Intermediate Temperature Proton Conducting Fuel Cells for Transportation Applications

ARPA-E Project (2012 Open)

Award No. DE-AR0000314

Project Start: Feb. 2013

Completed Q10

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Project Team

Team Member	Project Role
Ceramatec, Inc.	Prime
Location: Salt Lake City, UT Focus: Ion conducting ceramics Electrochemistry Advanced Materials	Materials Scale up Stack Testing
Los Alamos National Lab.	National Lab Partner
Location: Los Alamos, NM	Materials Development, Synthesis, & Characterization Cell Testing
Nissan Technical Center North America	Commercialization Partner
Location: Farmington Hills, MI	Cell validation System Modeling Requirement Definition

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Project Objectives

- Develop a proton conducting fuel cell based on Tin Pyrophosphate (TPP) that operates at 200 – 250 ° C
  - **Mid-Temp and Low RH will <u>simplify the Balance of Plant</u> in the system.**
  - **This simplification will <u>reduce significant portion of the Balance of Plant cost</u>.**

Project Target

- Fuel Cell Testing using thin, composite membrane
  - Demonstration of 25 to 50 cm^2 fuel cell
  - 500 mW/cm^2 at 200° - 250° C, relative humidity < 5%

Conclusions

- Reproducible, high conductivity in scaled up powder batches
  - Proton Conductivity of 0.1 S/cm
- High loading of TPP in polymer composite
- Single 5 cm^2 membrane performance of ~ 300 mW/cm^2 demonstrated (High Pt loading) – porous membrane
- Dense composite membrane fabricated
- Low Pt loading (0.2 mg/cm^2), 5 cm^2 cell demonstrated >400 mW/cm^2
- Early versions of cells demonstrated in 50 cm^2 size

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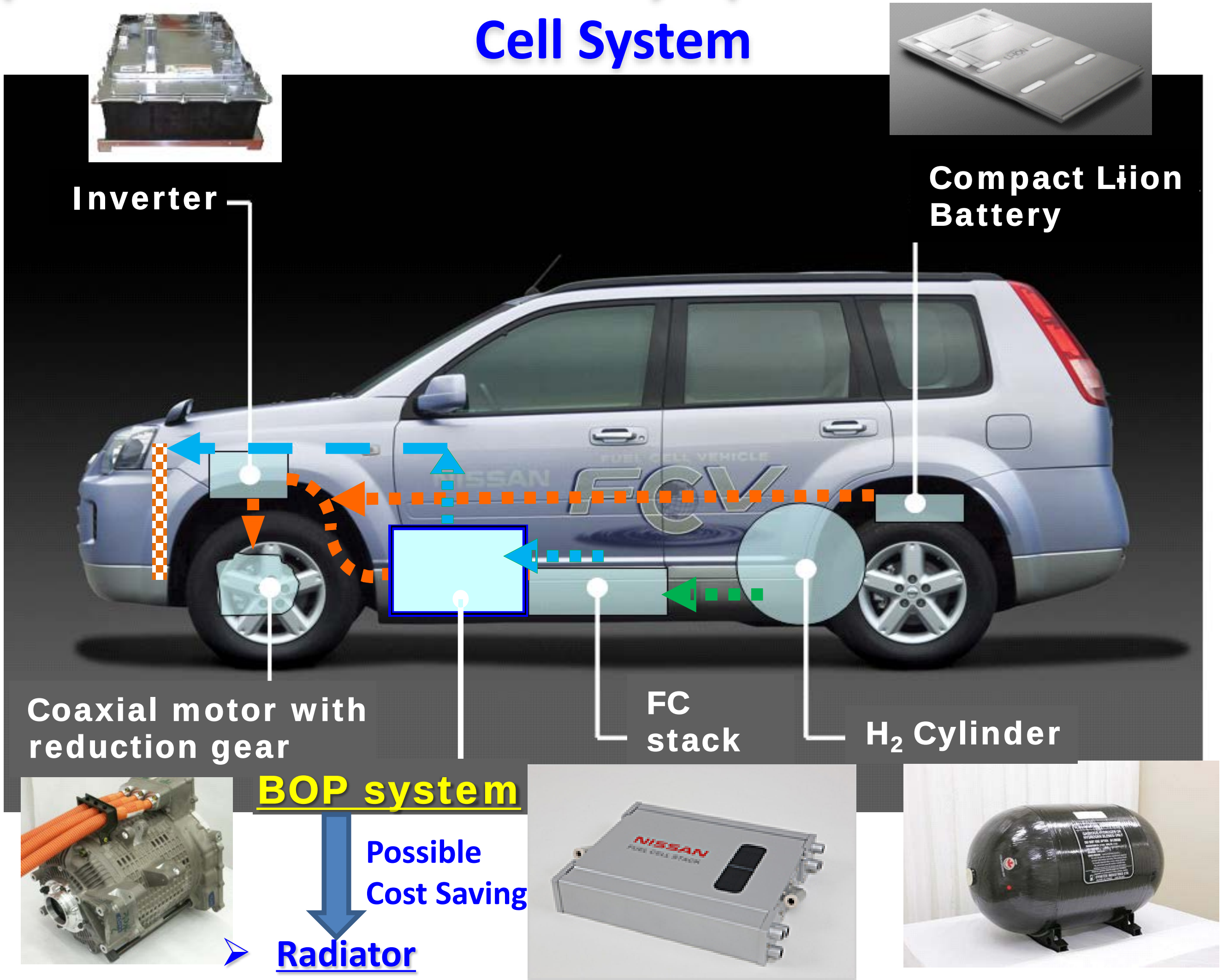
MOTIVATION

Mid-Temperature and Low Humidity Operation Benefits for the Fuel Cell System



BOP system

Possible Cost Saving

- Radiator
- Humidification
- Compressor-Expander Unit
- H_2 Purification

◀▪▪▪▪ Hydrogen
◀▪▪▪▪ Electricity
◀▪▪▪▪ Coolant

Mid temperature operation can lower the FC system cost by simplifying the Balance of Plant (BOP)

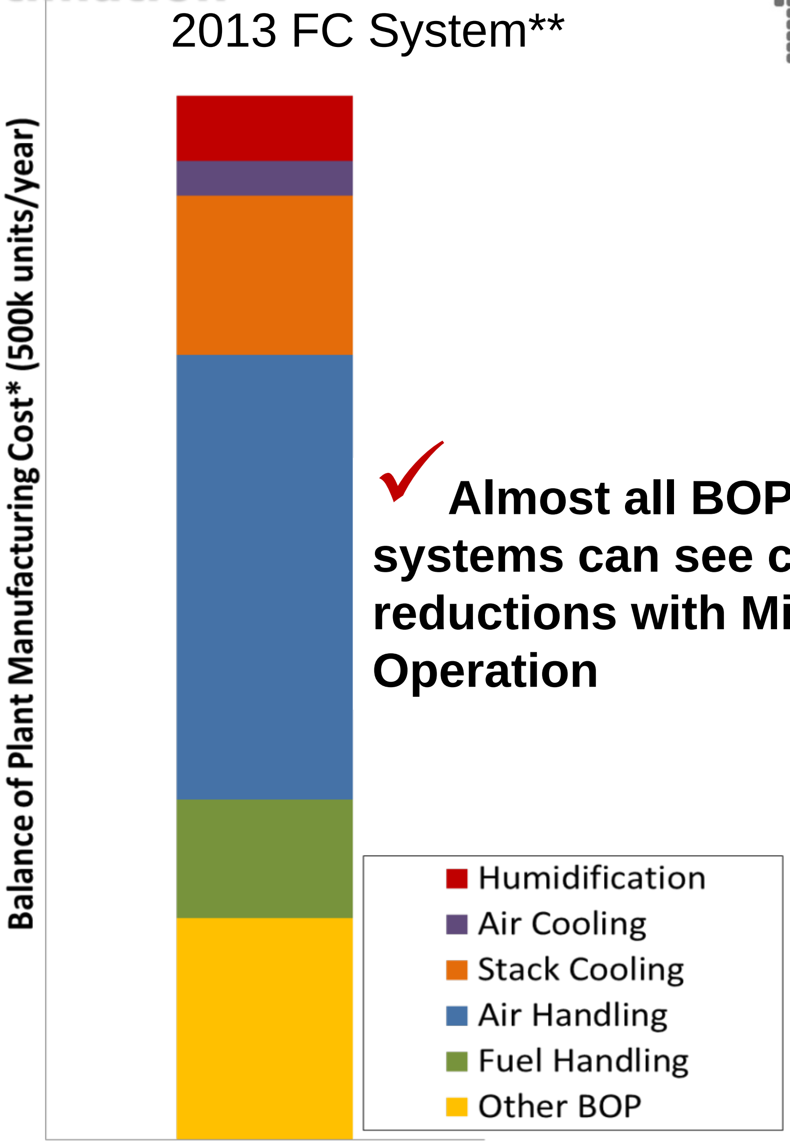
FCEV System-Level Modeling

Mid-Temp FCEV System Cost Estimation

Major Cost Saving component/system *

1. **Air Handling**
   - ✓ **Compressor**
   - ✓ **Expander**

2. **Water/ Heat Recovery**
   - ✓ **Humidifier**
   - ✓ **Radiator**
   - ✓ **Coolant Loop**



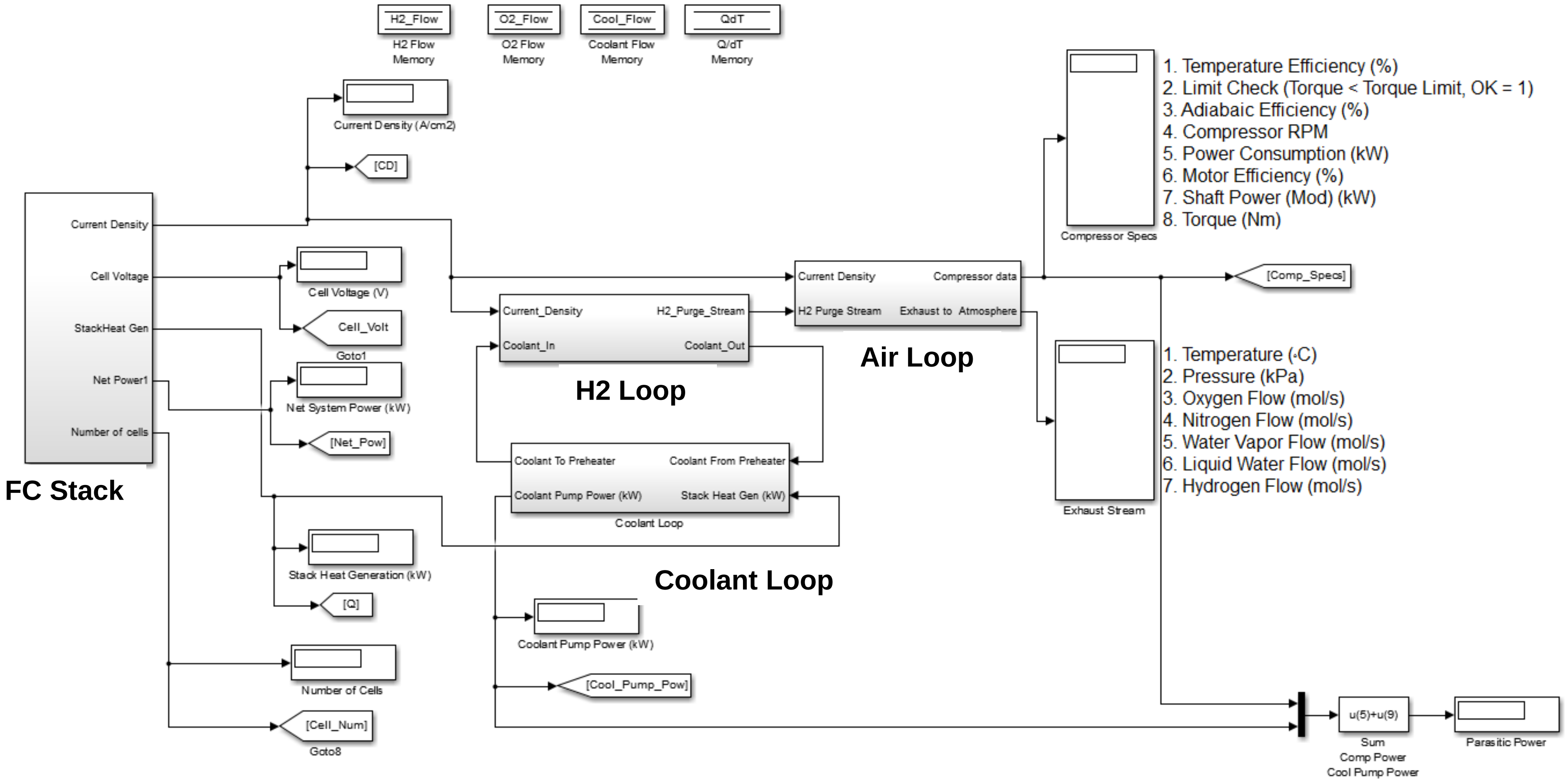
✓ **Almost all BOP sub-systems can see cost reductions with Mid-Temp Operation**

* Compared to conventional FC system

** James Brian D, " Fuel Cell Transportation Cost analysis Prelim Results" DOE Annual Review, May 2013

FCEV System-Level Modeling

Overall Model in Matlab+Simulink



FC Stack

H2 Loop

Air Loop

Coolant Loop

1. Temperature Efficiency (%)
2. Limit Check (Torque < Torque Limit, OK = 1)
3. Adiabaic Efficiency (%)
4. Compressor RPM
5. Power Consumption (kW)
6. Motor Efficiency (%)
7. Shaft Power (Mod) (kW)
8. Torque (Nm)

1. Temperature (◦C)
2. Pressure (kPa)
3. Oxygen Flow (mol/s)
4. Nitrogen Flow (mol/s)
5. Water Vapor Flow (mol/s)
6. Liquid Water Flow (mol/s)
7. Hydrogen Flow (mol/s)

- ☐ Lot more sub-layer and sub-systems also built-in

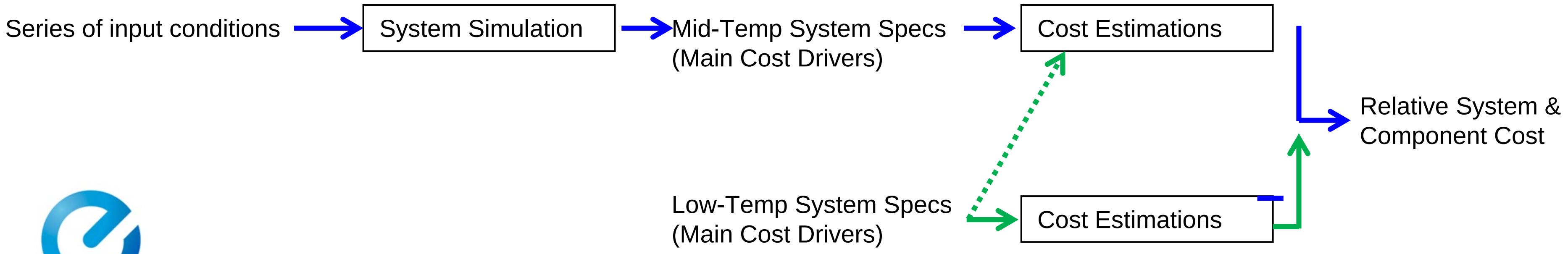
FCEV System-Level Modeling

Mid-Temp FCEV System Cost Estimation

- **System specifications are calculated from the system simulation.**
  - The necessary specification ranges for FCEV operation will be determined

- **The determined specs will be used to estimate the relative cost of the system components with respect to a Low-Temp FCEV System**
  - Main cost drivers to be determined and will be the focus of the simulation

  - **For Example**
    - The air compressor cost is a major cost driver for the system
    - Compressor cost is primarily determined by the required pressure ratio and the torque
      - These specs are calculated over a range of operating conditions



Series of input conditions

System Simulation

Mid-Temp System Specs
(Main Cost Drivers)

Cost Estimations

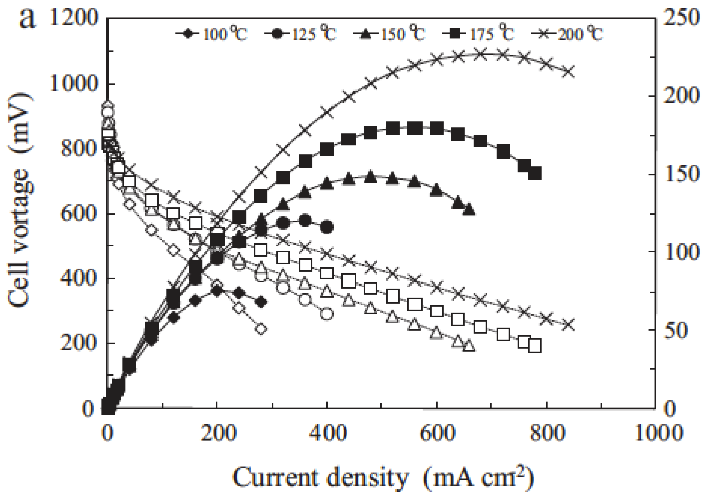
Low-Temp System Specs
(Main Cost Drivers)

Cost Estimations

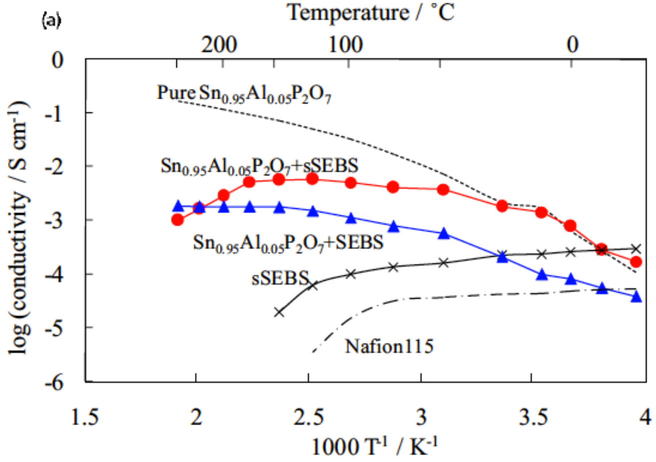
Relative System &
Component Cost

MEMBRANE MATERIAL

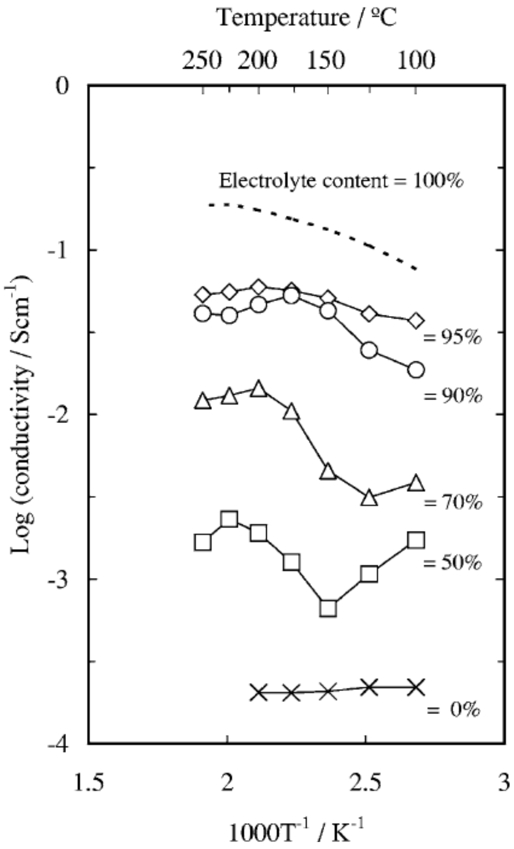
State of the Art – Indium Tin Pyrophosphate (ITPP Fuel Cells and Composite Membranes)



Y.C. Jin et al. / Journal of Power Sources 196 (2011) 4905–4910



Electrochemical and Solid-State Letters, **13** (2) B8-B10 (2010)



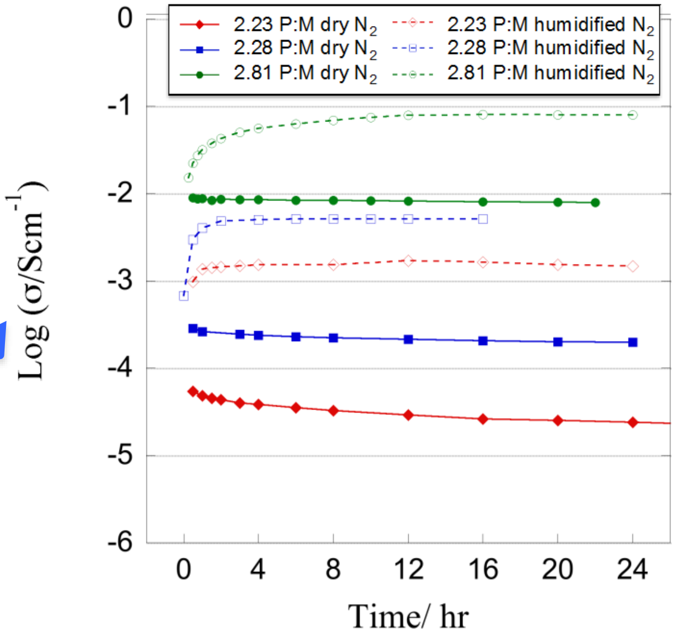
Journal of The Electrochemical Society, **154** (1) B63-B67 (2007)

Project Goals

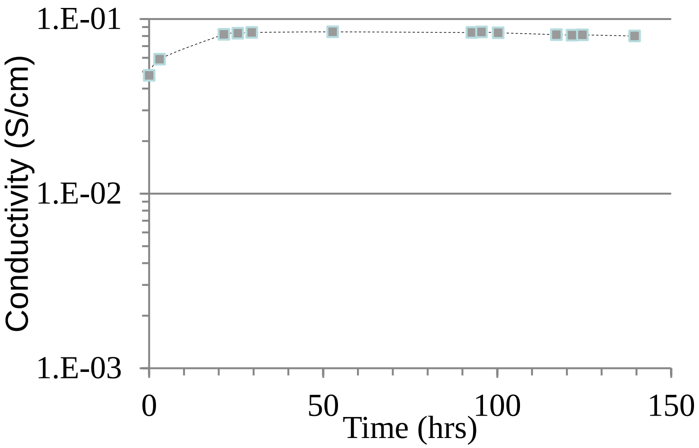
- ✓ Double State of the art power density
- ✓ Improve Conductivity 5 times

Conductivity of $In_{0.1}Sn_{0.9}P_2O_7$ with varying P:M

- High Proton Conductivity at Intermediate temp. in anhydrous reported for In-doped Sn pyrophosphates
- Inconsistent reproducibility in conductivity reported



Composition optimization for reproducible, high conductivity - LANL



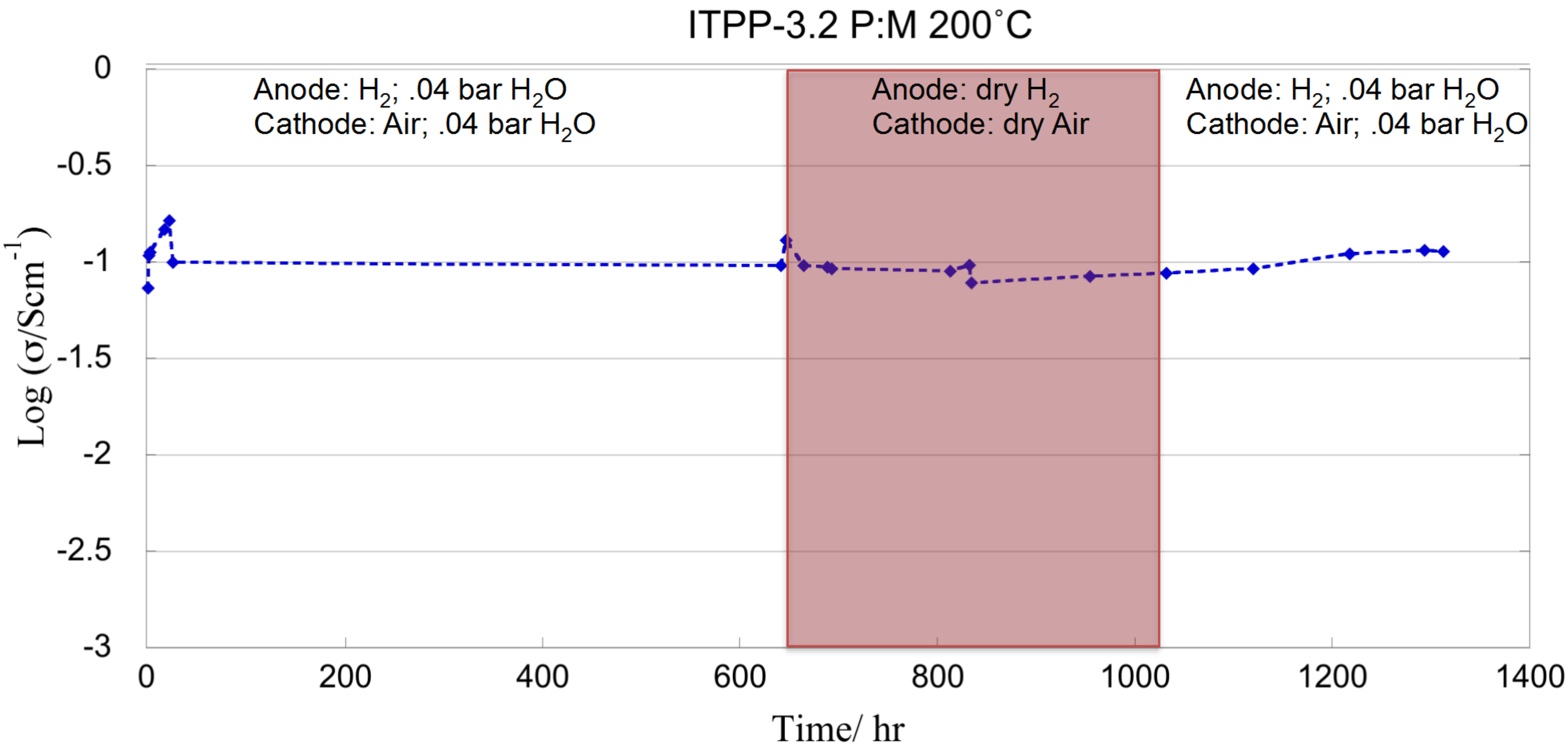
Batch scale up and high conductivity - Ceramatec

✓ Conductivity of nominal material (2.02 P:M) is *negligible* at 250˚C.

✓ P/M > 3; $\sigma \approx 10^{-1}$ Scm^{-1}

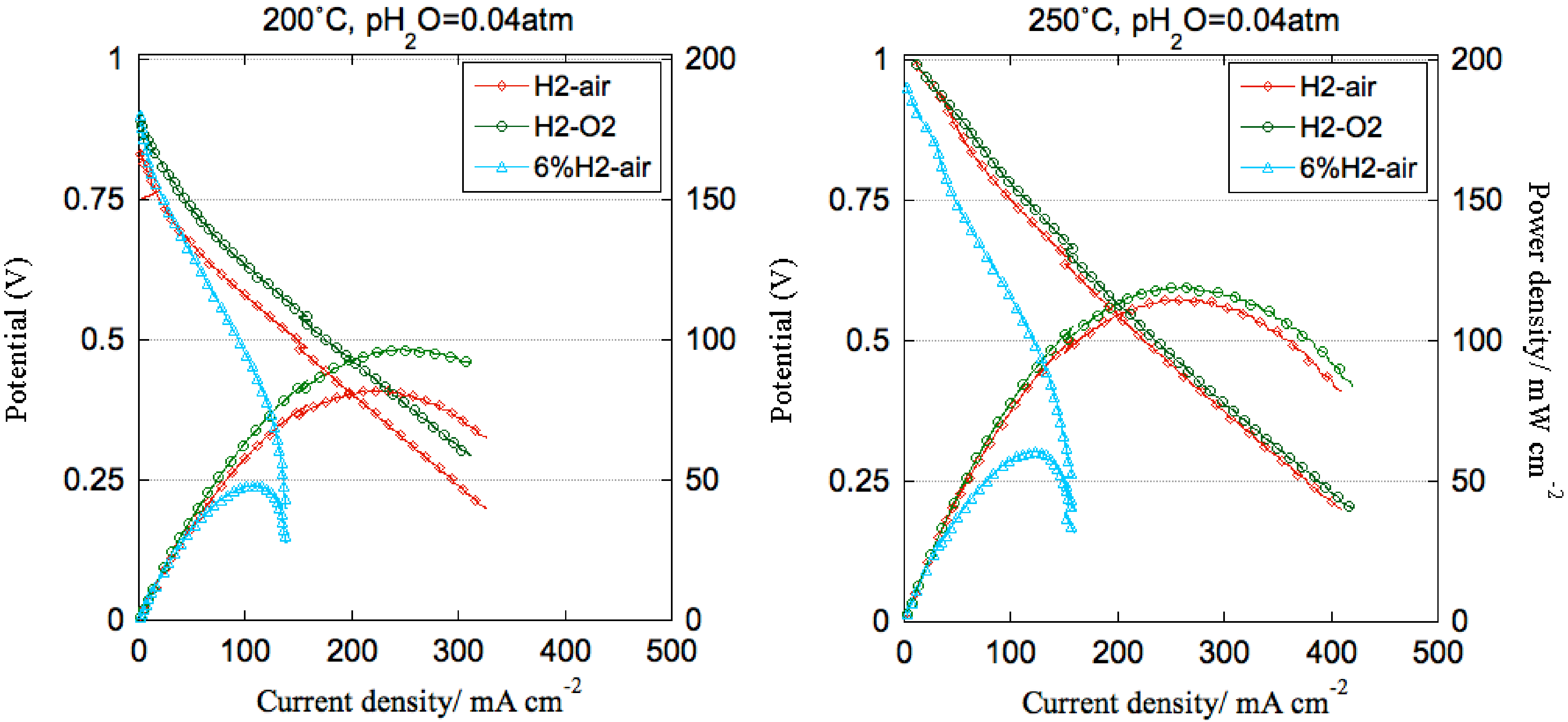
Kreller, C.R.; Wilson, M.S.; Mukundan, R.; Brosha, E.L.; Garzon, F.H. *ECS Electrochemistry Letters* 2013; 2(9): F61-F63.

Stability of Conductivity



SINGLE CELL TESTING

Electrolyte 1mm thick ITPP
Electrode: 10mg/cm^2 GDE + Phos Acid



- ✓ Anode performance is limiting in 6% H_2
- ✓ Electrolyte conductivity is critical

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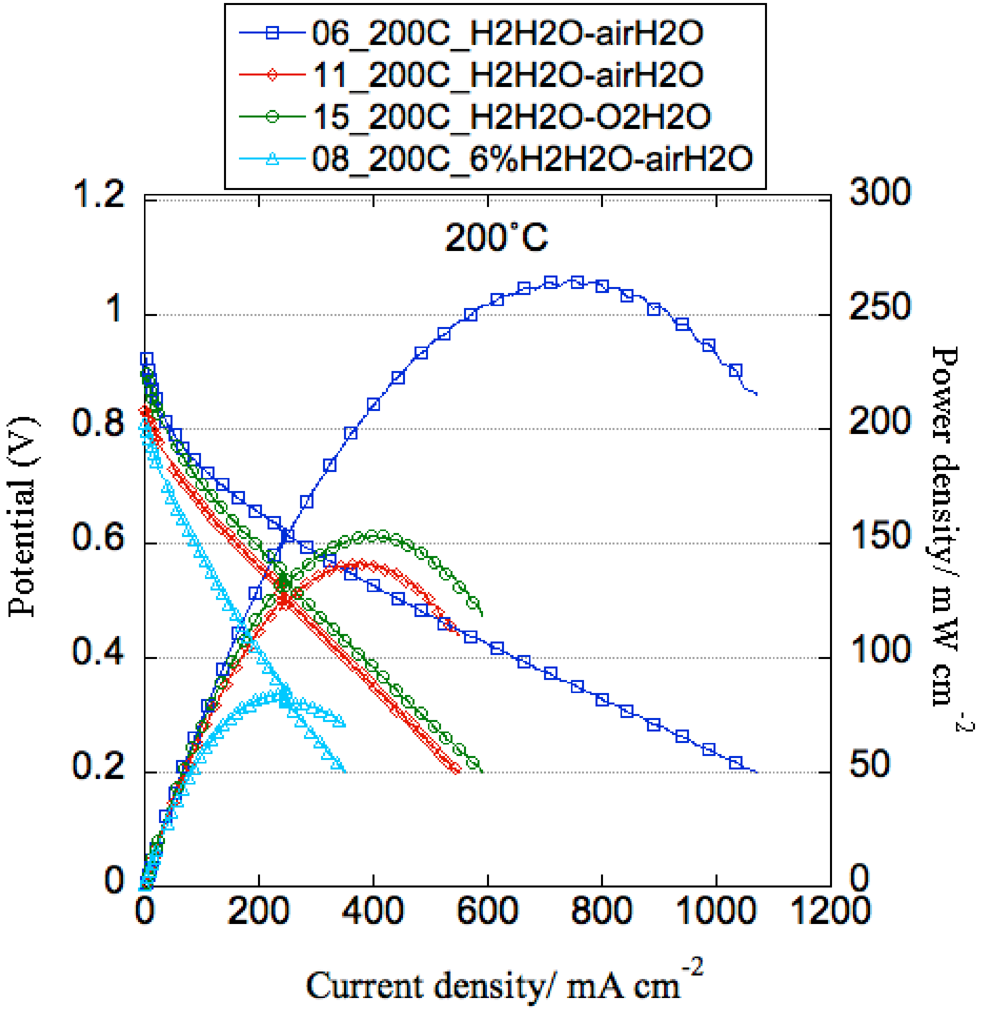
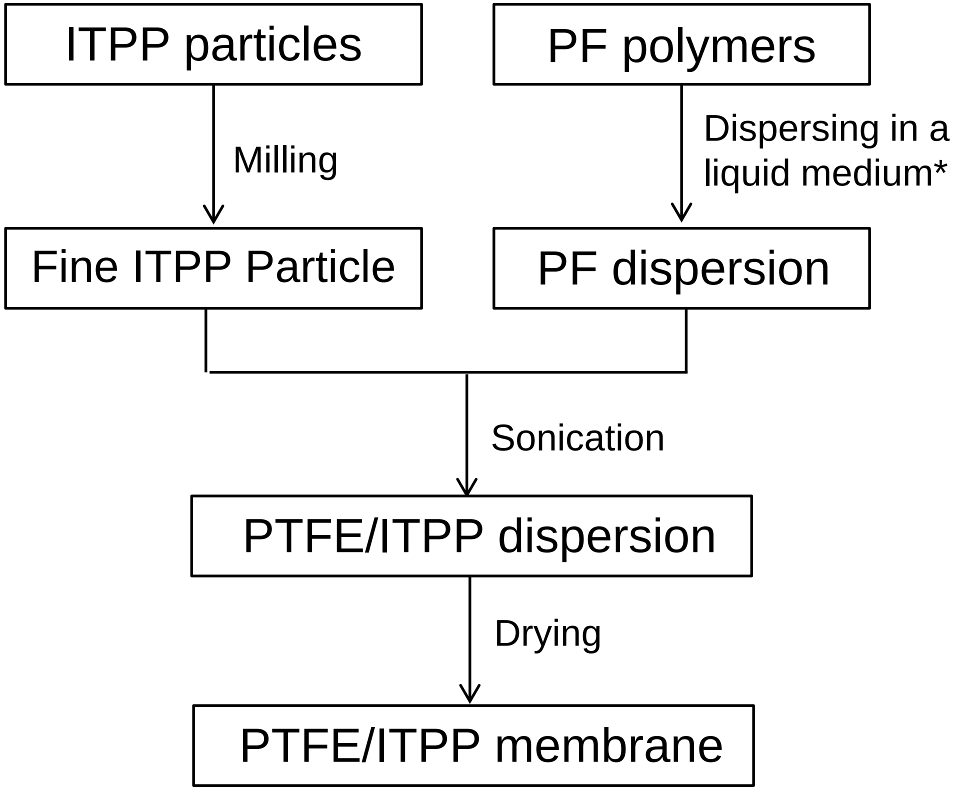
Electrolyte 0.025mm thick TPP 15wt% SiC whiskers
Electrode: Pt 10mg/cm^2 GDE + Phos Acid: 4µl cathode/2µl anode



- ✓ Significant performance improvement with thin electrolytes

Fabrication process of composite membranes



ITPP particles

Milling

Fine ITPP Particle

PF polymers

Dispersing in a liquid medium*

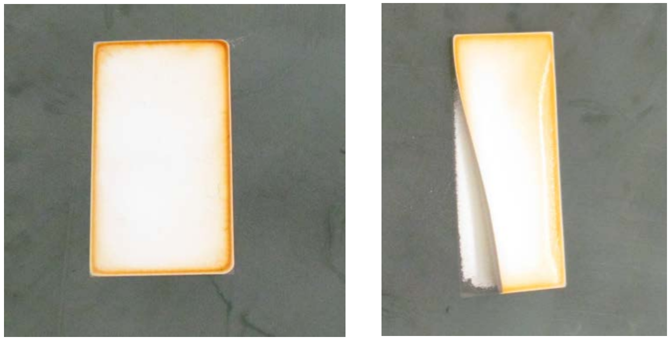
PF dispersion

Sonication

PTFE/ITPP dispersion

Drying

PTFE/ITPP membrane



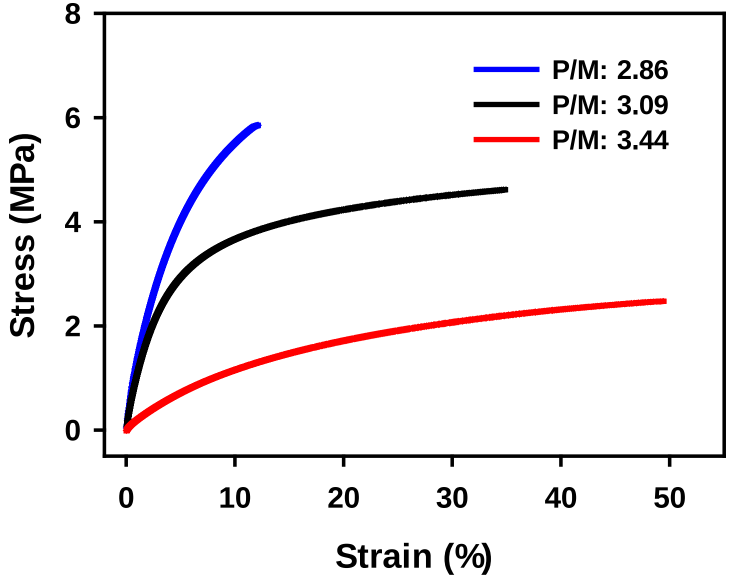
Cast composite membranes

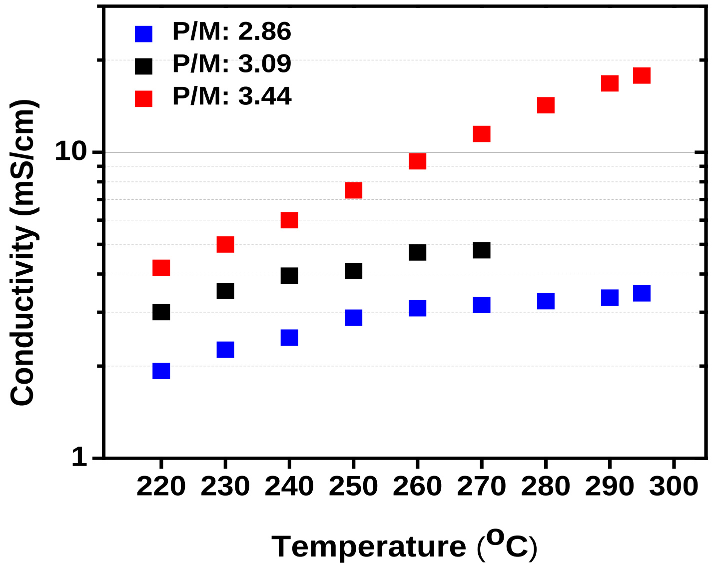
ITPP content: up to 90%

Thickness: 10 - 350 μm

Conventional sintering results in loss of proton conductivity

Effect of P:M ratio on mechanical and electrochemical properties


Stress-strain curves
(ITPP content: 75wt.%)


Proton conductivity
(ITPP content: 75wt.%)

- ✓ Elongation Strength ↑; Stress and Modulus ↓ with increasing P:M ratio
- ✓ Conductivity increased with P:M ratio
- ✓ Further optimizations are needed in terms of P:M ratio, ITPP content and casting solvent

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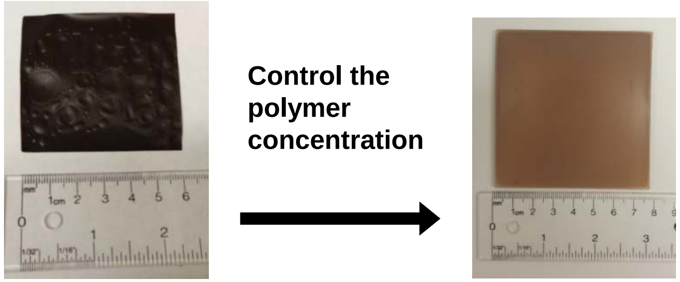
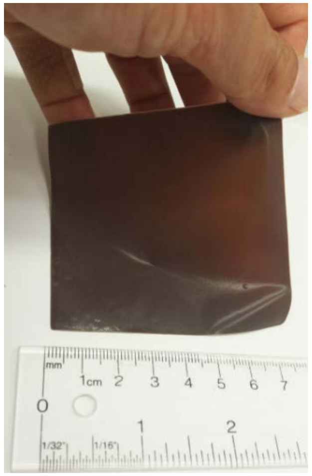
Large Area Membrane Fabrication

❑ Optimization of membrane formation : Issue of surface uniformity

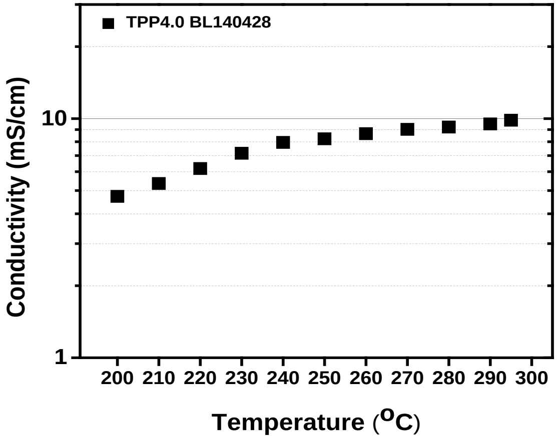
→ **PF polymer solution concentration: 5~8 wt%**

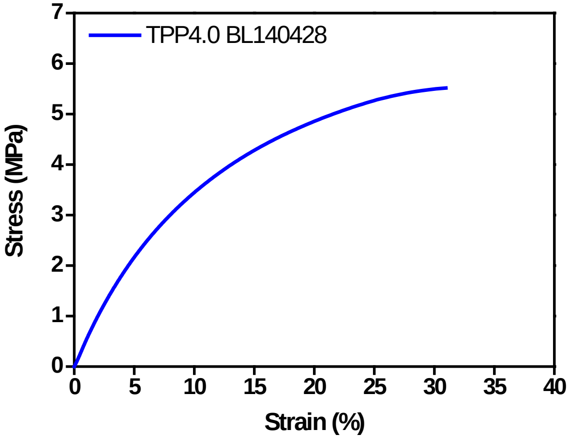

Control the polymer concentration

3 X 3 in^2 membranes
ITPP content: 75 %
Thickness: 50 μm ± 2



Proton conductivity & Mechanical property (Stress-strain curves)

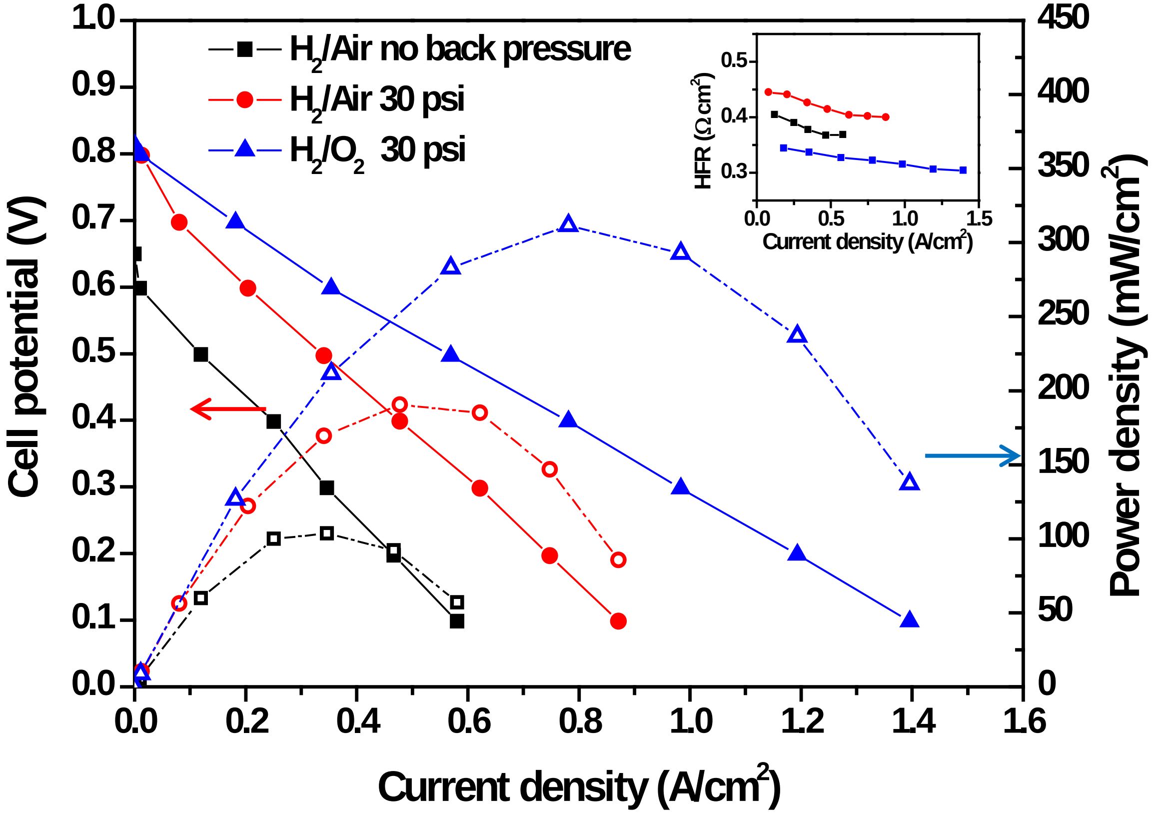




ITPP sample	Ceramatec sample # TPP4.0 BL140428 (P:M ratio : 3.28)
ITPP content	75 wt%
Casting temperature	140 °C
Casting time	4 h

Performance_TPP90wt%/PA

TPP90wt%/PA (electrode: Pt Black + TPP)



Sample	HFR (Ω cm2)	Conductivity (mS/cm)
H2/Air no back pressure	0.37 ~ 0.4	30 ~ 33
H2/Air 30 psi	0.40 ~ 0.44	27 ~ 30
H2/O2 30 psi	0.30 ~ 0.34	35 ~ 40

Condition

- Membrane thickness: 120 μm
- **Anode/Cathode/Cell Temp: 80/80/220 °C**
- H_2/Air (H_2/O_2): 200/200 sccm
- **Back pressure: varied (0-30 psi)**
- **Pt loading: 3.5 mg/cm²**

✓ **Best performance in H_2/O_2 condition with 30psi back pressure**

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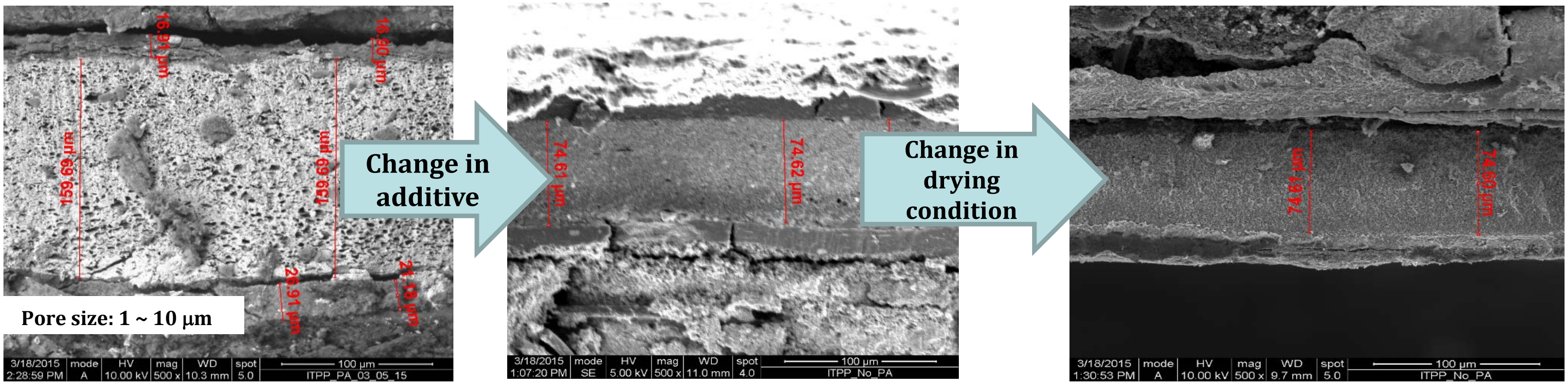
SEM images of TPP/PF composite membrane



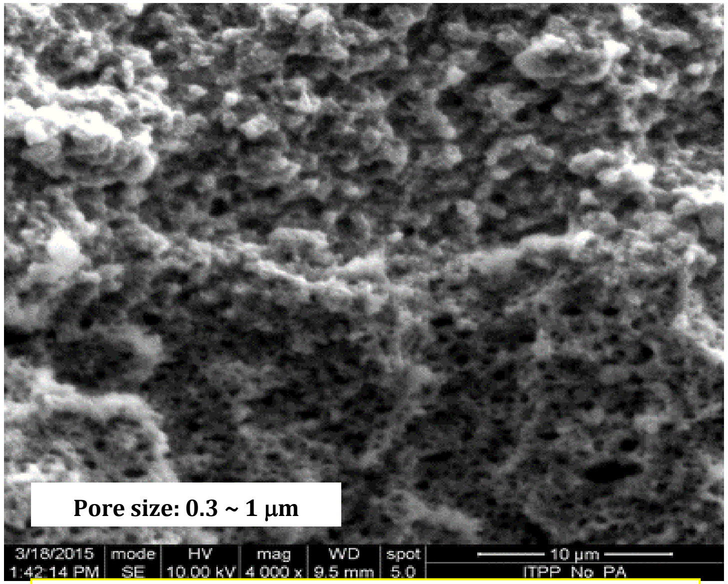
- Membrane thickness: 180 μm
- **No back pressure**
- **No humidification**
- H_2/O_2: 200/200 sccm
- **Pt loading: 0.2 mg/cm^2**
- Cell temperature: 200 °C
- OCV = 820 mV.

- Membrane thickness:120 μm
- **No back pressure**
- **No humidification**
- H_2/O_2: 200/200 sccm
- **Pt loading: 0.2 mg/cm^2**
- Cell temperature: 220 °C
- OCV = 840 mV.

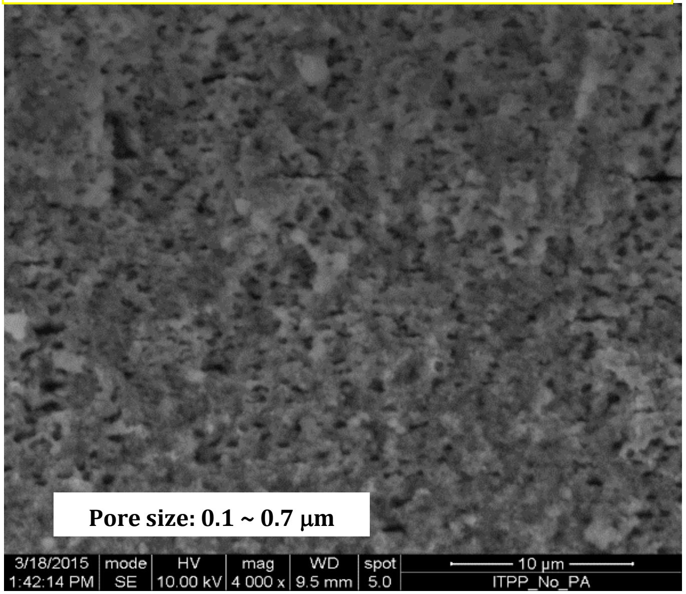
- Membrane thickness: 100 μm
- Back pressure: 30 psi
- No humidification
- H_2/O_2: 200/200 sccm
- **Pt loading: 0.2 mg/cm^2**
- Cell temperature: 200 °C
- OCV = 810 mV.

Membrane Porosity

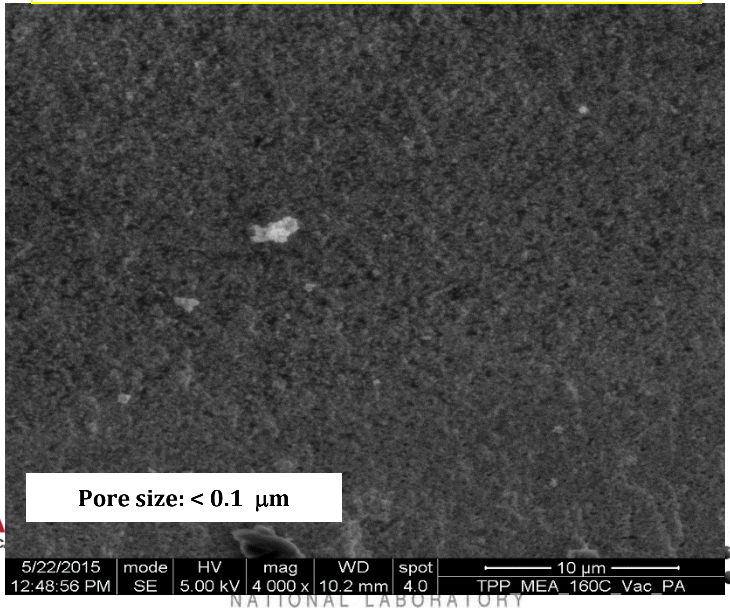
Initial Process


Pore size: 0.3 ~ 1 µm

Change in drying condition


Pore size: 0.1 ~ 0.7 µm

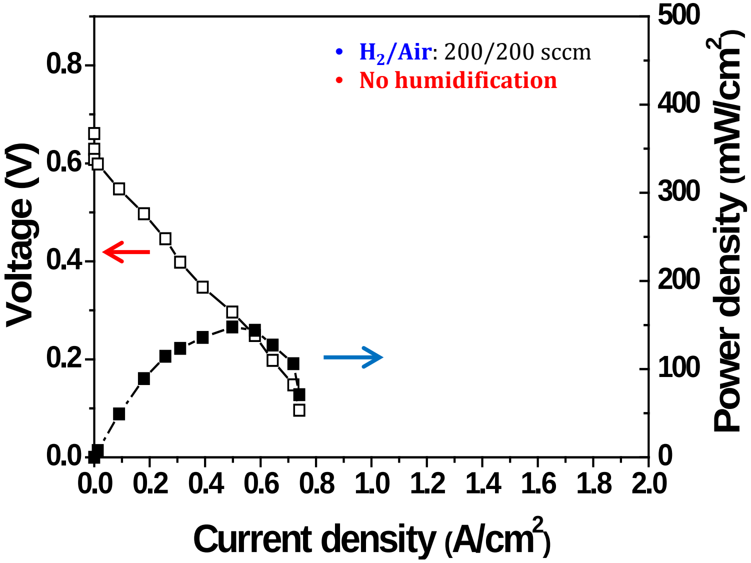
Change in drying condition and Temperature

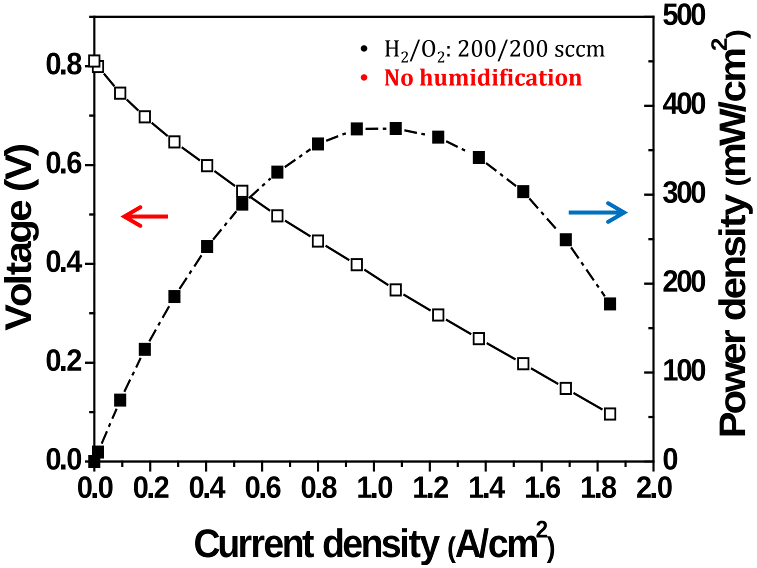

Pore size: < 0.1 µm

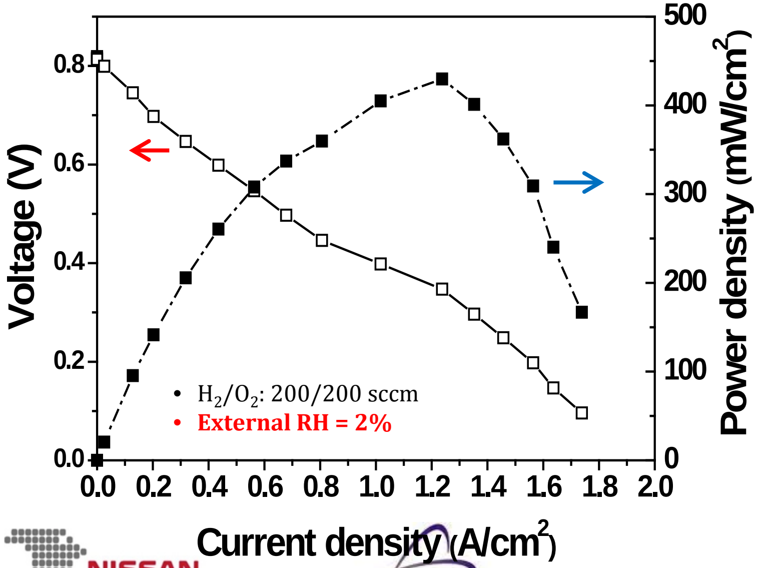
✓ Successfully prepared denser membranes

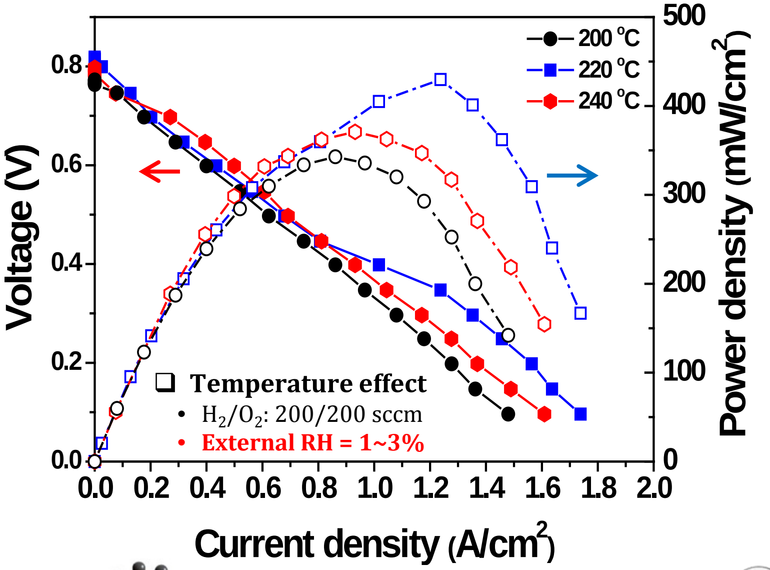
- Modified slip preparation and drying conditions

Updated Single Cell Performances with LANL Ionomer









❑ **Membrane**
- **TPP content: 90 wt%**
- **Thickness : 80 μm**
- **Drying condition changed**

❑ **Catalyst**
- **20wt% Pt/C (BASF)**
- **0.2 mg_{PGM}/cm^2 for each electrode**

❑ **Electrode**
- **No TPP particles**
- **Added H_3PO_4**
- **LANL developed ionomer**
- **Ionomer is stable at high temperature operation.**

❑ **Operating cond.**
- **Cell temp.: 220 °C**
- **Backpressure: 30psig**
- **Cell break-in: 24 h**

❑ **MEA preparation**
- **Active area: 4.4 cm^2**
- **PTFE gaskets**
- **High temperature GDL**
- **GDL painting without hotpressing**

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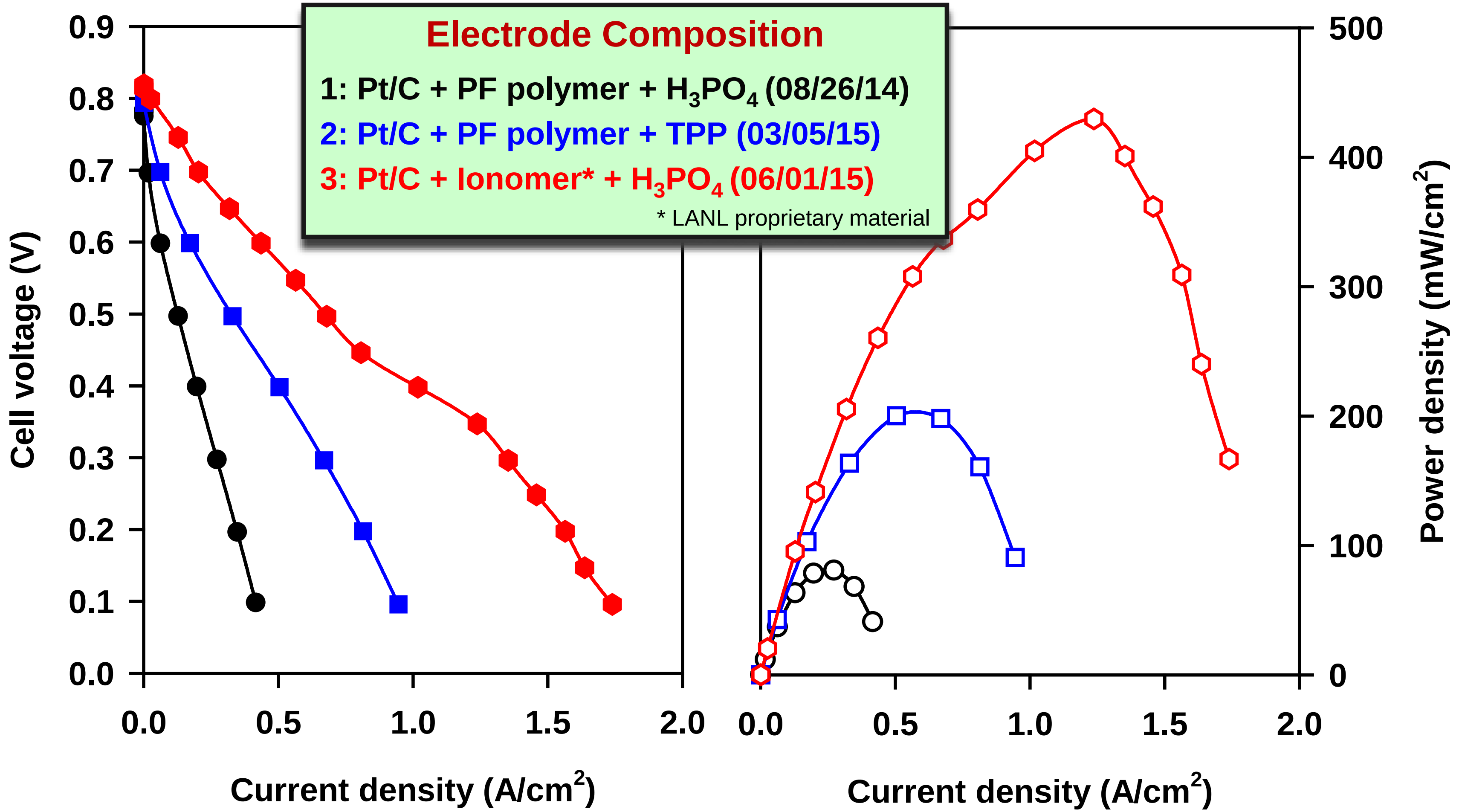
Electrode Optimization towards Better Fuel Cell Performance

Test conditions: H_2 (200 sccm)/O_2 (200 sccm); external RH = 0-2%; 5 cm^2 hardware
Operating temperature: 1: 240° C, 2: 230° C, 3: 220° C
Membrane TPP content: 90 wt.%; Membrane thickness: 80-180 μm
Catalyst: 20 wt.% Pt/C (BASF); catalyst loading: 0.2 mg/cm^2 for each electrode

● 1: 08/26/14
■ 2: 03/05/15
⬢ 3: 06/01/15



Electrode Composition

1: Pt/C + PF polymer + H_3PO_4 (08/26/14)
2: Pt/C + PF polymer + TPP (03/05/15)
3: Pt/C + Ionomer* + H_3PO_4 (06/01/15)

* LANL proprietary material

Conclusions

- Reproducible, high conductivity in scaled up powder batches
  - Proton Conductivity of 0.1 S/cm
- High loading of TPP in polymer composite
- Single 5 cm^2 membrane performance of ~ 300 mW/cm^2 demonstrated (High Pt loading) – porous membrane
- Dense composite membrane fabricated
- Low Pt loading (0.2 mg/cm^2), ionomer in GDE, 5 cm^2 cell demonstrated >400 mW/cm^2
- Early versions of cells demonstrated in 50 cm^2 size

Remaining Challenges

- Increase in OCV
- High performance cells in 25 cm^2 and 50 cm^2 size
- Design/build/test multi-cell stack
- Long term performance stability evaluation
- CO tolerance evaluation
- Complete cost model

Acknowledgement

- ARPA-E Team
  - Program Director: Dr. John Lemmon
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  - Tech to Market: Mr. Sven Mumme