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Title: MPA-11: Materials Synthesis and Integrated Devices; Overview of an Applied Energy Group

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MPA-11: Materials Synthesis and Integrated Devices

Overview of An Applied Energy Group

Andrew M. Dattelbaum
Group Leader

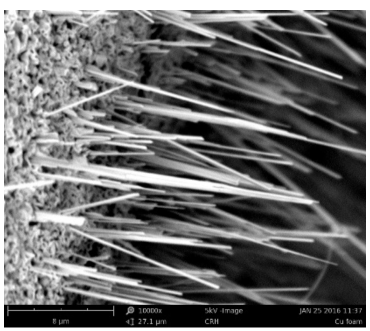
November 10, 2017

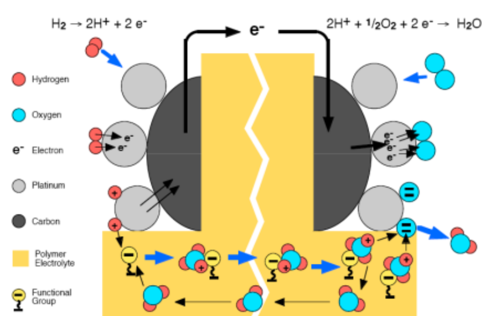
Materials Synthesis and Integrated Devices (MPA-11): An Applied Energy Group

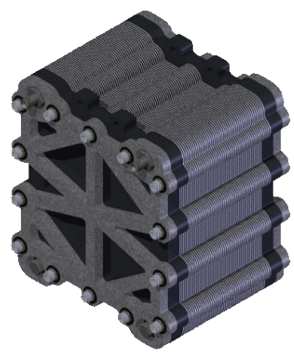
- Our mission is to provide innovative and creative chemical synthesis and materials science solutions to solve materials problems across the LANL missions.
- Our group conducts basic and applied research in areas related to energy security as well as problems relevant to the Weapons Program.

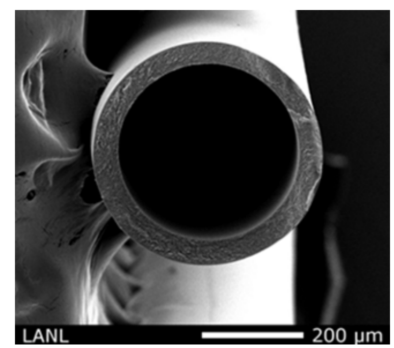
Areas of Specialization:

- Polymer Electrolyte Fuel Cells
- Acoustics Technology
- Weapons Aging and Safety
- Actinide Chemistry/Materials
- Polymer membranes for gas separations
- Nanomaterials synthesis of 2D materials
- Electrochemical-based gas sensor and devices









Los Alamos National Laboratory Overview

People

- 7,200 permanent employee
- ~3500 technical staff members
- 350 Post doctoral researchers
- 1,600 students

Place

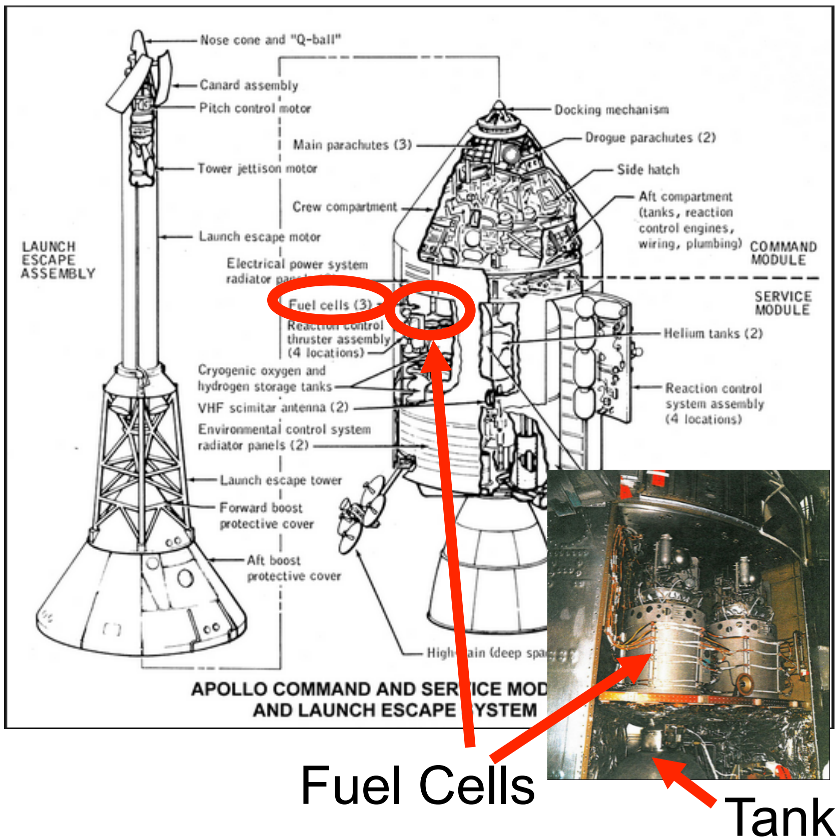
- 35 miles northwest of Santa Fe, NM
- 1,000 individual facilities,
- 47 technical areas
- 8.2 million square feet

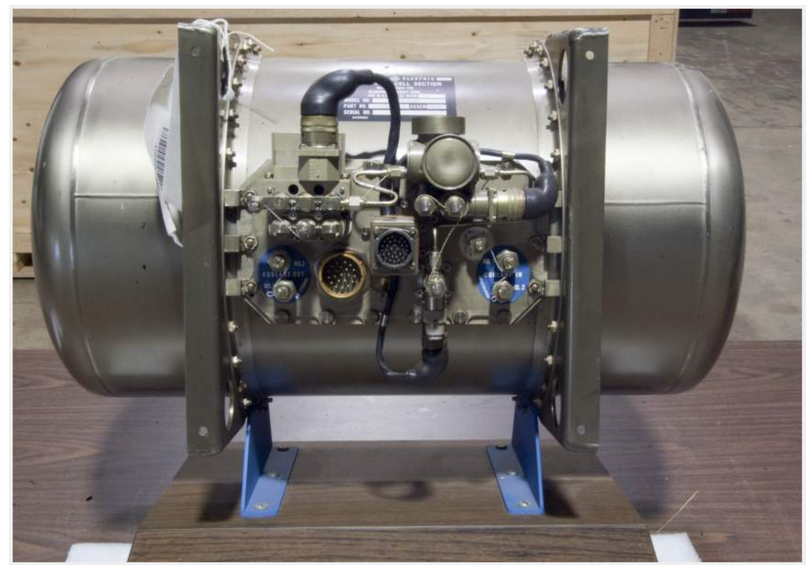
Budget (FY16)

- ~ $2.45 billion budget
- 65% Weapons program
- 4% DOE Office of Science
- 2% Energy programs
- 10% Work for others

Fuel Cells – Space Applications

- **Fuel Cells found their first applications in space**
  - Fuel cells first flew on Gemini space missions (PEM)
  - Apollo missions were powered by two/three fuel cells (Alkaline)
  - Space Shuttle had three fuel cells (Alkaline)





General Electric PEM fuel cell (test version) used on the two-astronaut Gemini spacecraft during seven missions in 1965-66.

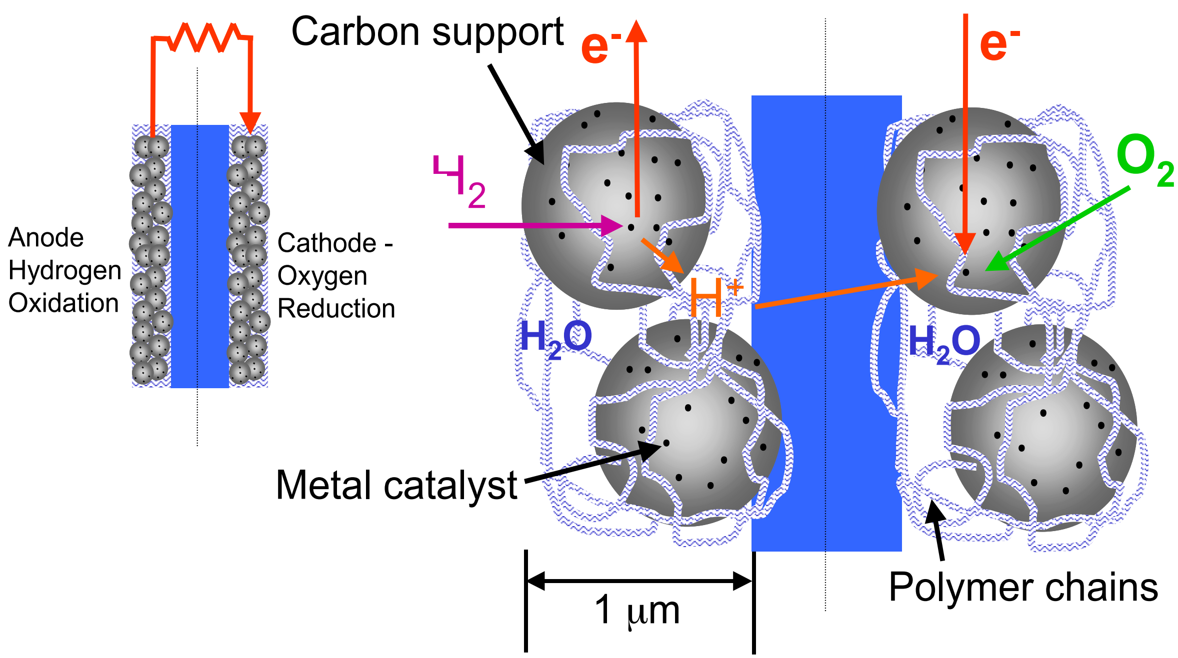
The Beginning of the DOE Fuel Cell Program…

1970s | A group from labs, government and industry met at Los Alamos to set the foundation for DOE fuel cell programs

Lab researchers taught scientists around the world how to fabricate fuel cell electrodes. Group from GM relocated to Los Alamos.

History of the LANL Fuel Cell Program

LANL Enabling Breakthrough Thin Film Electrode

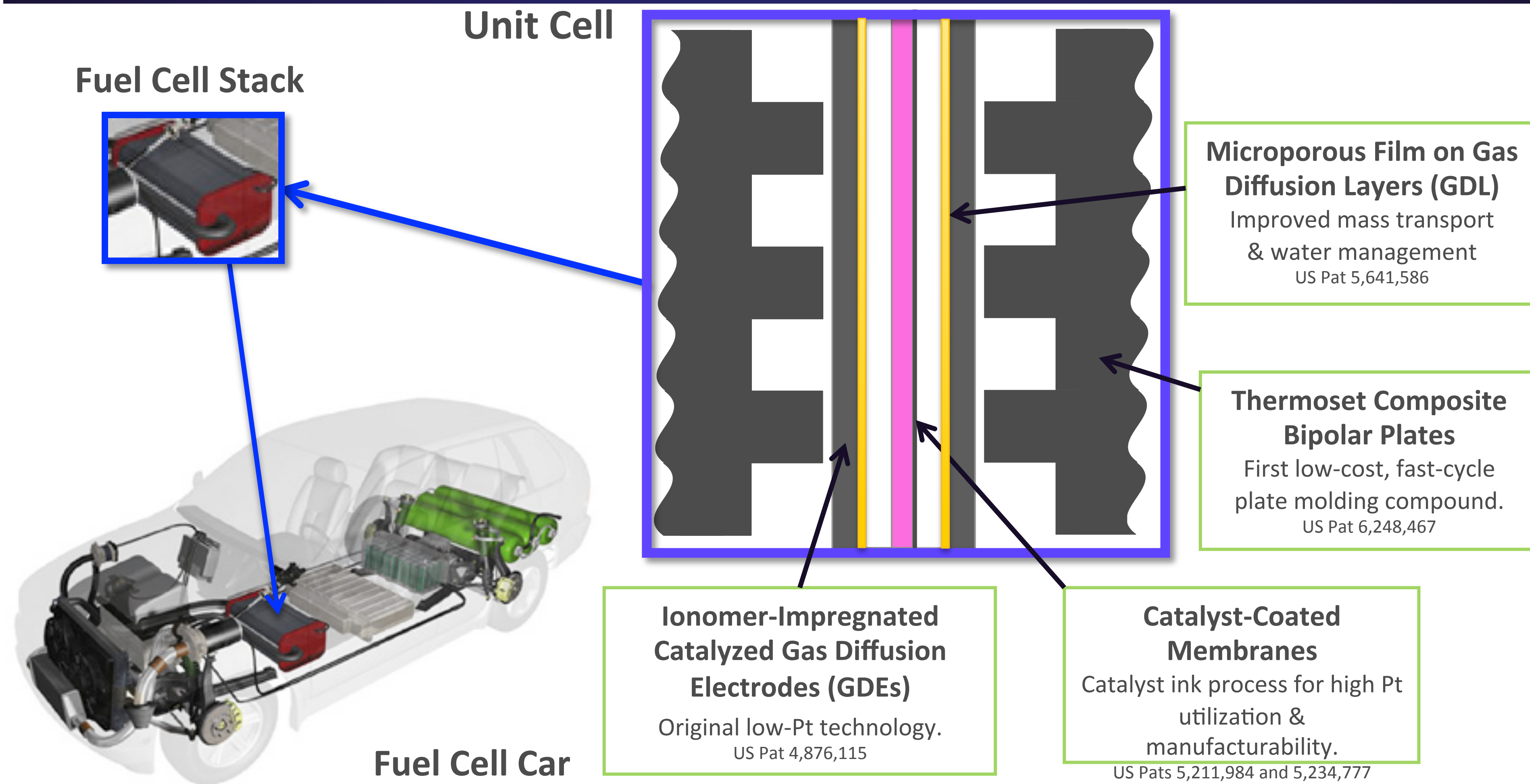


An electrochemically active reaction site must have reactant access to catalyst, available electronic and ionic conduction paths, and manage water

US Patents #4,876,115, #5,211,984 and #5,234,777

- One of longest running non-weapons programs at LANL (since 1977)
- The current DOE Fuel Cell Technologies Office (FCTO) program grew from the original Los Alamos program
- Program is primarily focused on polymer electrolyte membrane (PEM) technology for transportation
- LANL has the largest portion of the DOE EERE FCTO Fuel Cell Component R&D budget of any organization (NL or other)

LANL-Led Innovation in Fuel Cells



LANL's innovation in fuel cells technology has played a critical role in the technical viability of fuel cell stacks for FCEVs.

Fuel Cell Electric Vehicles (FCEVs) are on U.S. Roads TODAY!

Commercial FCEVs are here **today!**

Can reduce total GHG emissions 50-90% vs. today's gasoline vehicles

More than 1,100 FCEVs sold or leased in the U.S.

Why Fuel Cells for Transportation Applications?

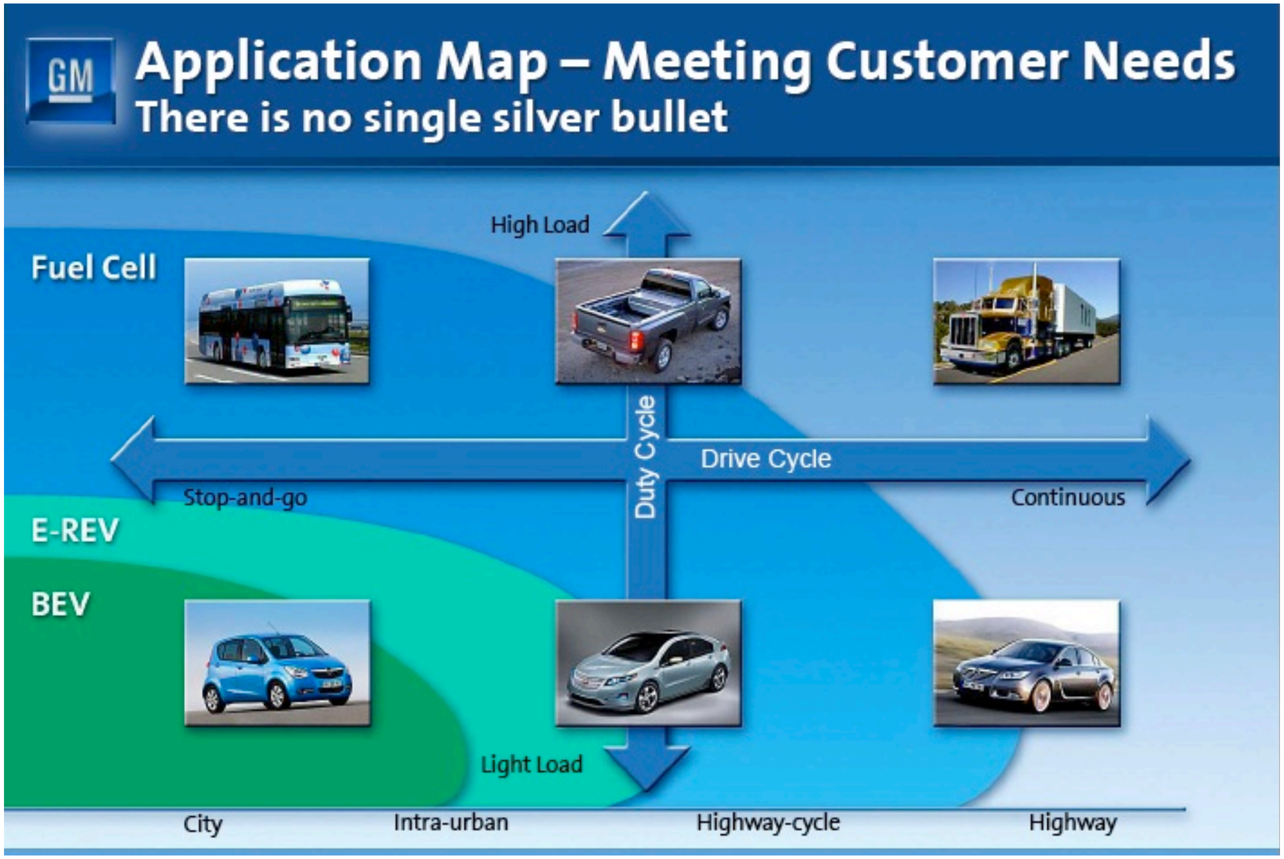
Hydrogen Enables U.S. Energy Security

Petroleum Diversification
~ 92% of Transportation

Hydrogen Production
Natural Gas Steam Reforming
Longer-term: Renewables
(wind, solar)

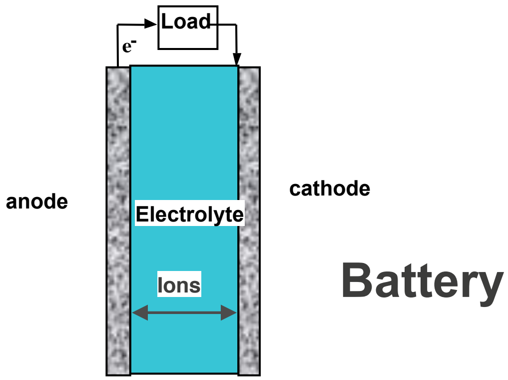
Green House Gas Emissions

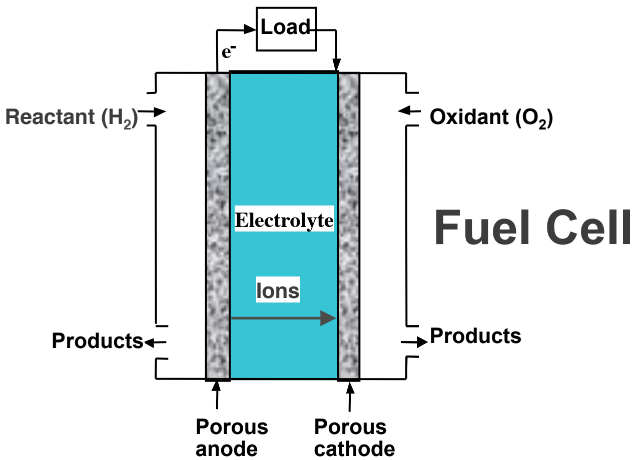
>50% with H_2 from
Distributed Natural Gas
>90% with H_2 from
renewable sources

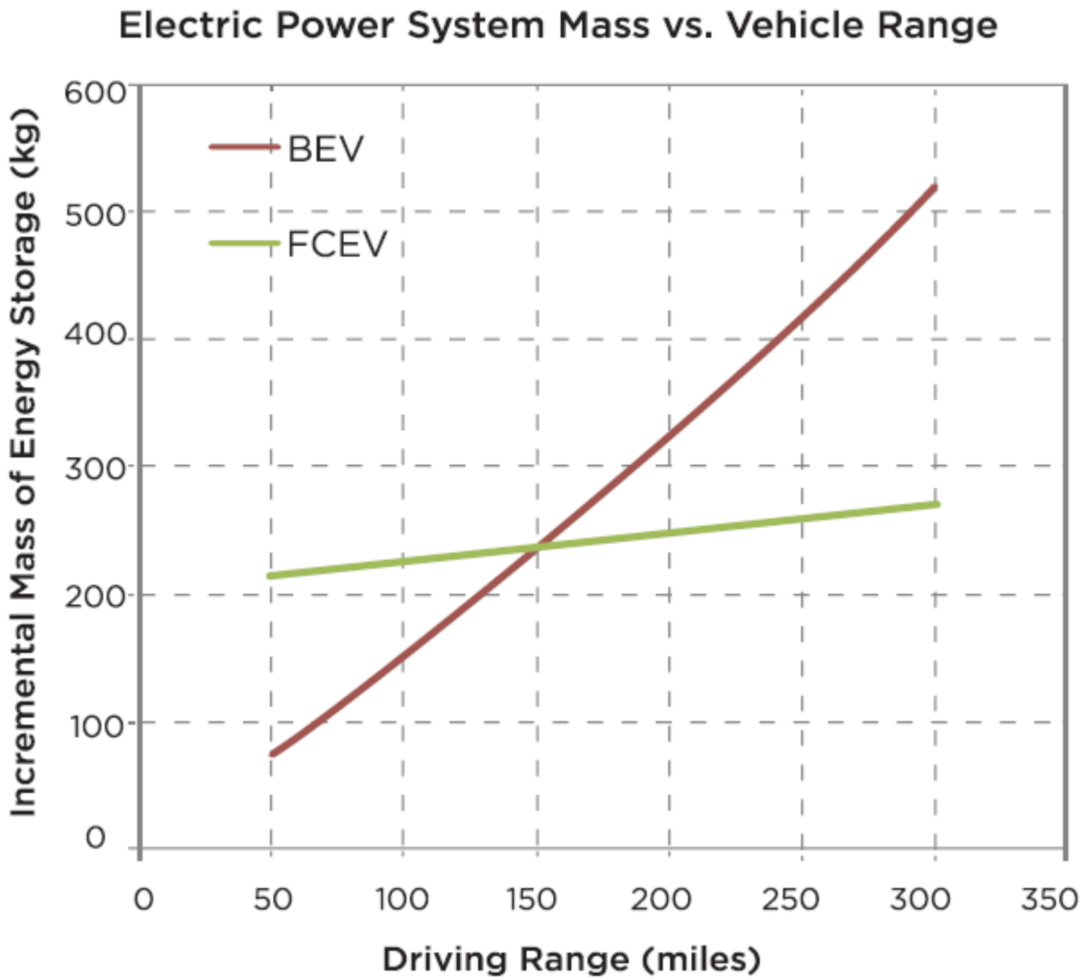


Source: http://hydrogen.energy.gov/pdfs/13005_well_to_wheels_ghg_oil_ldvs.pdf

Fuel Cell vs. Battery: A Range Advantage

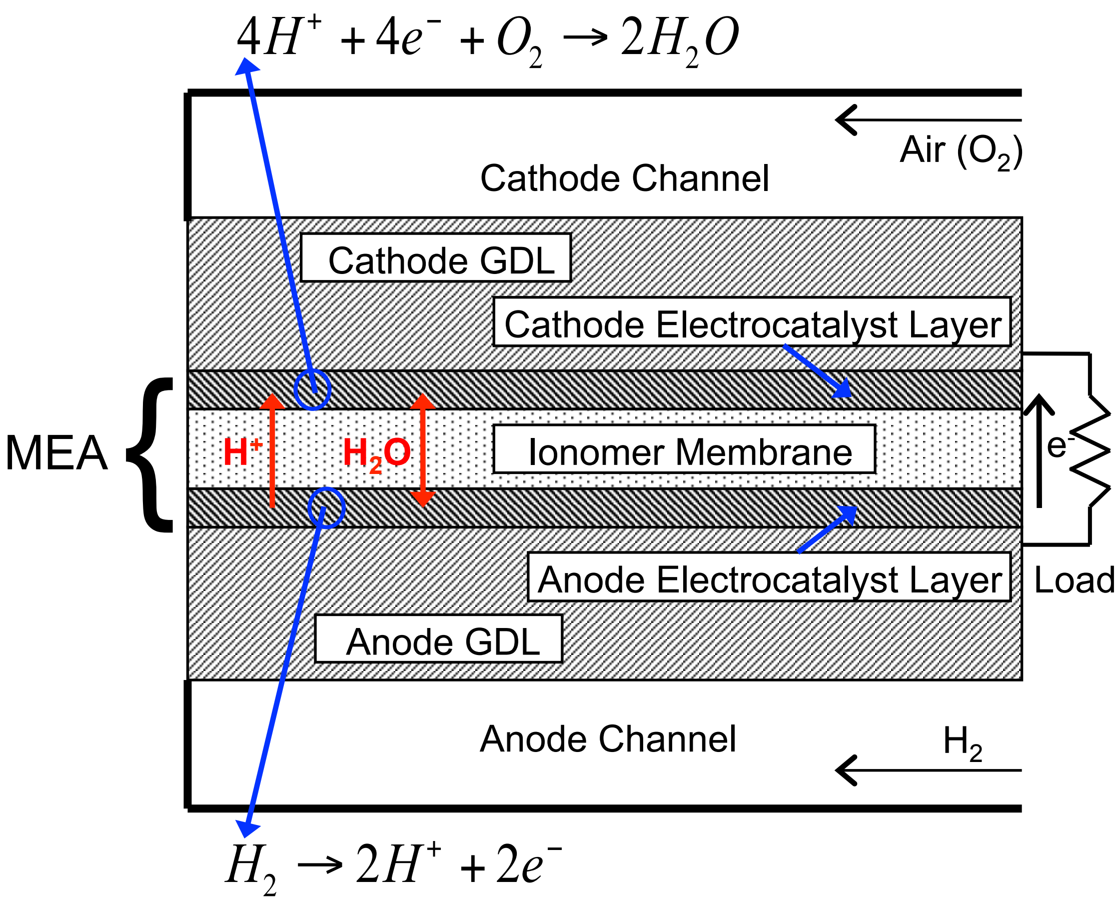






Advantages: energy density (up to >6000 Whr/kg based on fuel, batteries up to 150 Whr/kg), refuel versus recharge

The Components of a Polymer Electrolyte Membrane Fuel Cell (PEMFC)



Materials

Membrane: Perflourosulfonic acid (Nafion)
Durability, cross-over

Catalysts:
Anode: Pt
Cathode: Pt
Durability to cycling

Catalyst Support: N/A

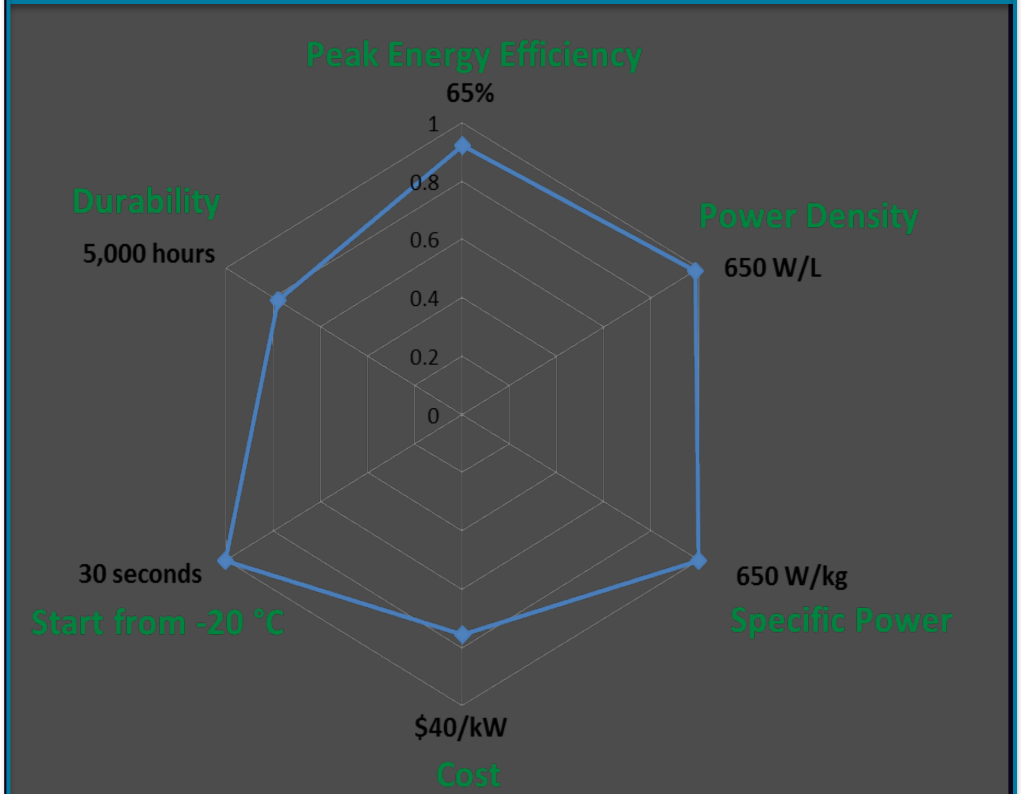
Gas Diffusion Layer: Carbon fiber with carbon micro-porous layer

Gaskets: PTFE,
Durability/Sealing

Bipolar Plate: Coated Metal
Corrosion resistance
Contact resistance

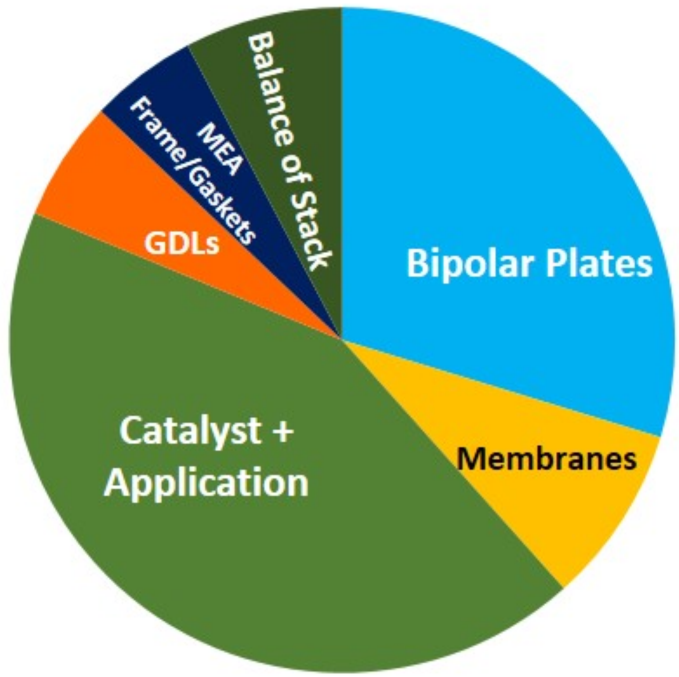
Fuel Cell Challenges

Durability and Cost are the primary challenges to fuel cell commercialization and must be met concurrently



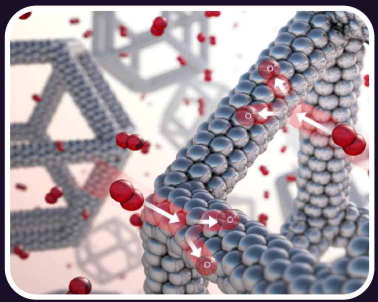
Improvements in multiple components are required to meet cost targets

PEMFC Stack Cost Breakdown*



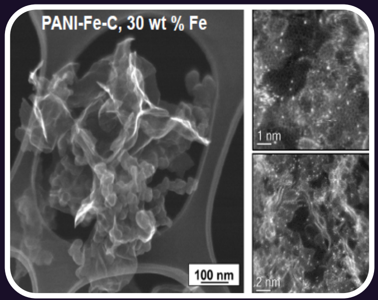
Catalyst cost is projected to be the largest single component of the cost of a PEMFC manufactured at high volume.

Approaches to Reduce Fuel Cell Costs



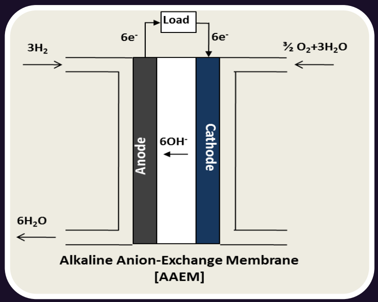
Low Pt Cathode Catalyst Development

- Near term Approach
- ANL, BNL, LANL, NREL



Non-PGM Cathode Catalyst Development

- Mid term
- LANL, ANL



Alkaline Membrane Fuel Cells

- Long-term
- LANL, SNL, NREL

LANL has leadership roles in two DOE National Lab consortia and applies fuel cells to NNSA applications

Fuel cell system targets set to be competitive with ICEVs.

Durability <u>and</u> Cost are the primary challenges to fuel cell commercialization and must be met concurrently

MPA-11 is also testing fuel cells for stockpile and GS applications

FUEL CELL FCPAD PERFORMANCE & DURABILITY

Rod Borup (MPA-11) is Director of the Consortium for Fuel Cell Performance and Durability

Los Alamos NATIONAL LABORATORY · Argonne NATIONAL LABORATORY · NREL NATIONAL RENEWABLE ENERGY LABORATORY · BERKELEY LAB · OAK RIDGE National Laboratory

ElectroCat Electrocatalysis Consortium

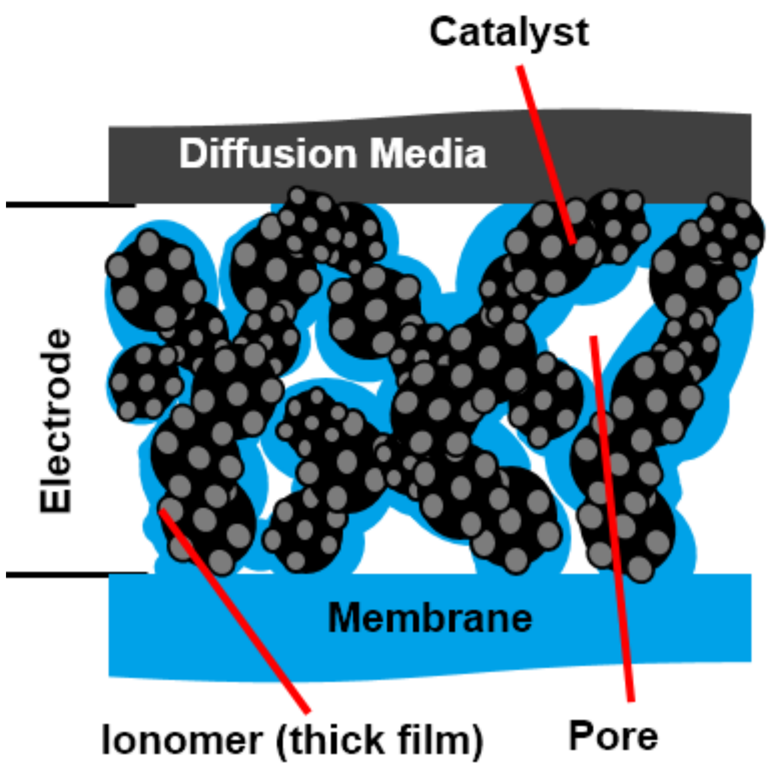
Project Focus: **PGM-free catalysts for automotive fuel cells**

Los Alamos NATIONAL LABORATORY · Argonne NATIONAL LABORATORY

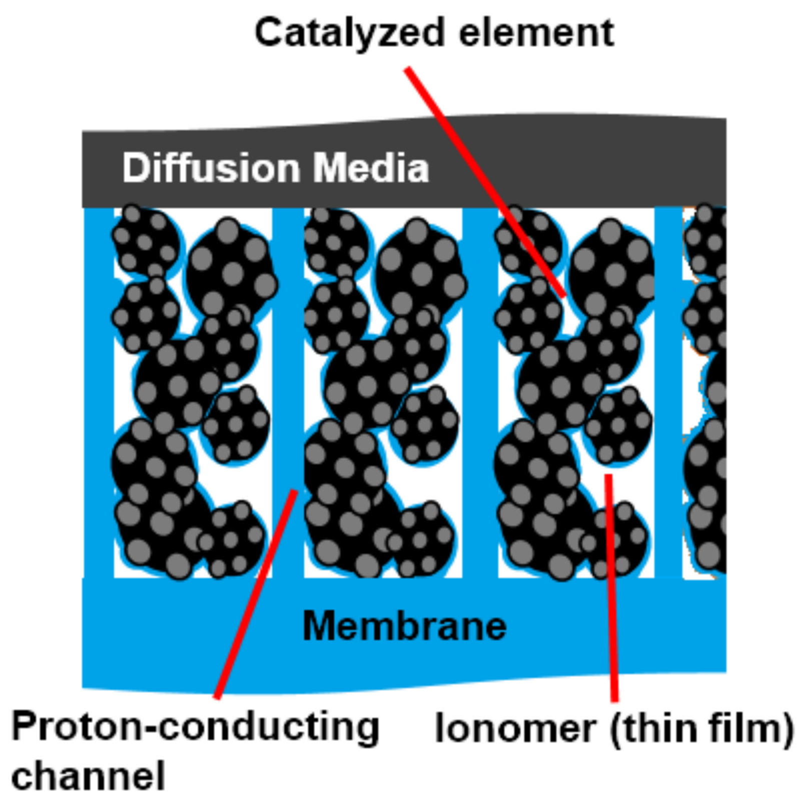
Piotr Zelenay (MPA-11) is Co-Director of ElectroCat – part of the DOE Energy Materials Network (EMN)

FC-PAD Highlight: Novel Array Electrode

Conventional Electrode*



Array Electrode*



- Array electrode relies on vertically-aligned ionomer channels for long-distance H^+ transport

  → Reduced catalyst layer sheet resistance

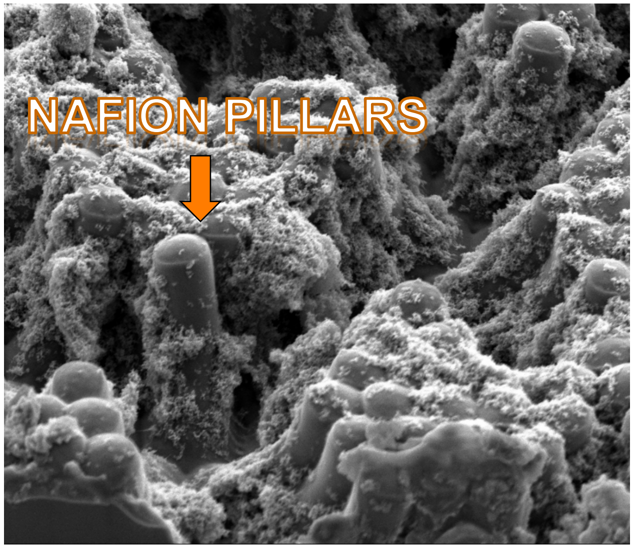
- Catalyzed elements can have reduced ionomer content

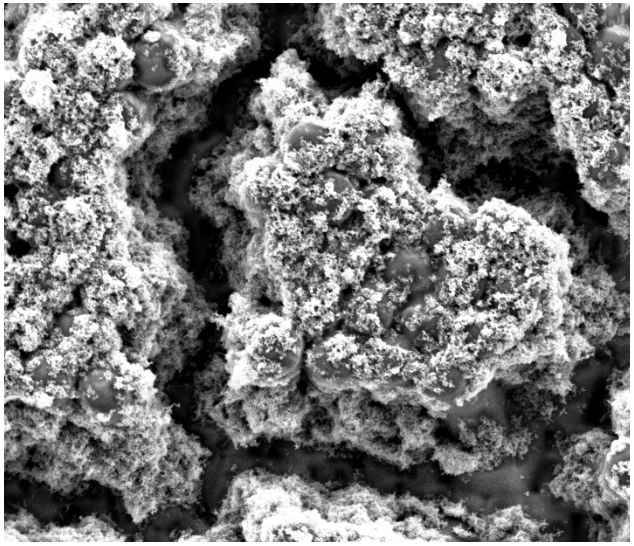
  → Reduced O_2 transport barrier

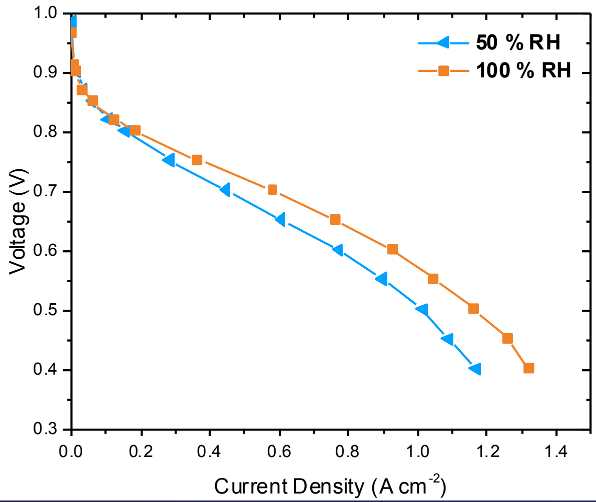
*not to scale

Catalyst Deposition and Fuel Cell Testing

Catalyst deposited around Nafion channels (SEM)



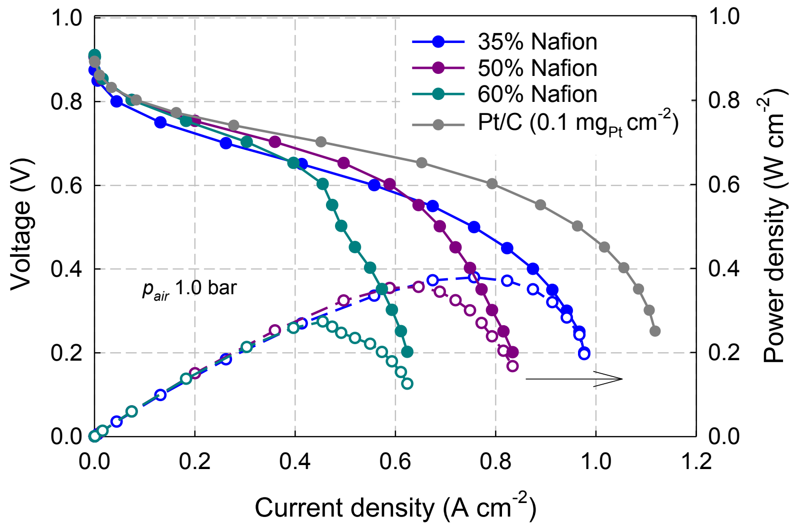




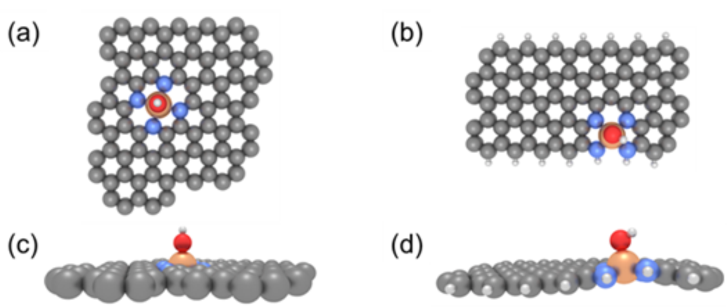
Nafion channels enable high performance under dry conditions – only ~10% difference between 50% and 100% RH performance

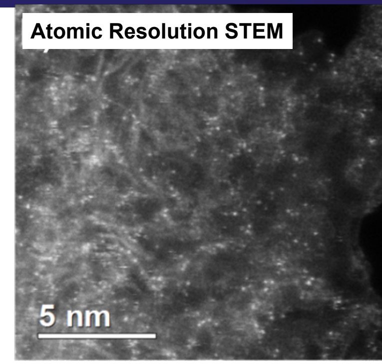
Insight into Active Sites of High-Performance PGM-free Oxygen Reduction Reaction (ORR) Catalysts

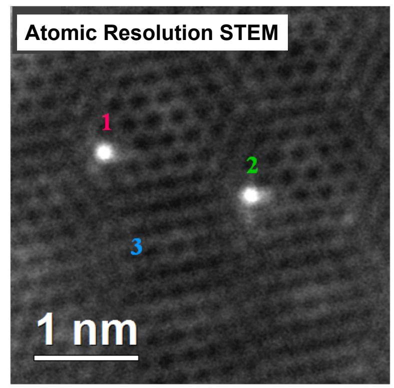
High-performance (CM+PANI)-Fe-C oxygen reduction reaction (ORR) catalyst with a hierarchical pore structure



DFT Model structures used in theoretical active-site studies
Confirms Fe-N_4 structure activity – most are likely at edge
(C – gray; Fe – bronze; H – white; N – blue; N – red)



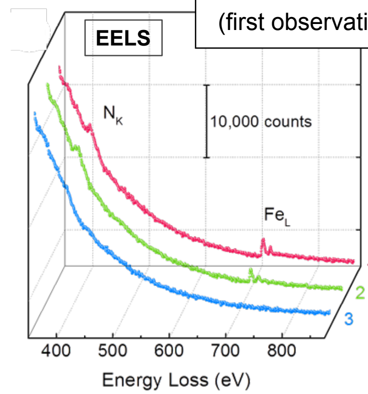




Advanced STEM and EELS characterization

Oak Ridge National Laboratory

N 79.5 at.%
Fe 20.5 at.%
↓
FeN_4
(first observation)



- ORR kinetics fuel cell performance matching that of a Pt catalyst at a loading of 0.1 mg cm^{-2}
- Proposed catalytic site (FeN_4) directly visualized for the first time using HR-STEM at ORNL
- Contributions of active sites associated with specific lattice-level carbon structures explored computationally and referred to the experiment

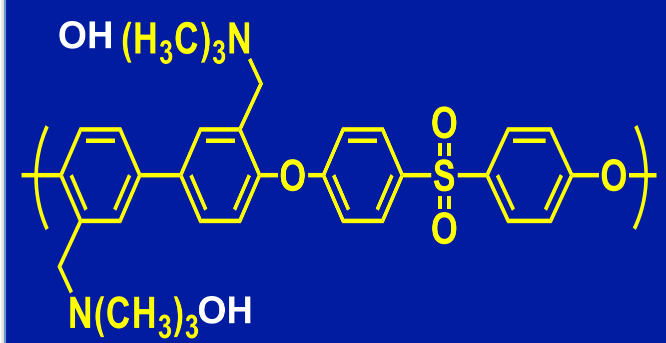
PI Piotr Zelenay, Science, 2017.

Alkaline conditions for Fuel Cell Systems

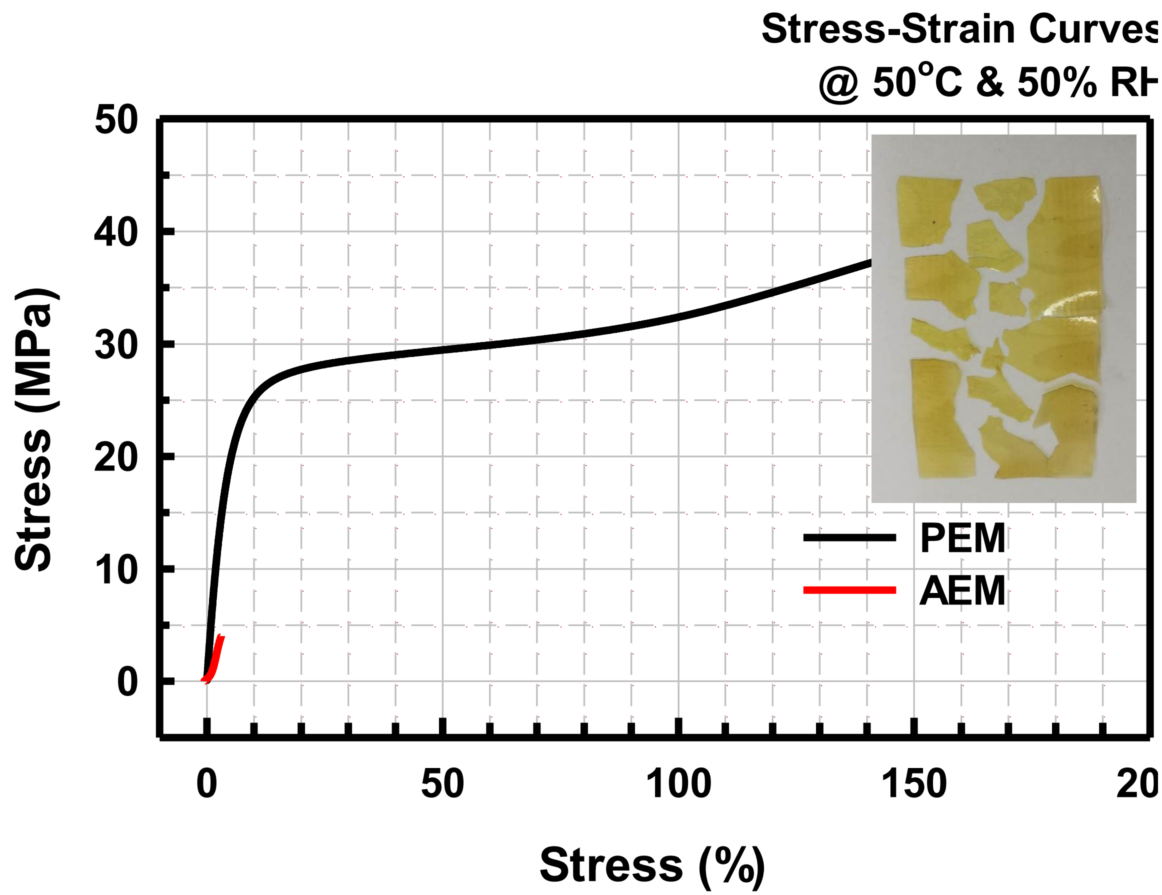
Nitrogen-containing carbon nanotubes can act as a metal-free electrode with a much better electro-catalytic activity….. than platinum for oxygen reduction in alkaline fuel cells” From Liming Dai et al. Science, 323, 760, Feb. 2009.

Membrane Embrittlement under high pH

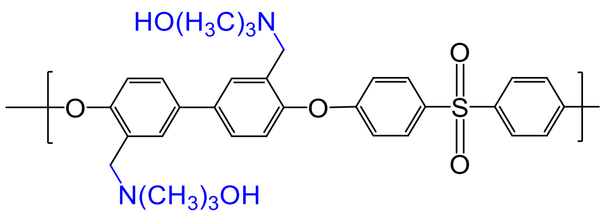
Alkaline membrane



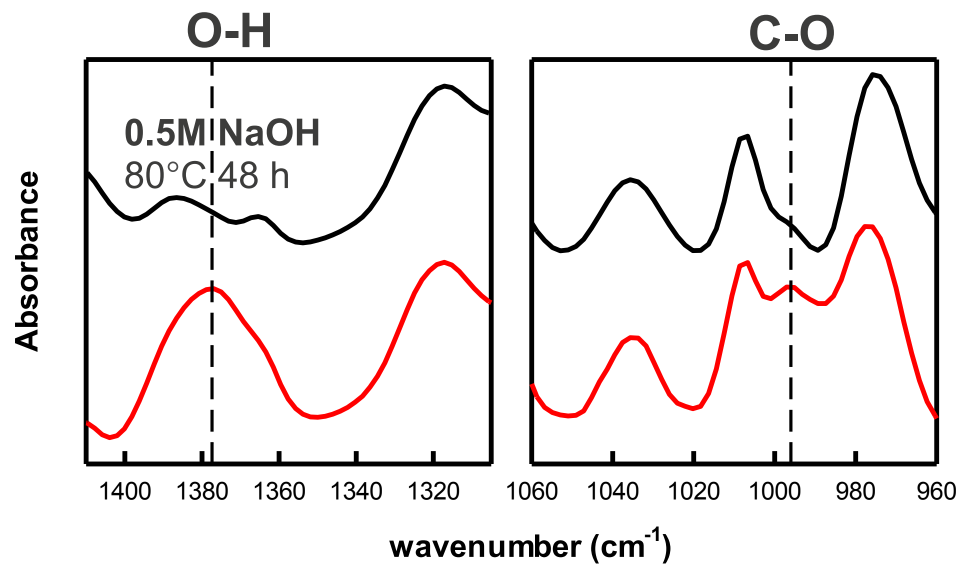
- IEC = 1.6 meq/g
- M_n = 42000 g/mol (prepolymer)
- Base treatment: 0.5M NaOH, 80˚C, 60 min



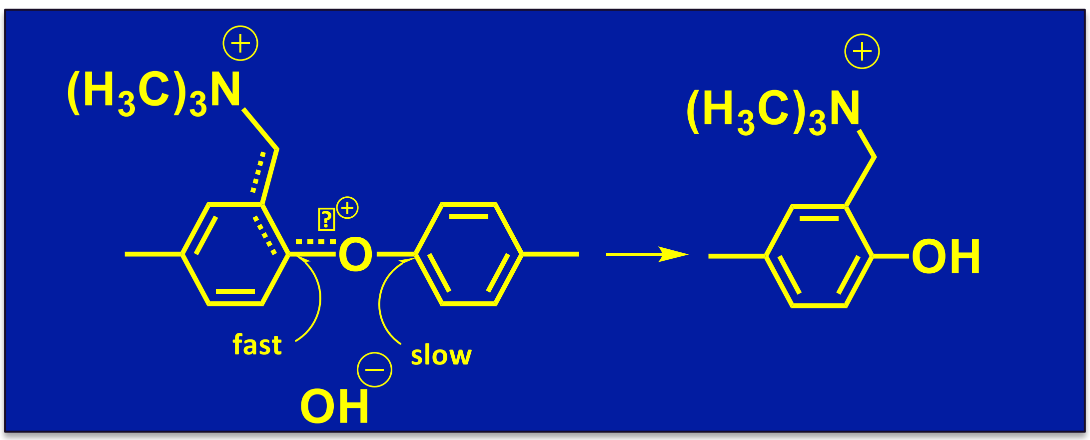
Determination of Degradation Mechanism



Increased phenolic OH peak at 1378 and 996 cm-1 after 0.5 M NaOH treatment



Proposed degradation mechanism*

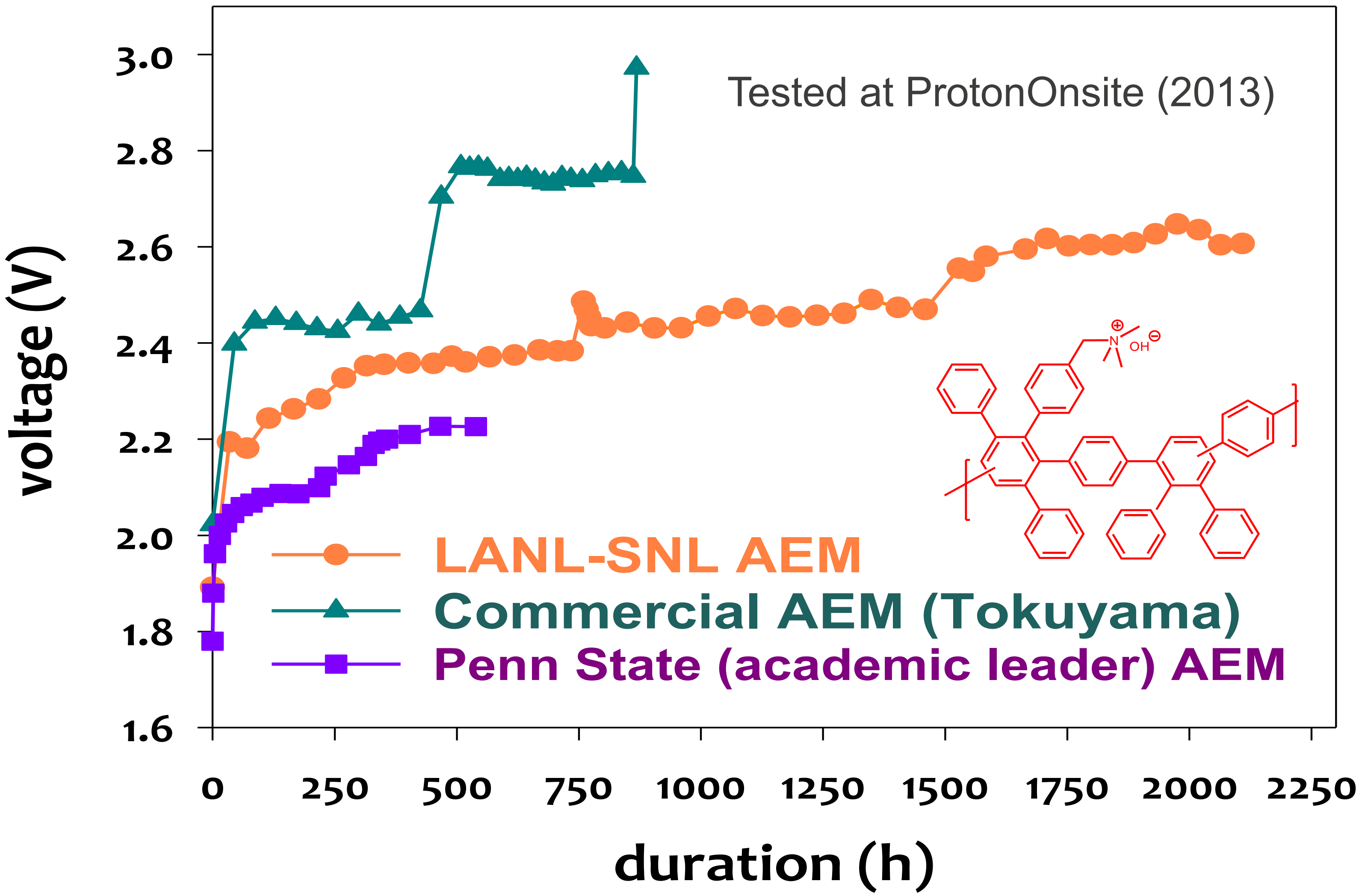


Solution:
Utilize Aryl-Free polymers to solve mechanical degradation issues

* *J. Memb. Sci.* 423, 438 (2012)

Stable Alkaline Membranes for Water Electrolyzers: Aryl-free Membranes

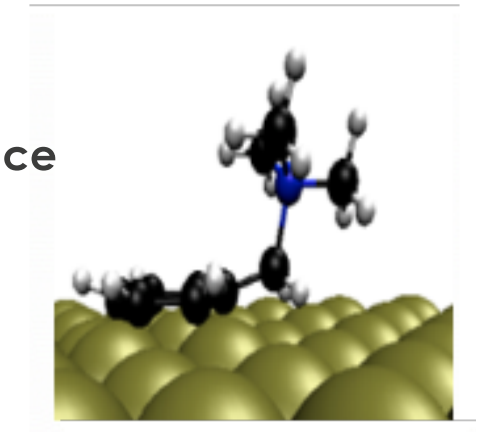
In-situ Membrane Durability Test



Alkaline membrane fuel cell (AMFC) research on catalyst electrolyte interface

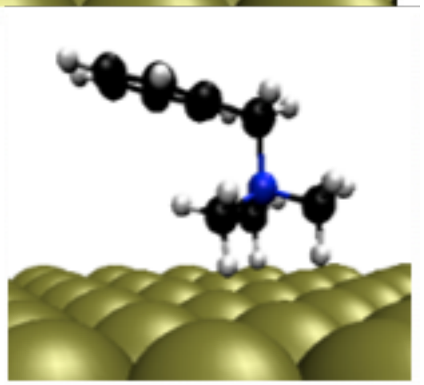
Benzene adsorption limits AMFC performance

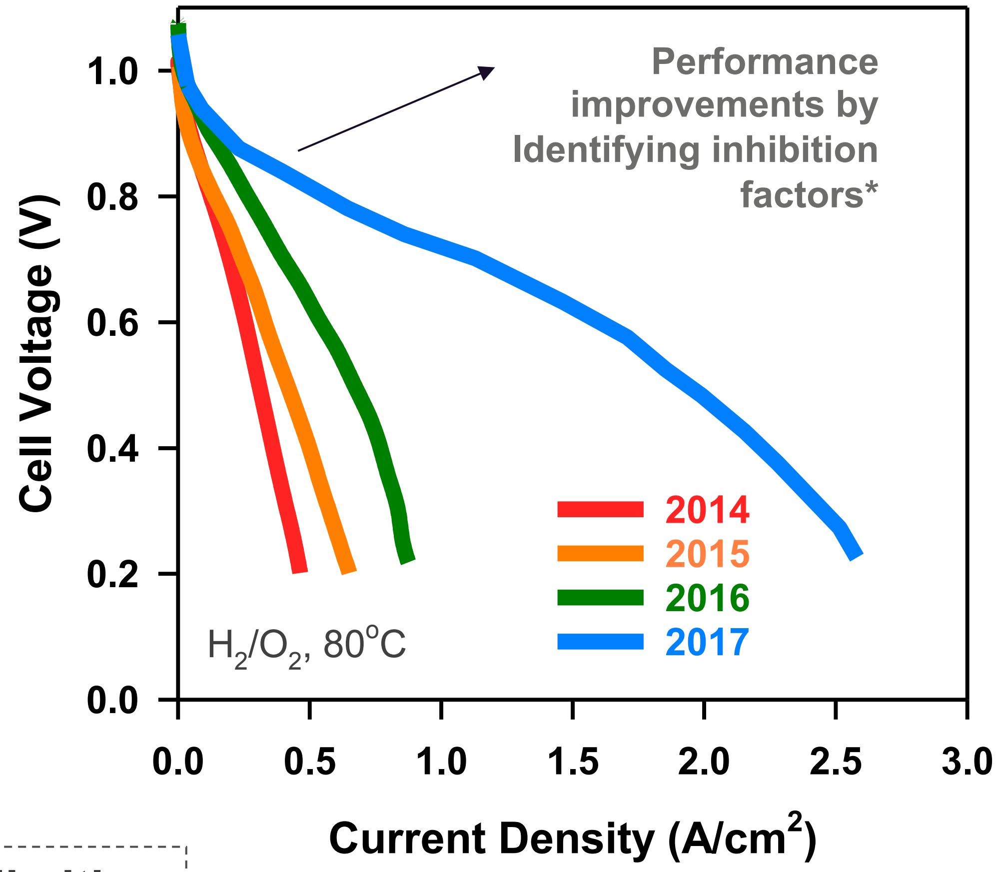
Matanovic et al. *J. Phys. Chem. Lett.* 2017, 8(19), 4918-4924.



Ammonium adsorption limits AMFC durability

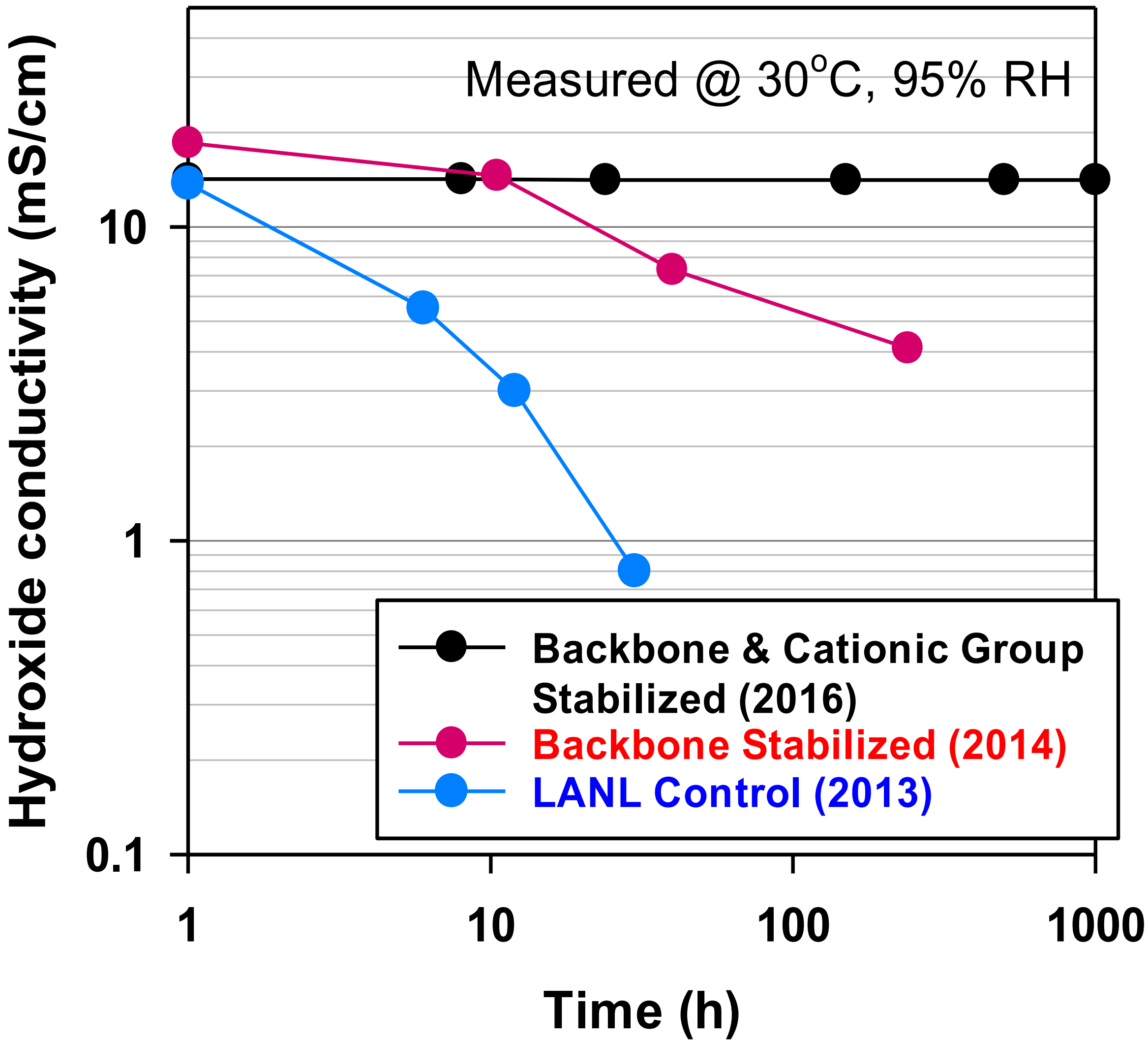
Chung et al. *J. Phys. Chem. Lett.* 2016, 7(22), 4464-4469.

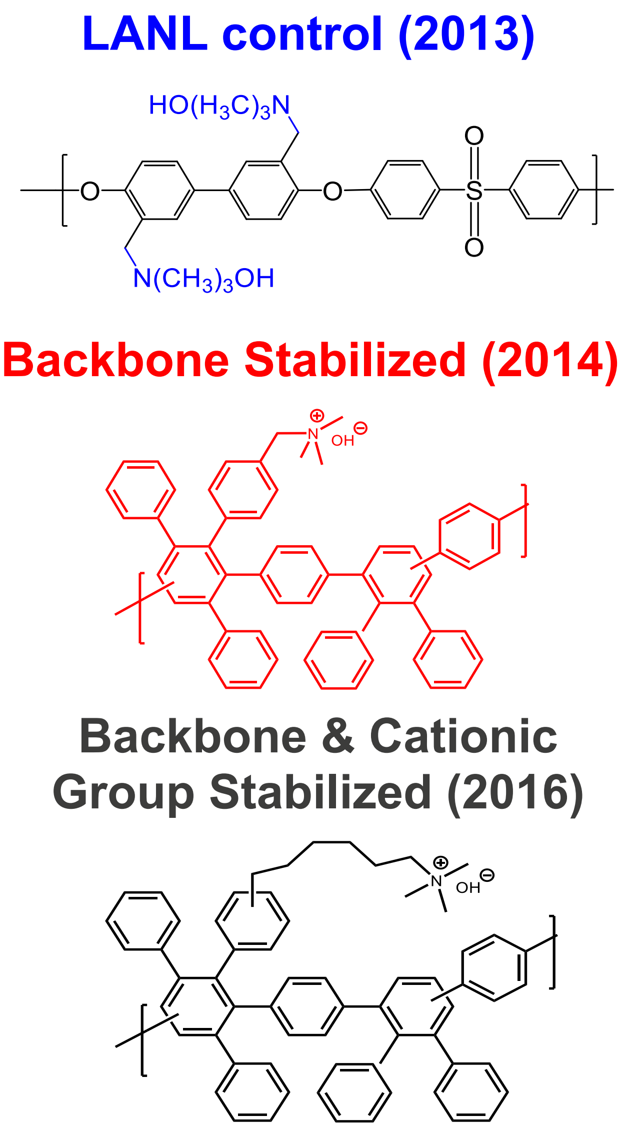




Identified performance and durability limiting factors (remove benzyl ammonium groups) of AMFC needed to reproducibly reach 1 W/ cm² peak power density

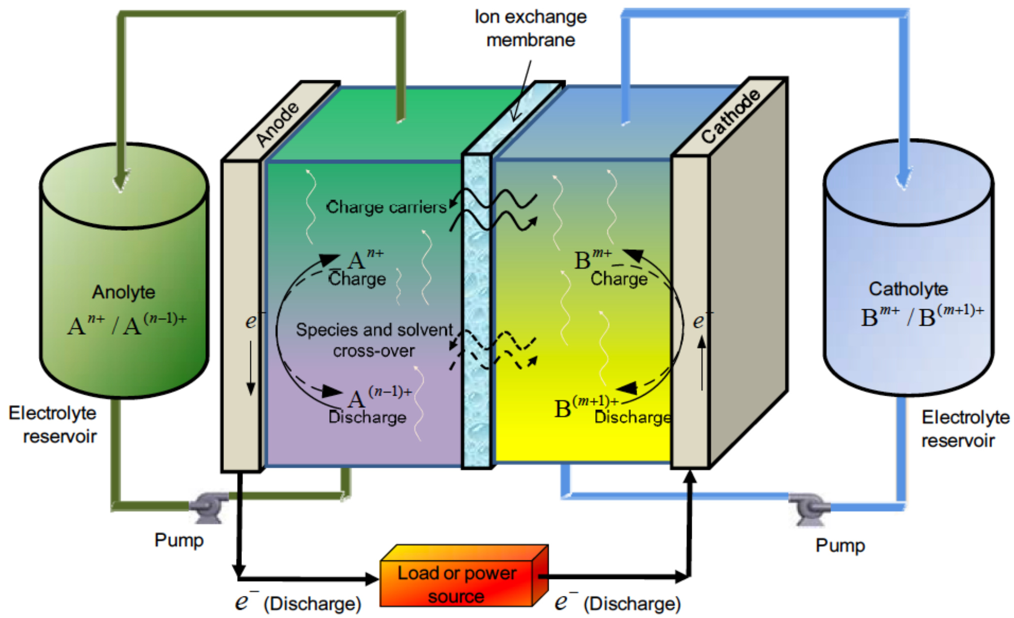
No degradation for backbone and cationic group stabilized AEM after 0.5 M NaOH treatment at 80 °C for over 1000h.





Grid Scale Energy Storage using Flow Cells (Redox Flow Batteries)

Need to maintain a robust and resilient electricity delivery system that incorporates significant intermittent renewable sources



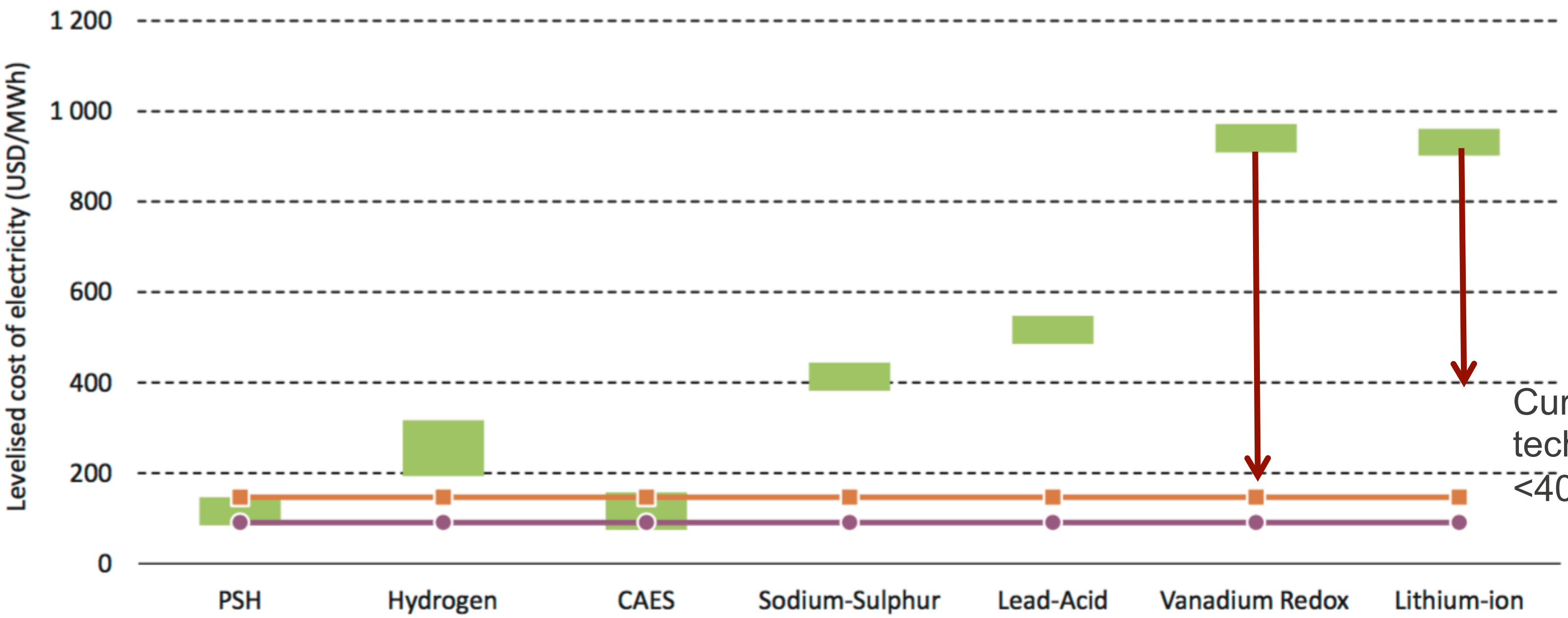
- Flow cells are uniquely scalable unlike other battery technology. Energy is determined by amount of electrolyte and size of tanks. Power is controlled by size of stack.
- Potential for high durability. Electrodes do not store energy or undergo chemical change
- Potential for high efficiency (>80% round trip efficiency possible)

State of the art: Vanadium redox flow batteries

$$V^{3+} \leftrightarrow V^{2+}$$

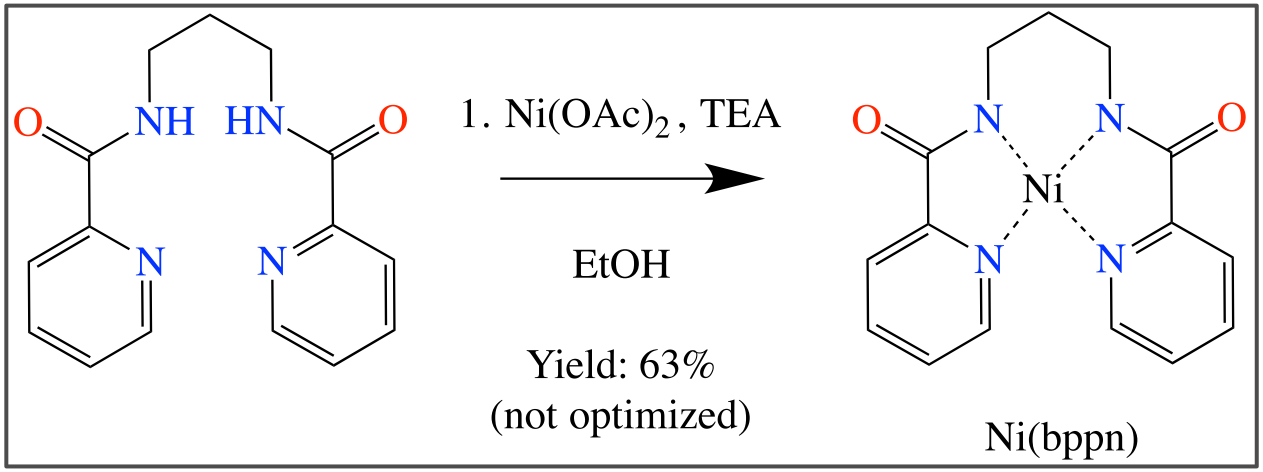
$$VO^{2+} \leftrightarrow VO_2^{+}$$

Limitations due to vanadium costs



Current Li-ion technology <400$/MWh

New Charge Carriers with high potentials and multi-electron redox properties

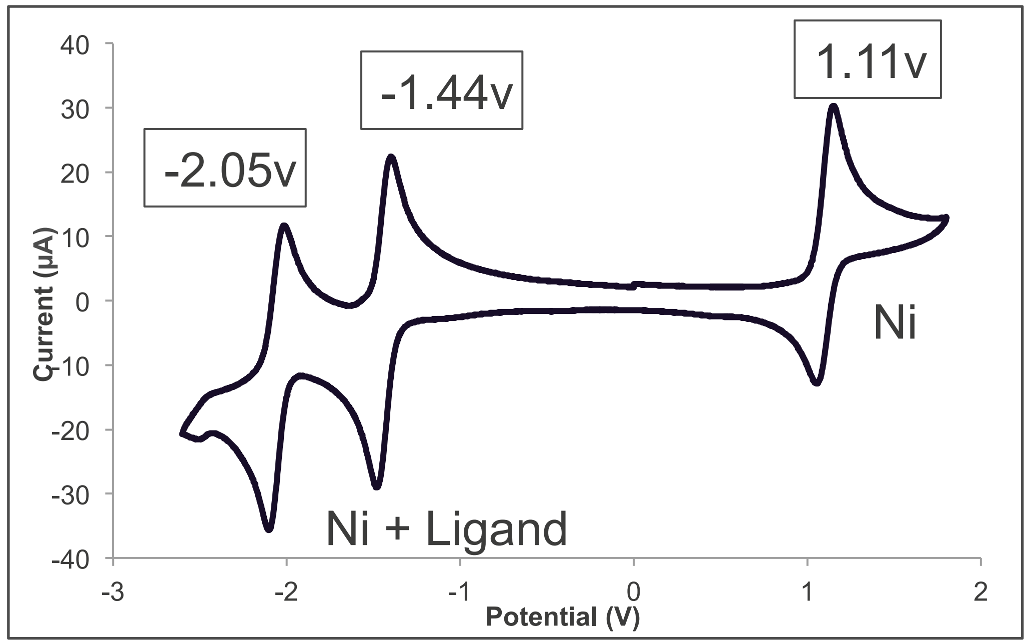


Ligand generated in good yield from inexpensive materials

Complex formation is simple and purification (crystallization) occurs in EtOH

CV in MeCN and TEABF shows greater than 3V potential is possible for the cell (ignoring overpotential and ohmics);
2nd stored electron is 2.5v

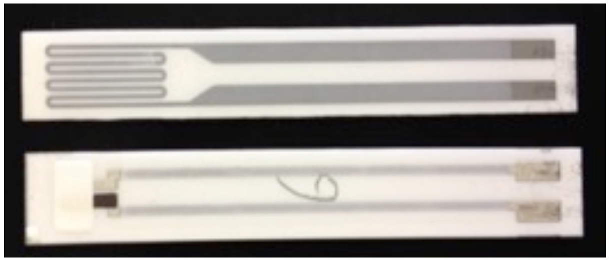
Could be used as catholyte and anolyte, eliminating need for expensive membranes

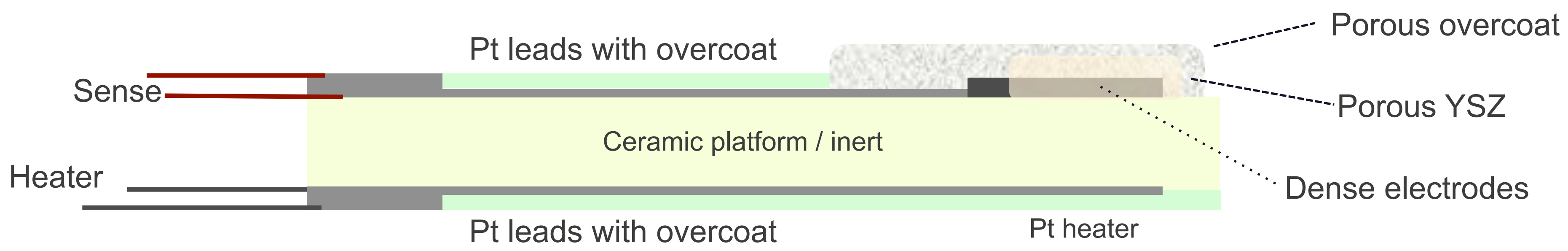


DOE VTO-sponsored electrochemical sensor project

Advantages:

- Significantly less complex sensor design
- Similar form factor as auto oxygen sensor
- No fugitive spacers needed / air reference channel and internal oxygen pumping cells not required
- Faster turn-on during start-up / protection against water induced thermal shock
- No pumping/diffusional channels to become blocked





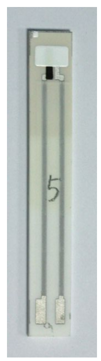
Electrochemical Sensors: NO_x/NH_3 Sensors for Vehicle applications

Problem: NO_x sensors that meet stringent vehicle requirements are not widely available:

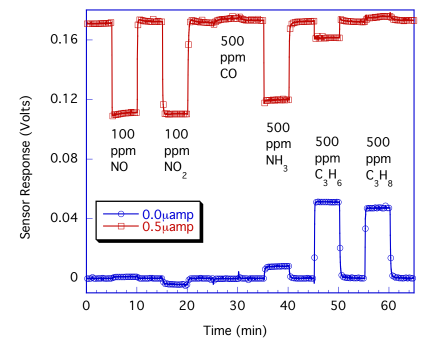
VDO/ NGK UniNOx Sensor ZrO2 -based multilayer sensor with 3 oxygen pumps Complex expensive sensor is the only commercial product available today	DOE-EERE-VT Funding LANL to commercialize NO_X/NH_3 sensors Collaboration with ORNL National Transportation Research Center

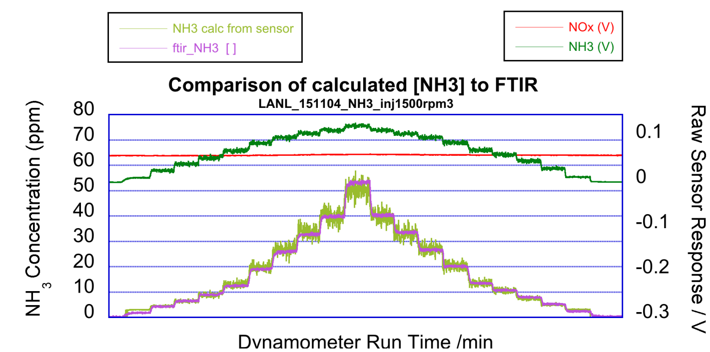
Transform LANL patented mixed-potential technology into commercial platform

Transform bulk LANL sensors to commercially manufacturable automotive platform.



Preserving unique sensor characteristics and excellent response sensitivity/ selectivity/stability





Sensor tracks FTIR NH_3 concentration

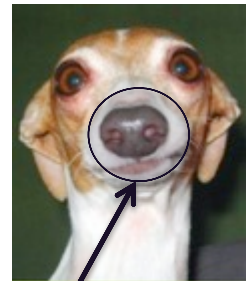
Current Status:

- Successfully incorporated LANL technology into ESL manufactured commercial platform and demonstrated in an engine dynamometer.
- Continental is evaluating LANL technology with assistance from DOE Tech to Market funding (matching).

Exploiting cross-sensitivity and stability of mixed-potential sensors: Design principles of olfaction used for decomposition of gas mixtures

In biological systems, cross-selective receptors work together to decode odors and odor mixtures.

Use Bayesian Inference models from multiple sensors to quantitatively de-convolute the concentration of each species of interest; Collaboration with Morozov Group, Rutgers University

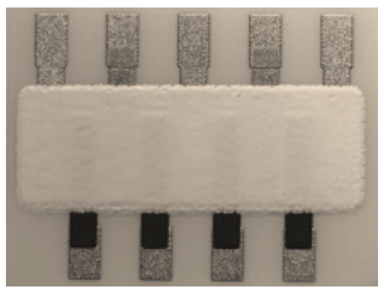


Still the best?

LDRD
innovation for our nation

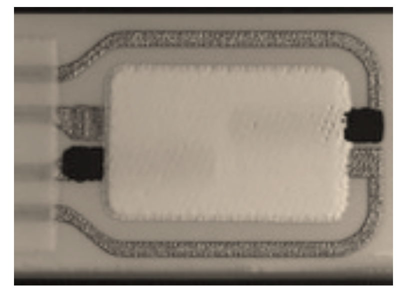
Flexible device to refine models

Each electrode is at a different temperature than the adjacent



Stick sensor to test models in engine exhaust

4 electrode, fixed T device for engine testing at NRTC

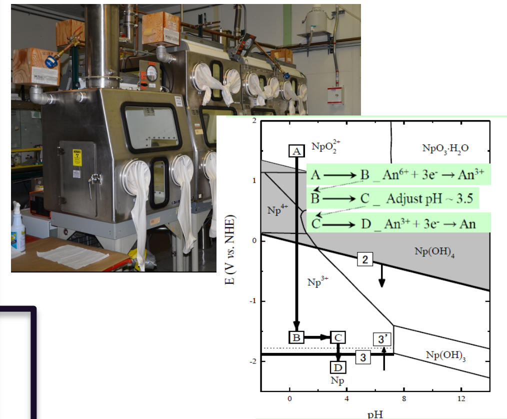


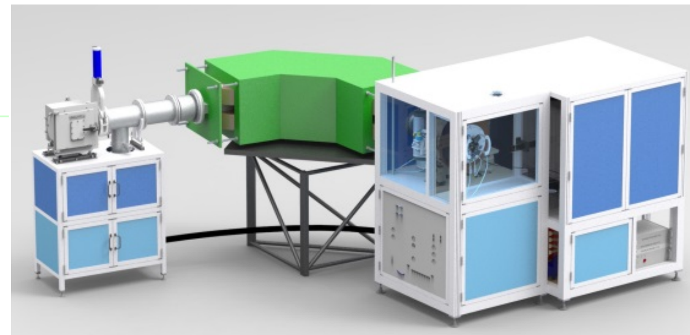
Results

- Model estimation of [C_3H_8], [NH_3], and [NO_2] with respect to [NO] in an extensive set of mixtures with max error 14.0% and average error of 1.8%.
- Predictions of each gas in 2- and 3-gas mixtures with 3.2% average error.
- Model can identify minimum number of sensors required for the application.
- Model is capable of predicting gas concentrations in complex mixtures with high accuracy.

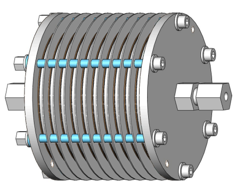
MPA-11 Impact on Future Stockpile Needs

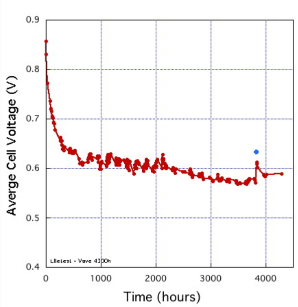
^{242}Pu Production to Support Pu Science and Engineering

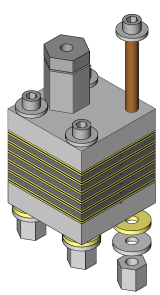




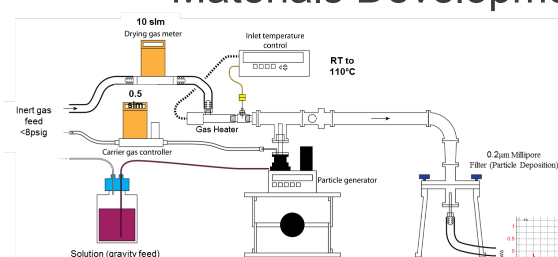
Materials and technologies for stockpile modernization

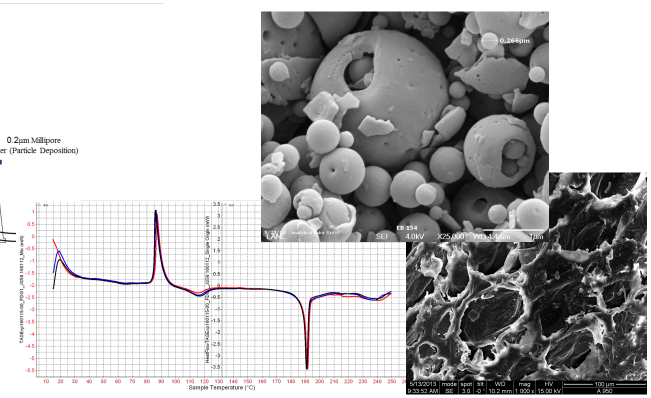






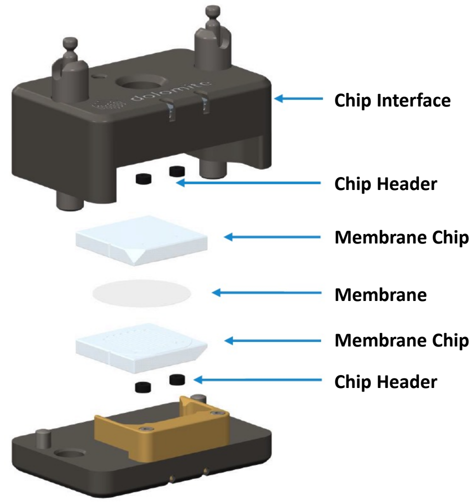
Materials Development and Manufacturing

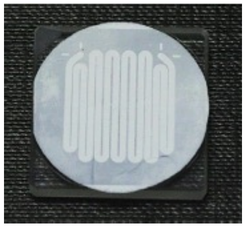


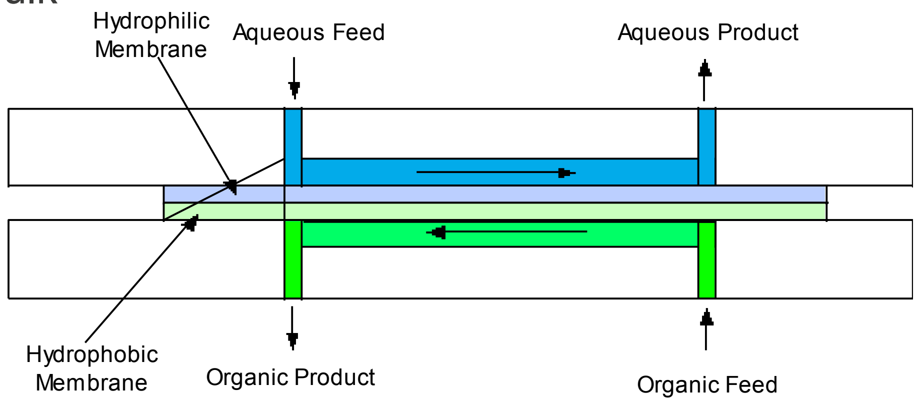


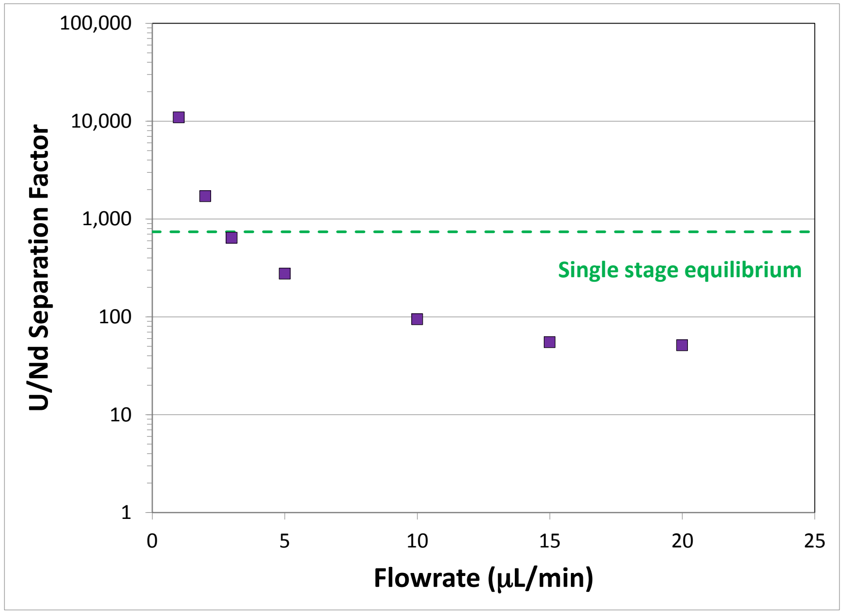
Advanced Actinide Separations

- **Microfluidics for actinide recovery and recycle**
  - Liquid-liquid extraction processes
  - Provides rapid mass transfer and heat transfer rates
  - Reduction in-process volumes,
    - decreases criticality concerns
    - Membranes provide excellent phase separation
  - Scalability: Recycle of exotic isotopes (^{242}Pu), up to bulk





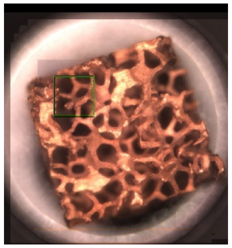




Separation factors of U(IV) from Nd (III) of more than 50 - 10,000 in a single contact!

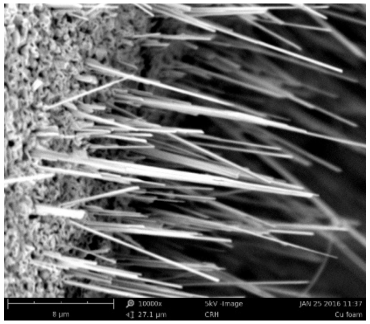
Materials Synthesis for National Security Needs

- **Thin film synthesis and chemistry**
  - PAD films of PuO_2, UO_2, and U_3O_8 films and associated chemistry for LEP, Surety, LDRD, AWE, DHS, NCT, and LLNL projects
  - Films provide low activity source of important nuclear materials for compatibility and reactivity studies in low level radiological facilities
- **Development of fluorinated oxide nanowires on porous copper for safe storage of nuclear materials**
  - Goals: hydrophobic, gas permeable, heat resistant filters for Savy cans
  - Approach: grow CuO nanowires on porous copper followed by fluorination
  - Collaboration with Nuclear Process Infrastructure Division (TA-55)



Porous Cu

600°C →



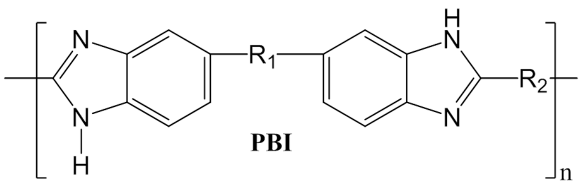
75nm diameter CuO nanowires

Fluorinating agent →

Contact angle > 120° on porous material

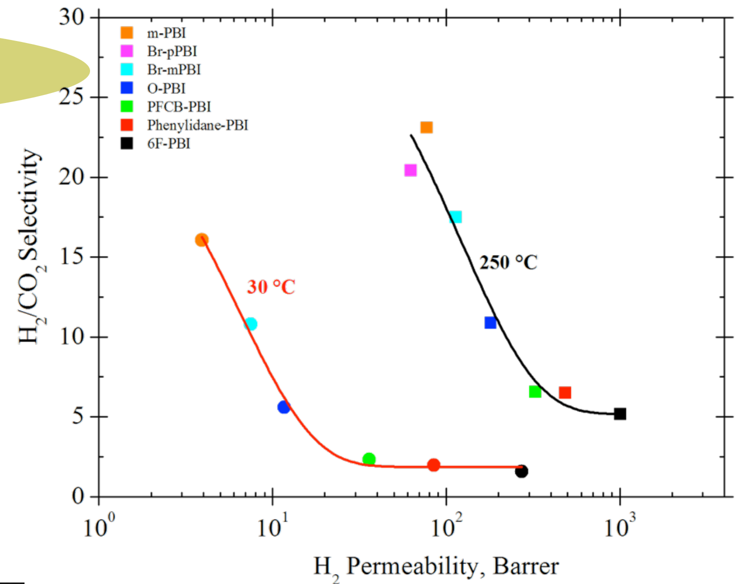
Barrier/Membrane Material Design & Deployment: Carbon Capture and Sequestration

Material Design for Controlling Small Molecule Transport and Separations

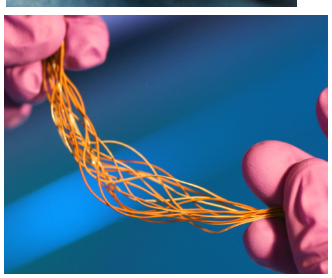


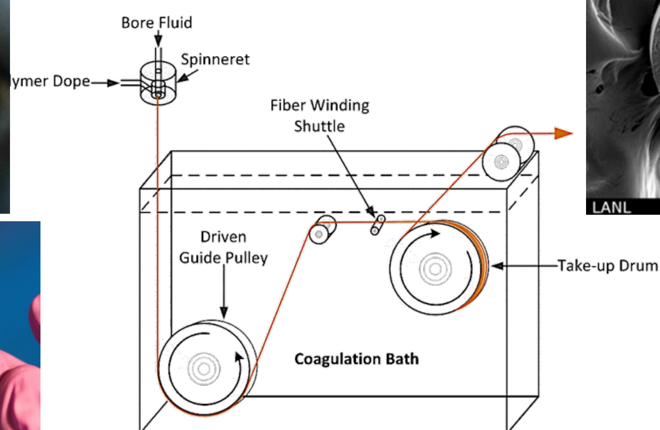
R_1, R_2: Bulky, large and high mobility functional groups ⇒
- Chain packing Efficiency
- Enhnace Fractional Free Volume
- High localized mobility
- Rigid and bent configurations

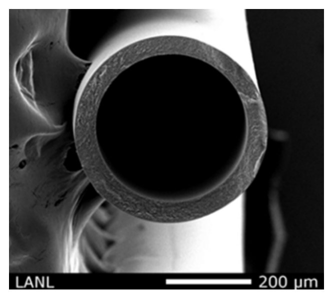
Material Design to Tailor Structure-Property Relationships



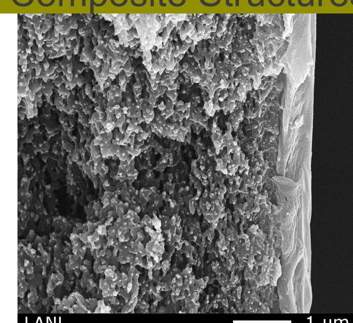
Materials Processing to Develop an Industrially Scalable Product Platform



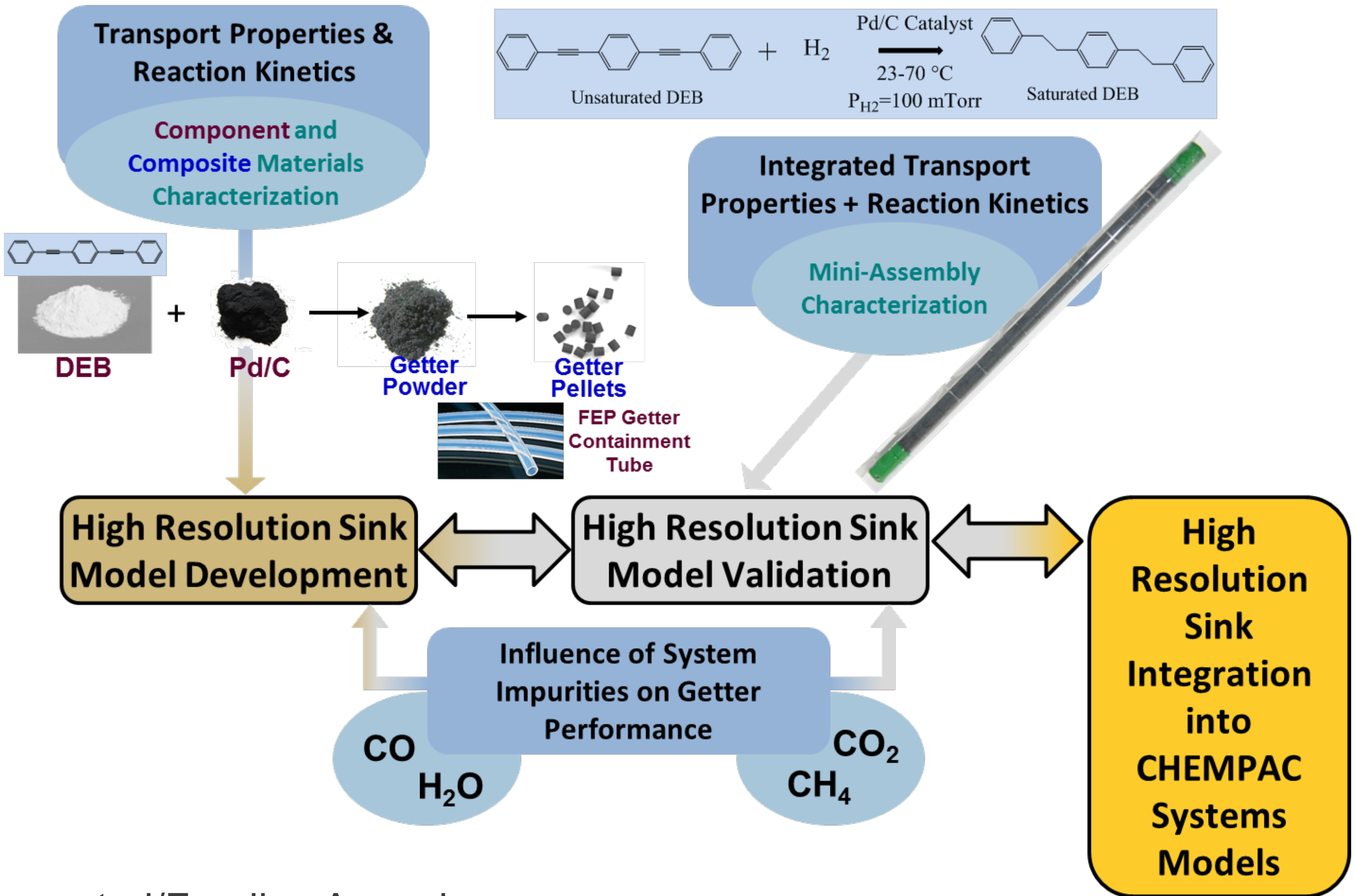




Morphology Optimization to Develop High Performance Composite Structures



Barrier/Getter/Adhesive/Structural Materials and Platform Characterization & Development for National Security Applications



Programs Supported/Funding Agencies:

B61-12 Life Extension Program
W76 Weapons Program
B61 Legacy Program
Campaign 8 - Enhanced Surveillance Campaign (ESC)

Acoustic Sensors Team:
Radial Vibration Modes of a Piezo-disk

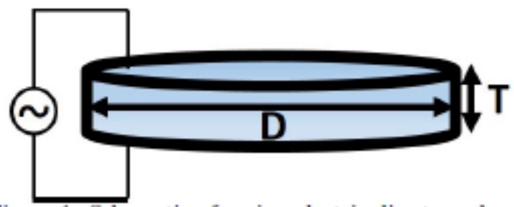
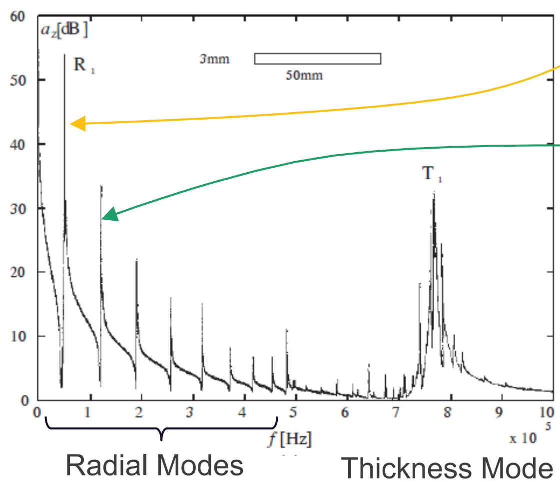
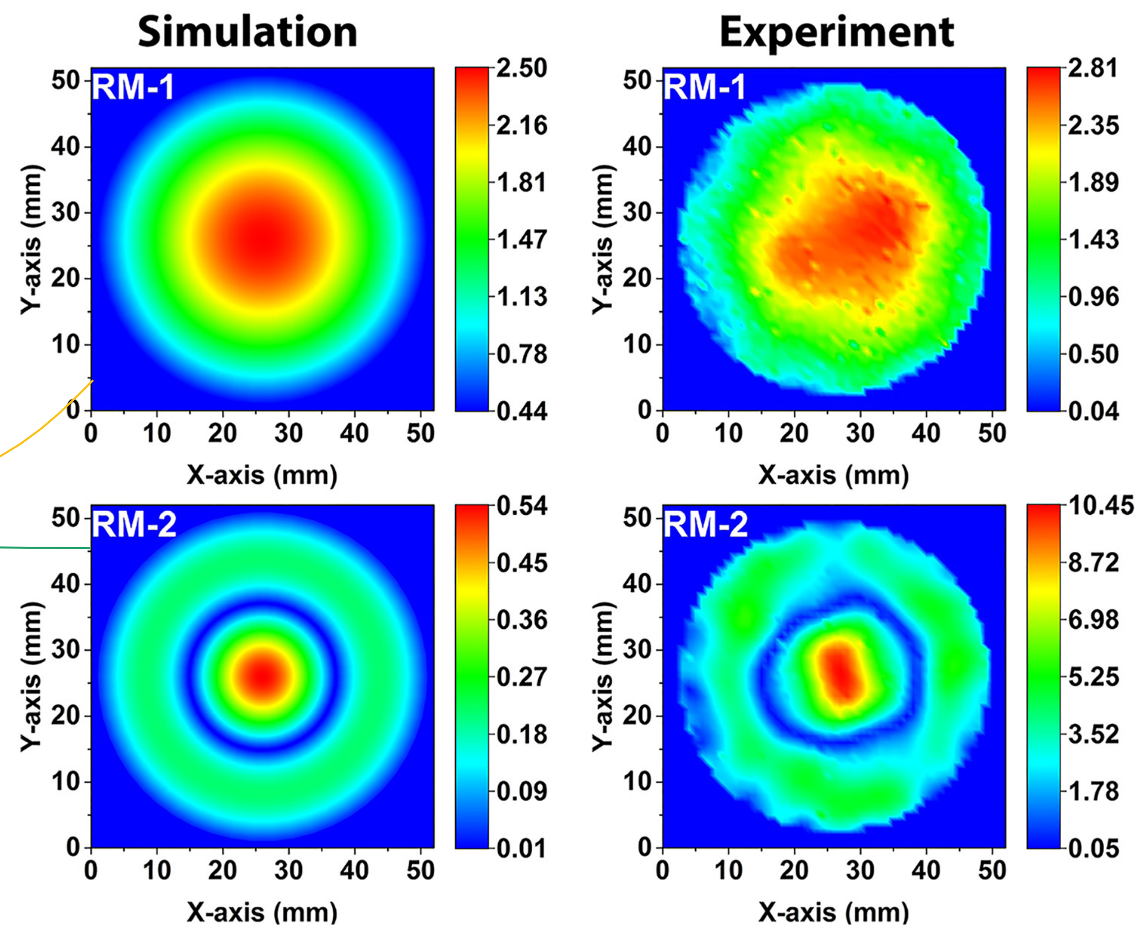


Figure 1: Schematic of a piezoelectric disc transducer.



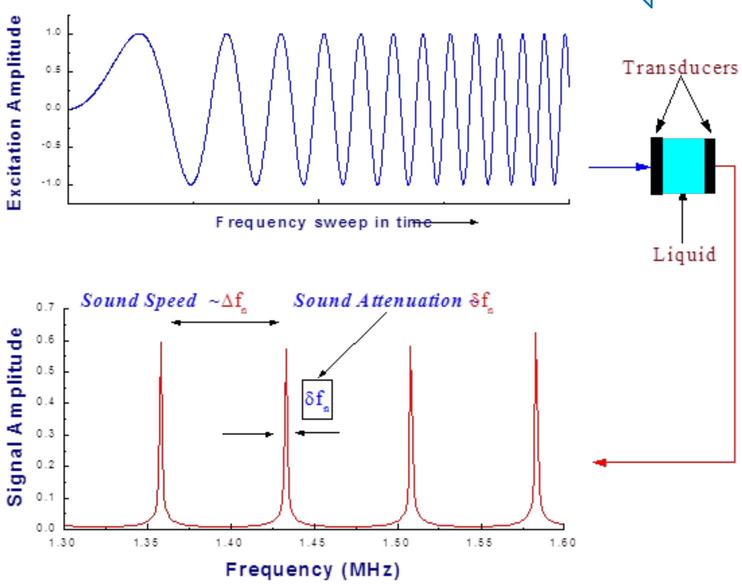
Surface Vibration



Much lower frequencies than the typical thickness mode resonance of a disk

Acoustic Sensor Technologies for Multiphase Metering
POC: Dipen Sinha

SFAI: Swept Frequency Acoustic Interferometry

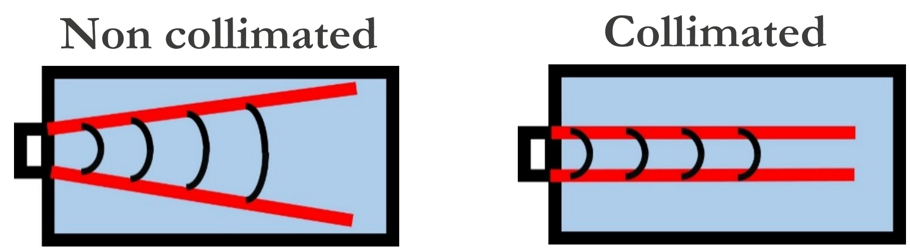


Derive multiple physical properties of fluids from a single, noninvasive measurement

Safire Meter

Low-frequency Ultrasonic Bessel-like Collimated Beam Generation

Why Collimated beam?

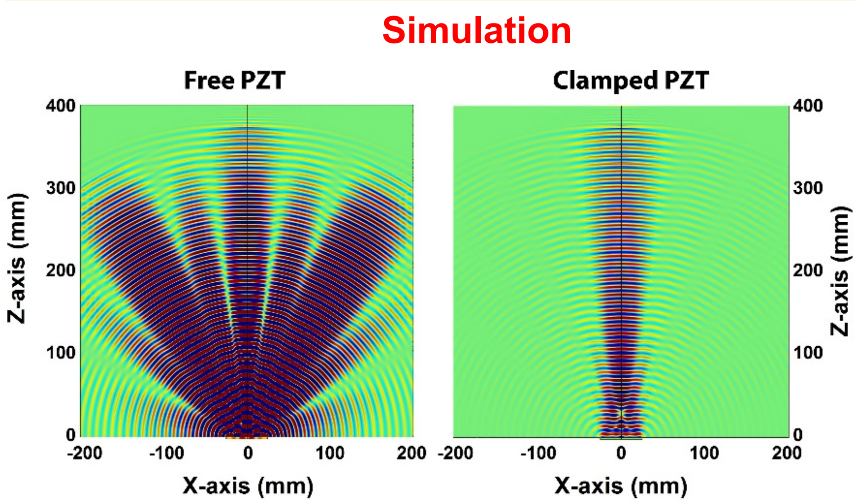


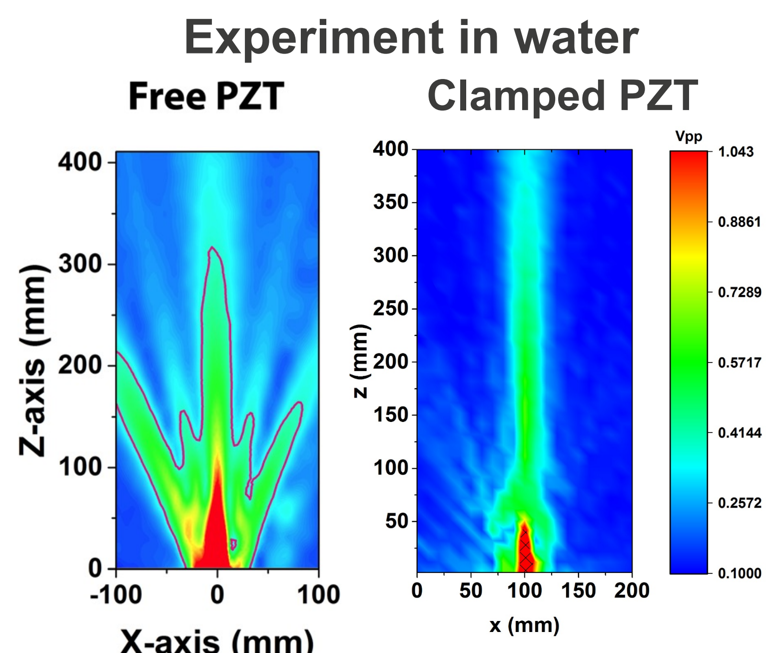
Applications

- ✓ Biomedical Imaging (through skull)
- ✓ Imaging concrete for bore-hole integrity applications
- ✓ Characterizing highly attenuating materials

Conventional approach: Bessel-like patterned piezo-disc to form Bessel pattern on a transducer (fabrication intensive technique)

Our Approach: uses natural vibration pattern of radial modes of piezoelectric disc transducer





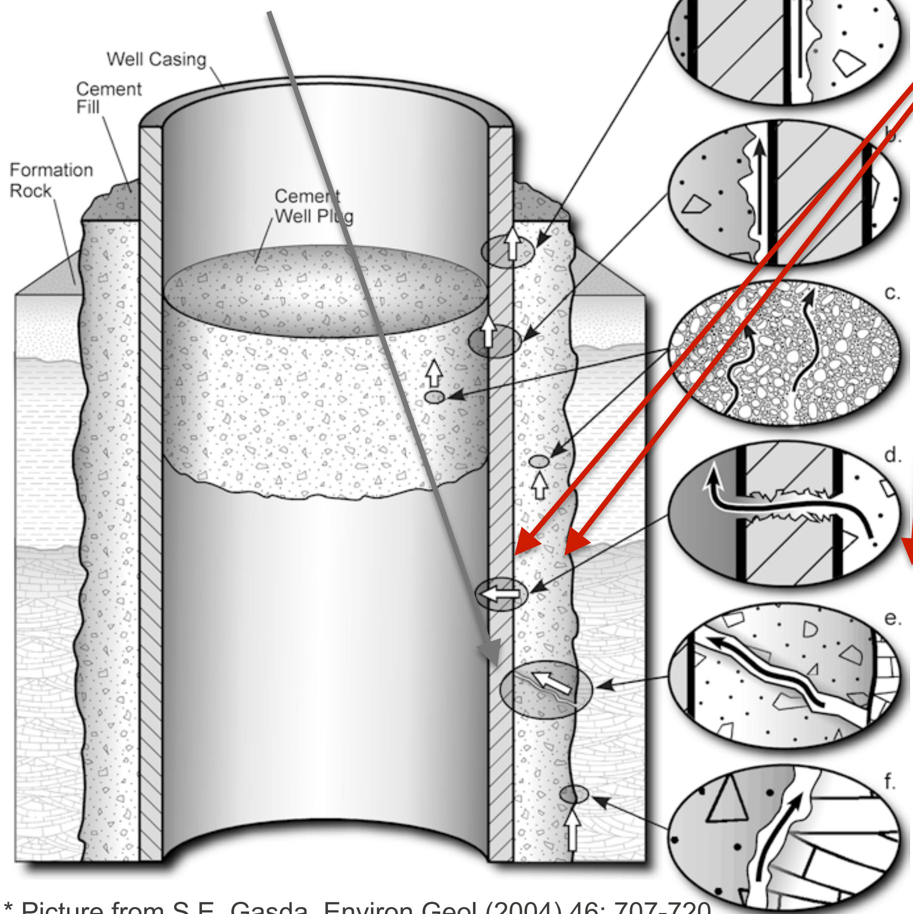
V. Chillara, C. Pantea, and D. Sinha, APL 2017, 064101

SubTer Program: High-Resolution 3D Acoustic Borehole Integrity Monitoring

The Problem: *Defects/fracture detection beyond casing with high resolution.*

Existing ultrasonic tools work well for casing inspection

We plan to extend applicability to: (1) casing-cement interface, (2) cement-formation interface, and (3) out in the formation (up to ~ 3 meters).

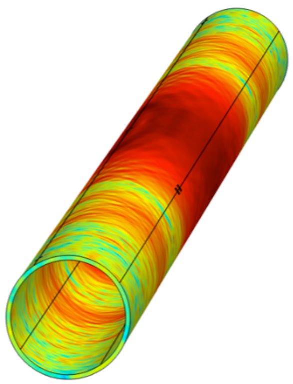


* Picture from S.E. Gasda, Environ Geol (2004) 46: 707-720

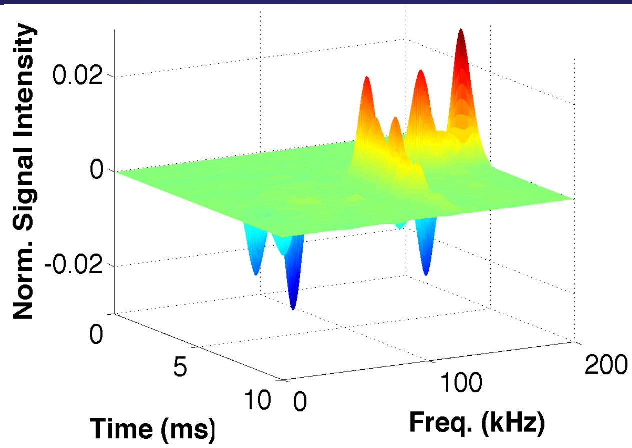
Comparison of existing techniques and the present approach

Method	Frequency (kHz)	Range (m)	Resolution (mm)
Standard borehole sonic probe, e.g. BARS (Borehole Acoustic Reflection Survey)	0.3-8	15	~ 300
Present approach	10-150	~ 3	~ 5
Ultrasonic probe, e.g. UBI (Ultrasonic Borehole Imager)	>250	casing	4-5

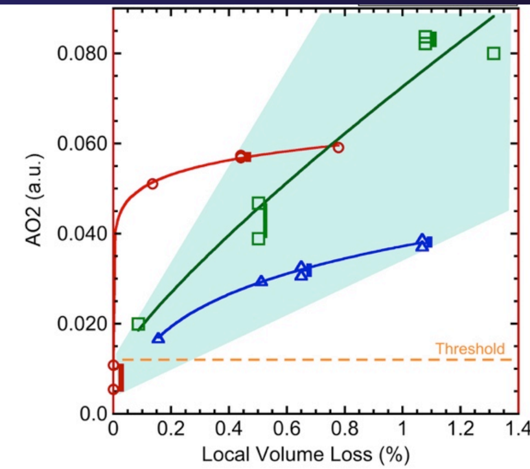
Acoustic Sensors: Acoustic Large Area Monitoring (ALArM) of Extended Mechanical Structures



Simulated Multi-Mode Acoustic Signal Propagation in pipe



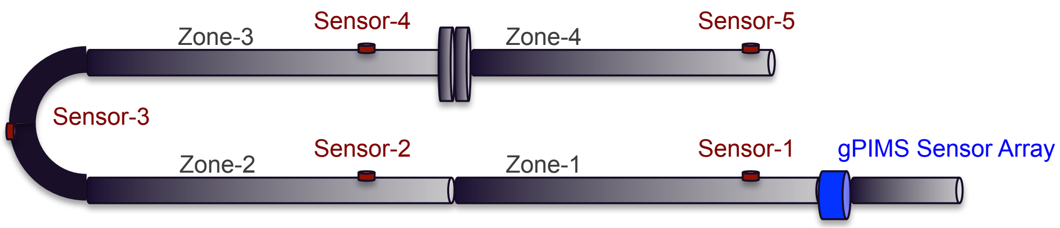
Example of Defect Detection with Freq-Timemixed-domain signal analysis



Detection of Local Vol. Loss of an extended structure, with sensitivity close to 0.1%

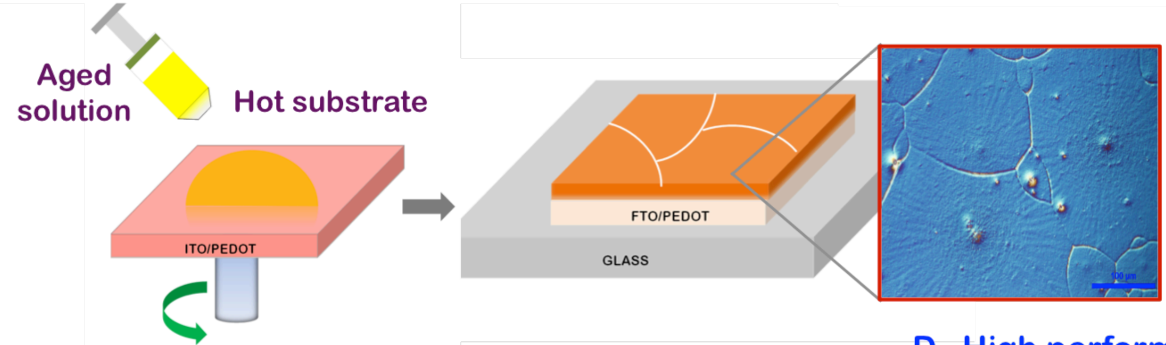
Field Tests in Houston, TX (2015-2016):

- 105'-long, 8"-Dia Sch-40 Steel pipe with 2 elbows, 8 welded joints, and 1 pair of flanges, held on10 stands,
- ALArM system (5 single sensors, spaced 25' over 100').

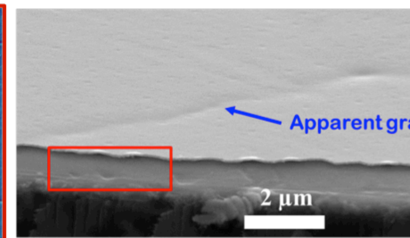


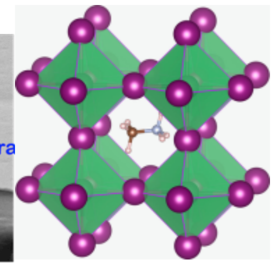
Hybrid Perovskites for Photovoltaic and Detector Applications
POC: Aditya Mohite, MPA-11

A Hot-casting method & optical image of large grains



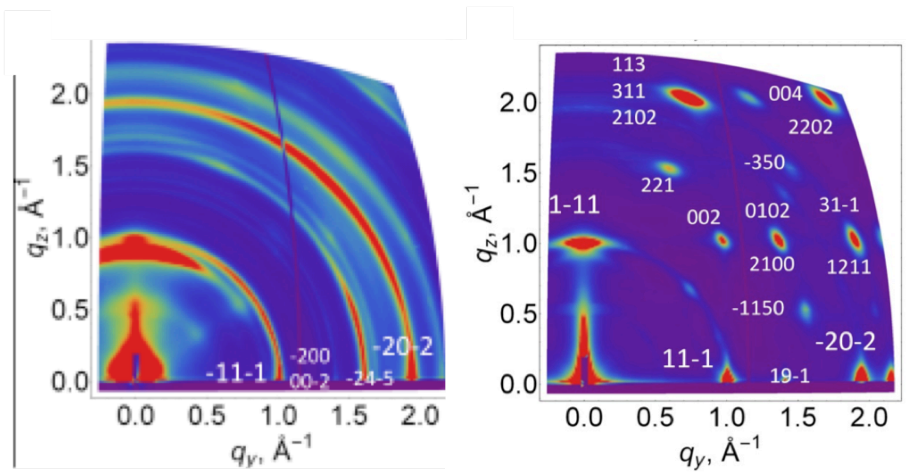
B Cross-sectional SEM shows bulk film



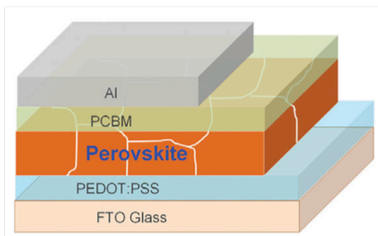


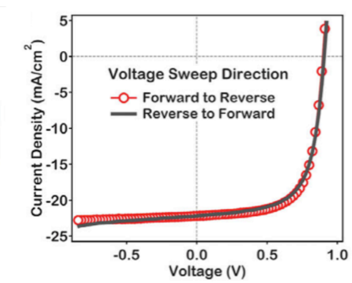
ABX_3

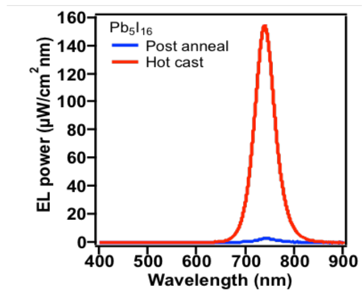
C Comparison of GIWAX of as-cast and hot-cast films



D High performance devices







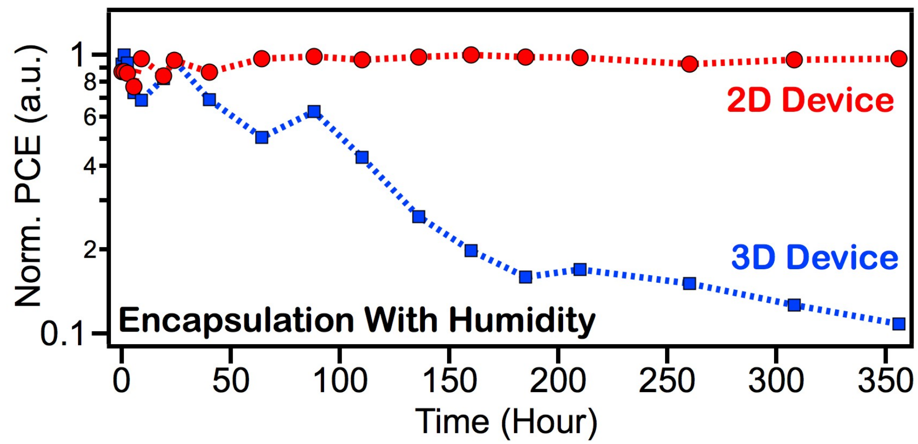
First in the world to grow large grain-size thin-films of hybrid perovskites:
Power conv. efficiency ~ 18%; Nie et al Science et al (2015)

2D vs 3D hybrid perovskite optoelectronics

High efficiency optoelectronic devices using 2D perovskites

>12% efficient solar cells

Intrinsically stable >2000hrs operating solar cells, Tsai/Nie, *Nature* 2016



3D: $MAPbI_3$ 2D: $(BA)_2(MAPb_4I_{13})$

***Efficient intrinsic process of exciton dissociation for n≥3*, Blancon, *Science* 2017**

Layer edge states drive exciton dissociation
Results in longer lived free carriers leading to stronger PL