Nanocomposite Electrodes for SAFC Stack Operating on Reformate

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SOFC Review Meeting
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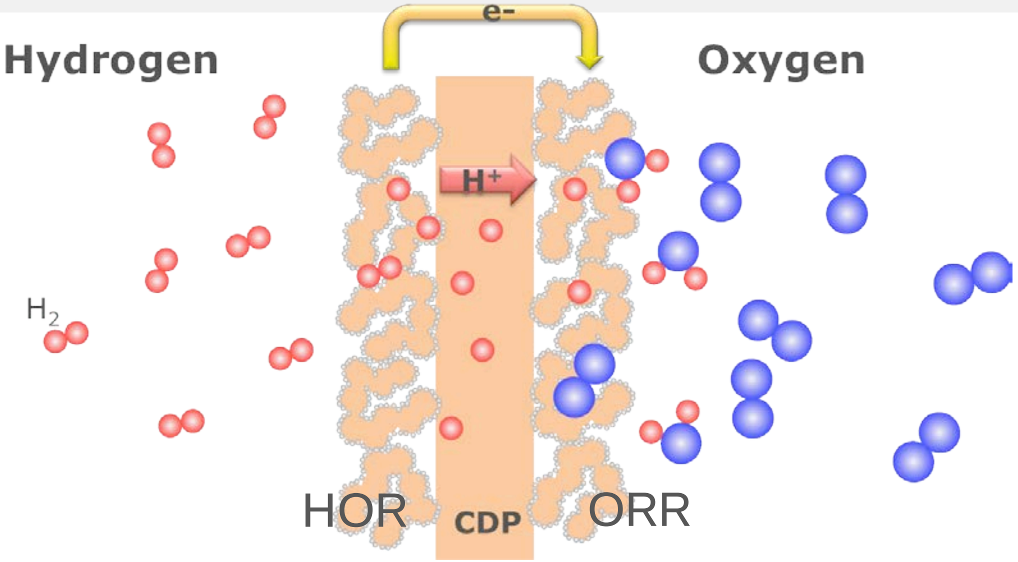
Solid Acids in Electrochemical Devices

Fuel Cell

$2H_2 + O_2 \rightarrow 2H_2O$

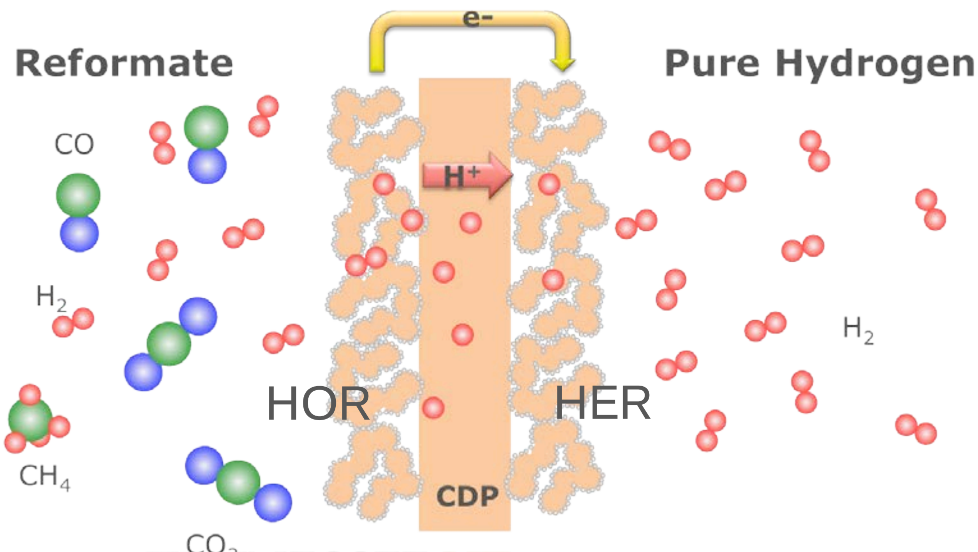
Produces electricity from fuel



Hydrogen Pump

$H_2 \rightarrow 2H^+ \rightarrow H_2$

Produces fuel from electricity

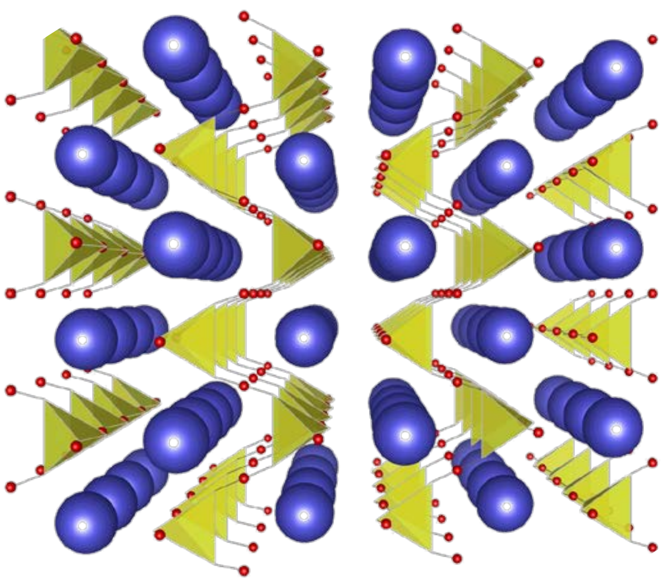


Superprotonic Solid Acid Electrolytes

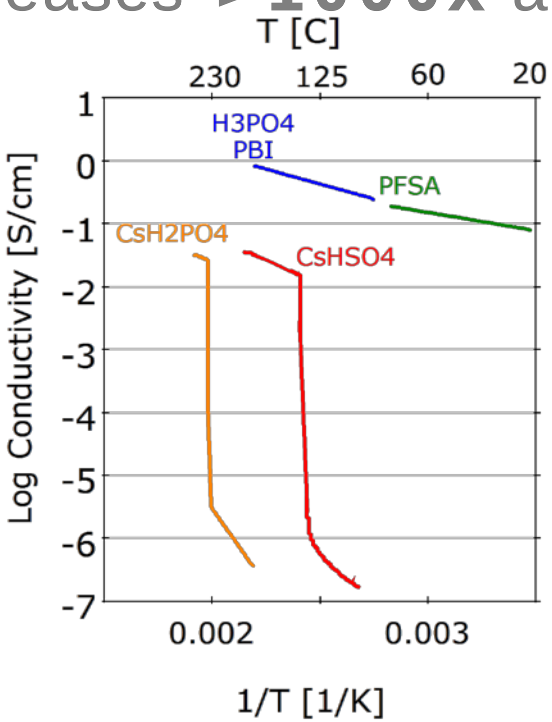
Hydrogen-bonded ionic solids

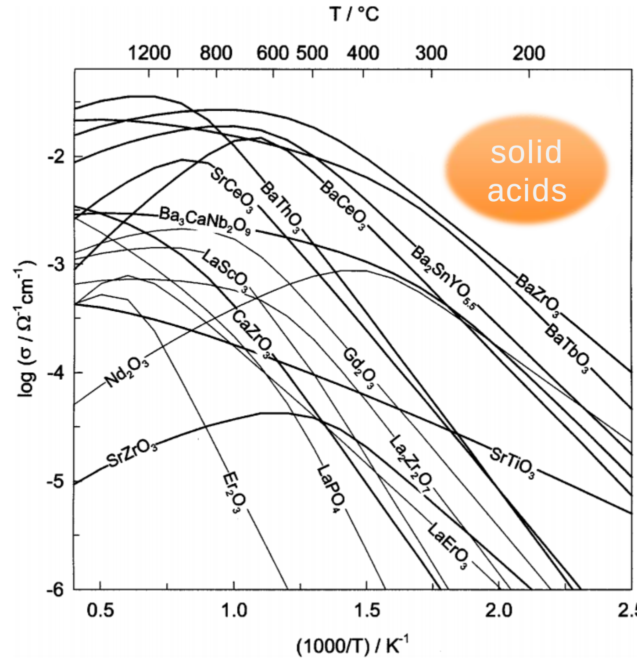
Polymorphic **phase transitions** at T>100 °C

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



CsH_2PO_4 (CDP)



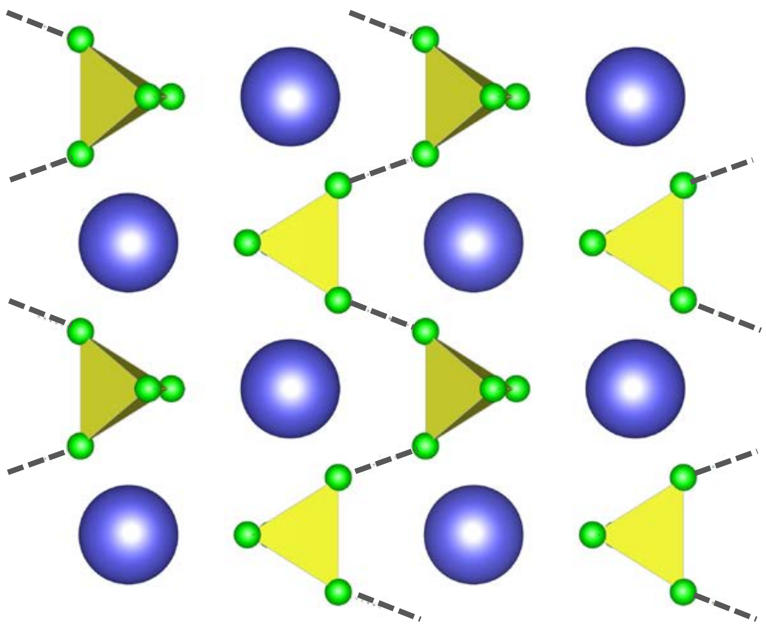


Proton Conducting Oxides
K.D. Kreuer, Annual Review of Materials Research 33, 333–359 (2003)

Solid acid fuel cells based on CDP operate at **240-260 °C** using **platinum catalysts**

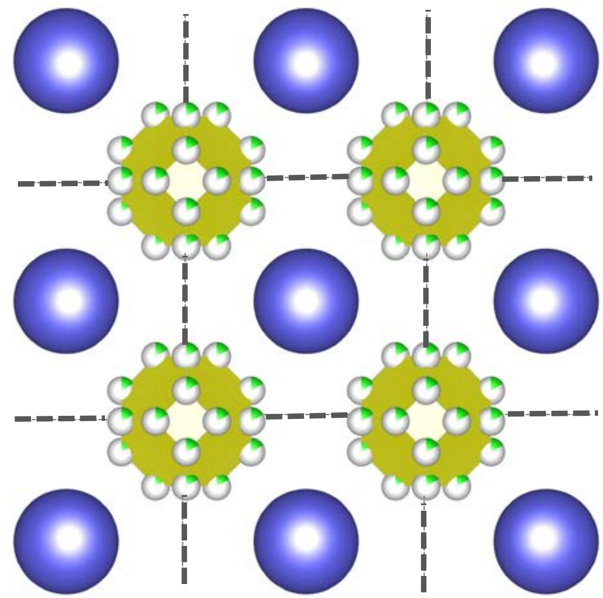
Crystal Symmetry Controls H^+ Conductivity in Solid Acids

Paraelectric (RT)



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

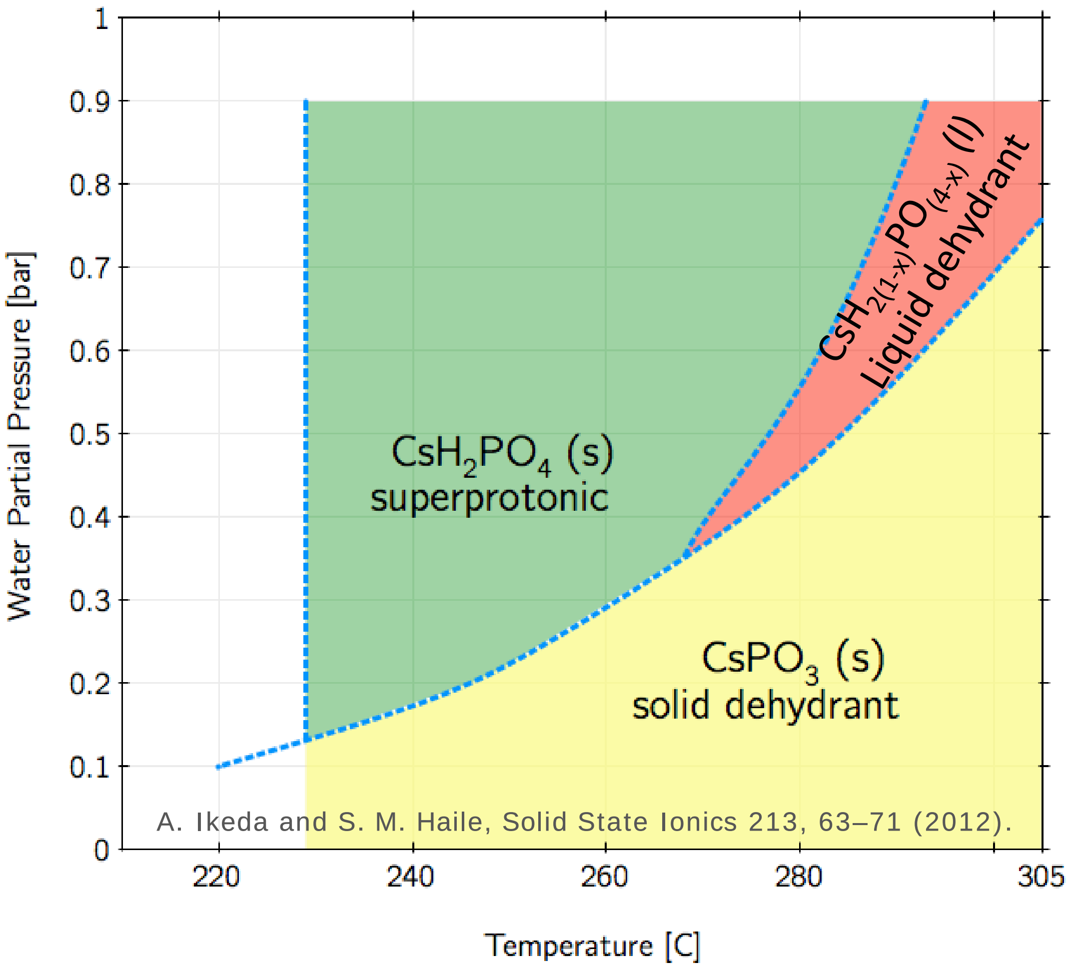
Superprotonic (>228 °C)



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

Operational Humidity Requirements

(Updated) CDP T-P_{H2O} Phase Diagram



$$CsH_2PO_4 \rightleftharpoons CsPO_3 + H_2O$$

Recent Progress in SAFCs

- ARPA-e REBELS program
- Natural gas in—power out
- CHP systems
- SOTA at start of project: electrodes with ~3 to 5 mg/cm^2 Pt
- Important target: lowered costs

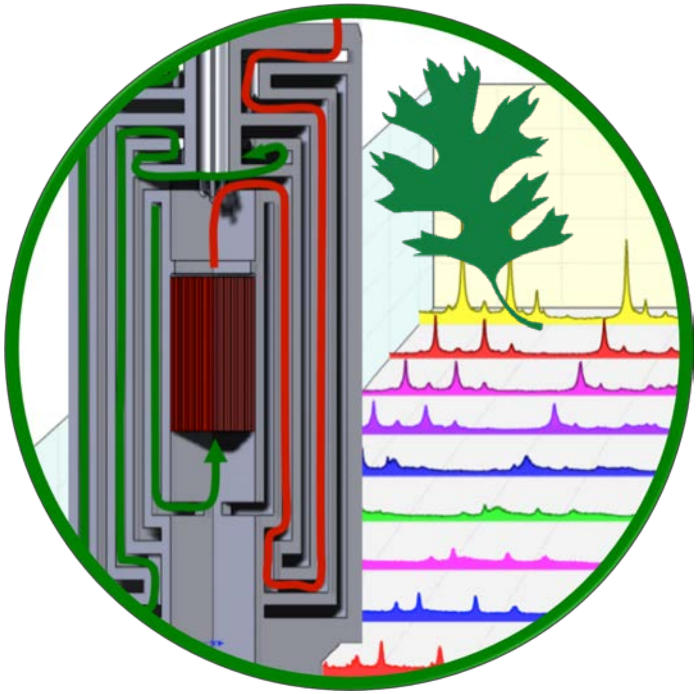
Major recent progress in improving Pt loading (decreased by 25 to 30x)

REBELS Project Team & Objectives

Oak Ridge National Lab
Natural gas reformer
Materials synthesis

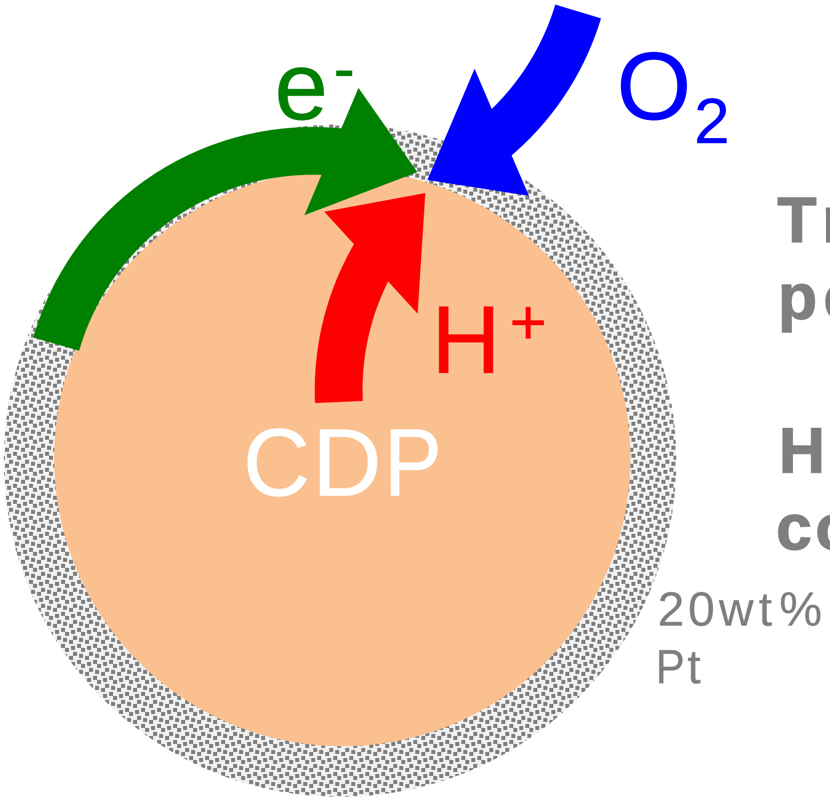
University of Tennessee
Nanocomposite Electrode Fabrication

SAFCell, Inc.
Stack Design and Fabrication



Development of a **solid acid fuel cell stack** incorporating **nanocomposite electrodes** operating on **externally reformed natural gas**

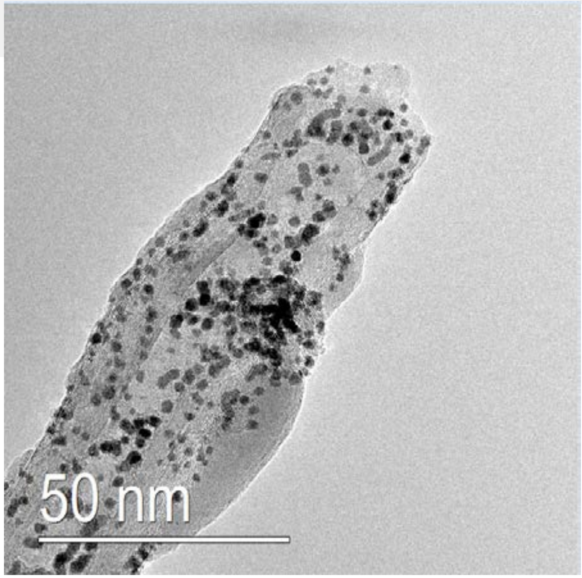
The Catalyst Problem in SAFCs

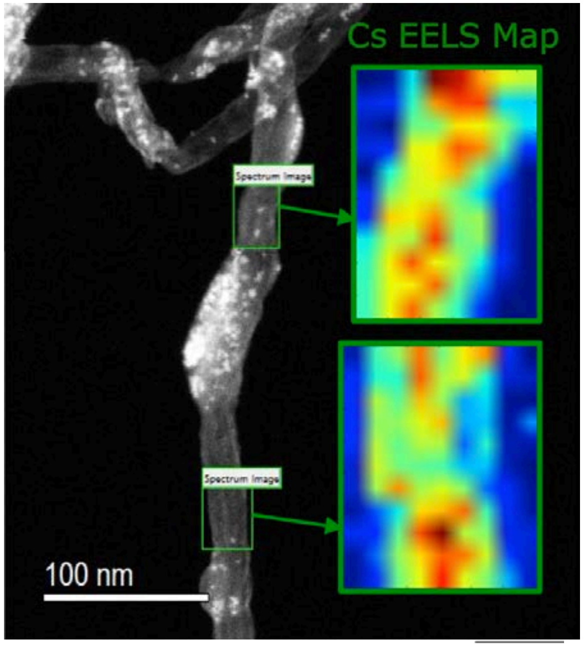


Triple point boundary at perimeter only

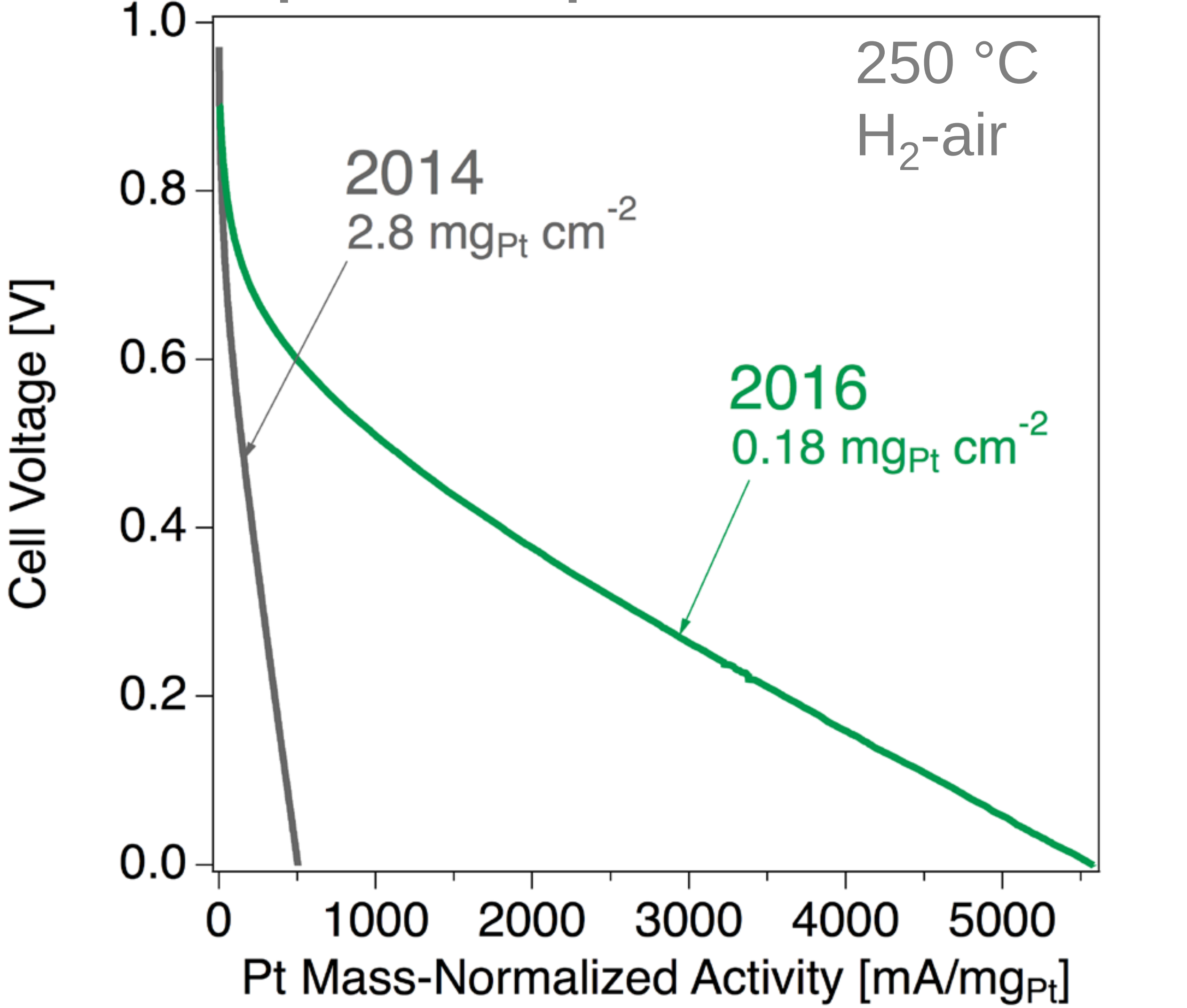
High Pt to maintain conduction

Breakthrough Electrodes



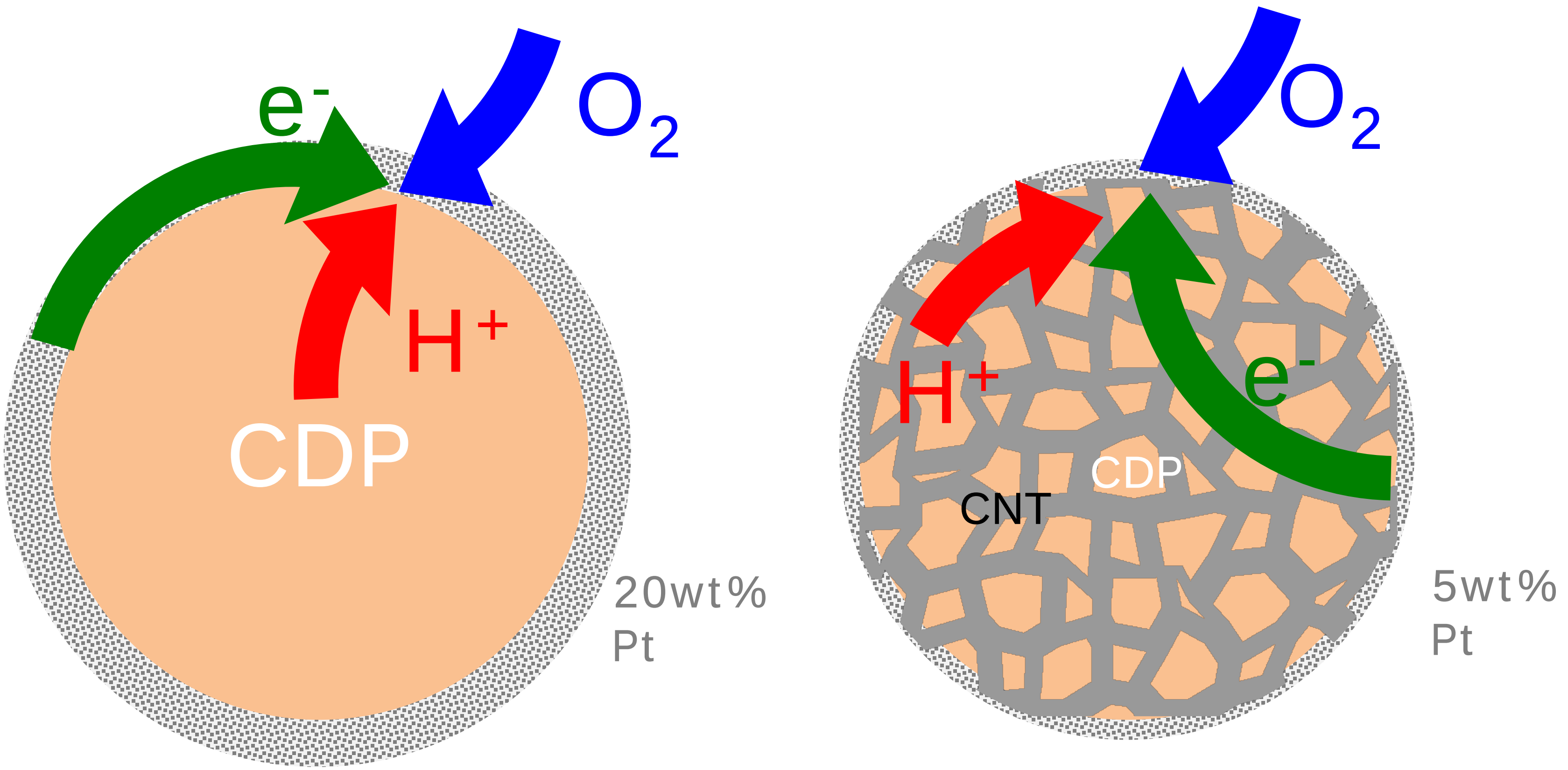


CsH_2PO_4-MWNT-Pt nanocomposite electrodes via aqueous / vapor infiltration



Task 1.1 Fabrication of Nanostructured Cathodes

M1.1.1 5 g of NC and PVD nanostructured cathodes with 0.75 mg/cm² Pt loading synthesized (Gen 1)



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

Task 1.1 Fabrication of Nanostructured Cathodes

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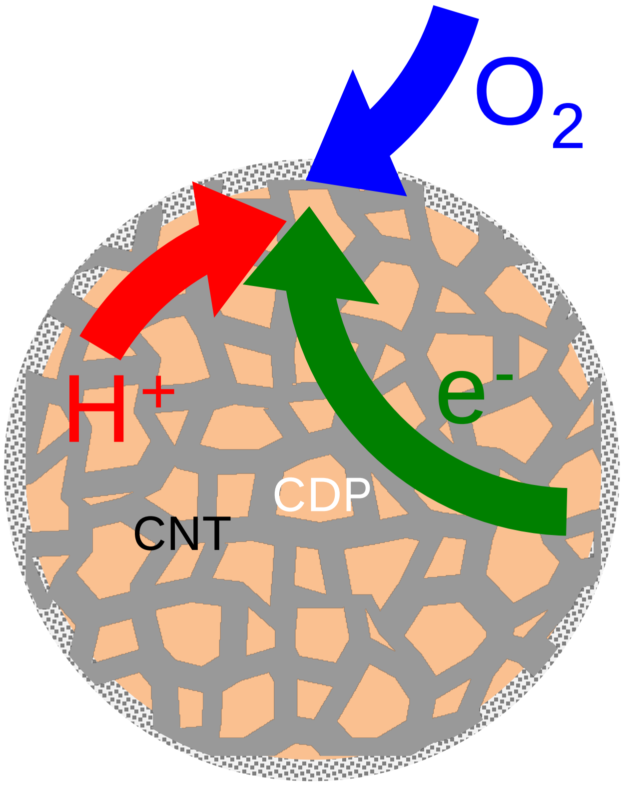
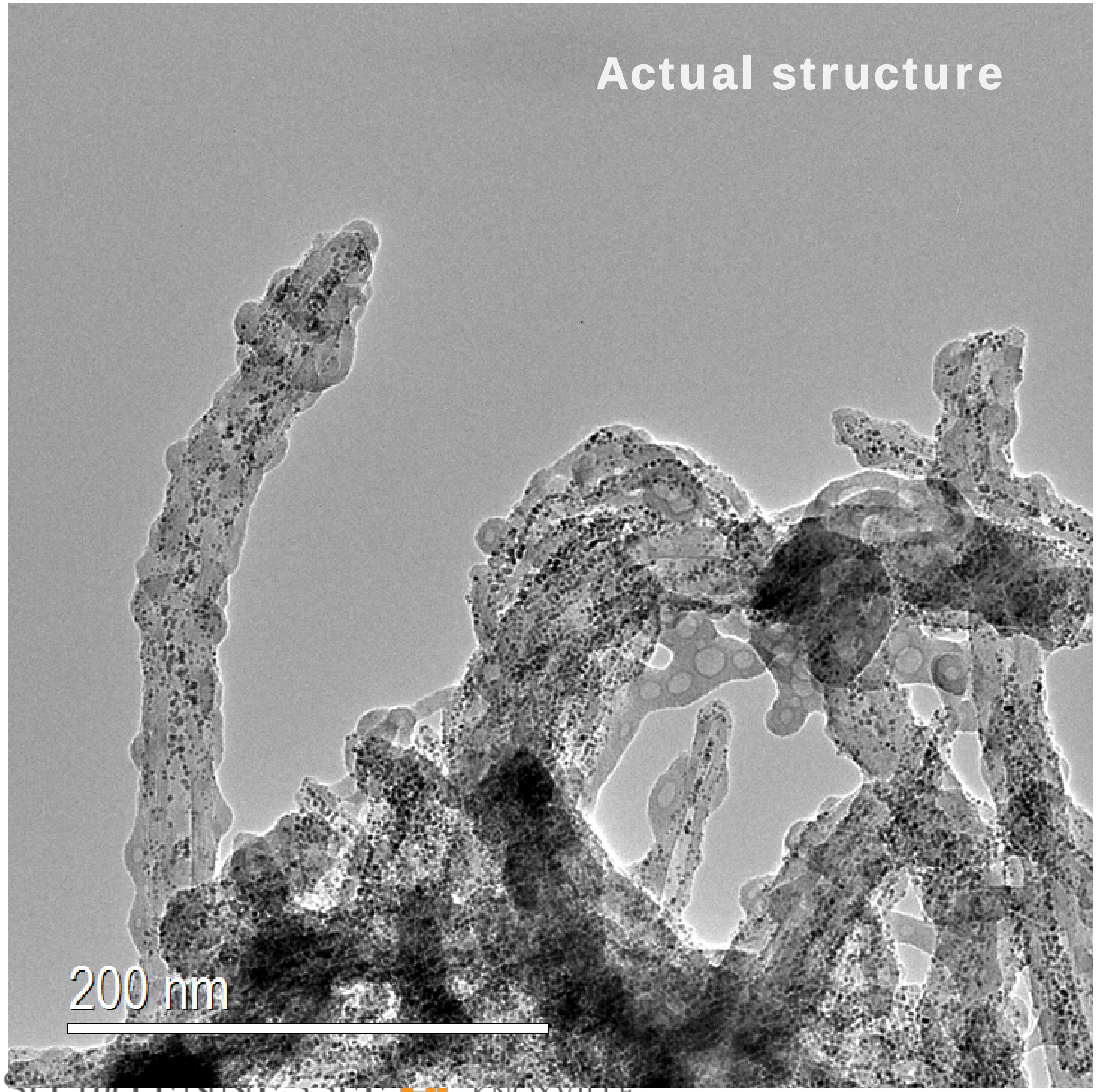
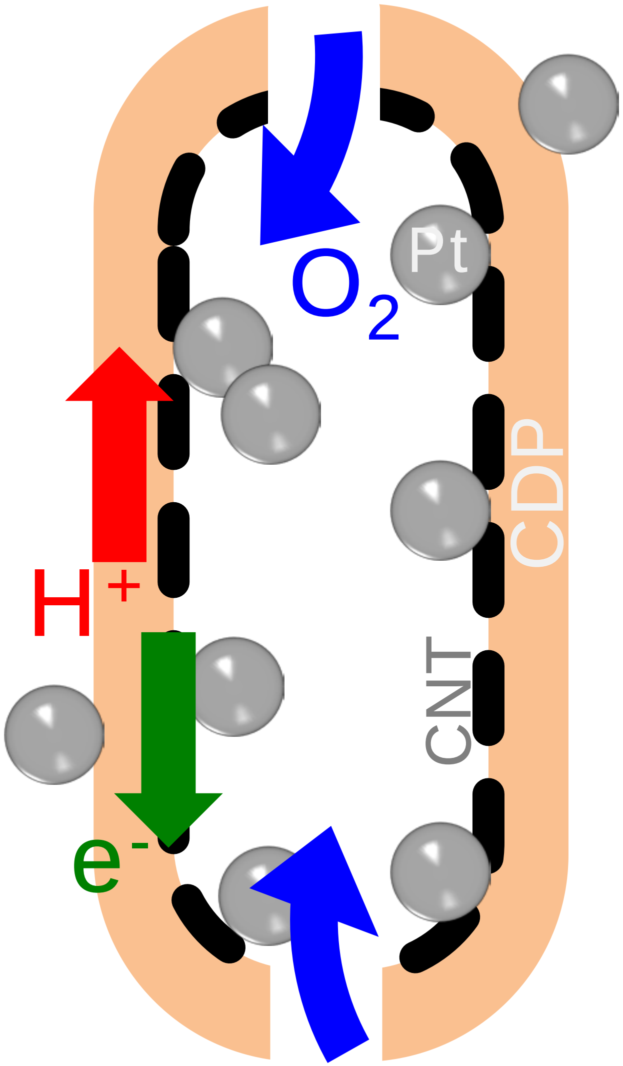
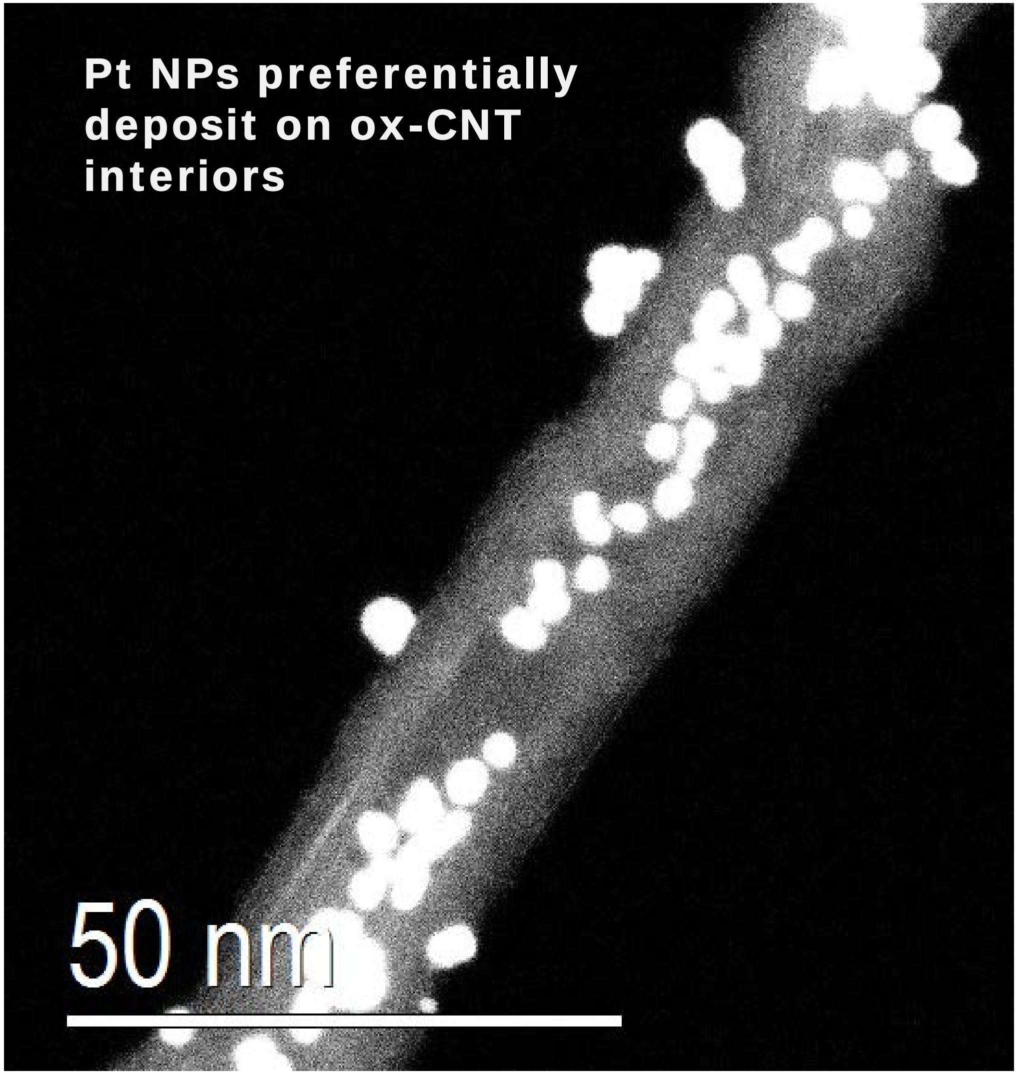


Assumed structure



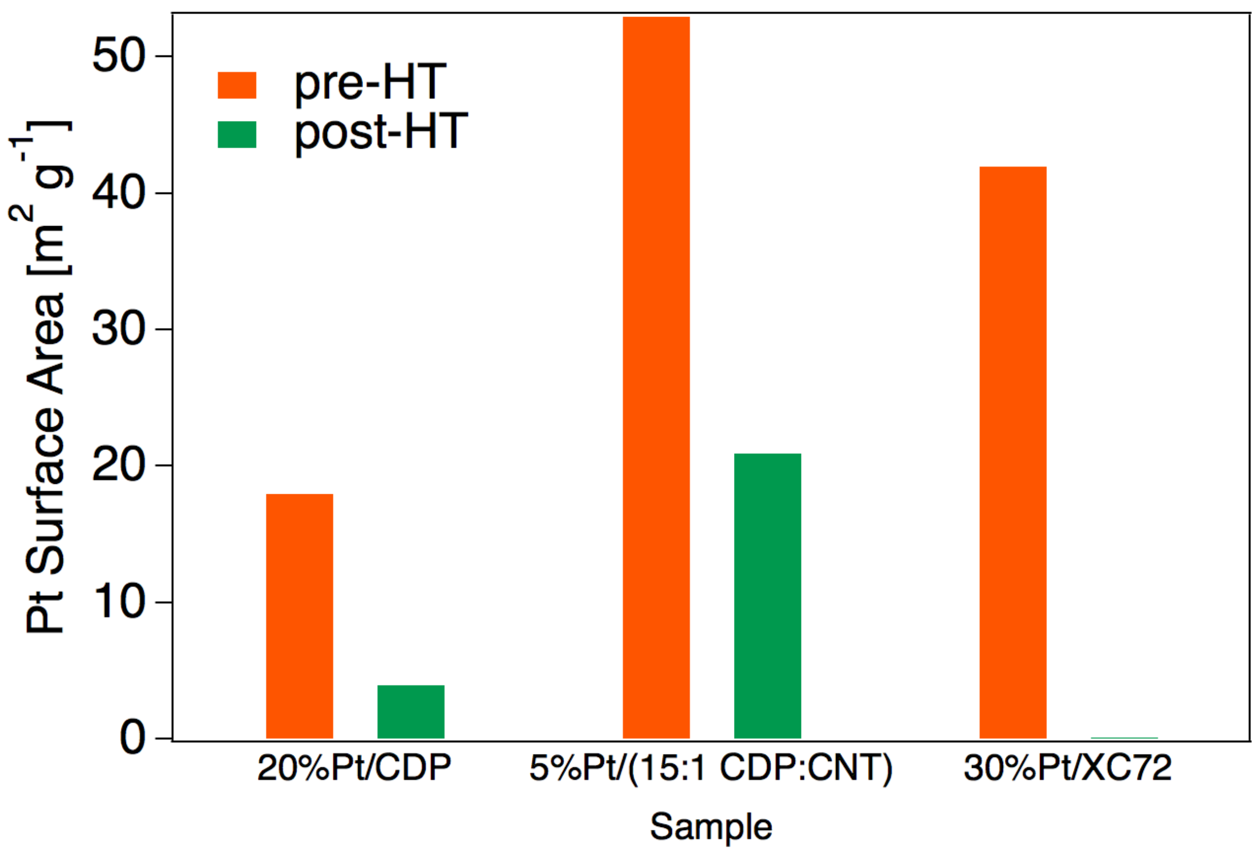
Gen 1.5: Inverted Structure?





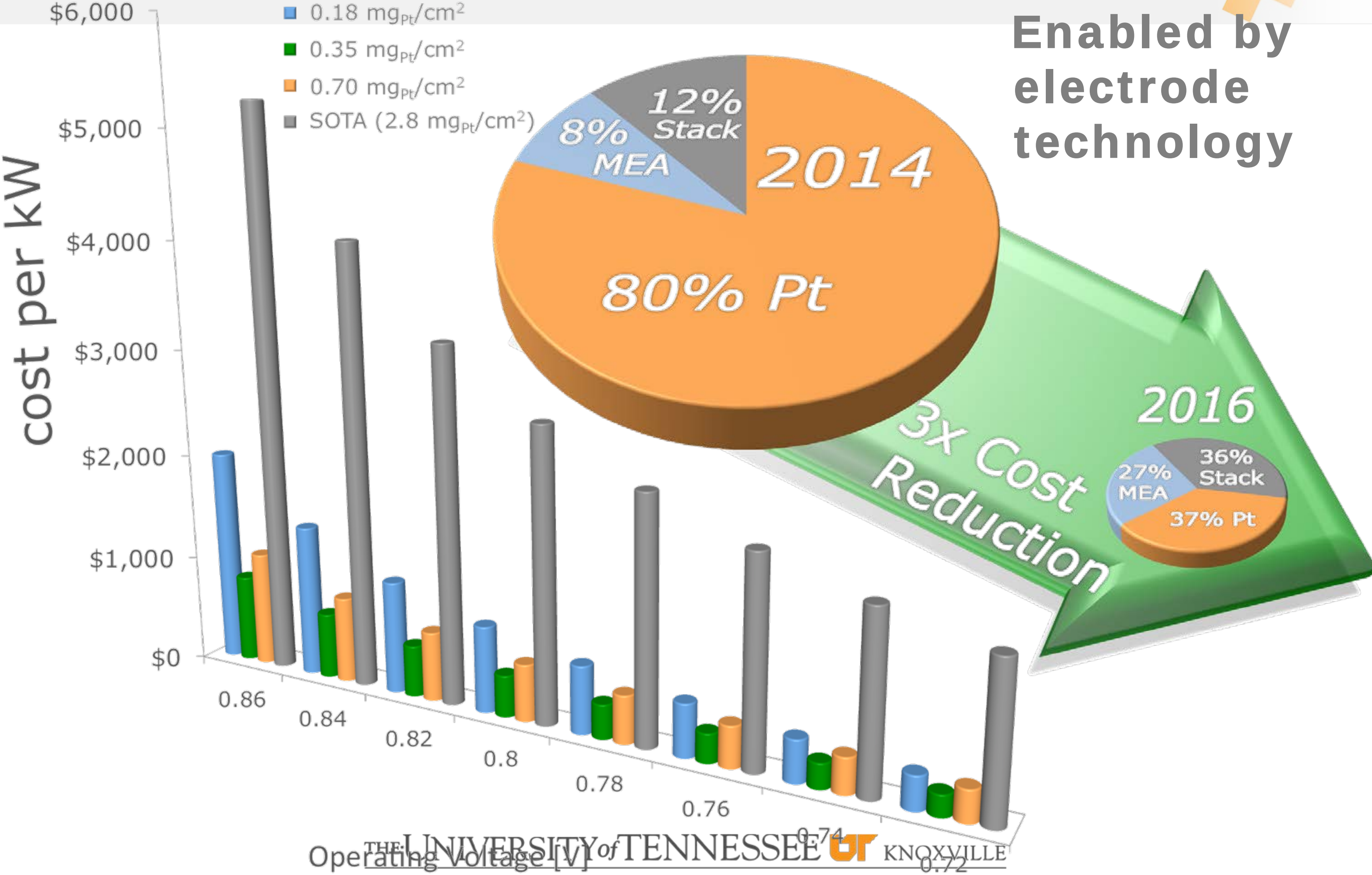
1.2 Physical Property Characterization

M1.3.1: 25% greater Pt specific surface area retention compared to baseline SAFC cathode after 16 hours at 250 C



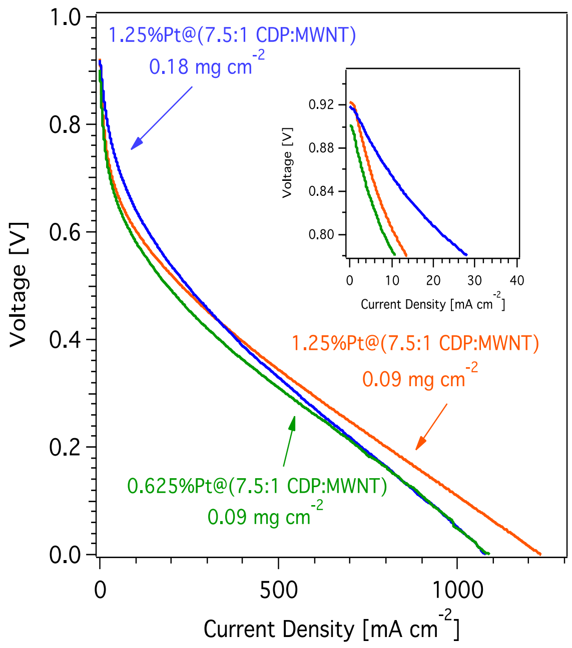
Target SA determined via static H_2 chemisorption

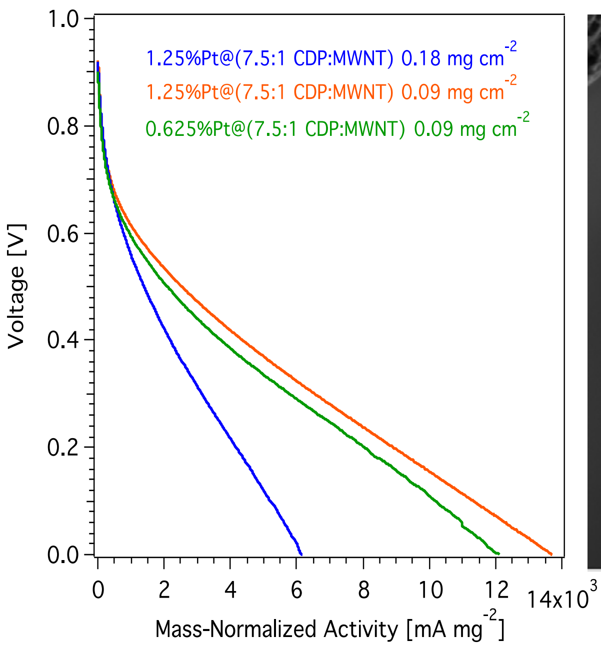
SAFC Stack Costs Reduced 3x

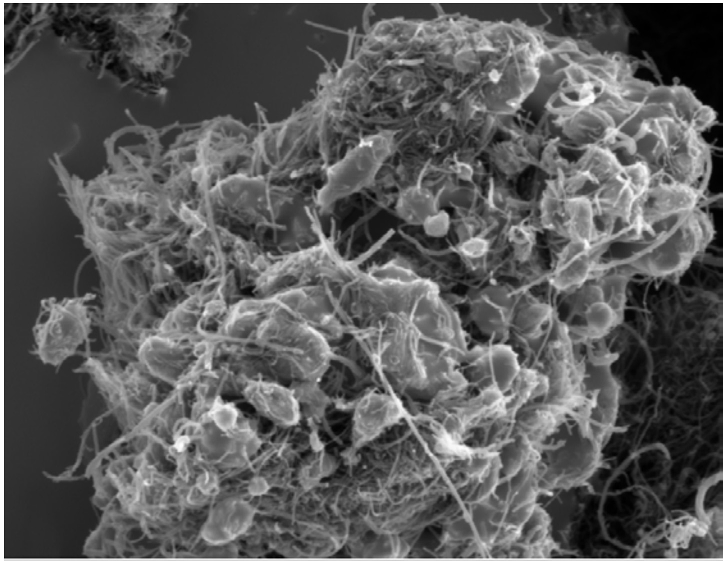


Enabled by electrode technology

Performance of Gen 3 Materials

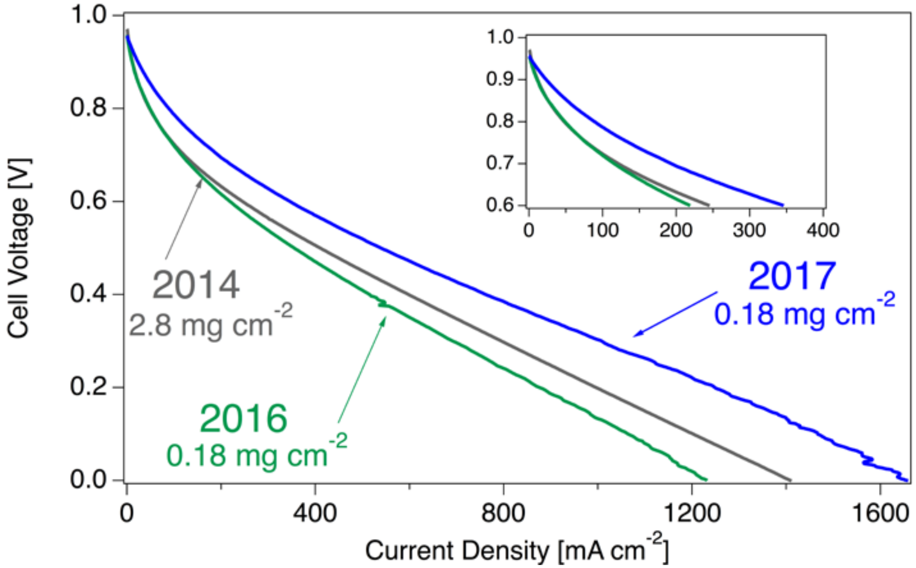


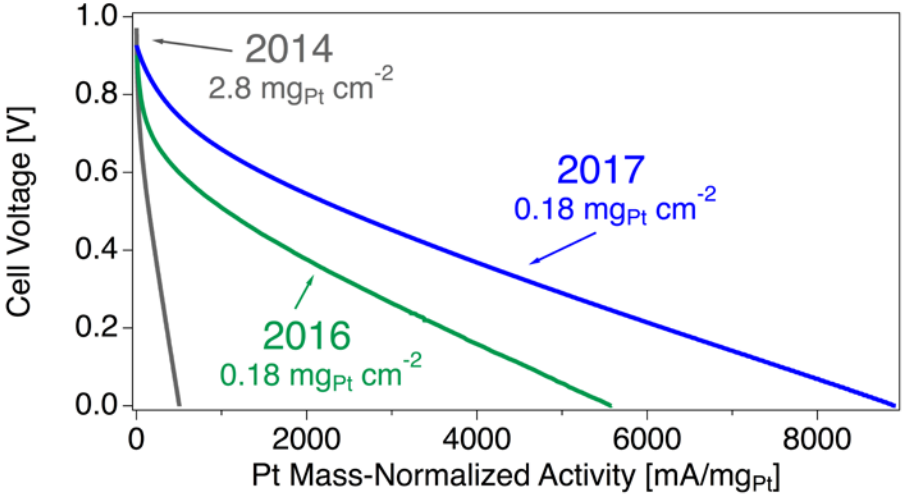




- Electrodes with 0.09 mg/cm^2 now prepared that can match SOTA performance

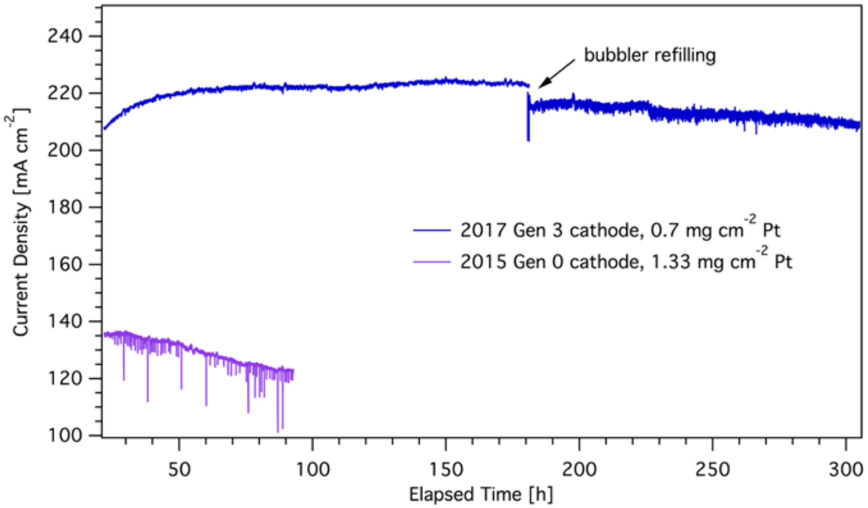
Progress on Cathode Performance





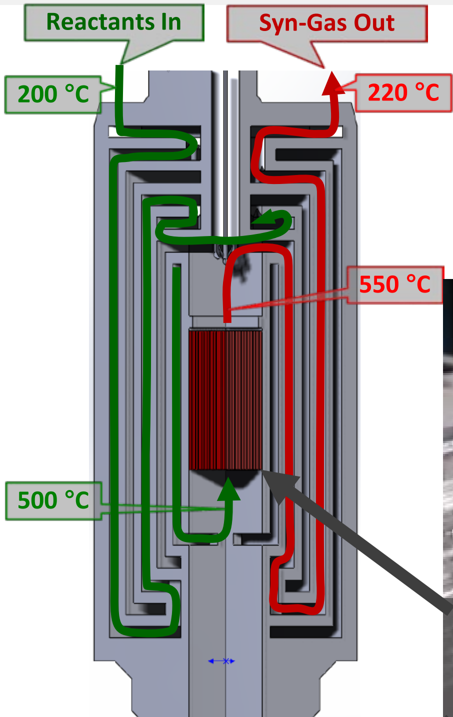
- At 0.78V, almost doubling of current density with ~16X less Pt from SOTA starting point

Recent Progress on Stability



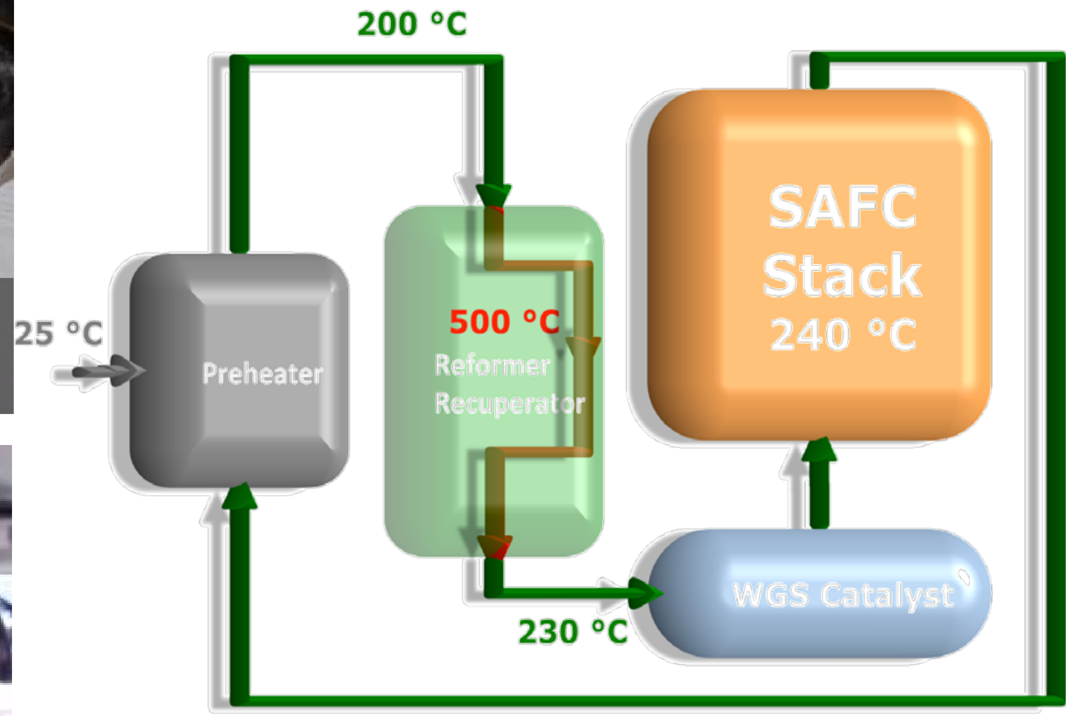
- Gen 3 cells typically degrade at -3 μA/cm^2/hr, over 10X slower than Gen 0
- Performance losses over time are strongly correlated with increase in ASR, ~10% over 200+ hours

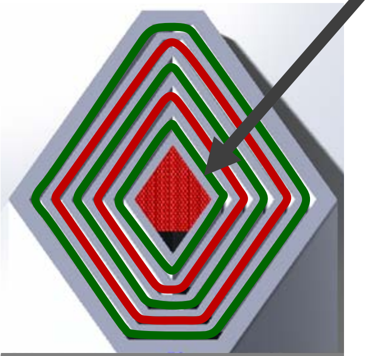
3D Printed Natural Gas Reformer Subsystem (Fuel Flex!)



3D printed stainless steel design for integration of 500 °C reformer with 250 °C SAFC stack

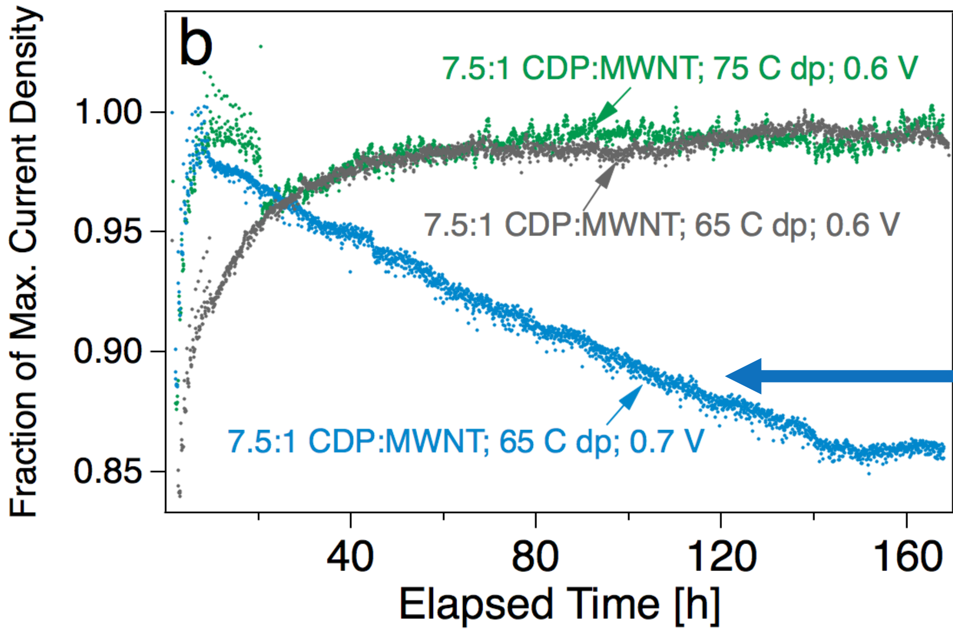
2%Rh/mullite monolith



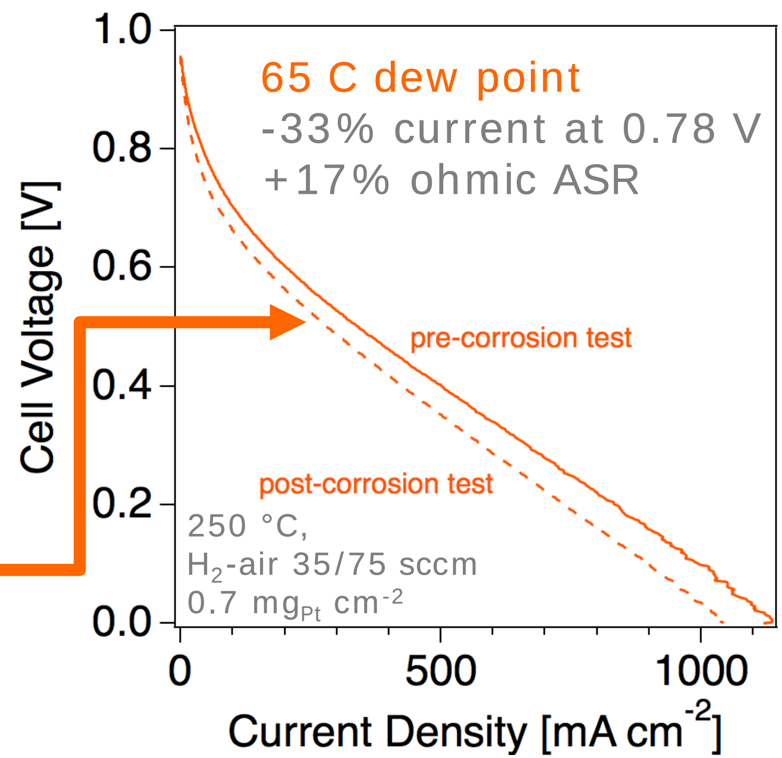


Nested-Annular Passages

Remaining Challenges

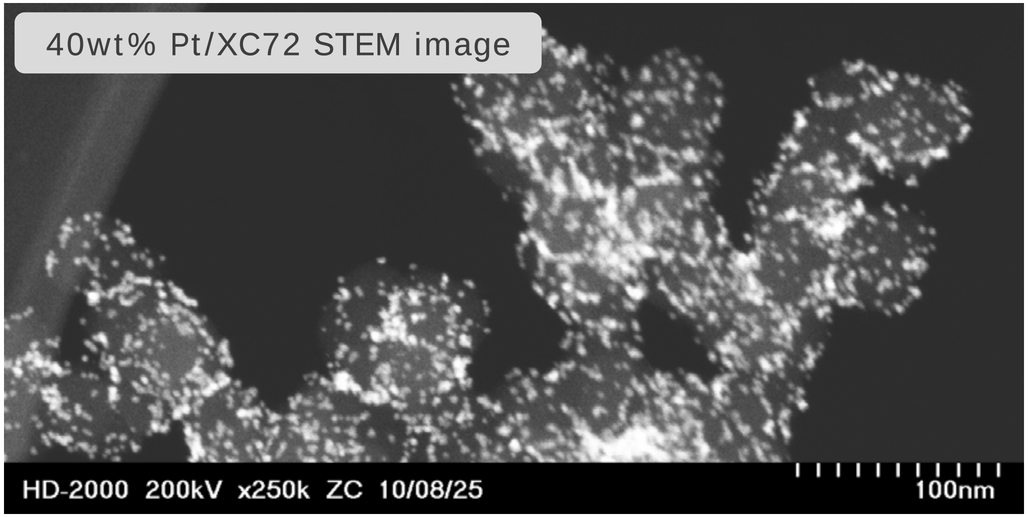


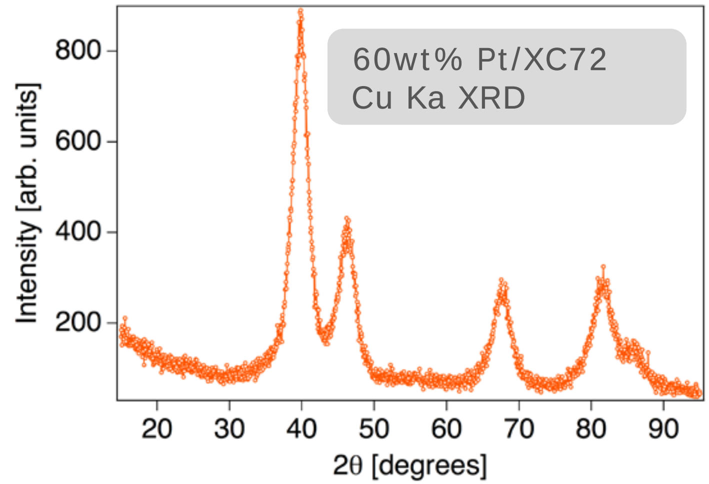
Electrode stability at **high efficiency** is lacking

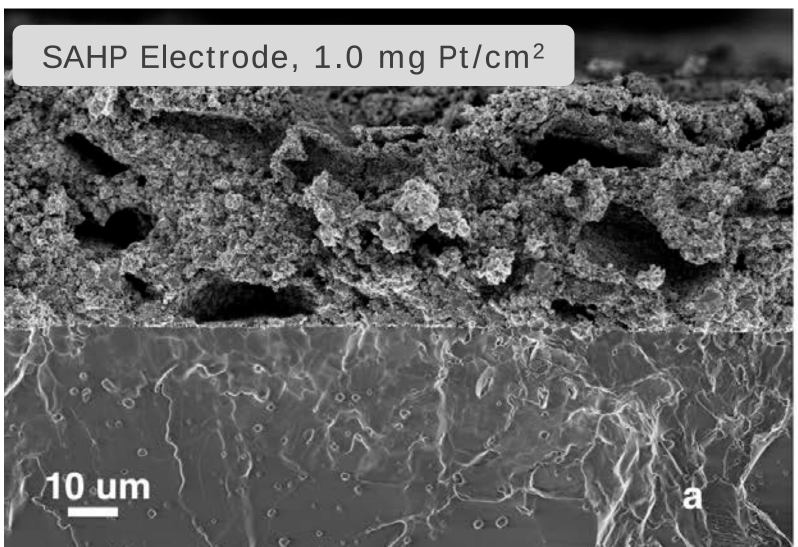


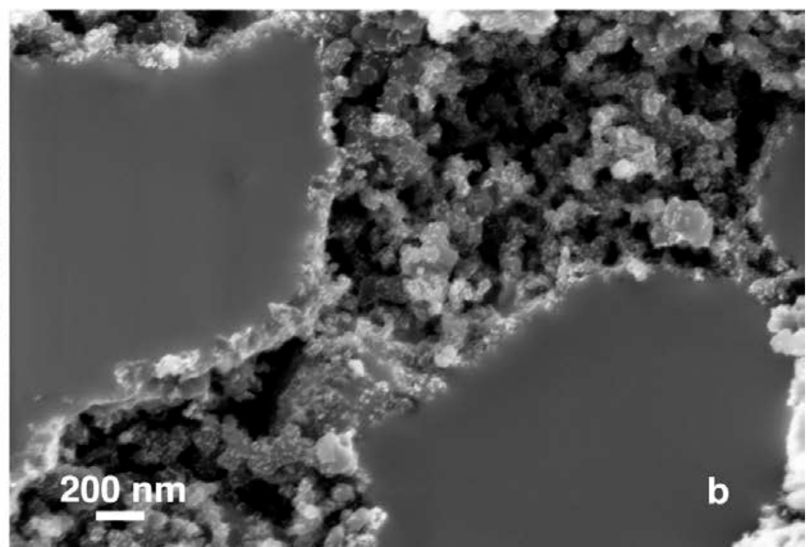
Carbon component has low **voltage stability**

Unlike Cathode, Carbon Supports may be a Viable Option for Anode



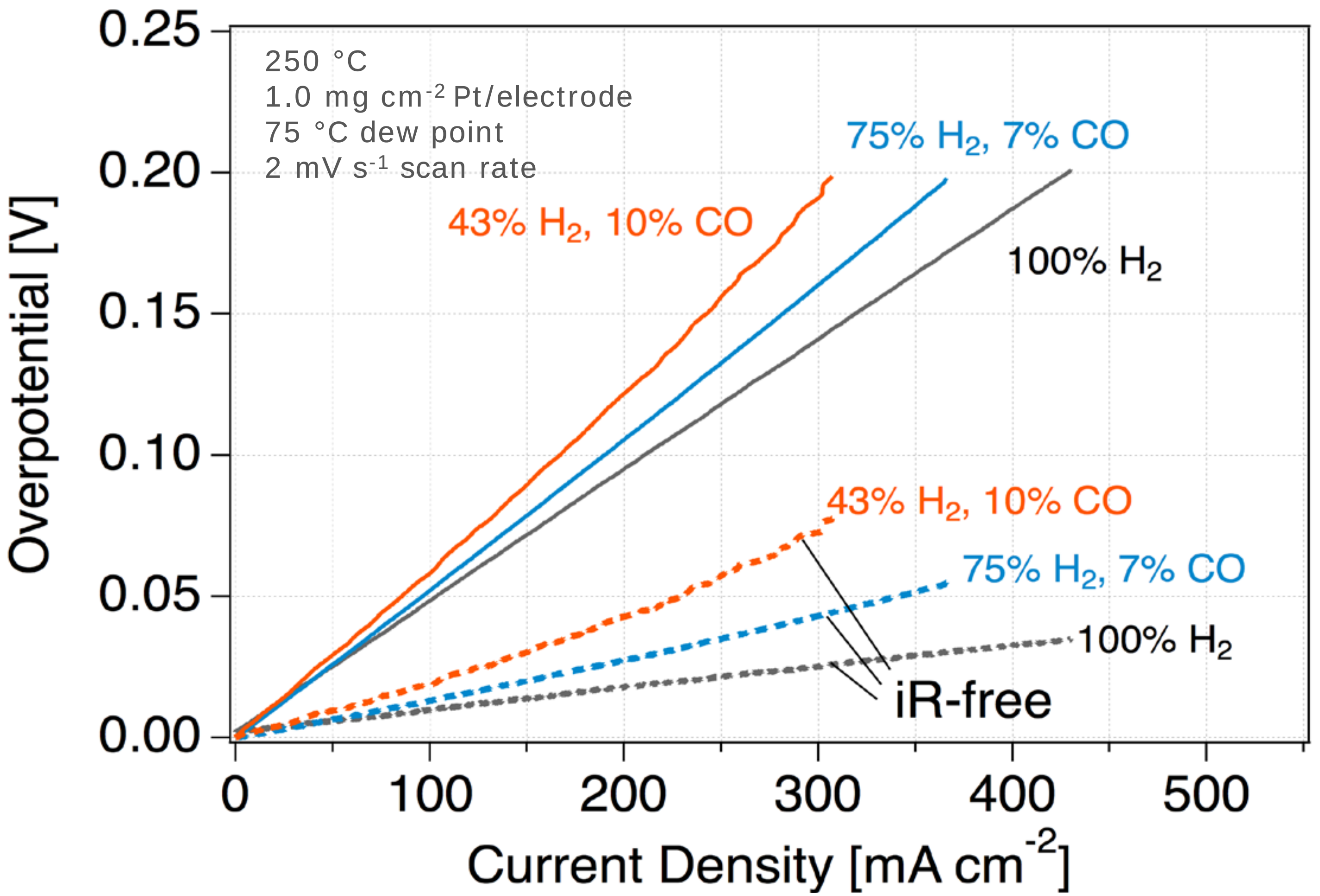




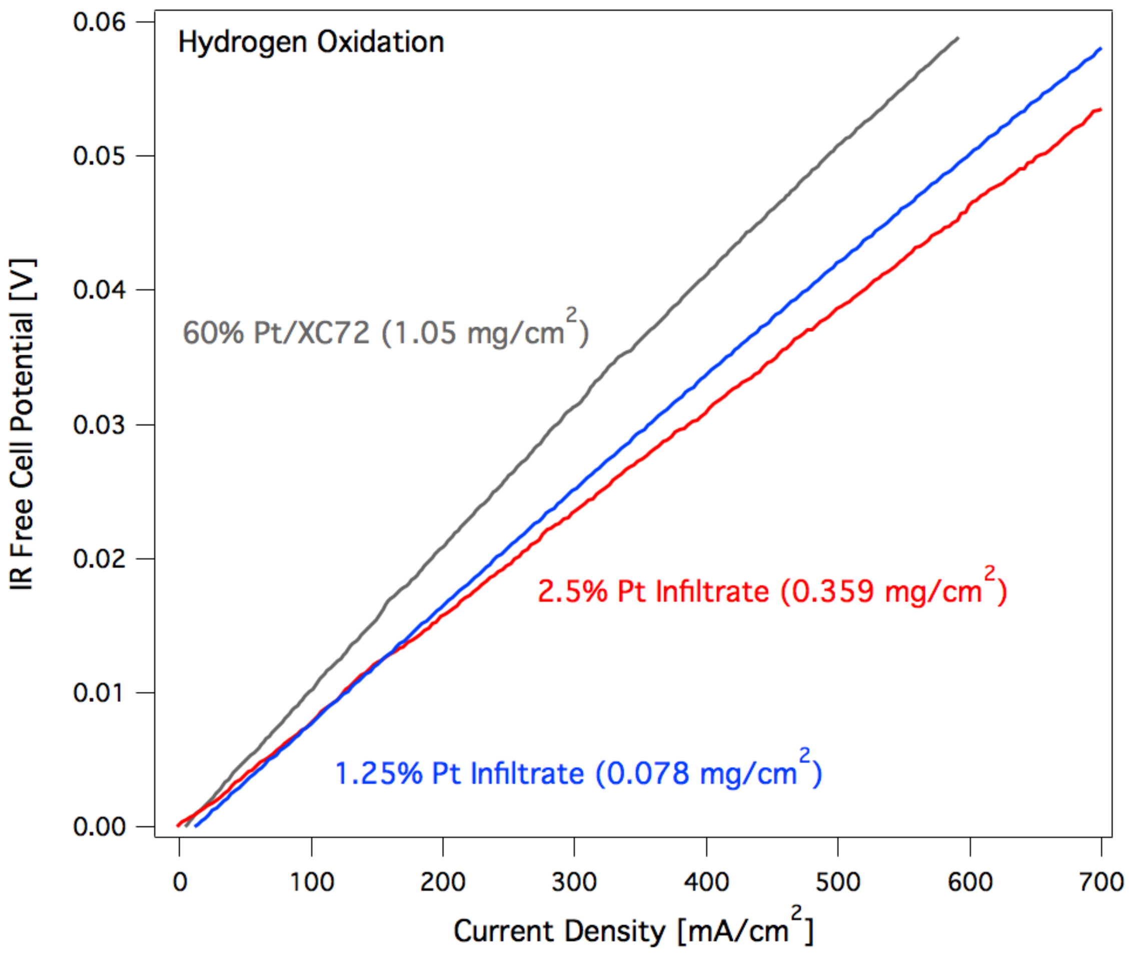


HOR Polarization in H_2 + CO

Simulated MeOH reformate	75% H_2, **7 % CO**, 18% CO_2
Simulated Propane Reformate	43% H_2, 37% N_2, **10 % CO**, 9.75% CO_2, 0.25% CH_4

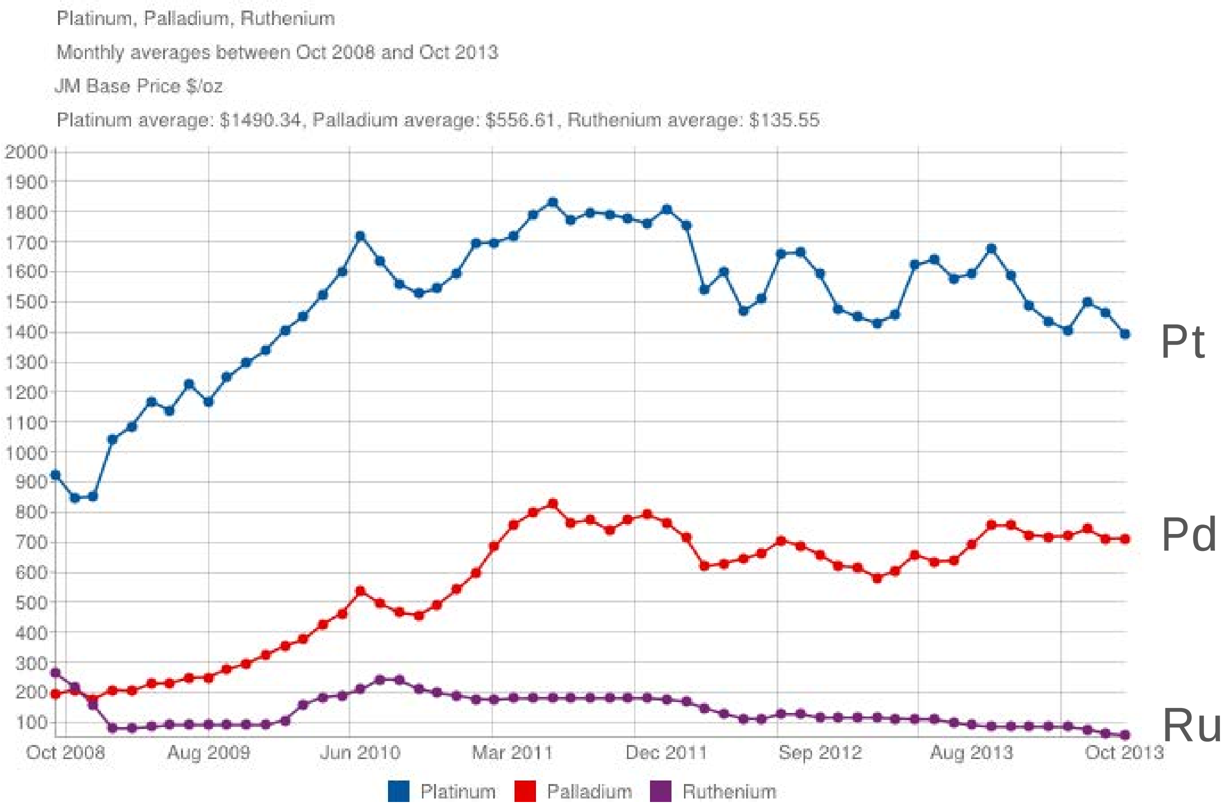


We can use similar CL construction approaches

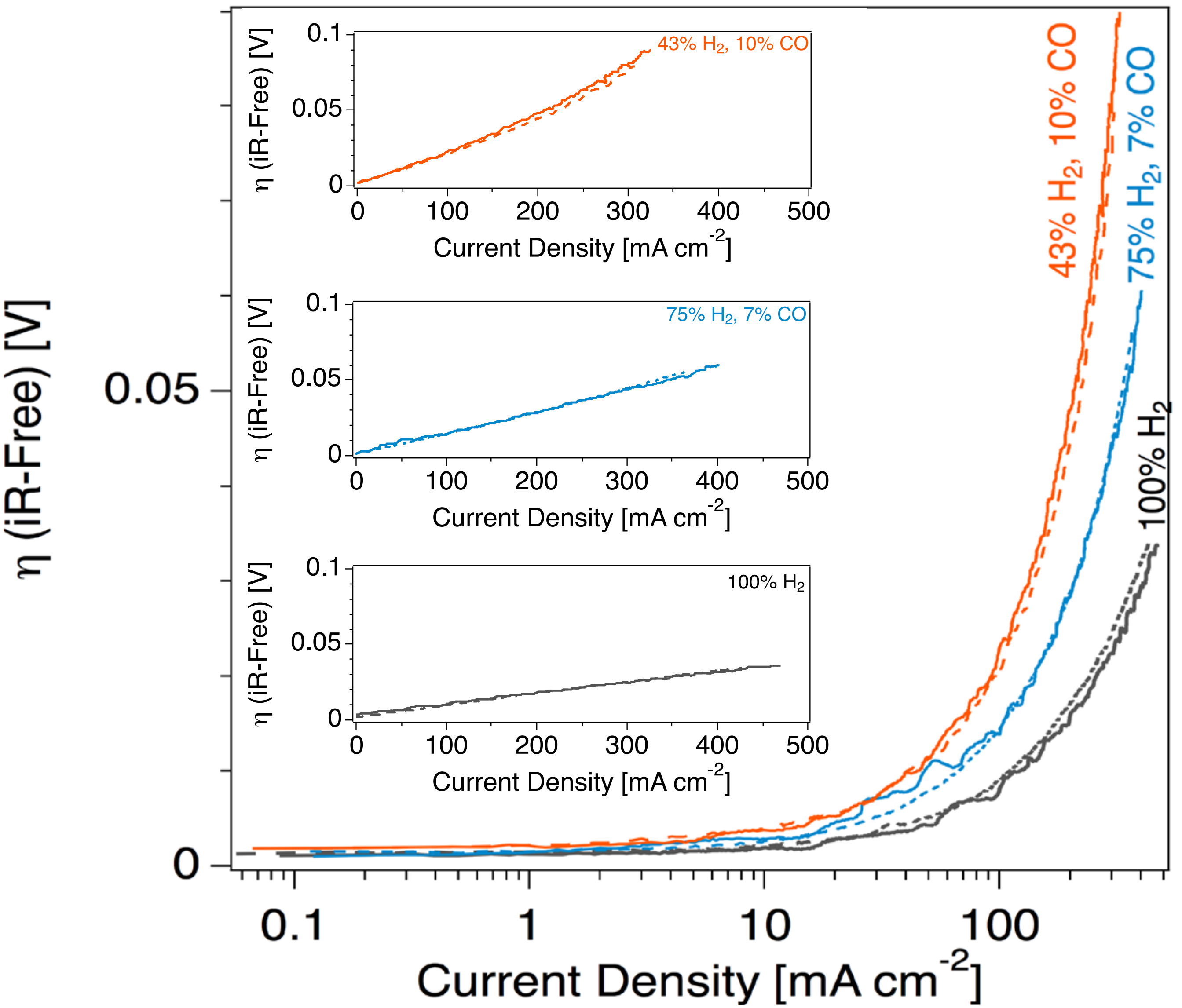


Alternatives to Pt for HOR?

In the absence of liquid acid, dissolution concerns are limited



Pd is Identical to Pt for HOR



250 °C
1.0 mg cm^{-2} 60wt%Pd/C
75 °C dew point
2 mV s^{-1} scan rate
1.0 mg cm^{-2} 60wt%Pt/C HER catalyst

Solid line: Pd
Dashed line: Pt

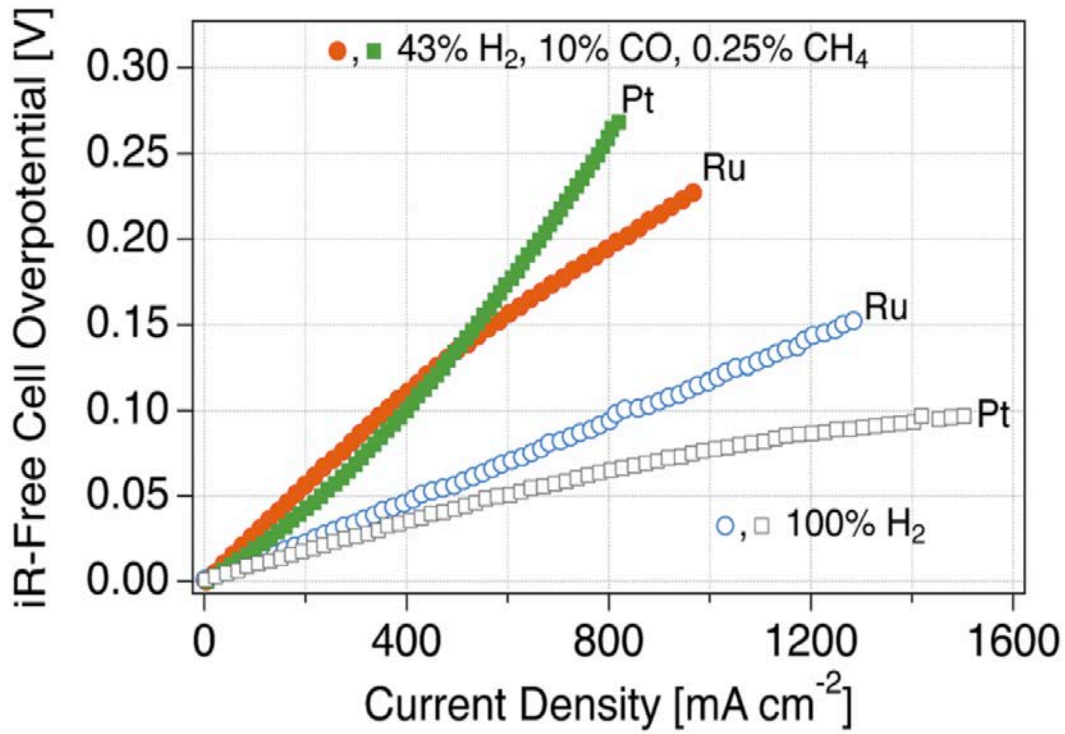
Ru outperforms Pt on Reformate Streams

Platinum

- Superior catalyst (on pure hydrogen)
- Lower performance on reformate streams

Ruthenium

- Ru ou performs Pt at lower overpotentials
- Water gas shift reaction or electrooxidation?

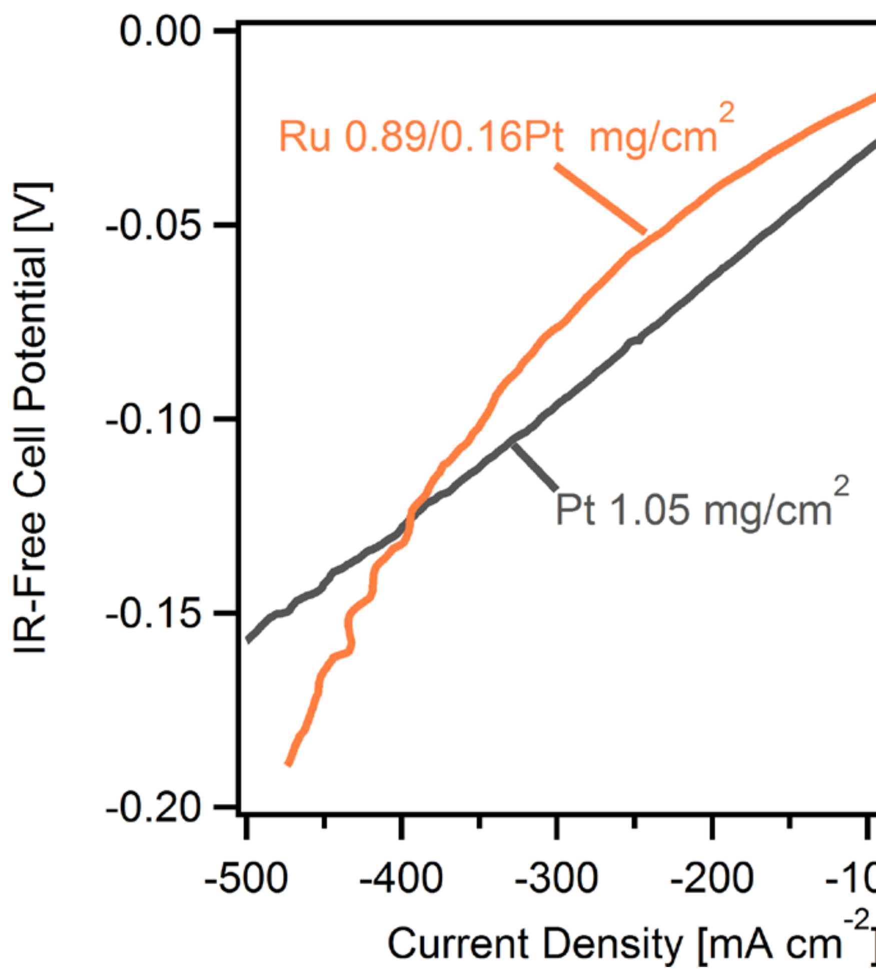


J. Mater. Chem. A, 2015, 3, 3984

Ru and Pt anodes are Superior on Reformate Streams

Ruthenium and Pt Electrodes

- Under reformate, similar performance to pure Ru
- Drastic decrease in Pt
- Higher Polarization still lead to higher Pt performance

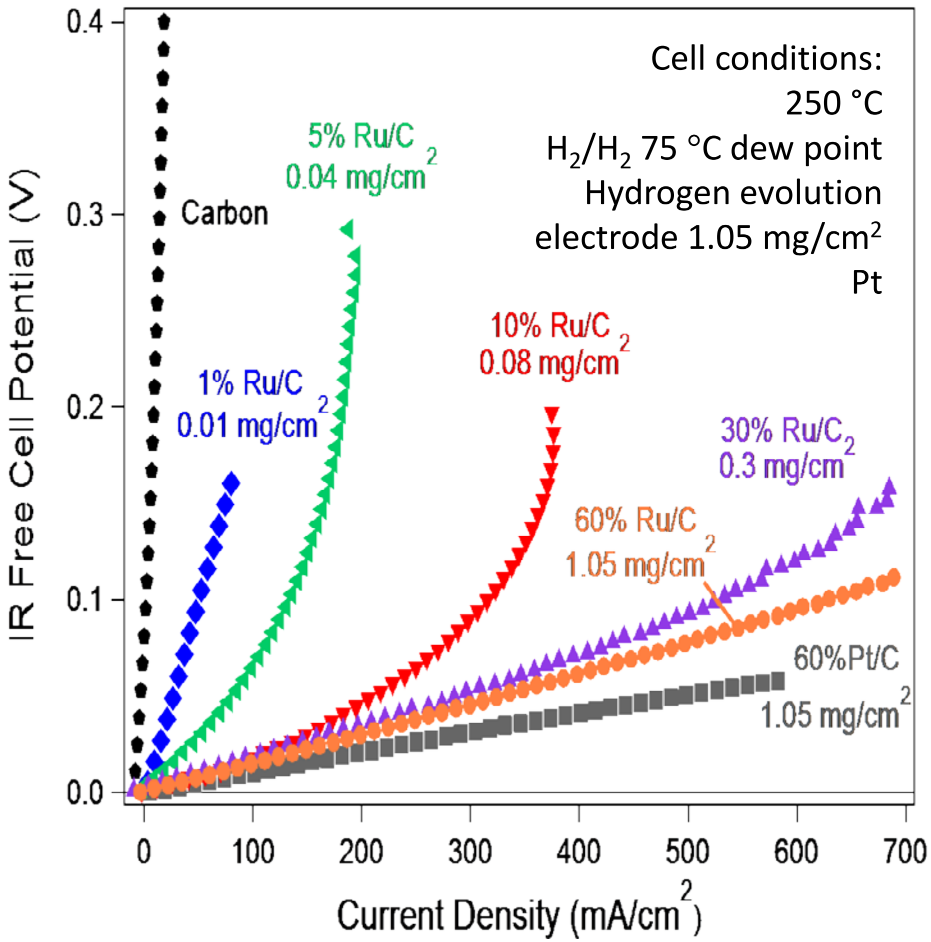


Cell conditions: 250 °C
Anode:
10%CO 43% H_2 0.25% CH_4 75 °C dew point
1.05 mg/cm^2 Ru
Cathode:
H_2 75 °C dew point
1.05 mg/cm^2 Pt

Hydrogen Oxidation Limited by Ru Metal Loading

Ruthenium HOR Electrodes

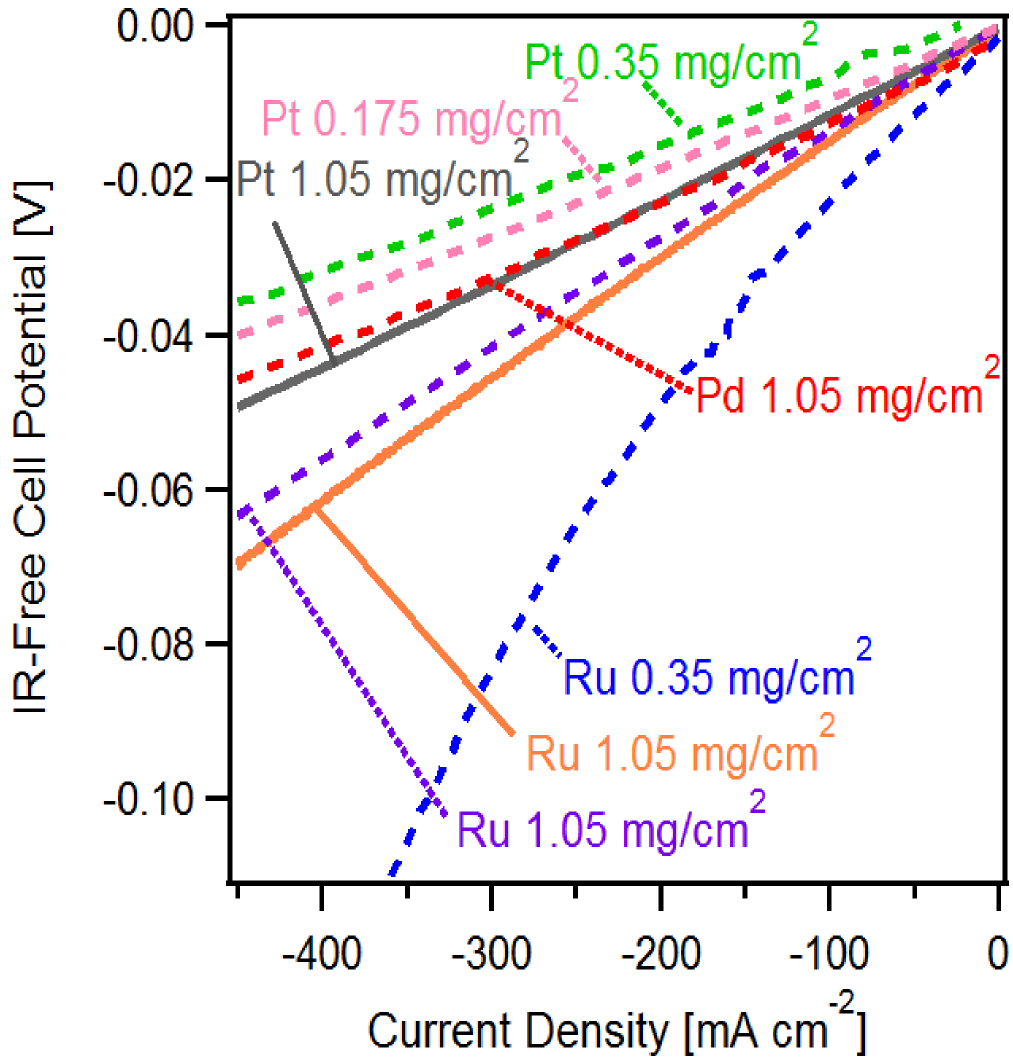
- Increasing the weight %Ru on supported carbon increases performance
- Mass transfer limitations in lower loadings of Ru



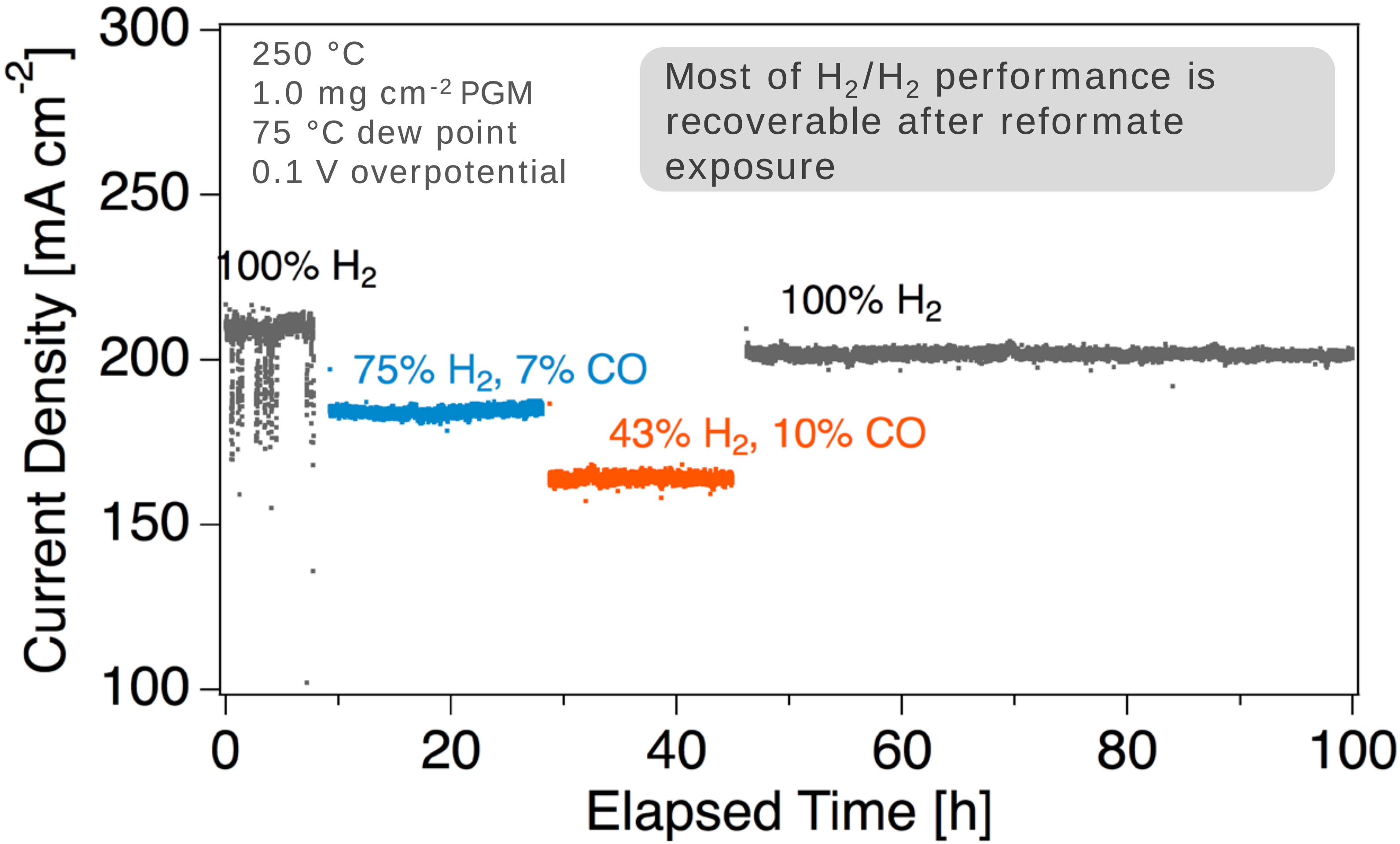
We can use similar CL construction approaches again

Dashed lines represent the infiltrated samples where straight lines represent the Vulcan supported samples.

All these tests were performed in hydrogen at 250°C.

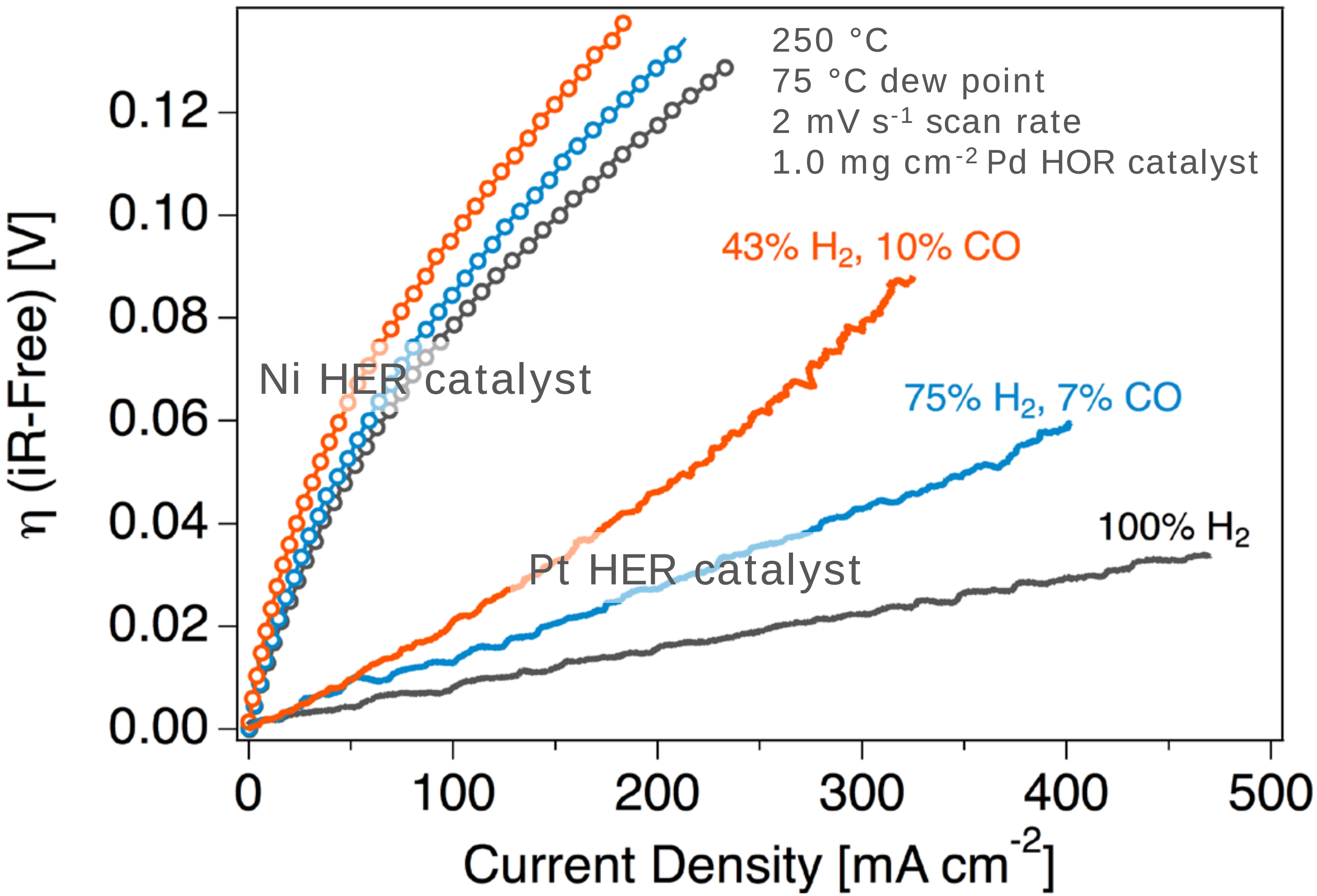


Stable Performance in Reformate



Pd (HOR) + Ni (HER) = Pt-Free

Opposite curvatures – activation vs. mass transport limitations



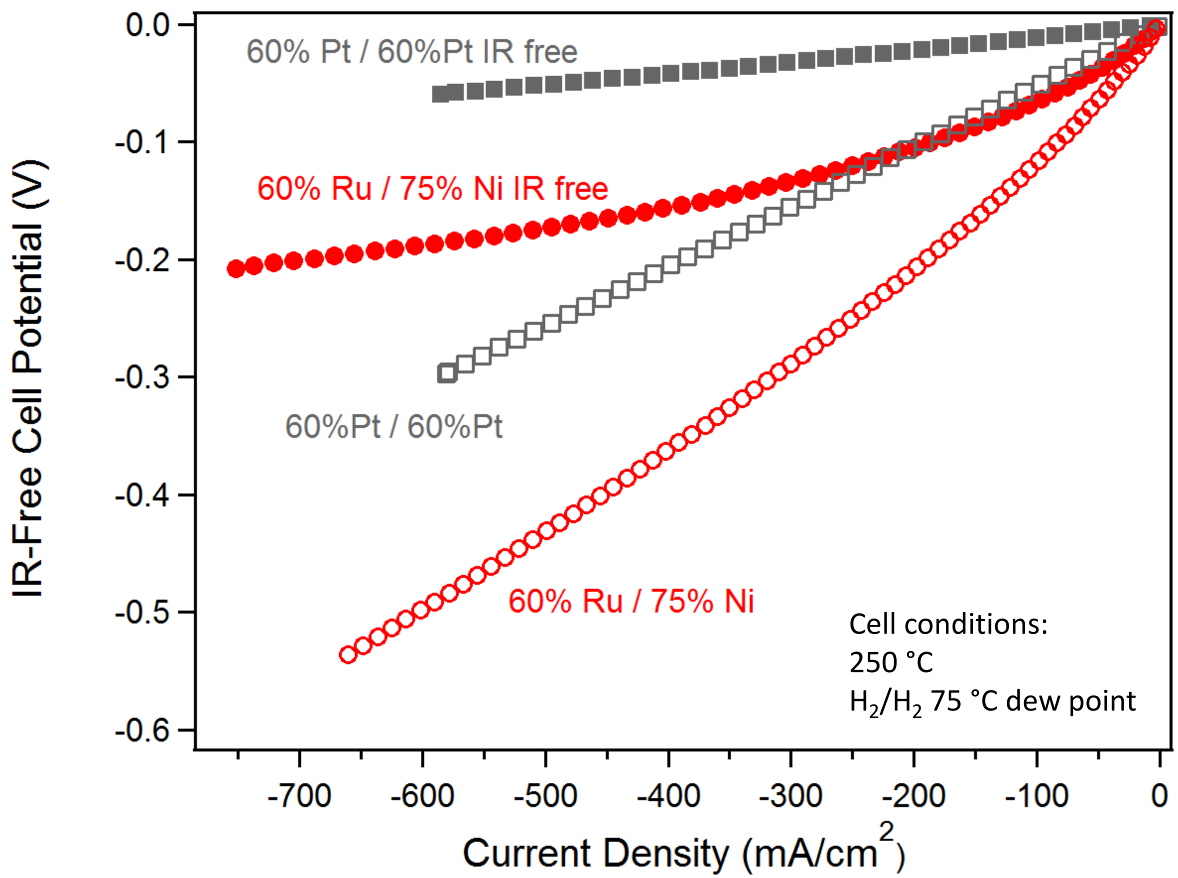
Ru/Ni SA Hydrogen Separation System

Pt/Pt

- Still shows the "better" performance
- System is still ohmically dominated
- Pt is expensive

Ru/Ni

- Performance less than Pt/Pt
- System still ohmically dominated
- Ru and Ni are both drastically cheaper than Pt



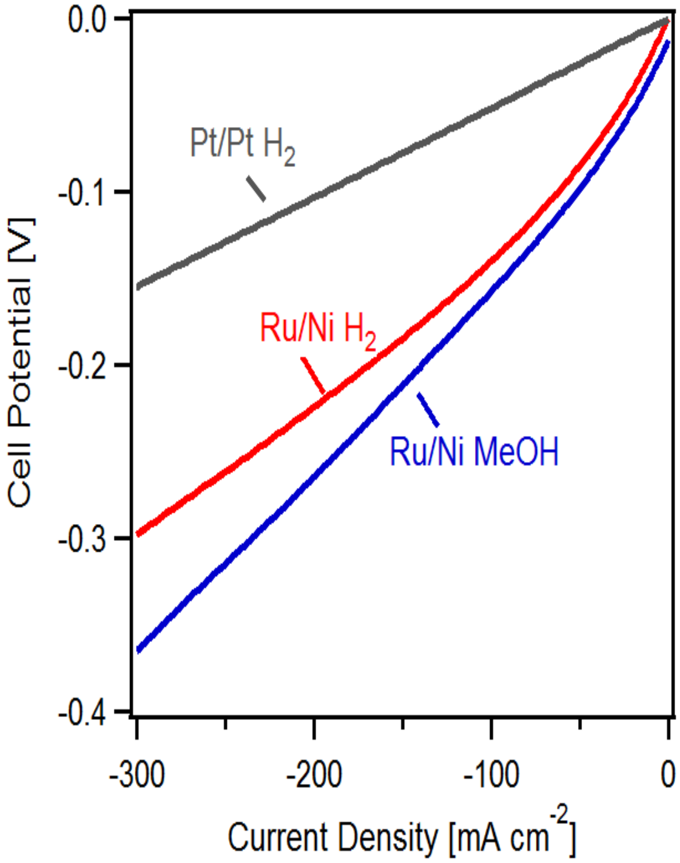
Metal loadings:

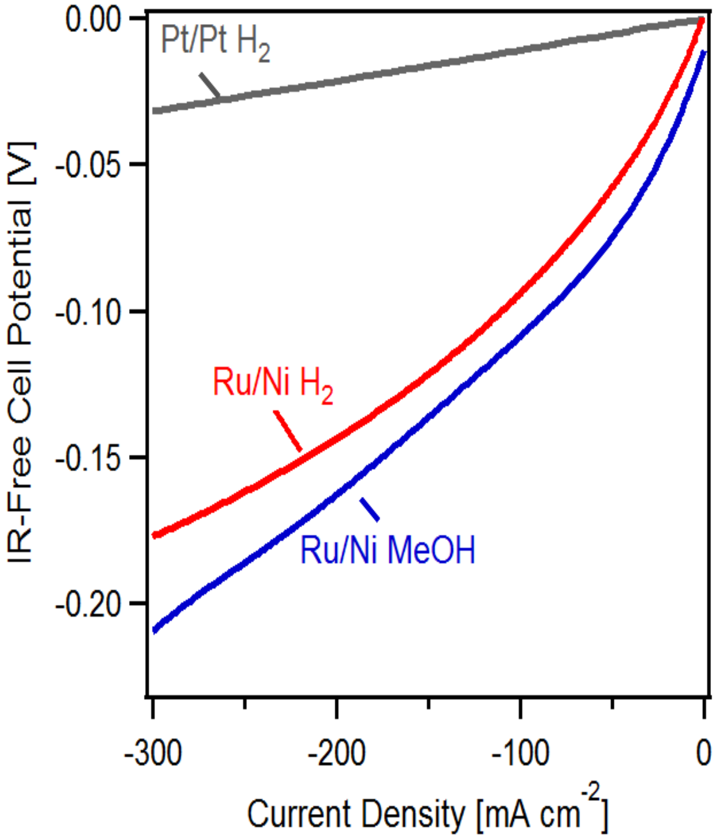
75% 2.10 mg/cm^2 (Ni)
60% 1.05 mg/cm^2 (Pt/Ru)

Direct Electro-oxidation Leads to Possibilities Beyond Reformed NG

- Direct electrooxidation leads to extended fuel possibilities for solid acid systems
- Dry coal gasification is great example of a CO rich fuel source
- Possibilities extend beyond a hydrogen source to a potential source of electricity
  - Direct CO fuel cell

Methanol to Hydrogen Cells

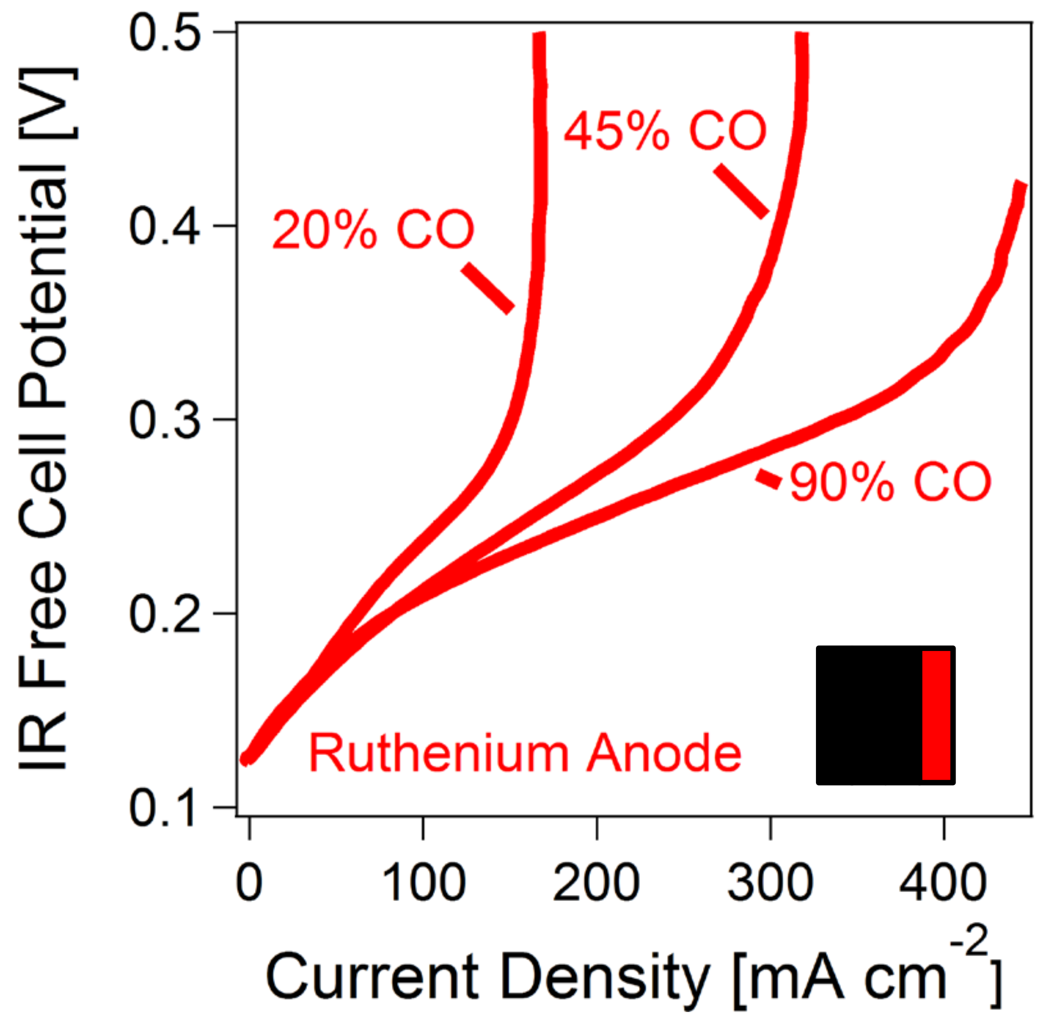




Hydrogen evolution polarization uncorrected for IR (a) and corrected for IR (b) for supported Ru anode (1.05 mg cm^{-2})and supported Ni cathode (2.5 mg cm^{-2}) on hydrogen and methanol.

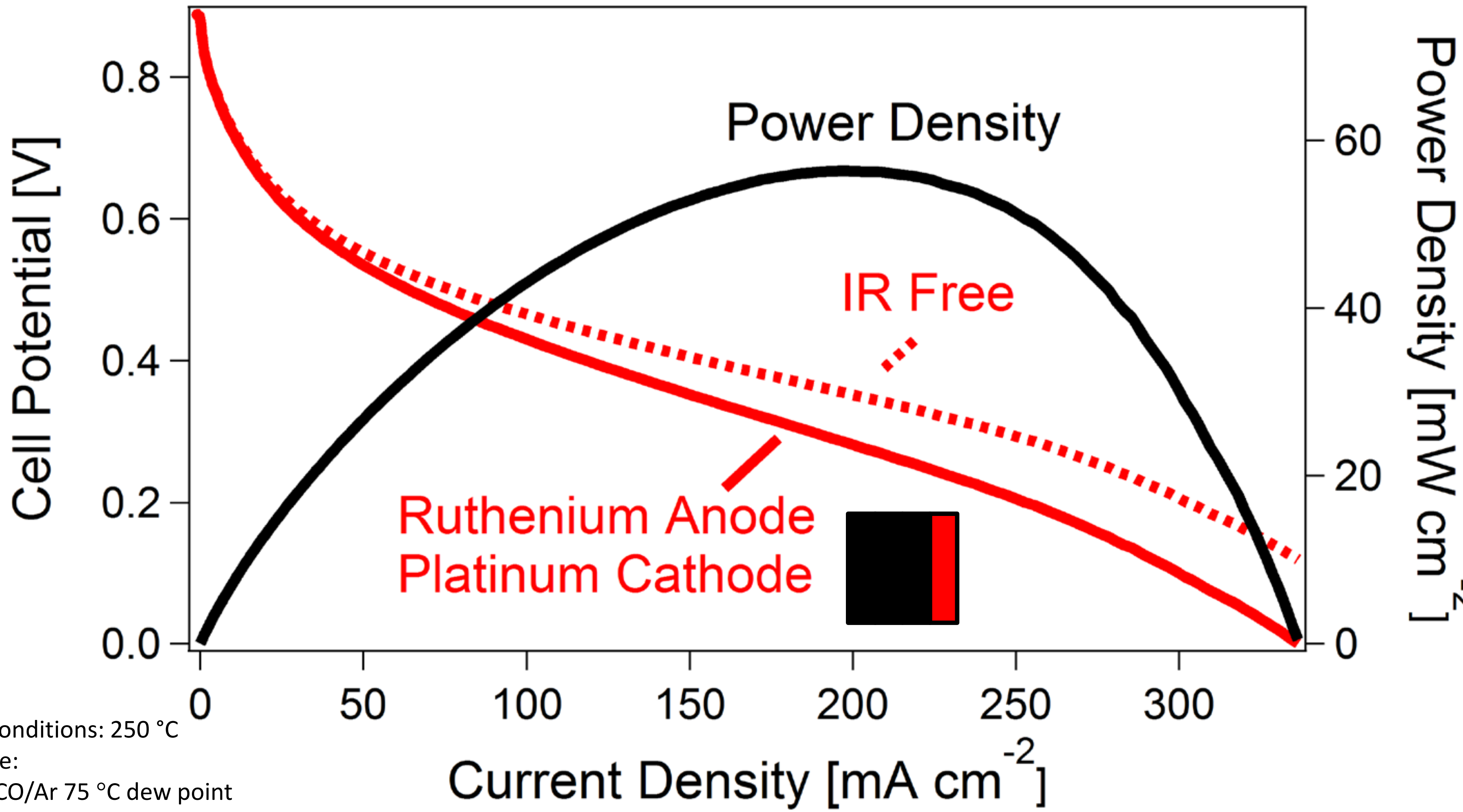
Ru Anode Performance Depends on CO Concentration

- Variable carbon monoxide (balance argon) feed stream to anode
- Hydrogen stream on cathode for reference
- No change in OCV



Cell conditions: 250 °C
Anode:
Variable CO/Ar 75 °C dew point
1.05 mg/cm^2 Ru
Cathode:
H_2 75 °C dew point
1.05 mg/cm^2 Pt

Direct CO Fuel Cell



Cell conditions: 250 °C
Anode:
90% CO/Ar 75 °C dew point
1.05 mg/cm² Ru
Cathode:
Air 75 °C dew point
1.75 mg/cm² Pt

Summary

- Advances in SAFC technology allow major decrease in Pt loading with improved performance.
- A number of non-precious (or less precious) metal catalysts are viable for HOR
- A Pd/Ni cell offers the prospect of Pt-free H2 production from streams containing 10% CO and 0.25% CH_4
- Ru looks promising for HOR
- More work needed to fully implement approaches from SAFCs

Funding Sources

- ARPA-e for SAFC work
- Office of Naval Research (N000141210887)
- NSF TN-SCORE (NSF EPS-1004083)
- Tennessee Governor's Chair Fund