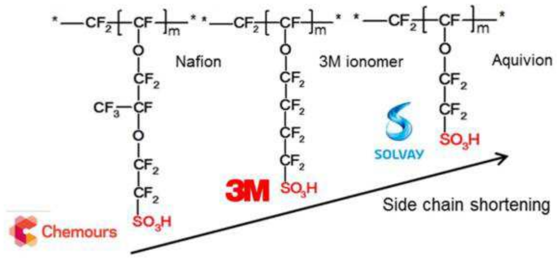
Comparison of complex viscosity (η*) obtained from frequency sweep tests on Nafion® at 240°C and different additive (1,2,4-Triazole) content

- Used as proton carriers in anhydrous PEM especially nitrogen based
- Amphoteric character, ability to form hydrogen bonds
- High boiling point, and water soluble.
- Bi-functional additives:
  - Protection of functional groups (SO_3H)
  - rheology modifiers (Plasticizers)
- Antifungal function and radical scavengers.

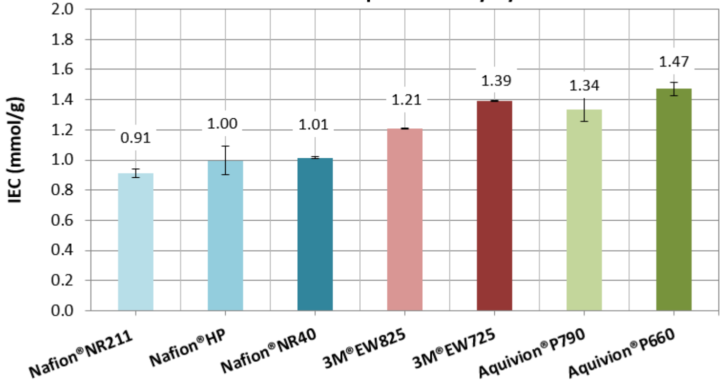
Process validation with different PFSA ionomers

lab-scale melt processing

Structure of different Perfluorosulfonic acid (PFSA) ionomers used as electrolytes in fuel cells



Ion Exchange Capacity of reference membranes and PFSA ionomers determined experimentally by titration



Micro-scale Cast Film Line *DSM-Xplore*

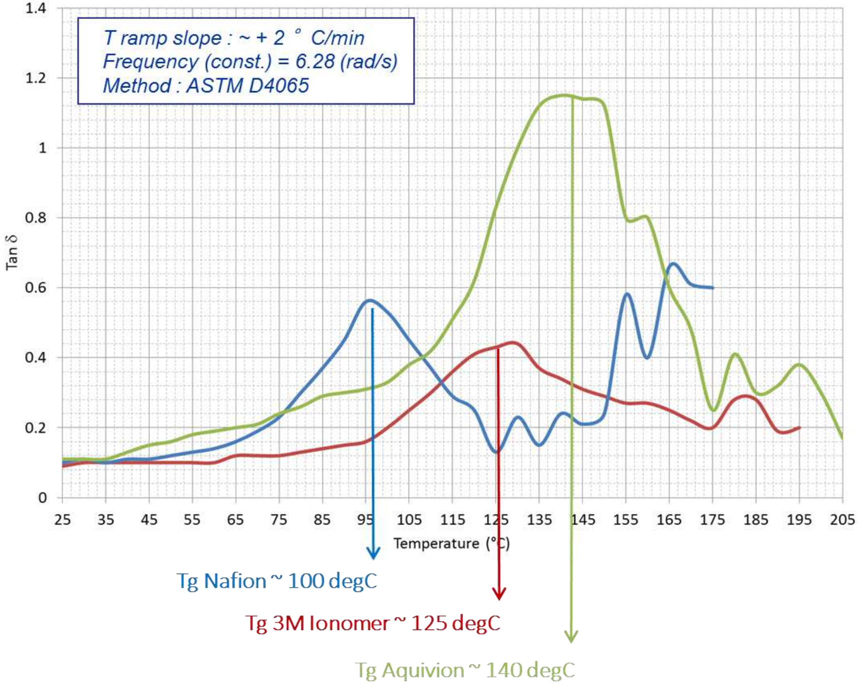
Formulation development
Materials prescreening
Batch volume: 5mL
Screw speed: 1-400 rpm
Film line with three slit dies (width / thickness)

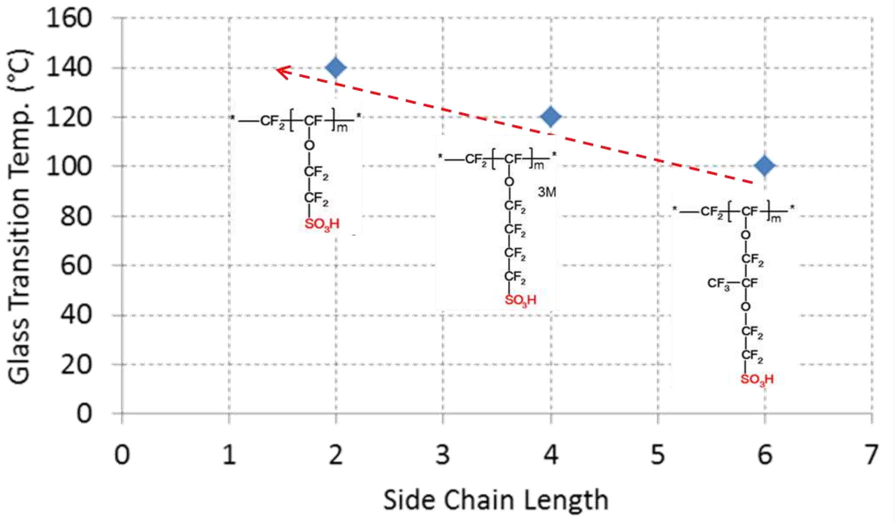
- 35 mm / 0.1, 0.2, 0.4 and 0.6 mm
- 50 mm / 0.1 and 0.2 mm
- 65 mm / 0.1 and 0.2 mm

Ionomers properties

Glass Transition Temperature (Tg)

DMTA analysis of PFSA ionomers with different side chain length

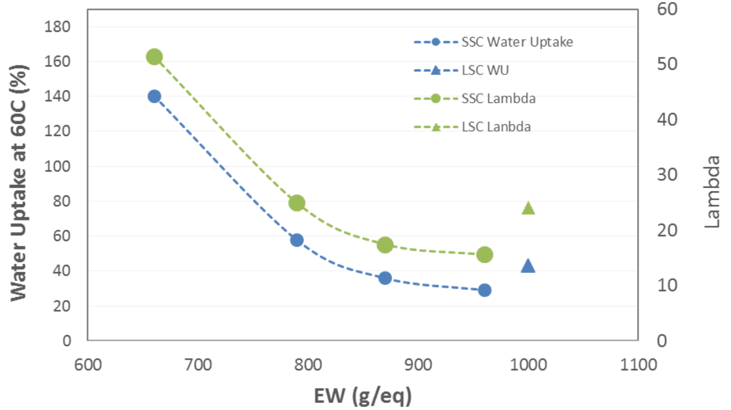


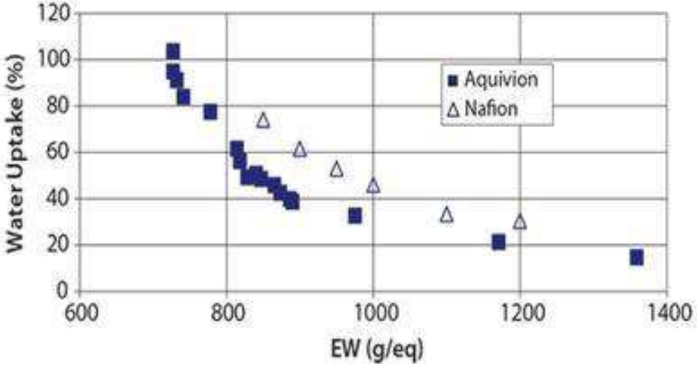


- The ionomer side-chain length strongly affects the glass transition temperature (*i.e.* the softening temperature) of the material.
- Higher Tg means higher operating temperature.

Ionomers Blends Approach

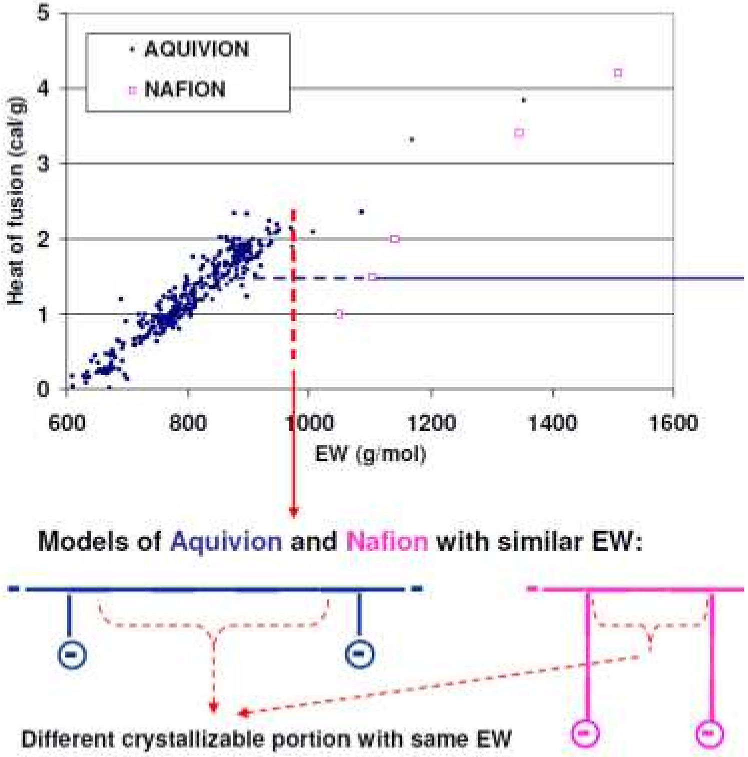
water uptake of SSC Aquivion® vs LSC Nafion®





Water uptake from liquid water at 100 °C for Aquivion® and Nafion® membranes as a function of the EW

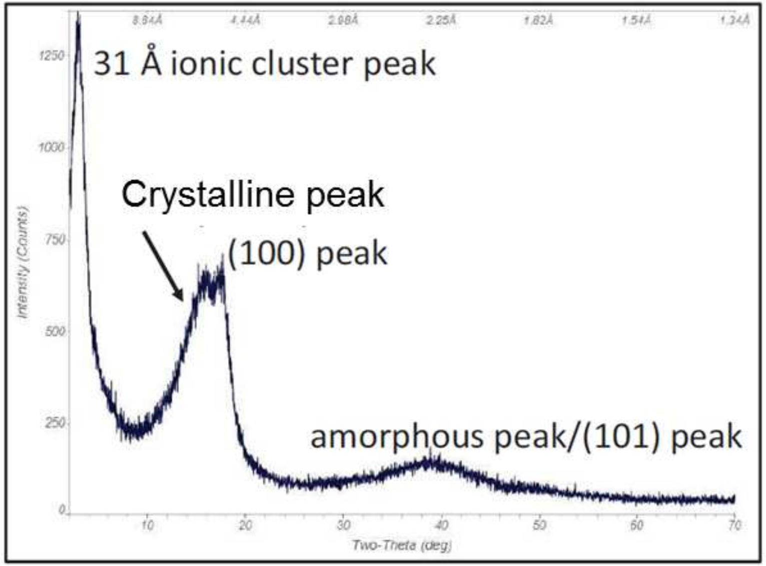
L. Merlo et all Solvay Specialty Polymers presentation 2012



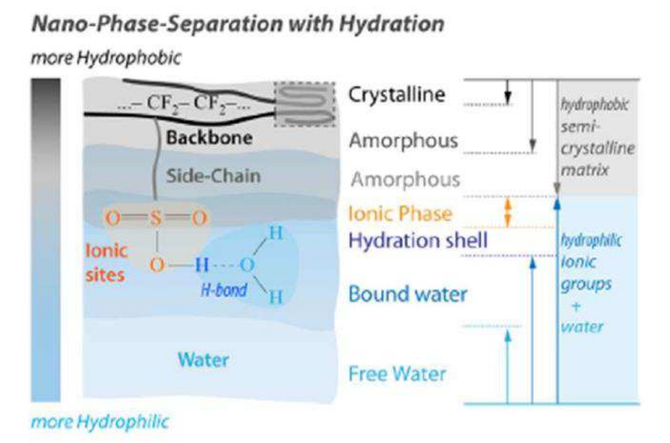
NRC-C

X-Rays Diffraction

Nafion® solution-cast



X-ray diffraction pattern for 10 micron D2020 DuPont Nafion PFSA film, annealed 2 hr. at 140 °C in N_2 (data collection at 23 °C, 40% RH).



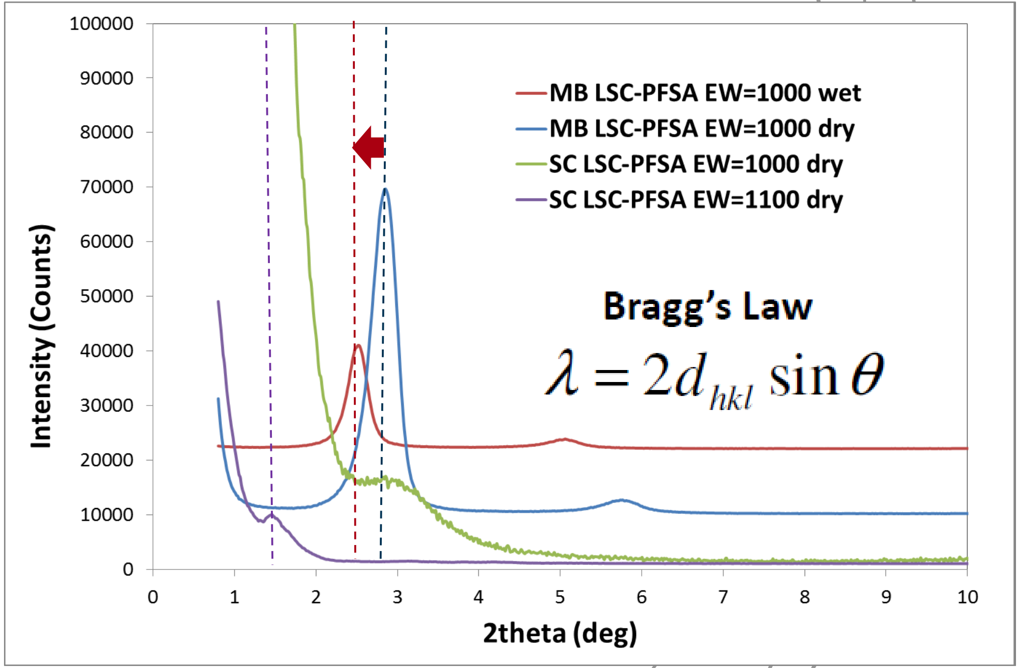
- Small-angle peak 2 theta = 1 – 3.5° associated with ionic domains clusters
- Diffraction peaks at 2 theta = 17.5° corresponds to d-spacing of 5.5Å can be deconvoluted to two peaks assigned to crystalline and amorphous domains in the main chain
- Diffraction peaks at 2 theta = 39.6°, d = 2.4Å is attributed to amorphous PTFE domains of Nafion®

T.N. Blanton et al. JCPDS-International Centre for Diffraction Data 2015 ISSN 1097-0002

X-Rays Diffraction

LSC-PFSA (Nafion®) solution-cast *vs.* Melt-blown

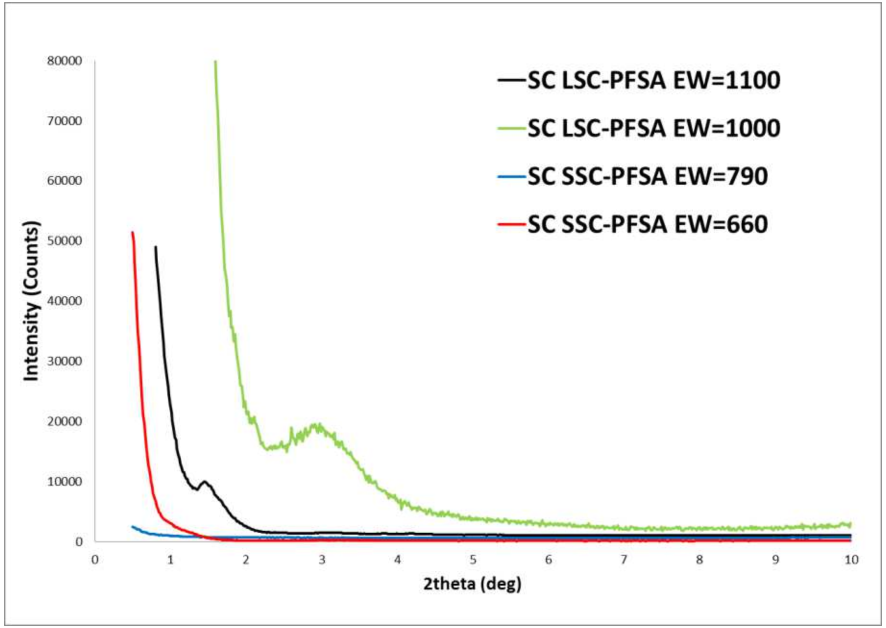
- Solution-Cast (SC)
  - LSC-PFSA (NRE211 (EW=1100) and D2020 (EW=1000)
  - Higher EW (lower IEC), lower 2theta, higher the distance between ionic domains
- Melt-Blown (MB)
  - Same 2 theta (2.9) and d-spacing (3 nm) as SC
  - Lower 2 theta after hydration (higher d) ⇨ ionic domains



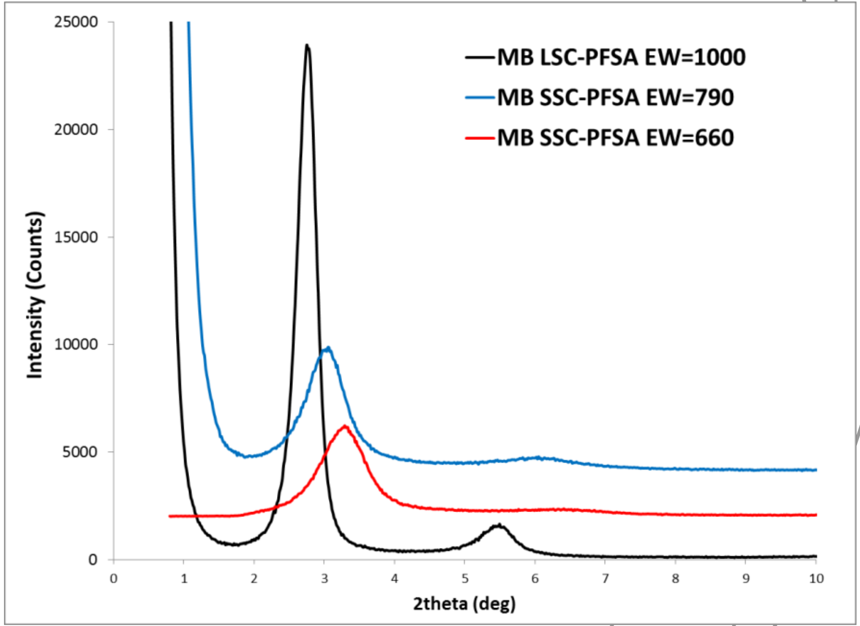
X-Rays Diffraction

LSC and SSC-PFSA solution-cast *vs.* Melt-blown

Solution-Cast

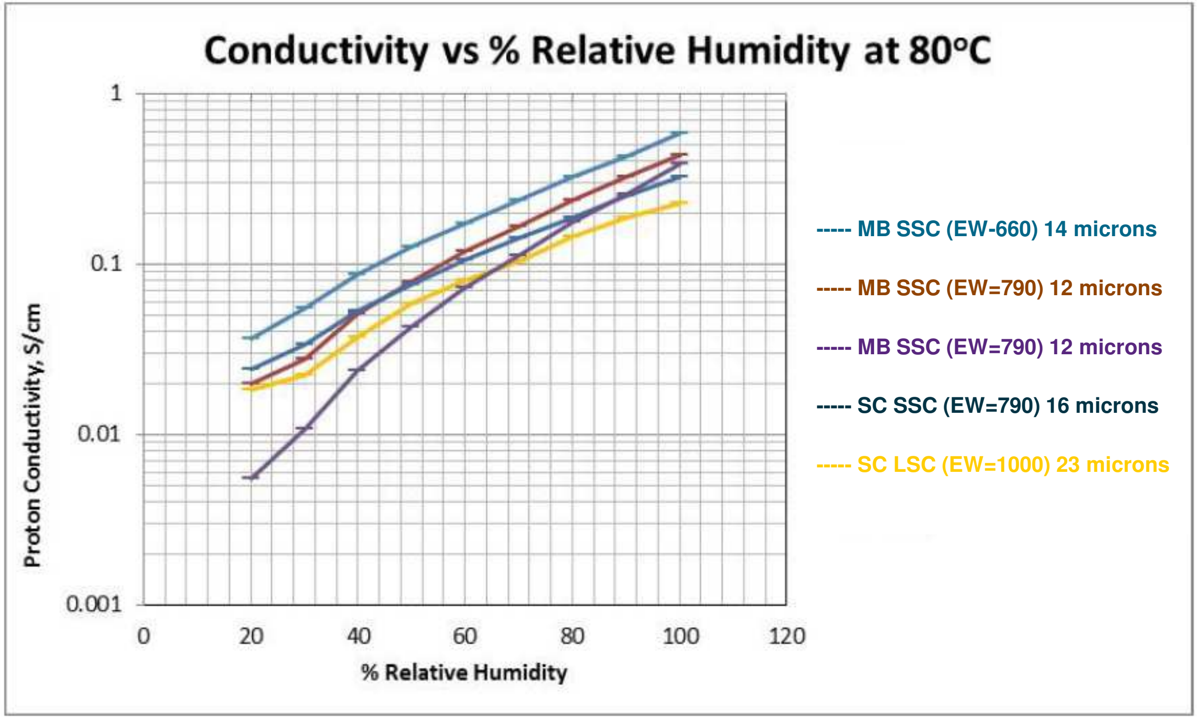


Melt-Blown



Proton Conductivity

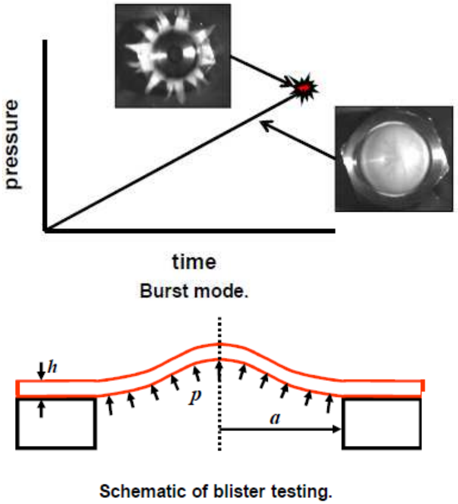
LSC and SSC-PFSA solution-cast *vs.* Melt-blown



- Melt-blown 12µm membrane matches the conductivity of the solution cast membrane
- As expected, MB membranes with lower EW are more conductive
- A 660EW melt-blown 12µm membrane has best-in-class conductivity

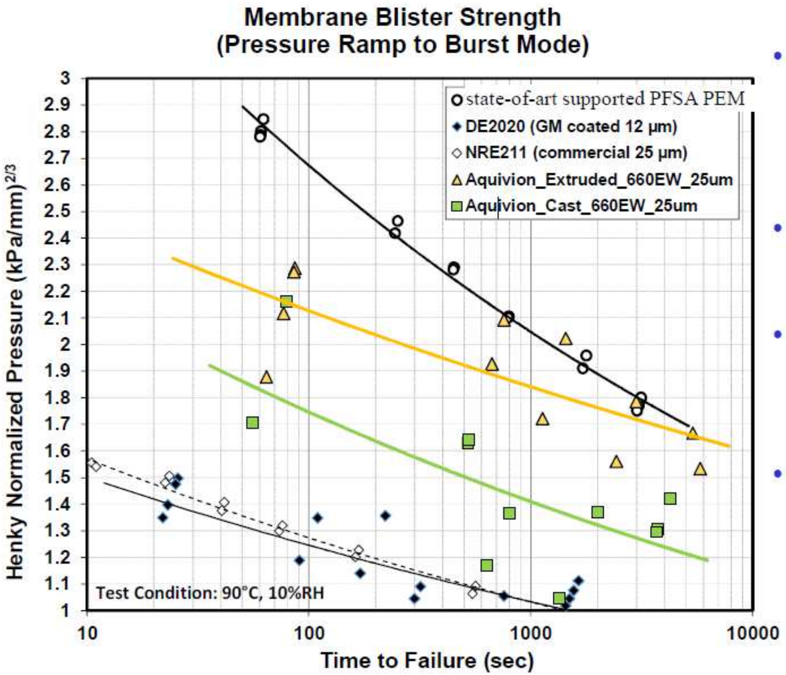
Ex-situ Mechanical Durability

LSC and SSC-PFSA solution-cast *vs.* Melt-blown



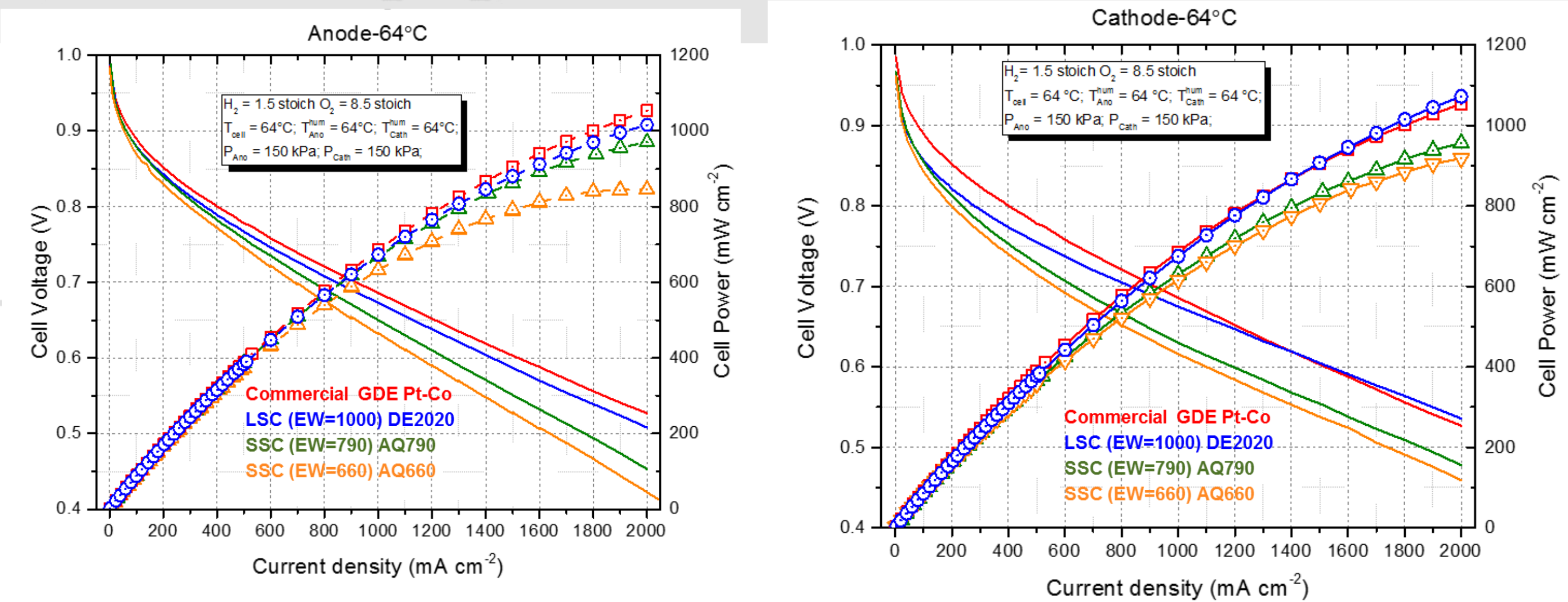
- 16 blister samples per test
- 6 Pressure ramp rates: 1, 0.2, 0.1, 0.05, 0.02, and 0.01
- kPa/sec.
- Test condition: 90°C, 10%RH

Mechanical Strength of PEM made of Aquivion 660EW – Cast vs. Extruded



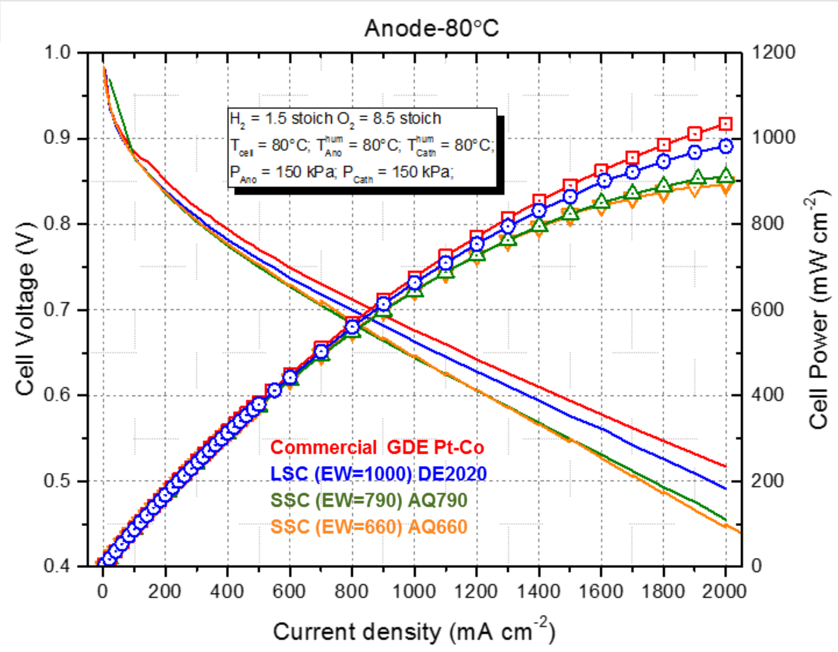
- Blister strength of Aquivion 660EW based membranes generally have higher blister strength than Nafion.
- Extruded membrane is stronger than cast membrane.
- Extruded Aquivion approaches strength of state-of-art supported PFSA PEM
- Blister burst strength from both cast and extruded membranes have high variability, suggesting quality or uniformity issues.

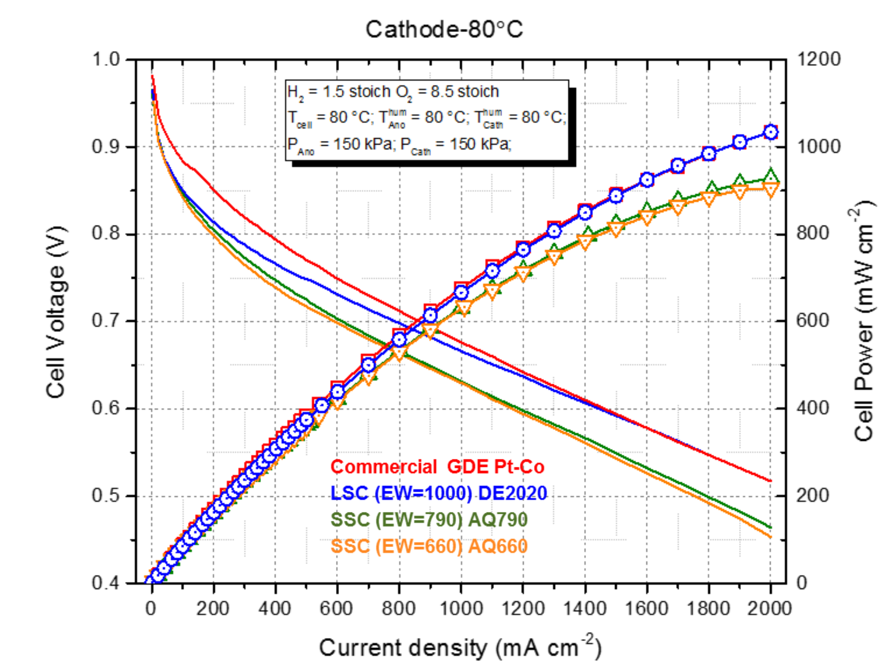
Integration of SSC in catalysts layers ($CCGDLs, H_2/O_2$)



Polarization and power density curves of single MEAs using different ANODES (Left) and CATHODE (Right) materials prepared by **CCGDLs**:
For all MEAs, approximately 0.2±0.05 mg_{Pt} cm^{-2} c and for Anode (left) and 0.5±0.05 mg_{Pt} cm^{-2} cathode (right) were used with commercial 25 microns membrane (Nafion® NR211). **I/C=0.8**

Integration of SSC in catalysts layers (CCGDLs, H_2/O_2)



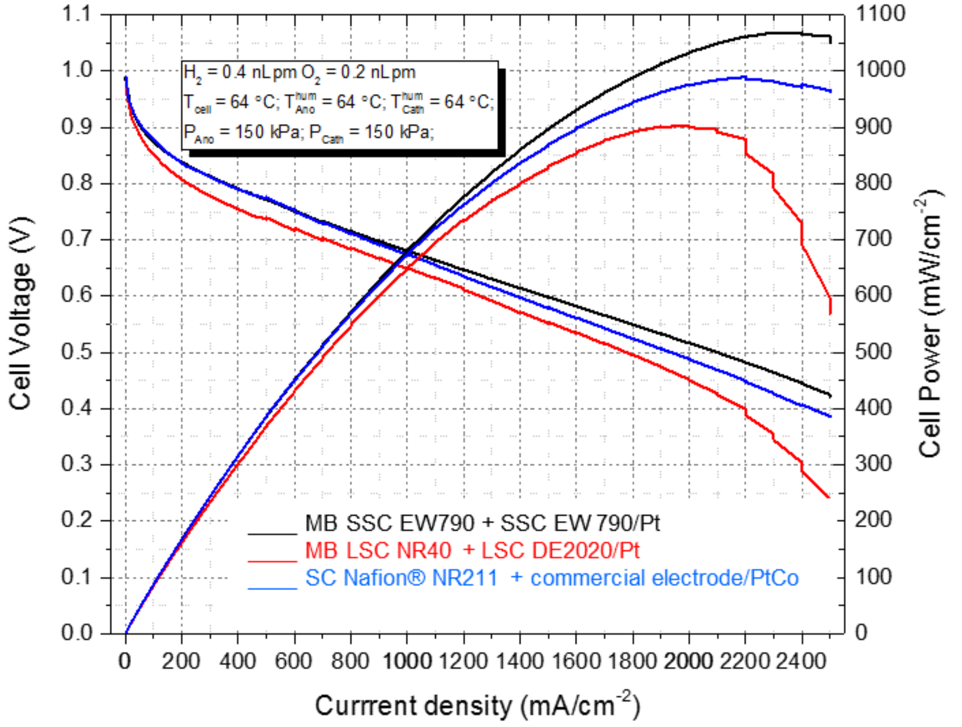


Polarization (lines) and power (symbols) densities curves of single MEAs using different ANODE (Left) and CATHODE (Right) materials prepared by **CCGDLs**: **Red lines and squares PtCo CCGDL commercial electrode**, **Blue lines and disks DE2020 ionomer I/C=0.8**, **Green lines and up-pointing triangles AQ790 ionomer I/C=0.8;** **and Orange lines and down-pointing triangles AQ660 ionomer I/C=0.8 .**

For all MEAs, approximately 0.2 and 0.5±0.05 mg_{Pt} cm^{-2} for Anode and respectively cathode were used and a commercial membrane type (Nafion® NR211).

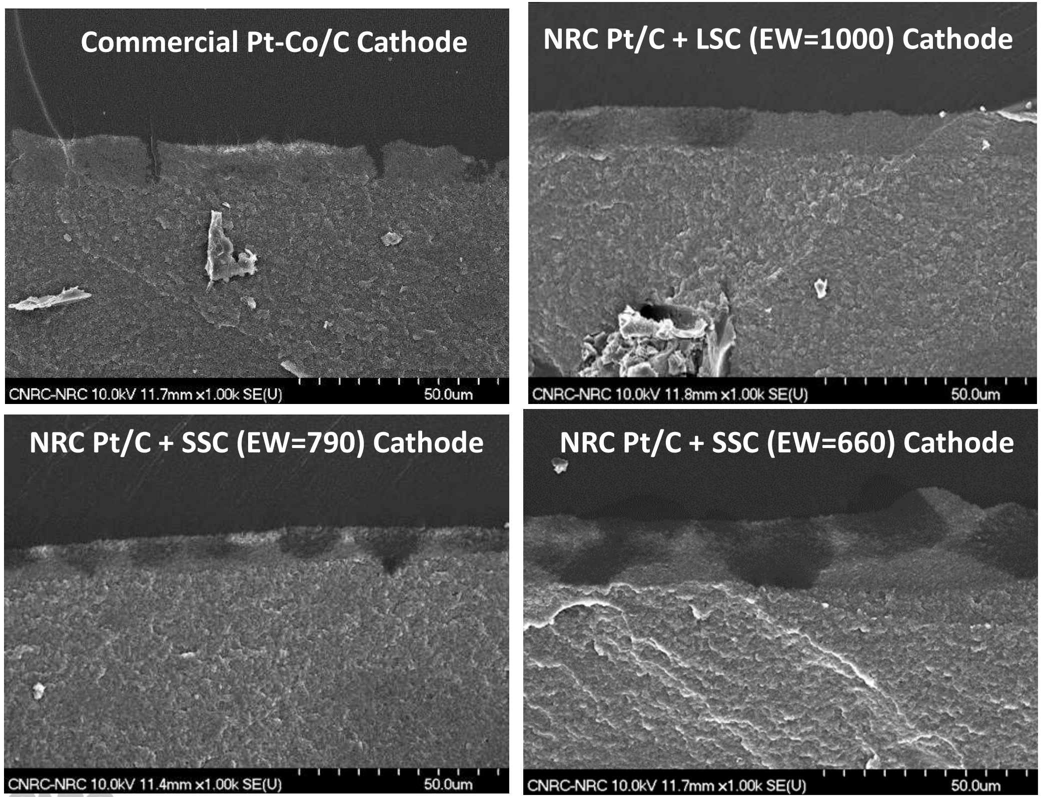
Integration of SSC in catalysts layers (CCGDLs, H_2/O_2)

Comparison of MEAs with same ionomer in membrane and GDE



- When integrating new materials, the entire MEA needs to be re-optimized, and testing protocols redesigned

Integration of SSC in catalysts layers (CCGDLs)



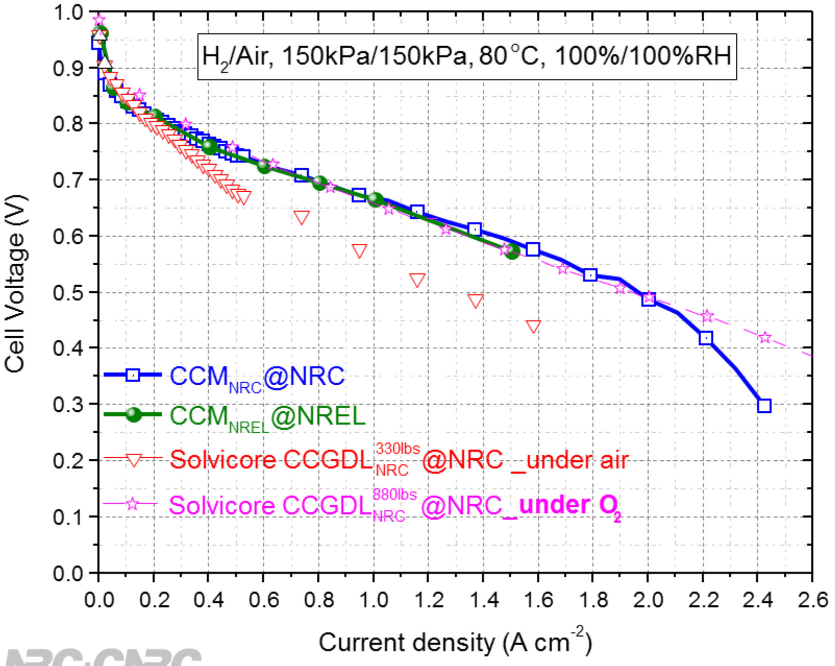
SEM cross-section images (x1000) of approximately 0.5±0.05 mgPt cm-2 cathodes prepared in this work by spray deposition on Gas Diffusion Layer. Top-Right DE2020 ionomer I/C=0.8 with 40 wt.% Pt/C, Bottom-Left AQ790 ionomer I/C=0.8 with 40 wt.% Pt/C and Bottom-Right AQ660 ionomer I/C=0.8 with 40 wt.% Pt/C. Darker zones in catalyst layers are agglomerates of ionomers (DE2020, AQ790 and AQ660). As a comparison, commercial cathode is presented in Top-Left.

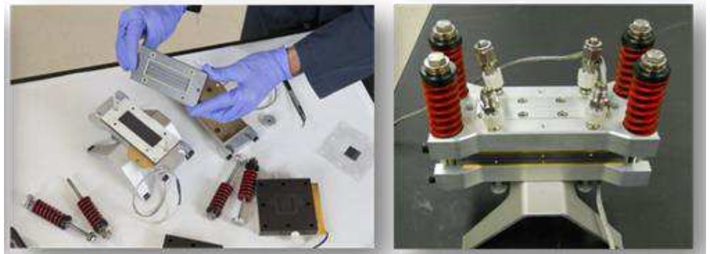
Fuel Cell Performance
CCM and CCGDL (Validation with NREL)

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

FUEL CELL SEMINAR & ENERGY EXPOSITION

Comparison of CCM and CCGDL under O_2 and air (NRE211 and D2020)

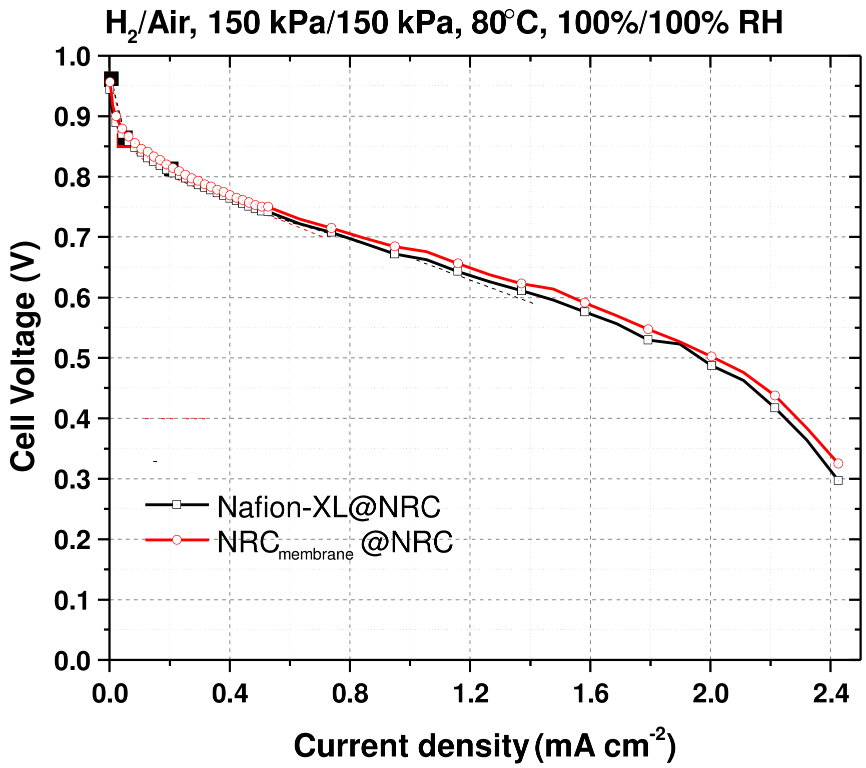


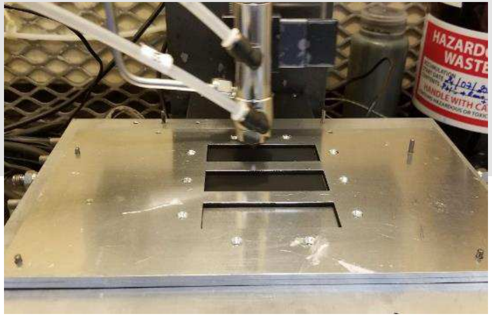


MEA @ NREL = 50 cm^2 square geometry
MEA @ NRC = 20 cm^2 rectangle geometry
Anode/Cathode: 0.15-0.2 / 0.5 mg_{Pt} cm^{-2}
NREL & NRC use their respective standard protocols for FC tests

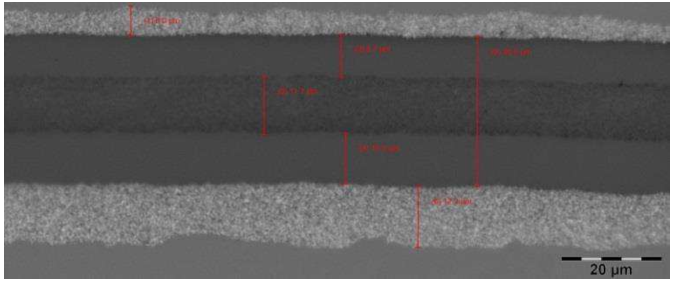
NRC·CNRC

Fuel Cell Performance
Catalyst Coated Membranes (CCM)





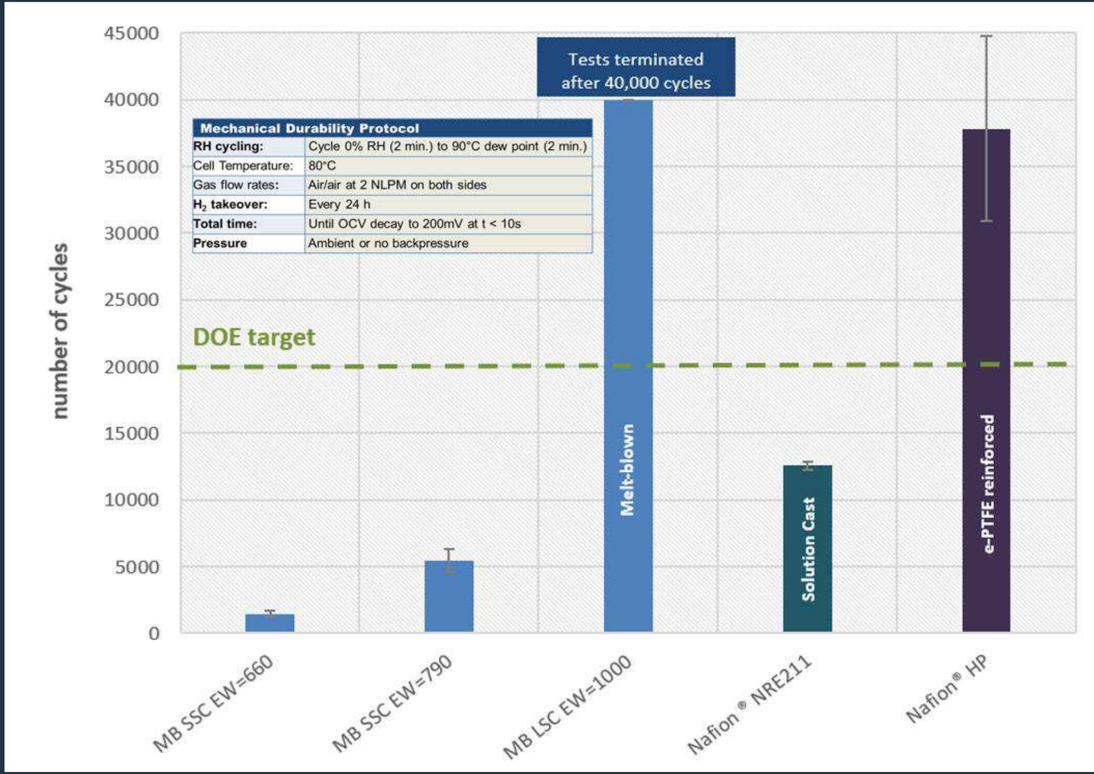
Spray deposition CCM



SEM cross-section of CCM with Nafion XL

Similar polarization curves membranes prepared with NRC process

Fuel Cell Performance
Mechanical Durability (ADT protocol)

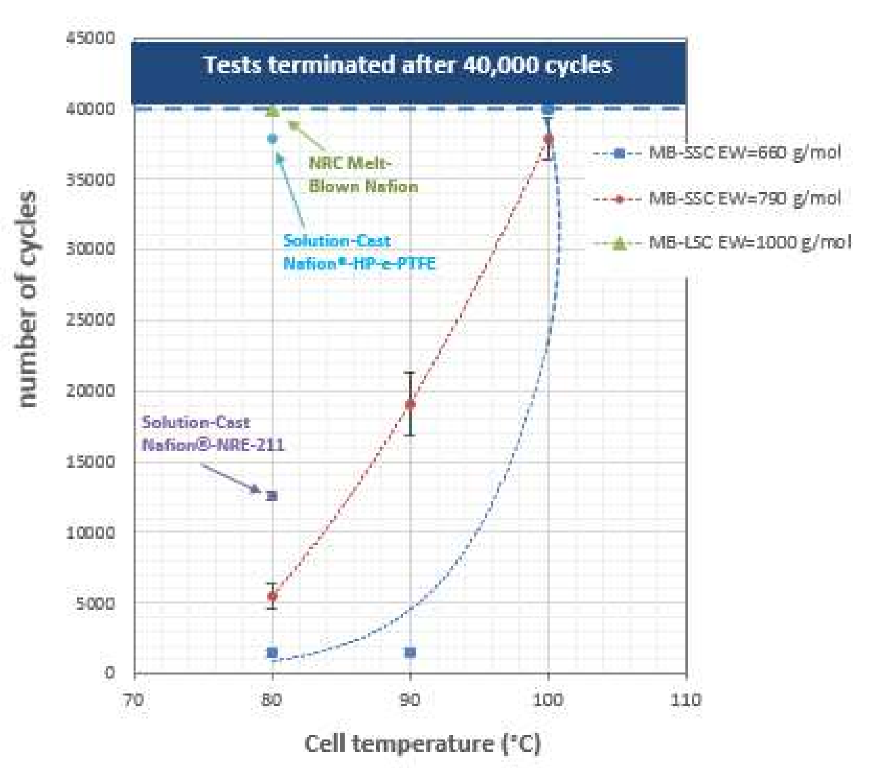


Fuel cell testing lab at NRC-Boucherville

- Melt-blowing process provides self reinforced membranes surpassing mechanical durability of e-PTFE reinforced solution-cast PEM
- The lower the EW the higher the IEC and gravimetric water uptake, and the higher H_2 permeability upon cycling

Fuel Cell Performance

H_2 permeability – high T and low RH



RH calculated from Buck equation

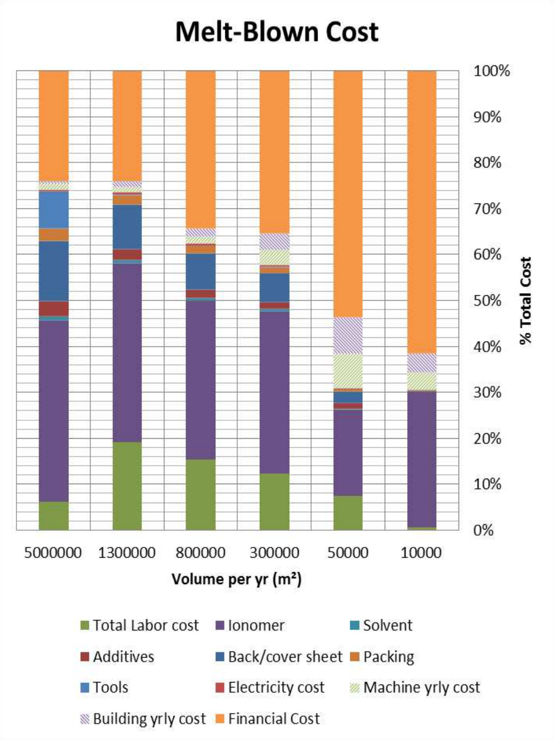
Dew point	Water Vapor pressure	Relative Humidity at Cell T =		
Hum Temp °C	kPa	80 °C	90 °C	100 °C
90	70.152	147.97%	100.00%	69.25%

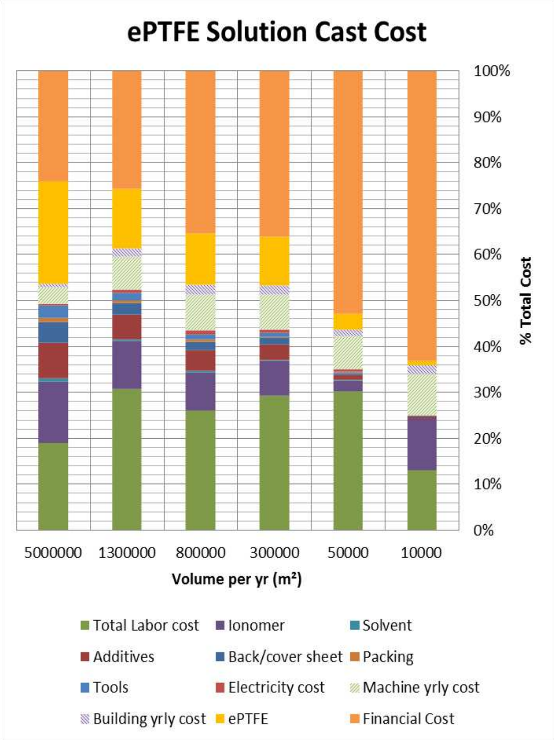
- Increasing cell temperature/ decreasing RH, improves drastically H_2 permeability upon cycling for SSC based membranes

NRC's PEM Manufacturing

Cost Analysis

Total Costs Drivers Comparison





- The cost of the solution cast process is driven by the financial cost, the labor, and the **e-PTFE**
- The cost of the Melt-Blowing process is driven by the financial cost, labor, and the **ionomer**

NRC's PEM Manufacturing

Cost Analysis

Veh Production/yr	Unit	1,000	5,000	30,000	80,000	130,000	500,000
Total yrly production*	m^2/yr	10,000	50,000	300,000	800,000	1,300,000	5,000,000
NRC's Melt-Blowing cost	\$/m^2	508.42	52.57	19.30	15.43	12.42	8.76
e-PTFE Solution Cast cost NRC study 2016	\$/m^2	1316.31	347.98	89.71	60.10	42.94	24.20
Actual cost Nafion XL, Nafion 211, Nafion HP (Ion Power Inc.)	\$/m^2	1600-2300					
e-PTFE Solution cast cost DOE study 2015 (B.D. James)	\$/m^2	268	74.00	45.00	30.00	27.00	16.00

** 80 kW FC stack for automotive (FCEV), with 10 m^2 of PEM / stack*

M. Toupin, A. Mokrini. World Electric Vehicle Journal Vol. 8 - ISSN 2032-6653 (2016)

Conclusions and outlooks

- A new manufacturing process developed and successfully used for PEM with different PFSA ionomers (side chain length and EW)
- For all APR scenarios considered, the melt-blowing cost advantages are significant (60 to 80% cost reduction)
- DOE membranes cost target for 2020 (20 \$/m^2) is achieved with this process at an intermediate APR of 30,000 FCEV/year
- Capital Investment for equipment of e-PTFE solution cast process is much higher that melt-blowing process, due to lines duplication requirements for solution cast process to increase production . e-PTFE elimination from melt-blown process brings significant cost saving
- New challenges and opportunities for further developments: Integration and optimisation of SSC in CL, activation and testing protocols, QC, etc.

Acknowledgments

NRC·CNRC F. Vachon, R. Chaouch, F. Perrin, R. Chenitz, M.Toupin

SOLVAY L. Merlo, C. Oldani, E. Favretto

GM C. Gittleman, T. Fuller, R. Jiang, Y-H. Lai,

NREL NATIONAL RENEWABLE ENERGY LABORATORY M. Ulsh, S. Mauger, M. Wang

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Thank you!