Nanocomposite Electrodes for a Solid Acid Fuel Cell Stack Operating on Reformate

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Pittsburgh, PA

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ARPA-E REBELS Program

OAK RIDGE National Laboratory

Project Team and Objectives

ARPA-E REBELS Category 1 Project

Project Outline

100 W stack prototype

CsH_2PO_4 electrolyte

Reformed natural gas fuel

Major Objectives

Electrical Efficiency >50%

Pt loading < 0.1 mg/cm^2

Current > 225 mA/cm^2 at 0.78 V

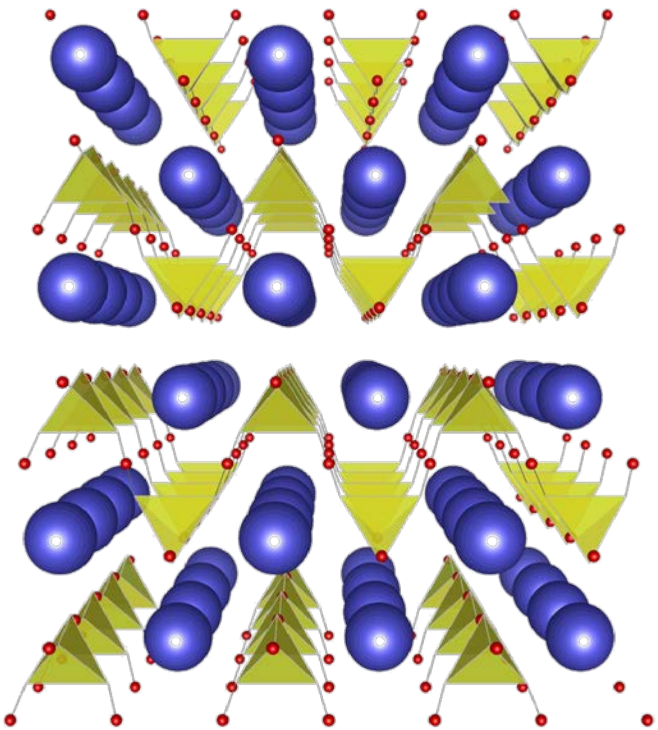
Superprotonic Solid Acids

Hydrogen-bonded ionic solids

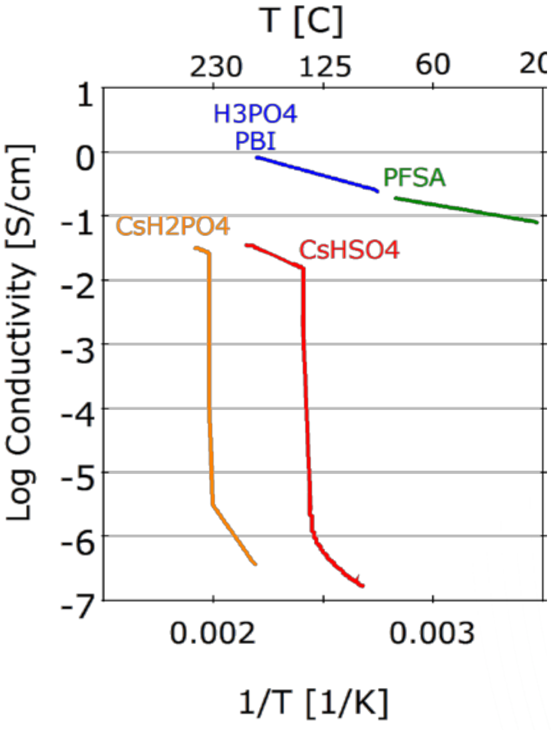
Polymorphic **phase transitions** at T>100 °C

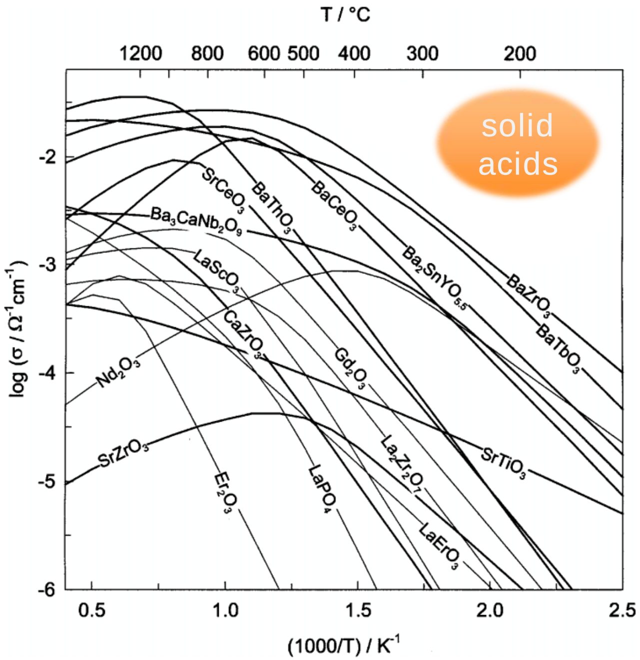
H^+ conductivity increases **>1000x** across phase transition

Water soluble



CsH_2PO_4 (CDP)

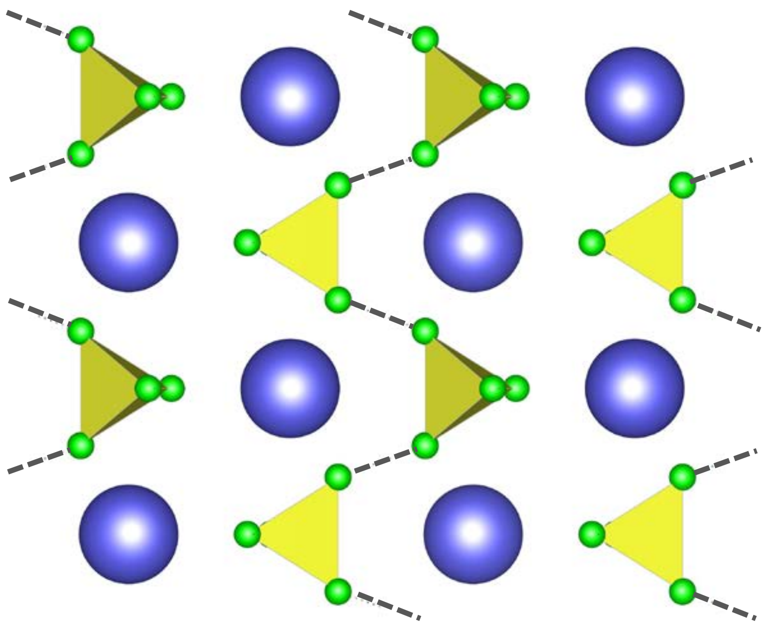




Proton Conducting Oxides
K.D. Kreuer, Annual Review of Materials Research 33, 333–359 (2003)

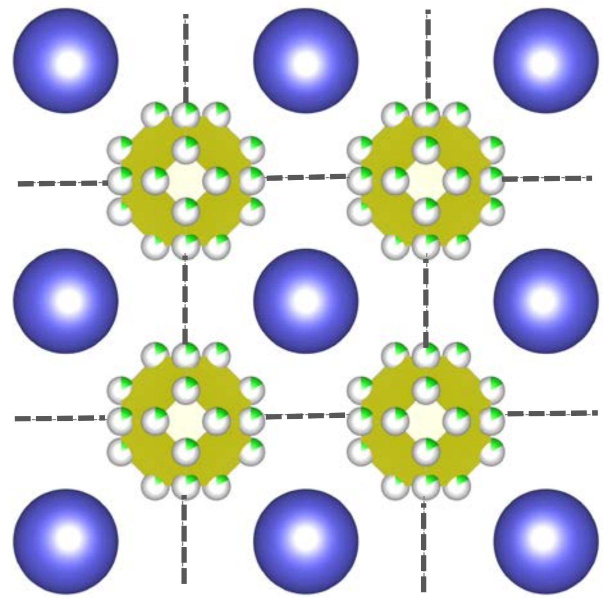
Crystal Symmetry Controls H^+ Conductivity

Paraelectric (RT)



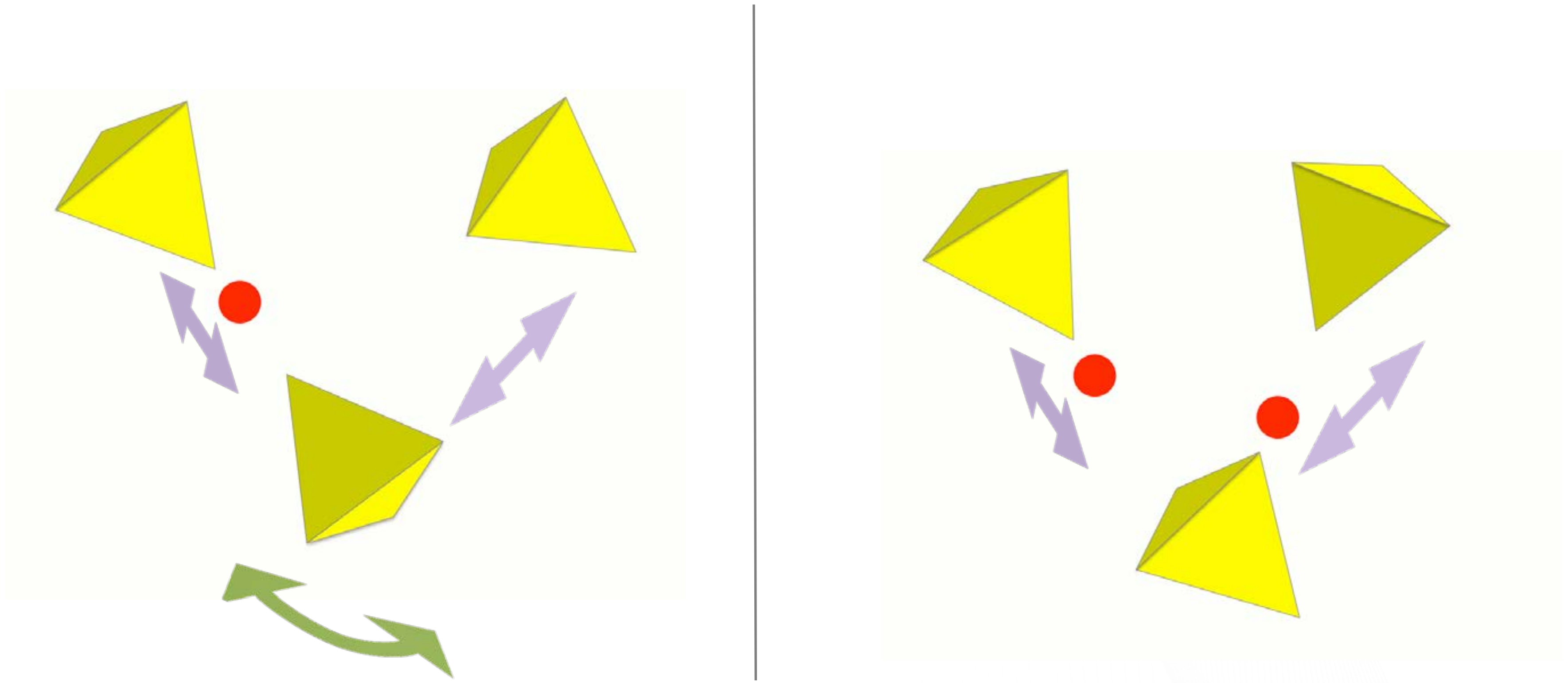
4 Oxygen sites per unit cell
4 H-bonds (----) possible per tetrahedron

Superprotonic (>228 °C)



24 Oxygen sites per cell, each with 1/6 occupancy
6 H-bond (----) orientations possible per tetrahedron

Proton Transport in Superprotonic CDP



Bulk proton transport includes both **oxyanion reorientation** and **hydrogen bond transfer**

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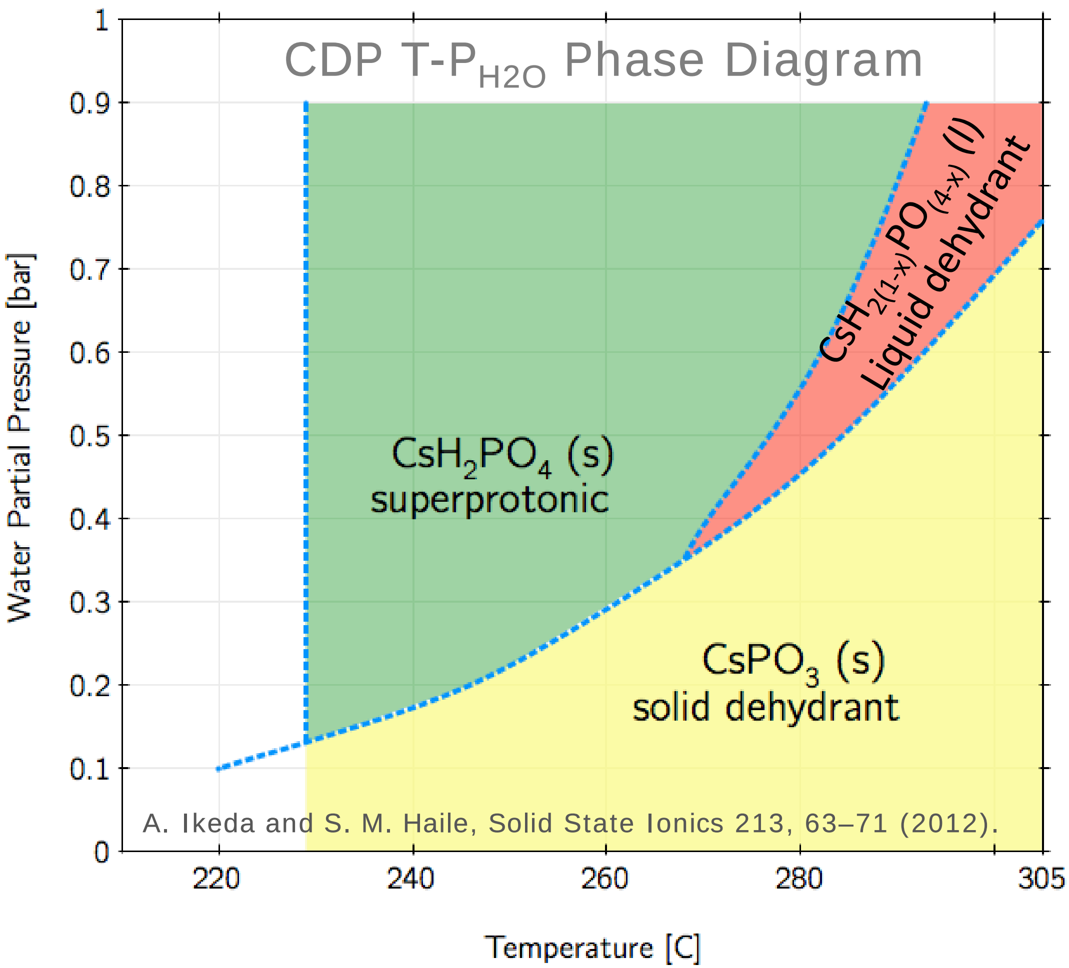
Temperature and Humidity Control Requirements

$$CsH_2PO_4 \rightleftharpoons CsPO_3 + H_2O$$



Water solubility

- Must keep humidity below dew point of water
- $P_{H2O} < P_{H2O}(T_{dew})$

Superprotonic transition temperature

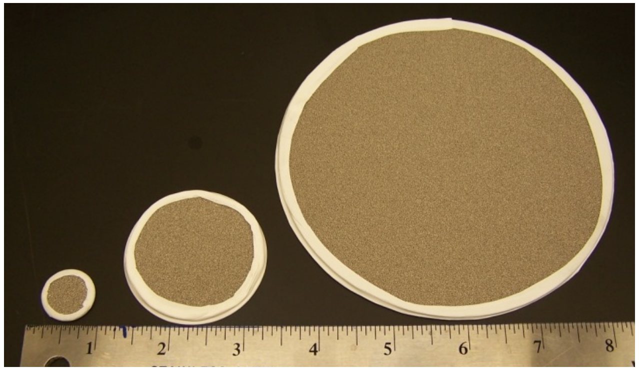
- No fuel cell operation until $T > 231°C$
- Requires independent system for heating upon start-up

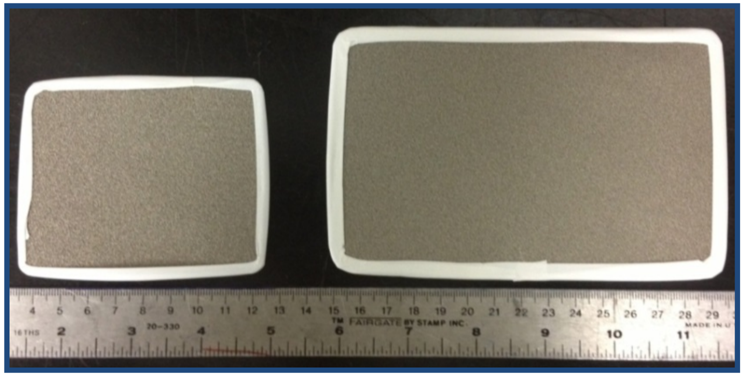
Dehydration temperature

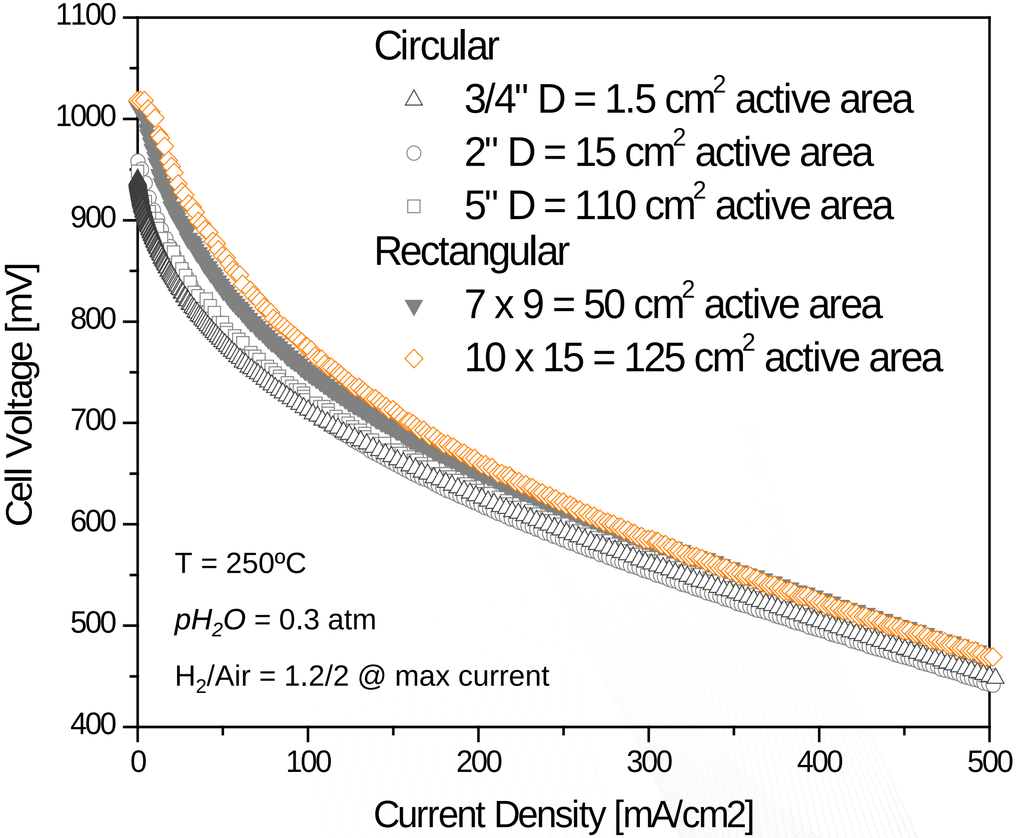
- Both fuel and air streams must be hydrated
- Maximum operating temperature $T_{dehyd} \sim 280°C$

Solid Acid Fuel Cells (SAFC)
CsH_2PO_4 Electrolyte, Pt Catalysts

SAFCell



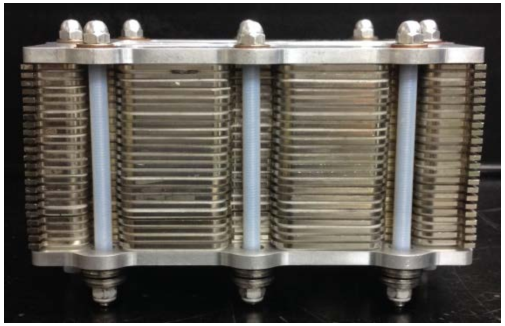




SAFCell SAFC Products
10 W to 1,500 W stacks

SAFCell

Portable power



Premium & auxiliary power

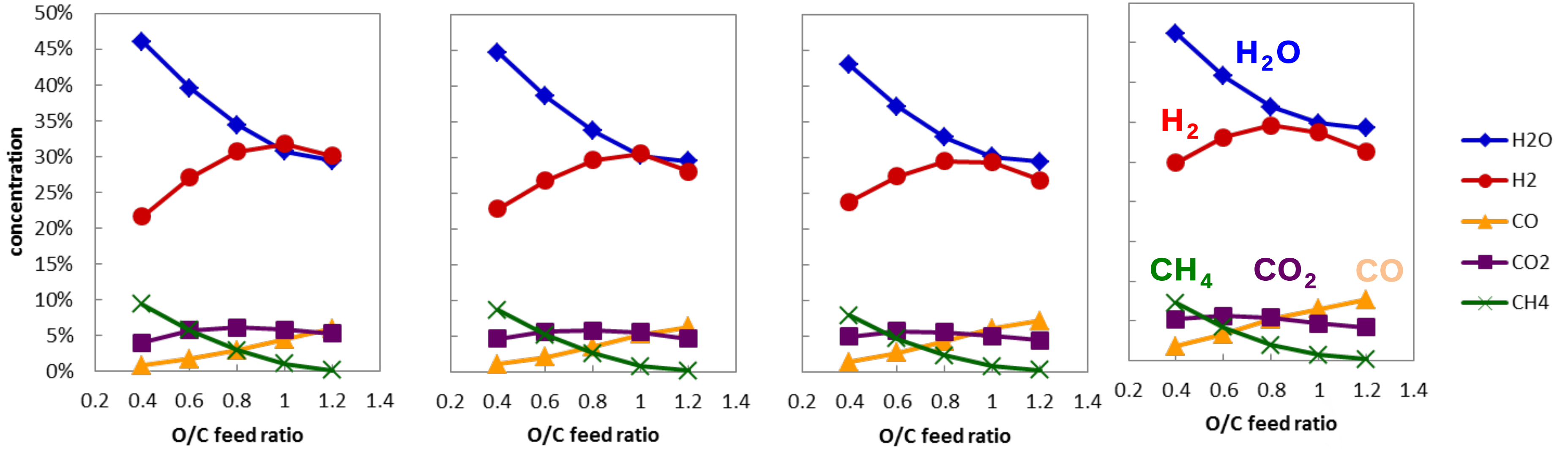
10-100W 100-300W 500-1500W

Stack power

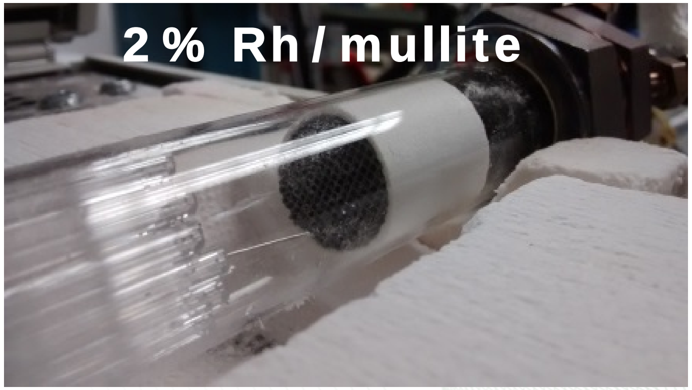
Aluminum and stainless steel hardware, polymer seals

ORNL Natural Gas Reformer

nominal inlet T: 475 °C **525 °C** **575 °C** **625 °C**



- Light-off T > 450 °C
- O/C ratios control reforming process
  - low: steam reforming (endothermic)
    - low CH_4 conversions, H_2 yields
  - high: partial oxidation (exothermic)
    - high CH_4 conversions, H_2 yields



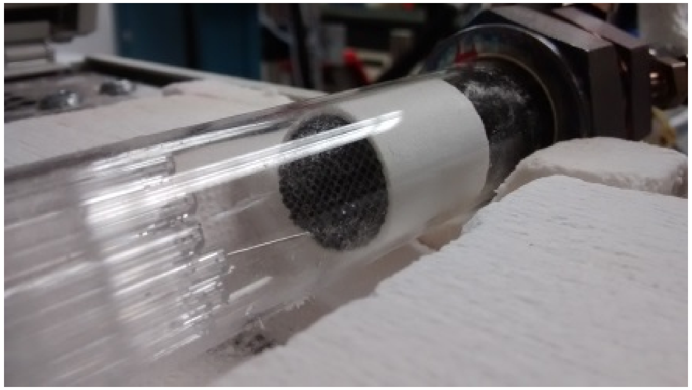
Reformer Efficiency Greater Than 80%

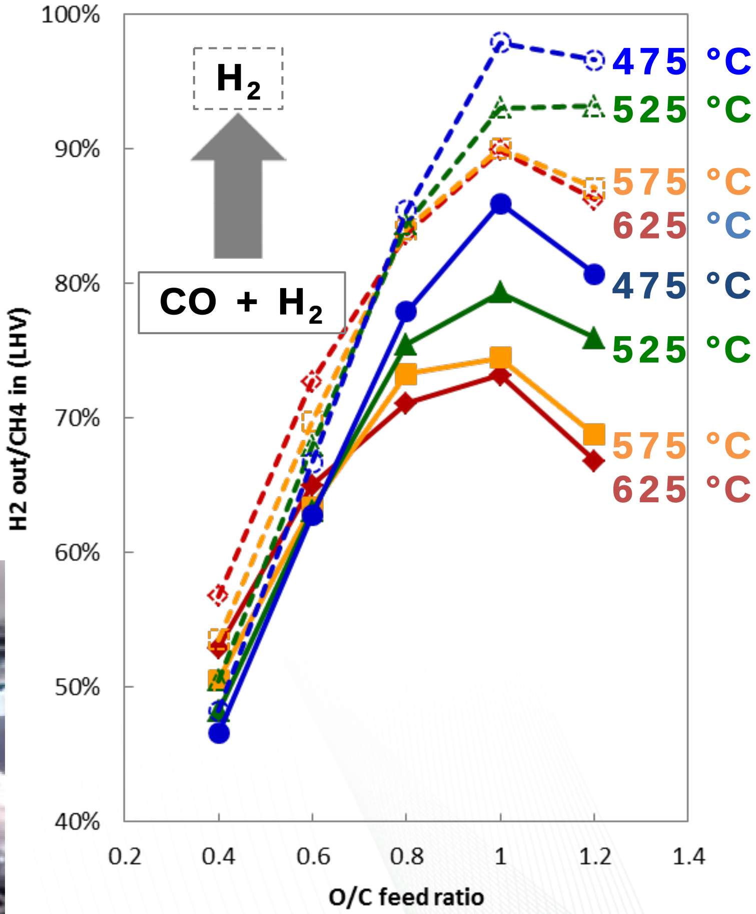
Optimal efficiency at O/C = 1

- 85% fuel energy converted to H_2 (LHV basis)

- 98% inlet fuel energy converted to H_2 if all CO shifted to H_2 over downstream WGS catalyst

WGS catalysts can be integrated into MEA





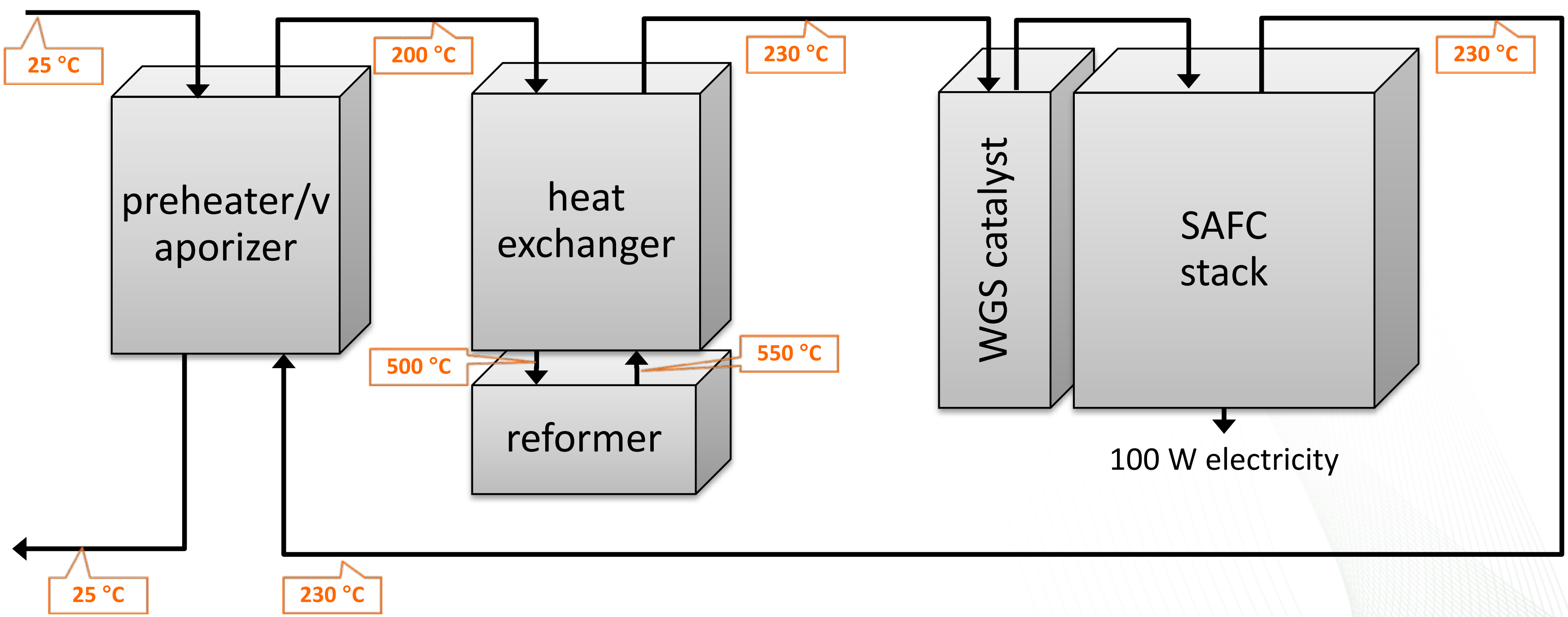
System flows, Compositions, Temperatures

flow (slpm)	gas	mole fraction
0.37	CH_4	16%
0	CO	0%
1.1	H_2O	47%
0.18	O_2	8%
0.69	N_2	30%

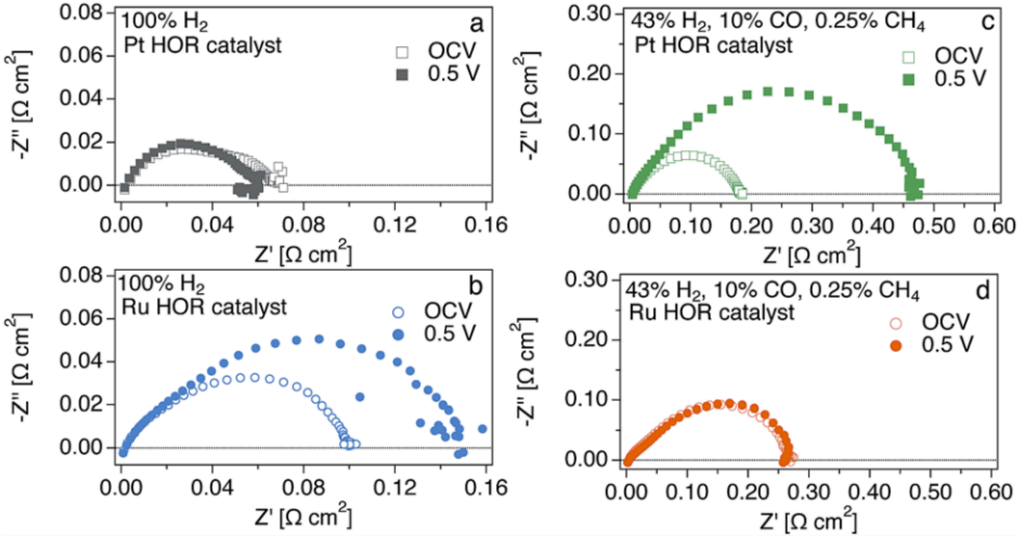
flow (slpm)	gas	mole fraction
0.96	H_2	33%
0.14	CO	5%
0.88	H_2O	30%
0.23	CO_2	8%
0.69	N_2	24%

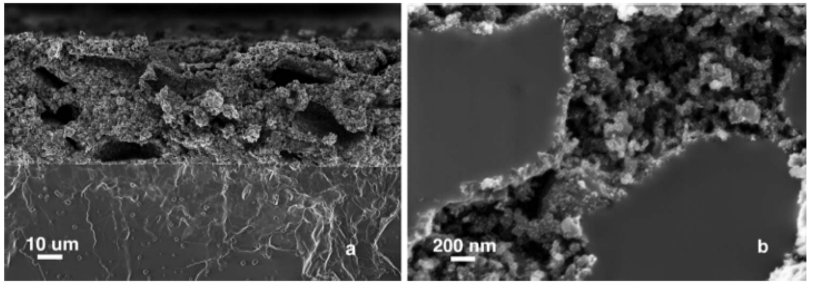
flow (slpm)	gas	mole fraction
1.1	H_2	38%
0	CO	0%
0.74	H_2O	25%
0.37	CO_2	13%
0.69	N_2	24%

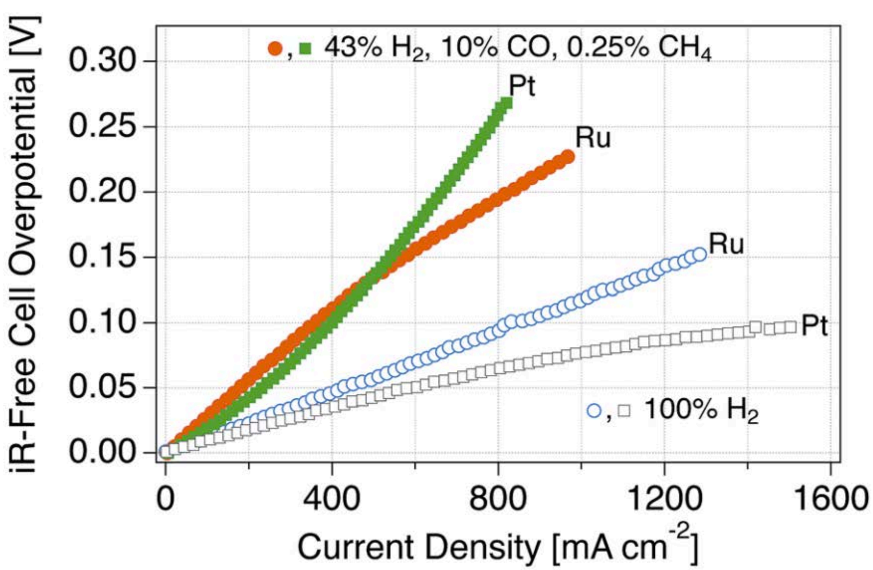
flow (slpm)	gas	mole fraction
0.18	H_2	9%
0	CO	0%
0.74	H_2O	37%
0.37	CO_2	19%
0.69	N_2	35%



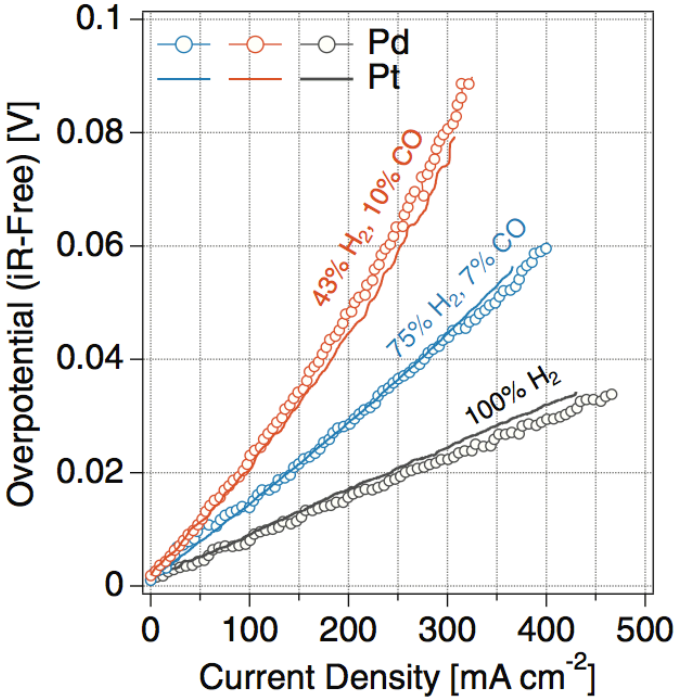
SAFC Anodes







A. B. Papandrew, R. W. Atkinson III, R. R. Unocic, and T. A. Zawodzinski, Journal of Materials Chemistry A, 3, 3984 (2015)



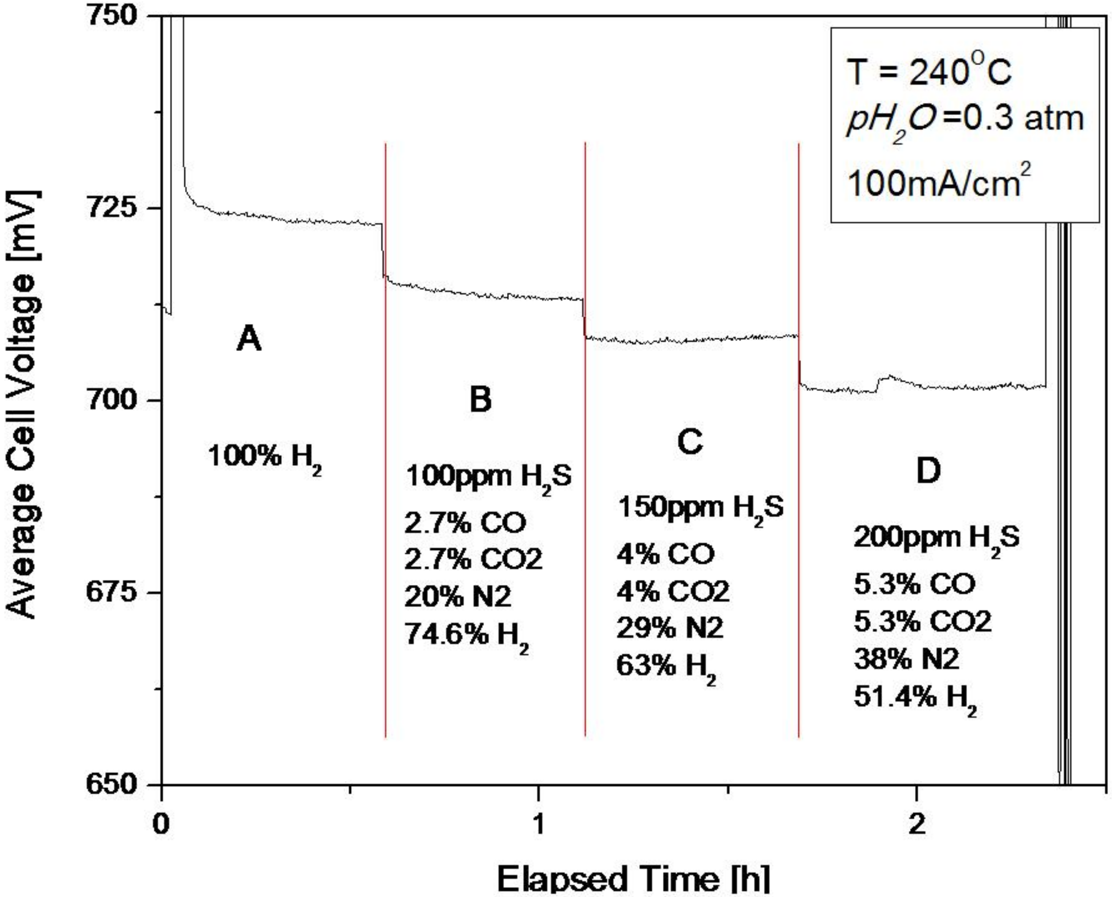
A. B. Papandrew, D. L. Wilson III, N. M. Cantillo, S. A. Hawks, R. W. Atkinson III, G. A. Goenaga, and T. A. Zawodzinski, Journal of the Electrochemical Society, 161, F679 (2014)

CO, CO_2 and H_2S Tolerance at the Stack Level

SAFCell

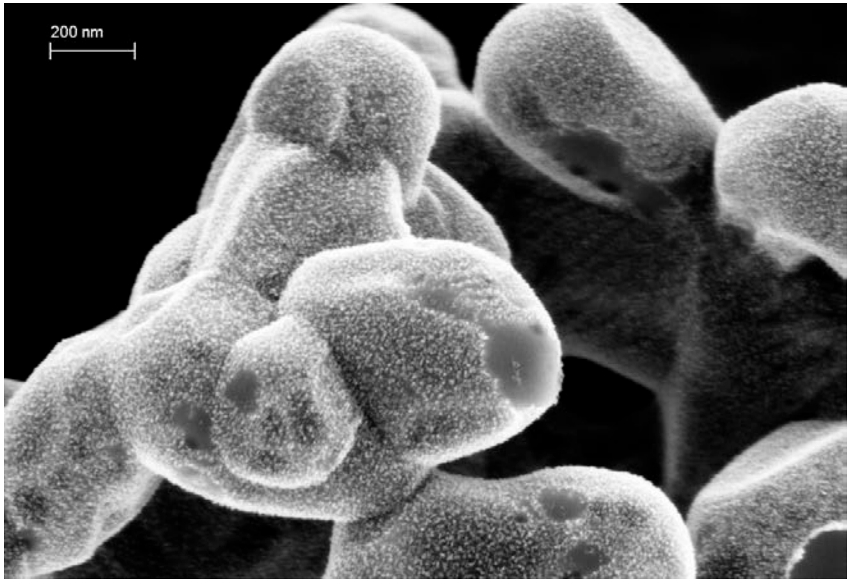
- Minimal effect of impurities on performance
  - Mostly H_2 dilution effect
  - 20 cell stack (2" MEA)
- Gas flow/compositions
  - Cathode:
    1.5 LPM air + 0.3 bar H_2O
  - Anode
    0.6 LPM + 0.3 bar H_2O
- Stack stabilty under high CO & H_2S confirmed
  - 5.3% CO & 200ppm H_2S

20 cell SAFC stack

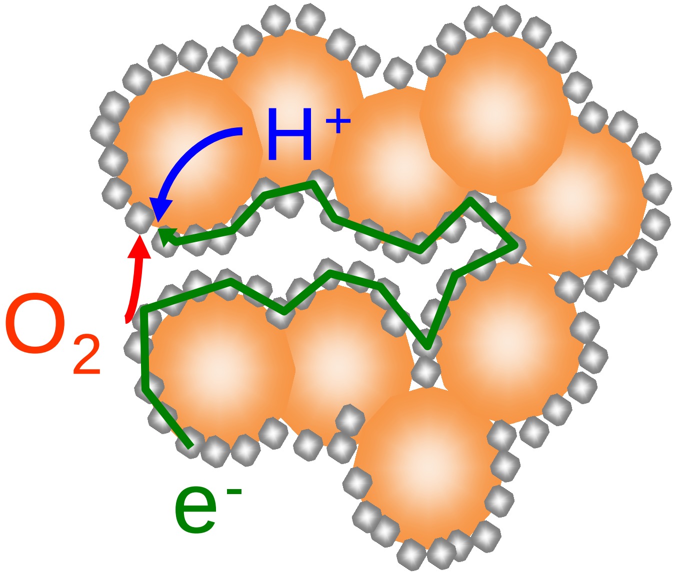


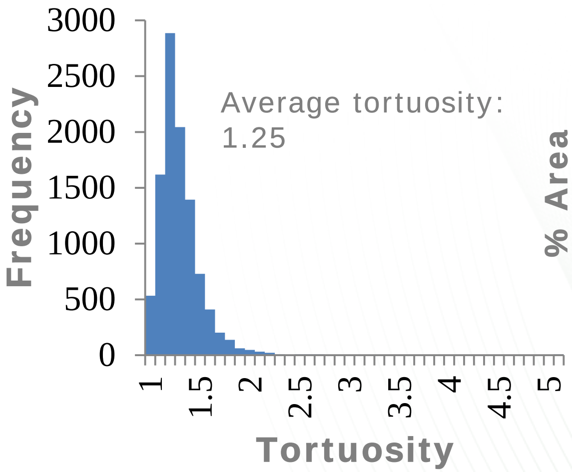
State-of-the-Art SAFC Cathode

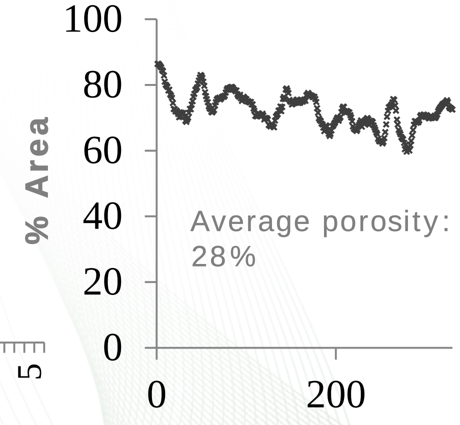
Pt is the ORR catalyst and the sole electronic phase



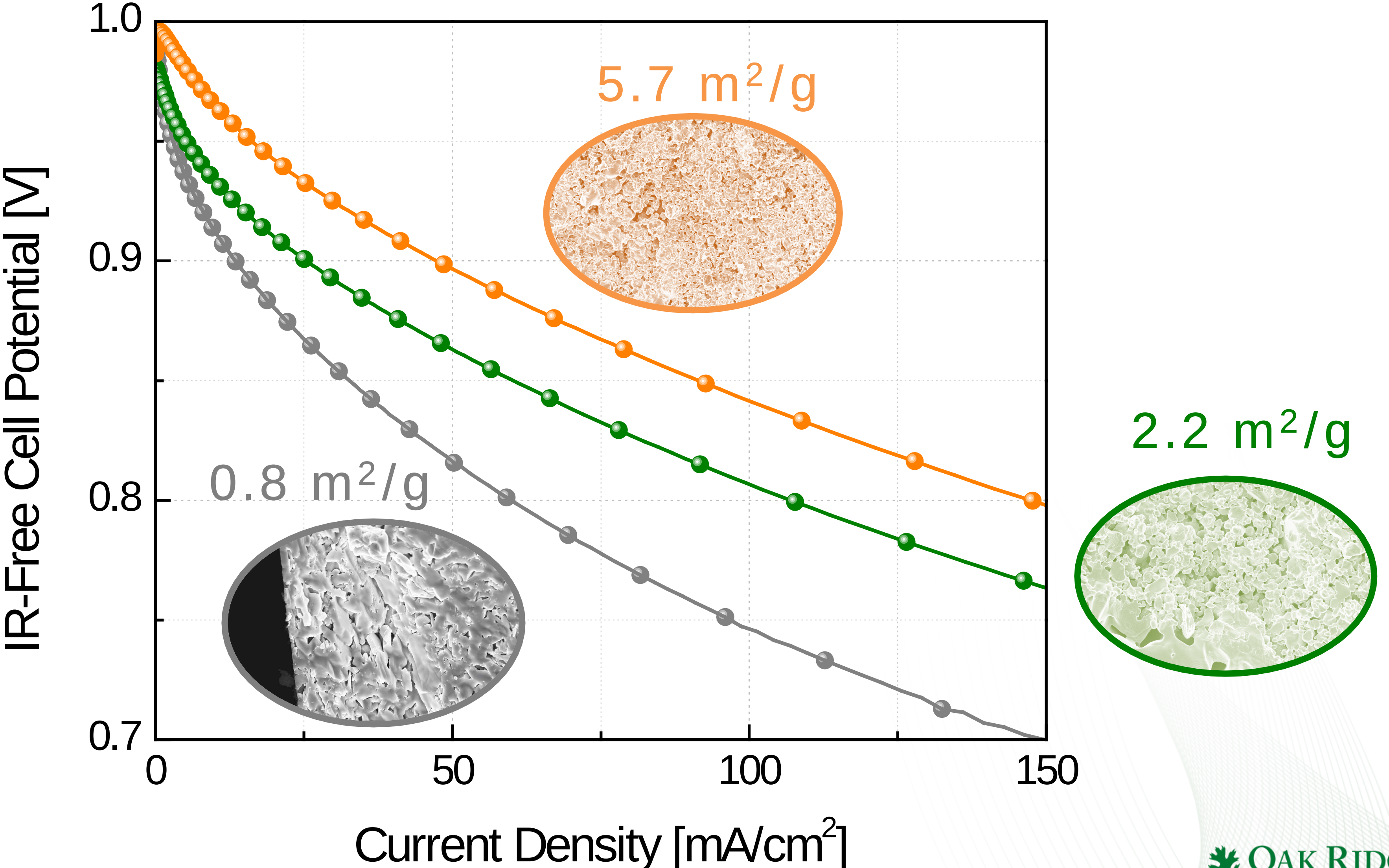
SEM-FIB Tomography Reconstruction







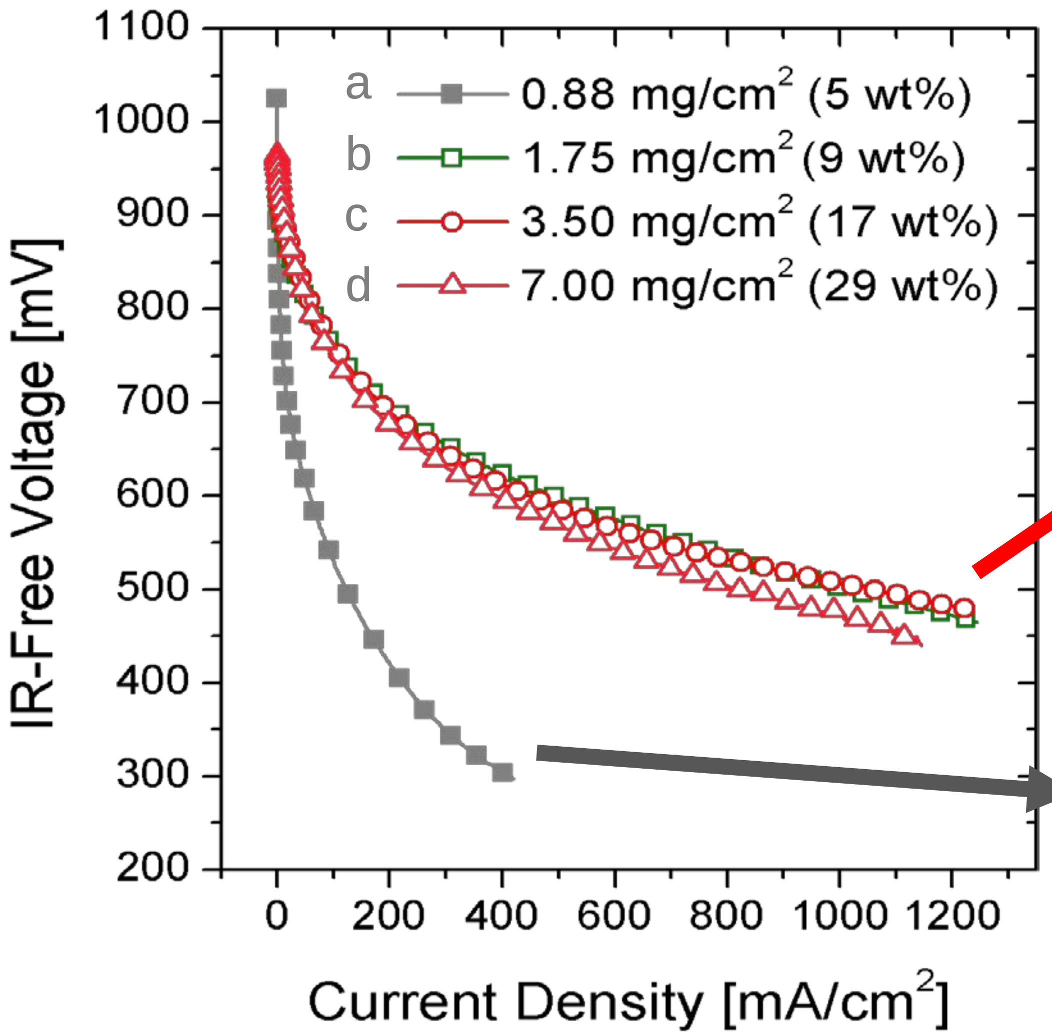
Electrolyte Surface Area Has Large Effects on Cathode Performance

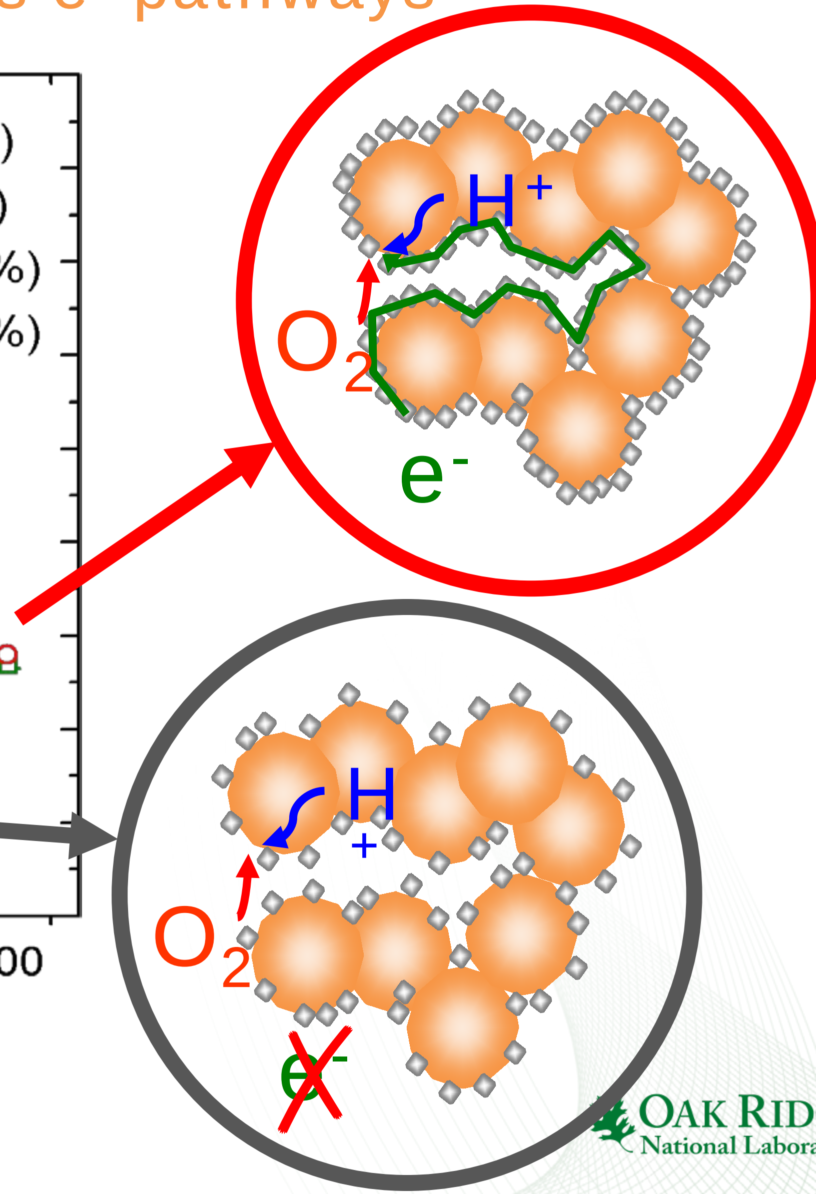


C.R.I. Chisholm, D.A. Boysen, A. B. Papandrew, *et al,* Electrochem. Soc. Interface 18, 53-59 (2009).

Baseline Cathodes at Lower Pt Content

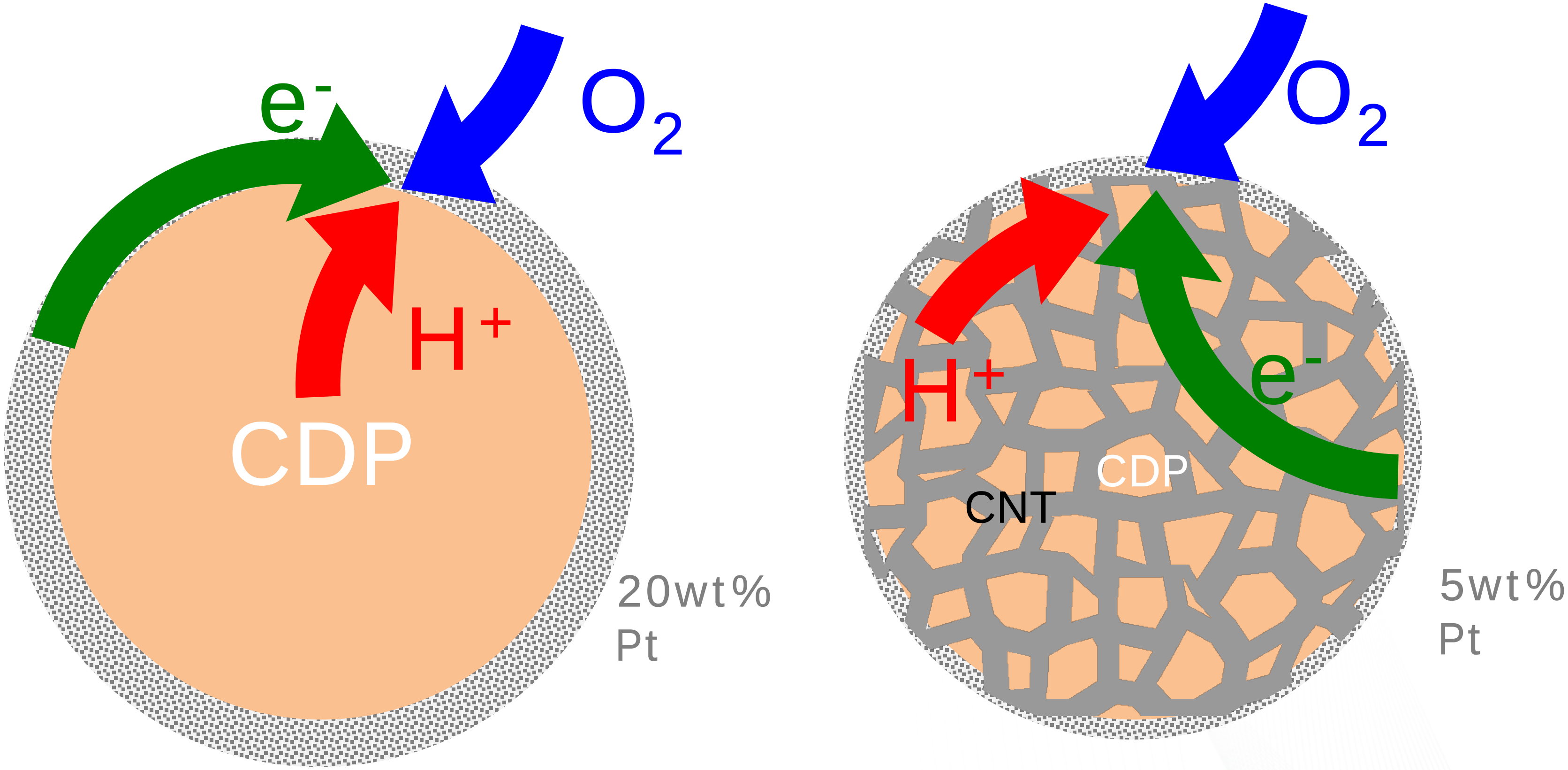
Sub-critical Pt coating limits e⁻ pathways





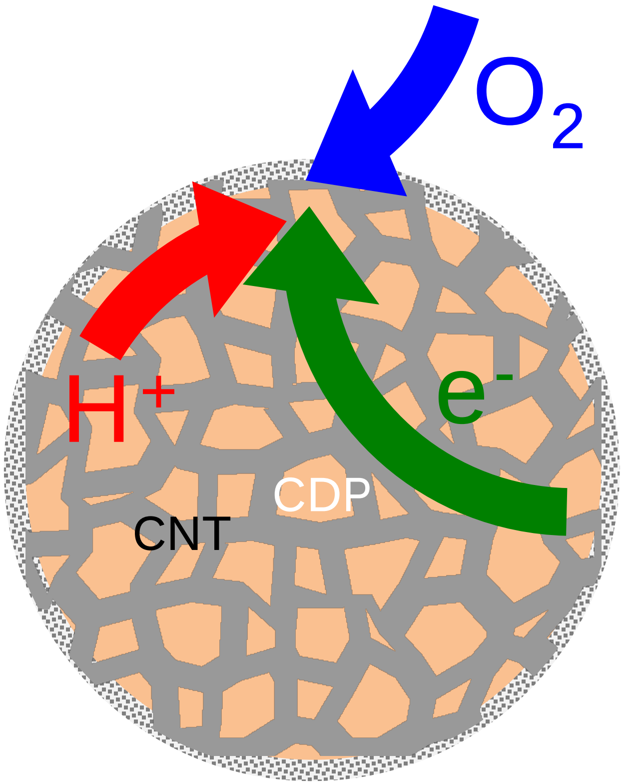
A.B.Papandrew, C.R.I.Chisholm, R.A.Elgammal, M.M.Ozer and S.K.Zecevic, Chemistry of Materials, 23, 1659 (2011)

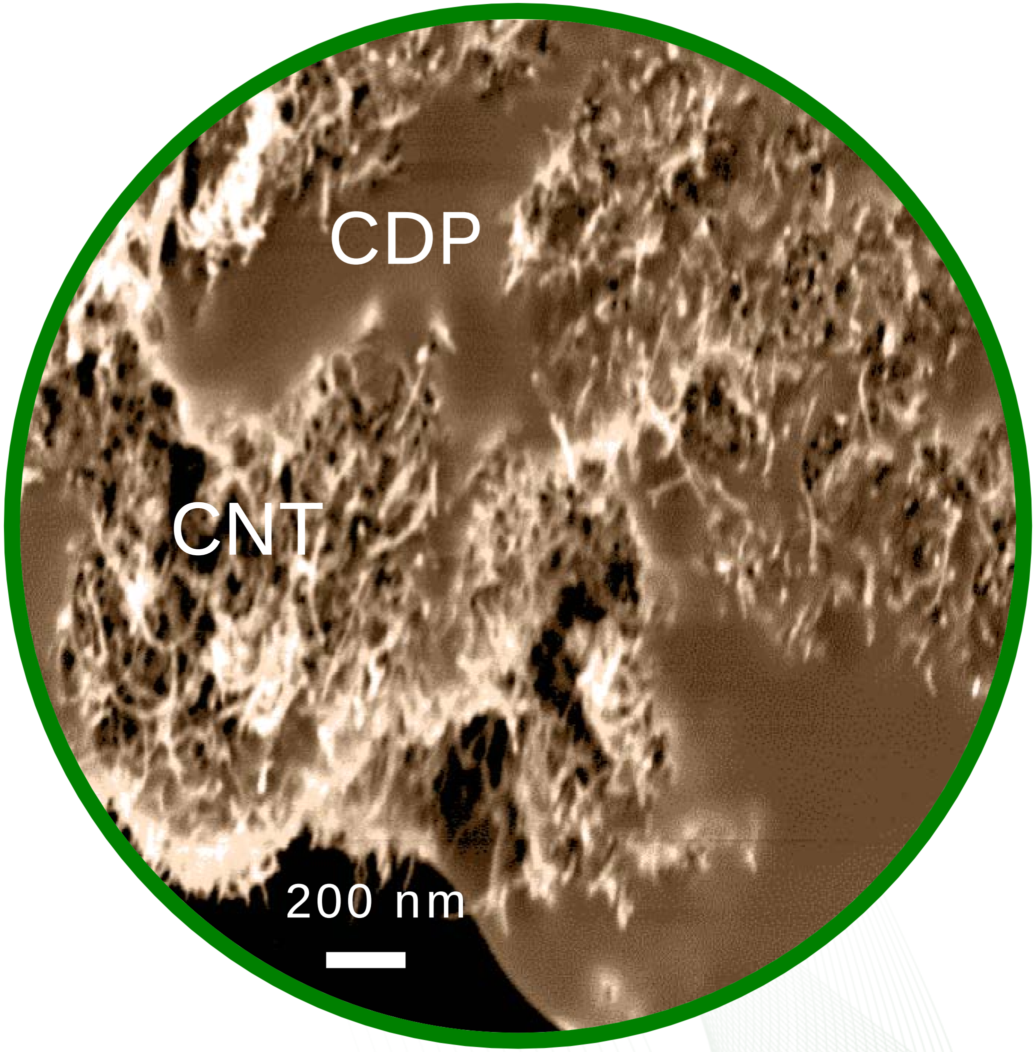
Advanced Cathode Architecture



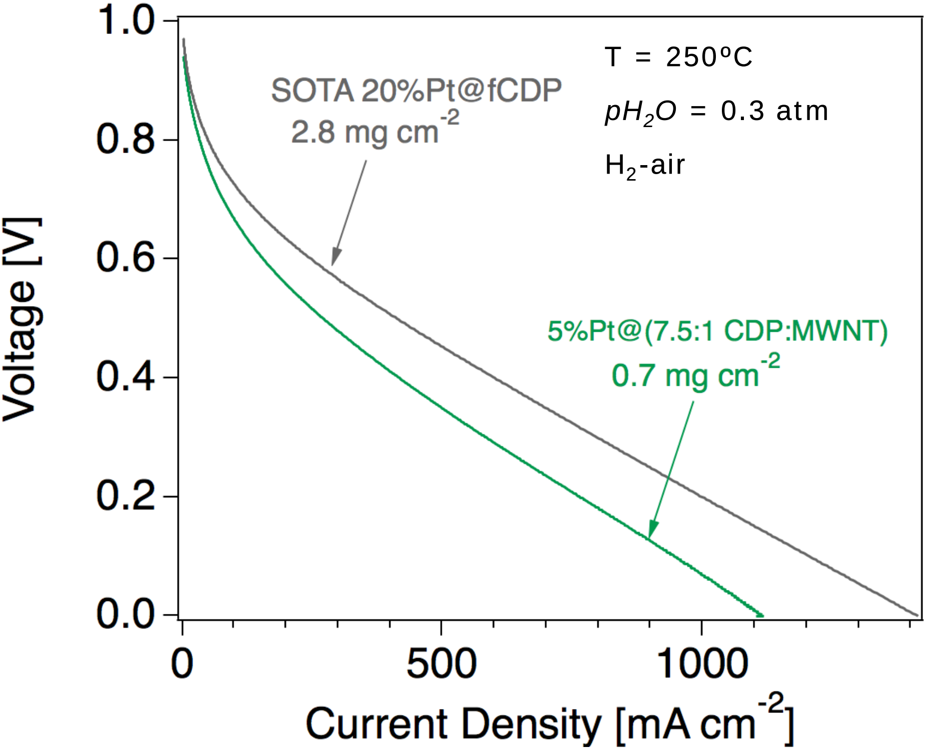
"Mixed conductor" eliminates the problem of conductivity loss at low Pt content

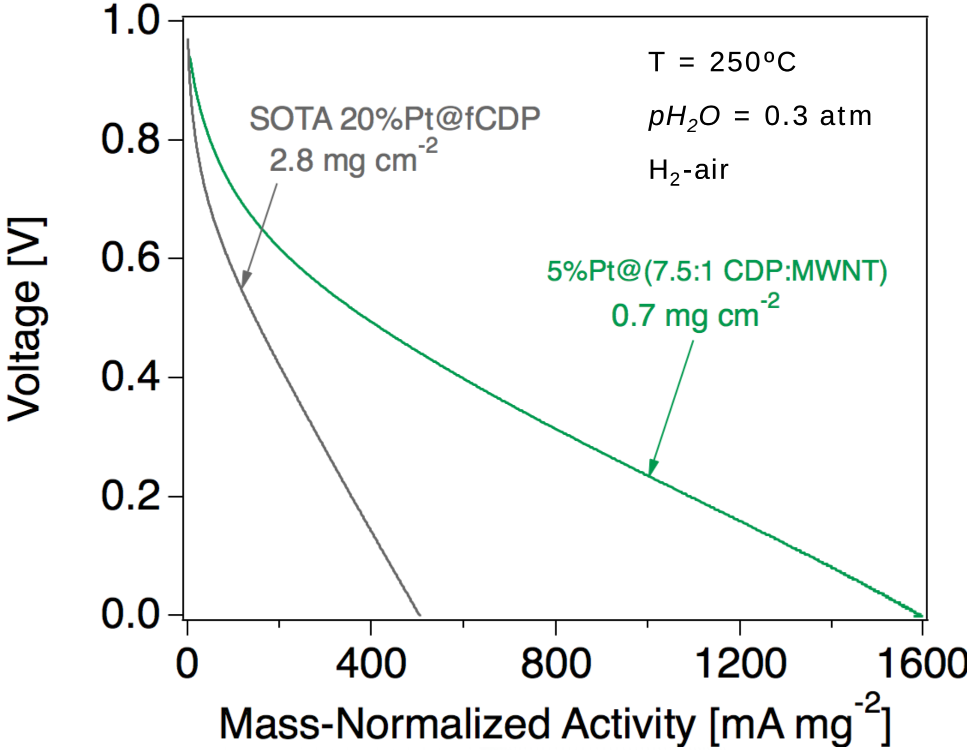
Advanced Cathode Architecture





Advanced Electrodes Dramatically Reduce Pt Content



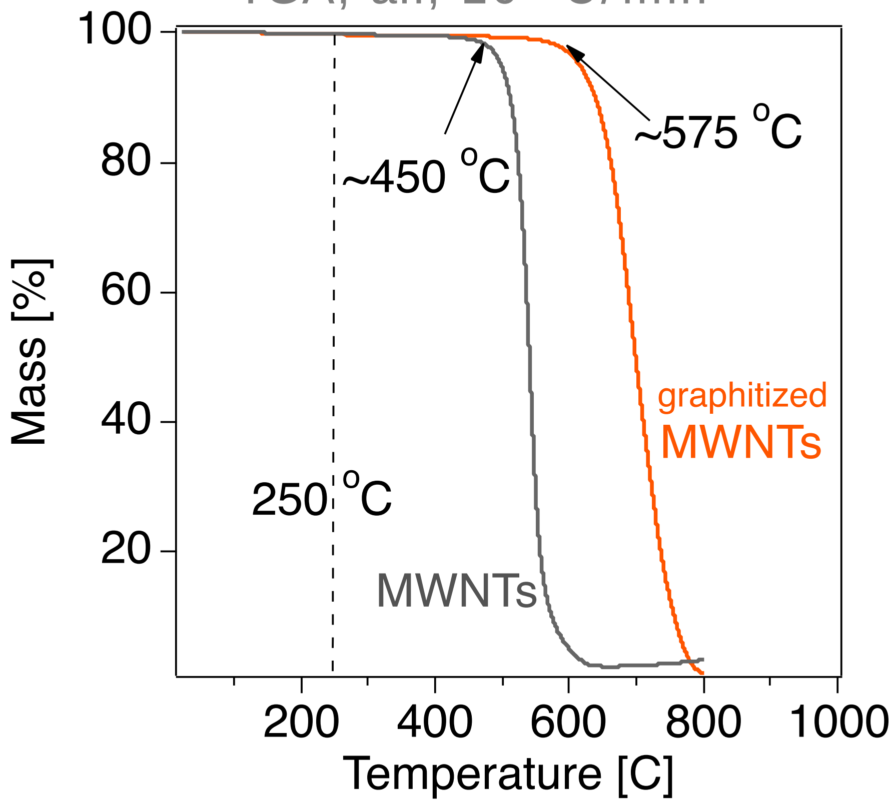


Very recent results suggest improvement to parity with SOTA electrode performance at 0.7 mg cm^{-2}

Carbon Corrosion Must Be Confronted

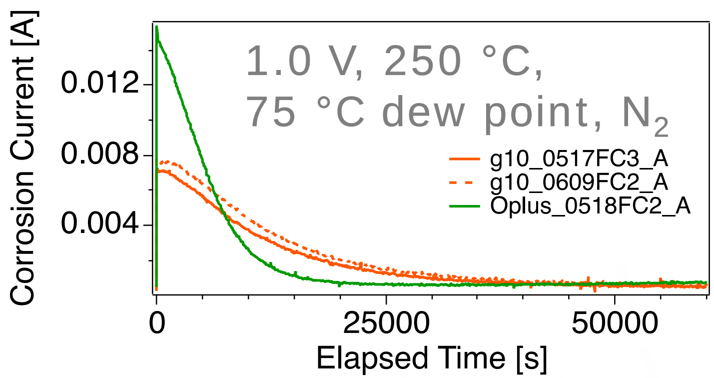
Chemical stability of MWNTs is adequate…

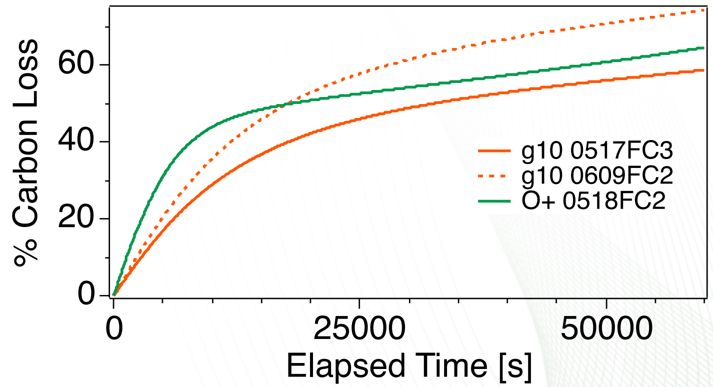
TGA, air, 10 °C/min



…But *electrochemical* stability is the issue

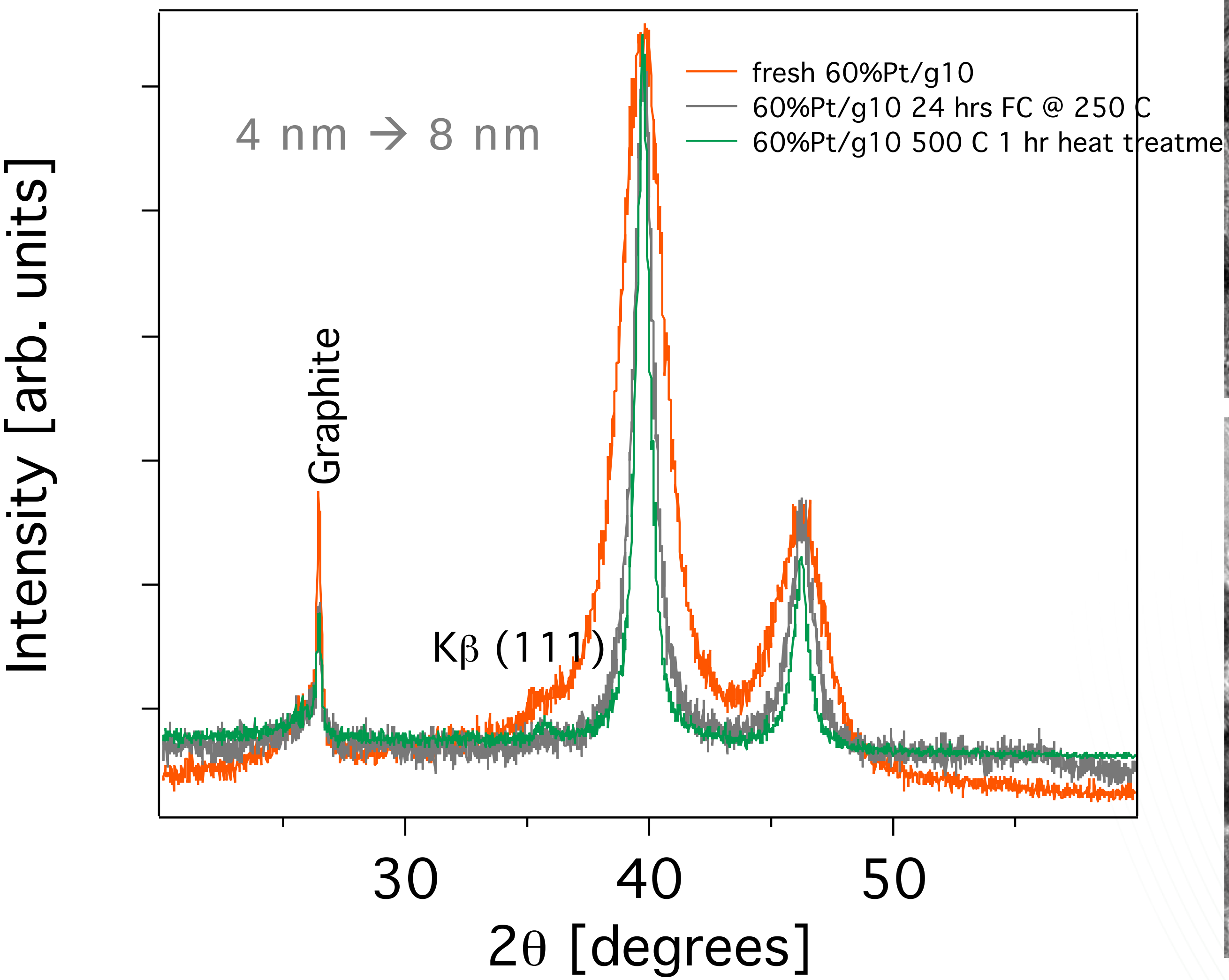
$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$$

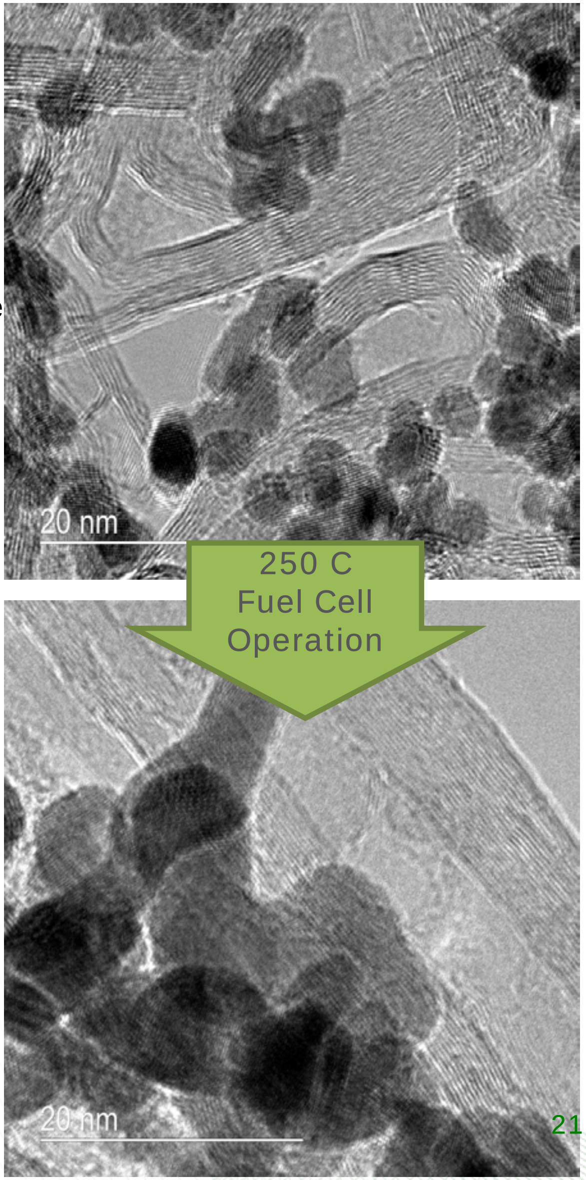




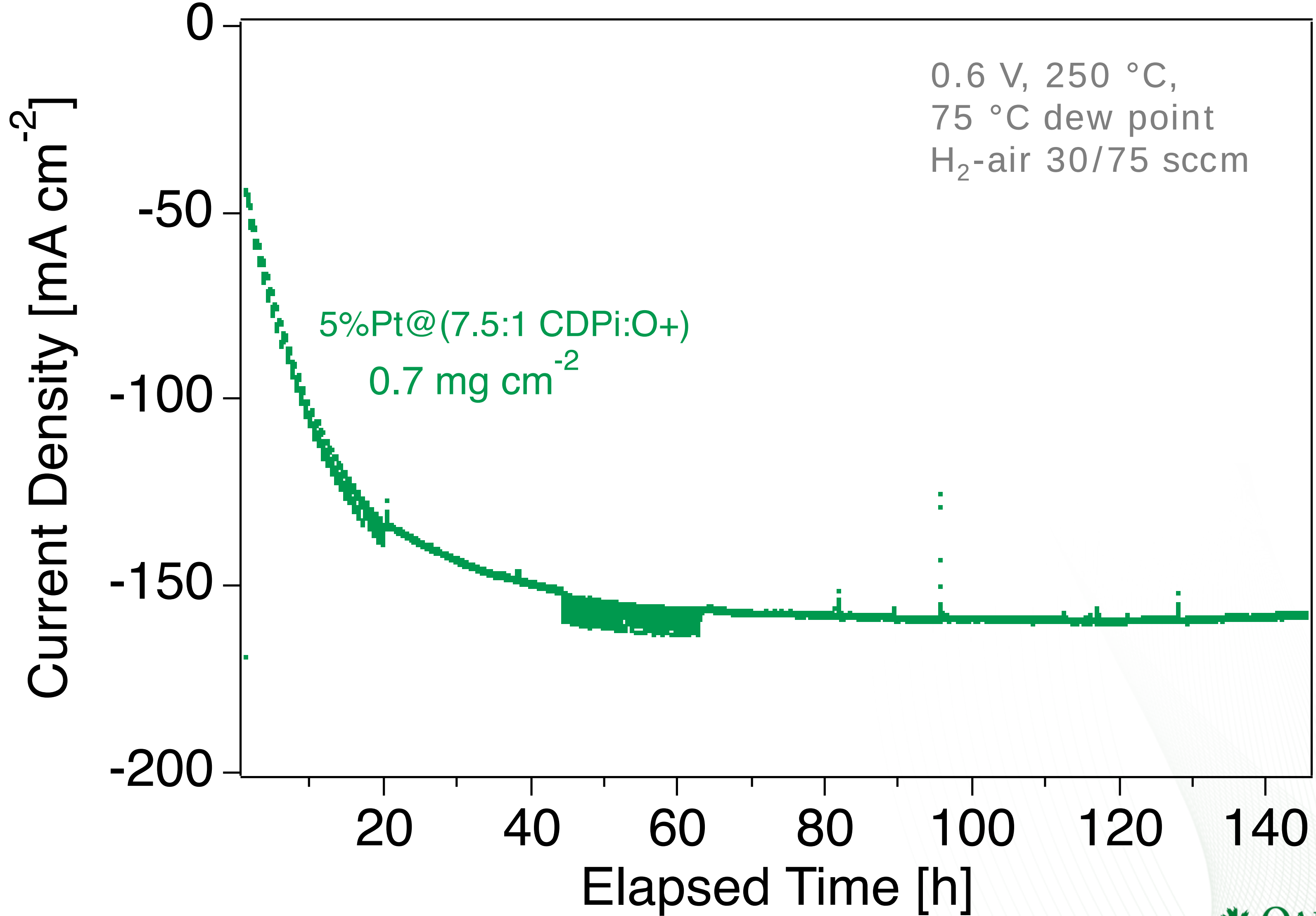
Pt Particles Coarsen During Operation

Lower Pt content in advanced electrodes may mitigate this effect





Advanced Cathodes Over 100+ hrs



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Summary

- ORNL, UTK, and SAFCell are developing a reformed NG fuel cell system based on the CsH_2PO_4 electrolyte
- Anodes have low impedance and are impurity tolerant
- Cathode activity is a key obstacle
- Nanocomposite electrode architectures using MWCNTs suggest 75% reduction in Pt is possible

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Ramez Elgammal
Ondrej Dyck

Calum Chisholm
Hau Duong
Mandy Abbott
Fernando Campos

Project Summary

Timeline

Project start date: 10/1/14

Project end date: 9/30/17*

*project continuation determined annually by DOE

Percent complete: 20%

Partners

University of Tennessee

SAFCell, Inc.

Budget

Total project funding: $3050k

- Federal share: $2750k
- Recipient share: $300k

FY15 amount: $1002k

Barriers

Reduction of Pt loading

- Target: 0.1 mg/cm^2

Cathode Activity

- Target: 225 mA/cm^2 at 0.78 V