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Electrochemical Separation, Pumping, and Storage of Hydrogen or Oxygen into Nanocapillaries Via High Pressure MEA Seals

Mitchell L. Solomon, Philip Cox, Nicholas R. Schwartz, Gregory E. Chester, and Justin J. Hill

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UNITED STATES AIR FORCE

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14. ABSTRACT

High-density storage of gases remains a major technological hurdle for many fields. The U.S. Department of Energy (DOE), for example, reduced their hydrogen storage targets for automotive applications due to the inability of technologies to reach the system-level targets. Without significant improvements in hydrogen storage density, hydrogen as a transportation fuel remains unfeasible. In other fields, the low volumetric and gravimetric storage densities of oxygen gas cylinders can be cumbersome or prohibitively expensive for applications like terrestrial and marine breathing apparatus' or manned space exploration. Emerging technologies, such as sorbents and chemical complexes, show potential for gas storage. However, the ability to achieve application-specific gas delivery rates and high storage densities, while operating reversibly at ambient temperature, remains elusive.

In contrast, it may be possible to achieve high gas storage densities and potentially high gas delivery rates using nanocapillaries when used in conjunction with a membrane electrode assembly (MEA). Hoop stress calculations show that the pressure tolerances of cylinders are inversely proportional to the radius. Indeed, glass microcapillaries have already theoretically and experimentally demonstrated the capacity to achieve DOE hydrogen storage targets at a materials-level. This technology can be further improved by reducing the capillary radius to the nanoscale; however, the capping and pressurization of the gas in micro- or nanocapillaries remains problematic.

Presented here is the fabrication of nanocapillary arrays capped by an MEA for highly reversible storage of gases with the potential for high rate pumping and high-density storage. Very high aspect ratio and densely packed nanocapillary arrays are produced through aluminum anodization. The nanocapillary arrays are capped with either a PEM or an alkaline (anion) exchange membrane (AEM) complete with catalyst nanoparticles on either side of the membrane to form an MEA. This MEA is used to provide controllable electrochemical pumping of gas species into and out of the nanocapillaries. The MEA also serves as a high pressure seal. A theoretical discussion of the potential volumetric and gravimetric storage densities in nanocapillary arrays will be presented together with experimental results of electrochemical gas compression into lab-scale devices. The evaluation of both commercial catalyst materials and fabricated nanoparticle catalysts (<10 nm) for gas pumping will be discussed. A discussion of the electrochemistry within nanocapillaries compared to planar MEAs will be given including the charge transport/transfer processes. The potential failure mechanisms and the technical obstacles to the implementation of our electrochemical membrane approach, together with the current state of the technology and overall storage capacities, will be presented.

15. SUBJECT TERMS
Nanocapillaries, templates, hydrogen storage, oxygen storage, electrochemical self-assembly, electrochemical gas compression, nanotechnology, carbon nanotube, nanoparticle, membrane electrode assembly

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October 14, 2015

228th ECS Meeting, Phoenix AZ

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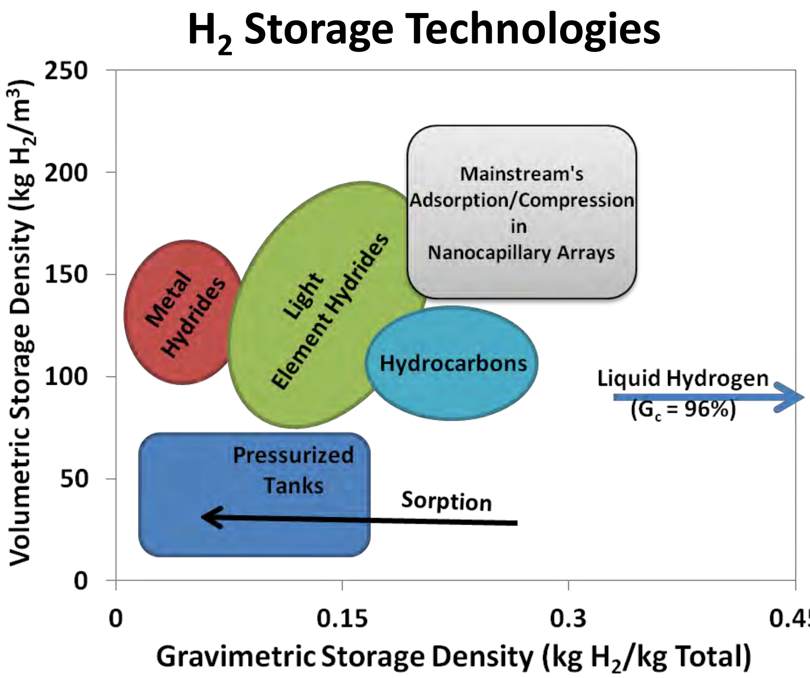
Solutions Through Advanced Technology® MAINSTREAM ENGINEERING

- **Electrochemical self-assembly of alumina nanocapillary arrays**
  - ***Provides <u>segregated</u> high pressure vessel (30,000 psi = 2x DoE H_2 targets)***
- **Integrate CNT into and cap nanocapillary with a polymer**
  - ***Adds hoop strength and sealing and reversible gaseous pumping***
- **Use ion exchange material as polymer and convert cap to a MEA**
  - ***Both seals the nanocapillaries and allows for electrochemical gas compression***

Gas Storage Technologies

- **Hydrogen Fuel Source**
  - Clean
  - Abundant
  - Highest Specific Energy

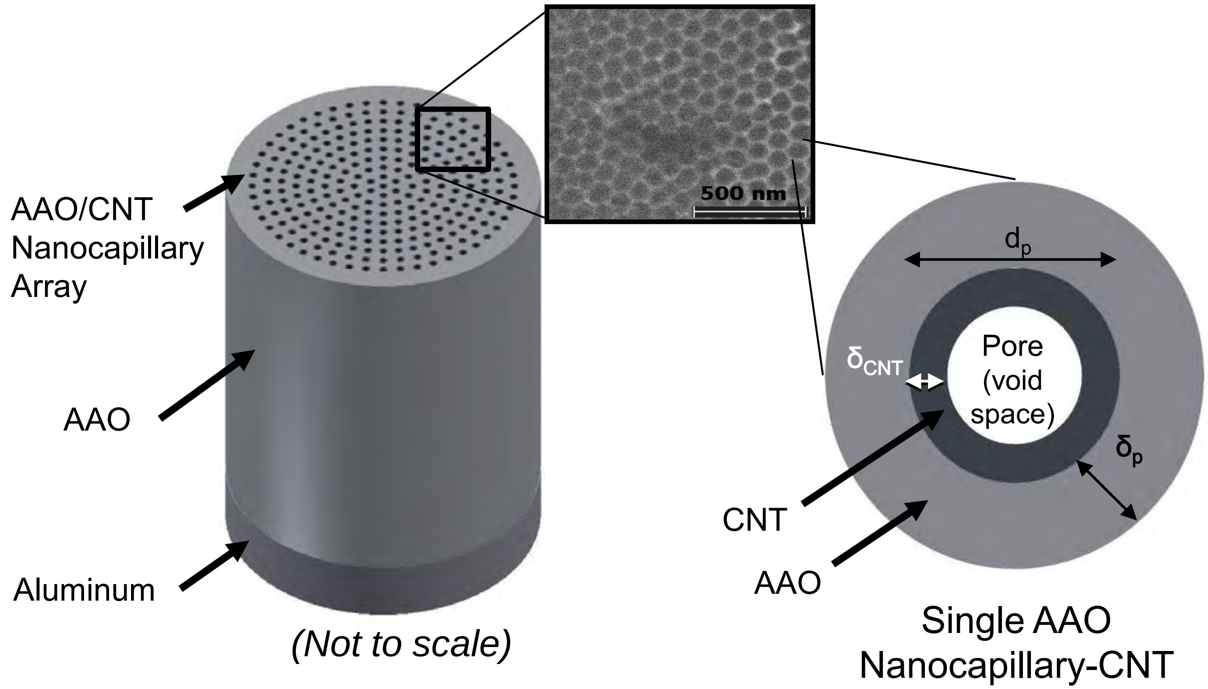
- **Technological Hurdle: Storage Density**
  - Hydrogen – Volumetric Energy Storage for automotive applications
    - DoE Targets for Automotive H2 Storage for 2020*
      - G_c = 1.8 kWh/kg (5.5 wt% hydrogen)
      - V_c =1.3 kWh/L (40 g-hydrogen/L)
  - Oxygen – Gravimetric Energy Storage
    - Mobile, personal oxygen supply
      - Aerospace, SCUBA, First Responders



*US Department of Energy, Energy Efficiency and Renewable Energy **2012**.

Nanocapillary Gas Storage

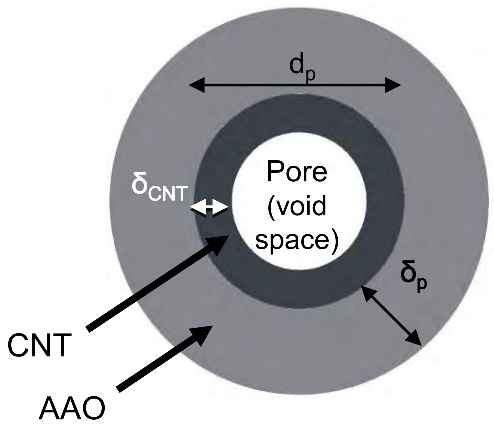
- **Glass Microcapillaries[1-3]**
  - >1,700 bar (24,600 psi)
- **Circumferential Stress**
  - Proportional to
    - Pore radius
    - Wall thickness



Nanocapillary Pores → Larger Pressure Tolerances

[1]N. Zhevago, V. Glebov, *Energy Convers. Manage.* ***2007***, *48, 1554.*
[2]N. Zhevago, E. Denisov, V. Glebov, *Int. J. Hydrogen Energy* ***2010***, *35, 169.*
[3]N. Zhevago, A. Chabak, E. Denisov, V. Glebov, S. Korobtsev, *Int. J. Hydrogen Energy* ***2013***, *38, 6694.*

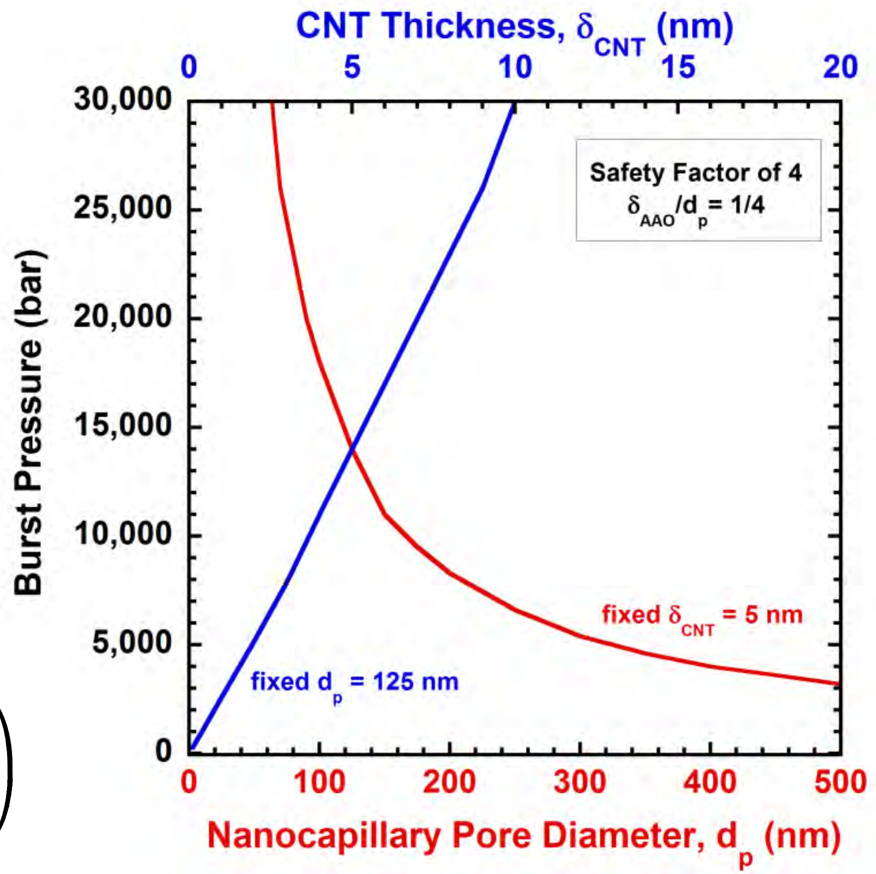
Theoretical Pressure Tolerances of Nanocapillaries



Single AAO Nanocapillary-CNT

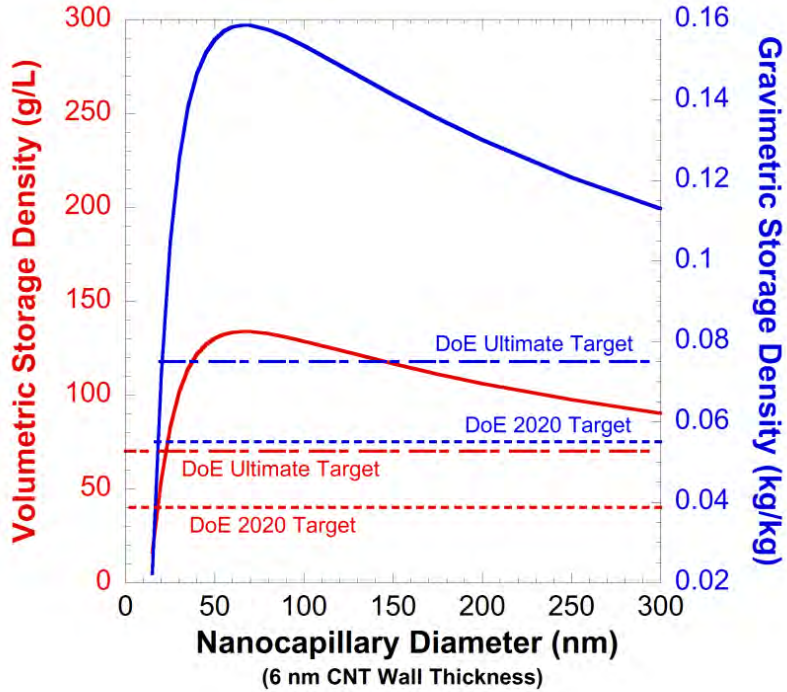
(Not to scale)

$$P_{\text{burst}} = \sigma_{nt} \frac{2\delta_{nt}}{d_{nt}} \left(1 + \frac{E_p}{E_{nt}} \frac{\delta_p}{\delta_{nt}} \left(\frac{d_{nt}}{d_p} \right)^2 \right)$$

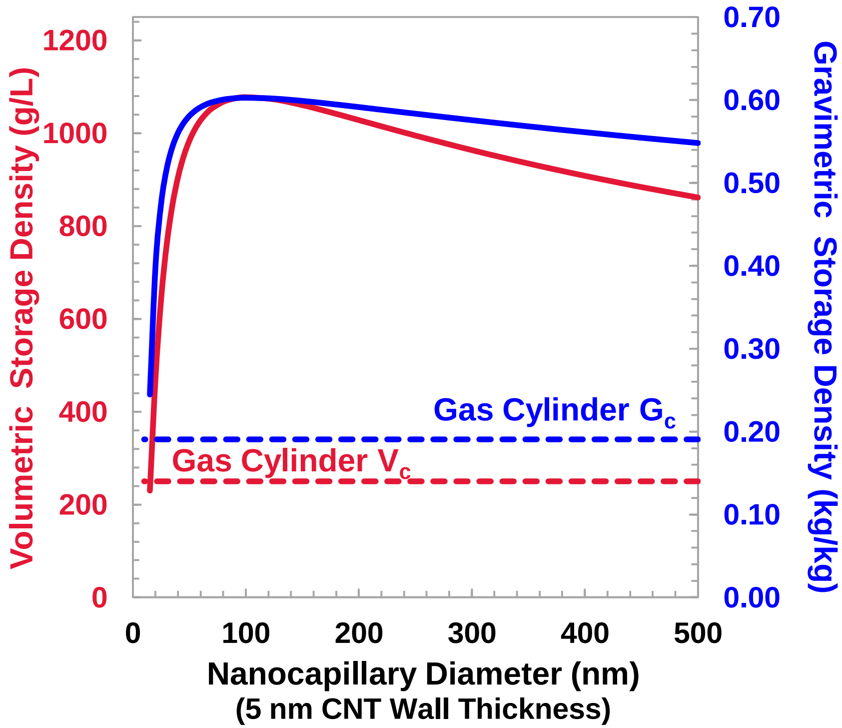


Theoretical Gas Storage Densities

Hydrogen



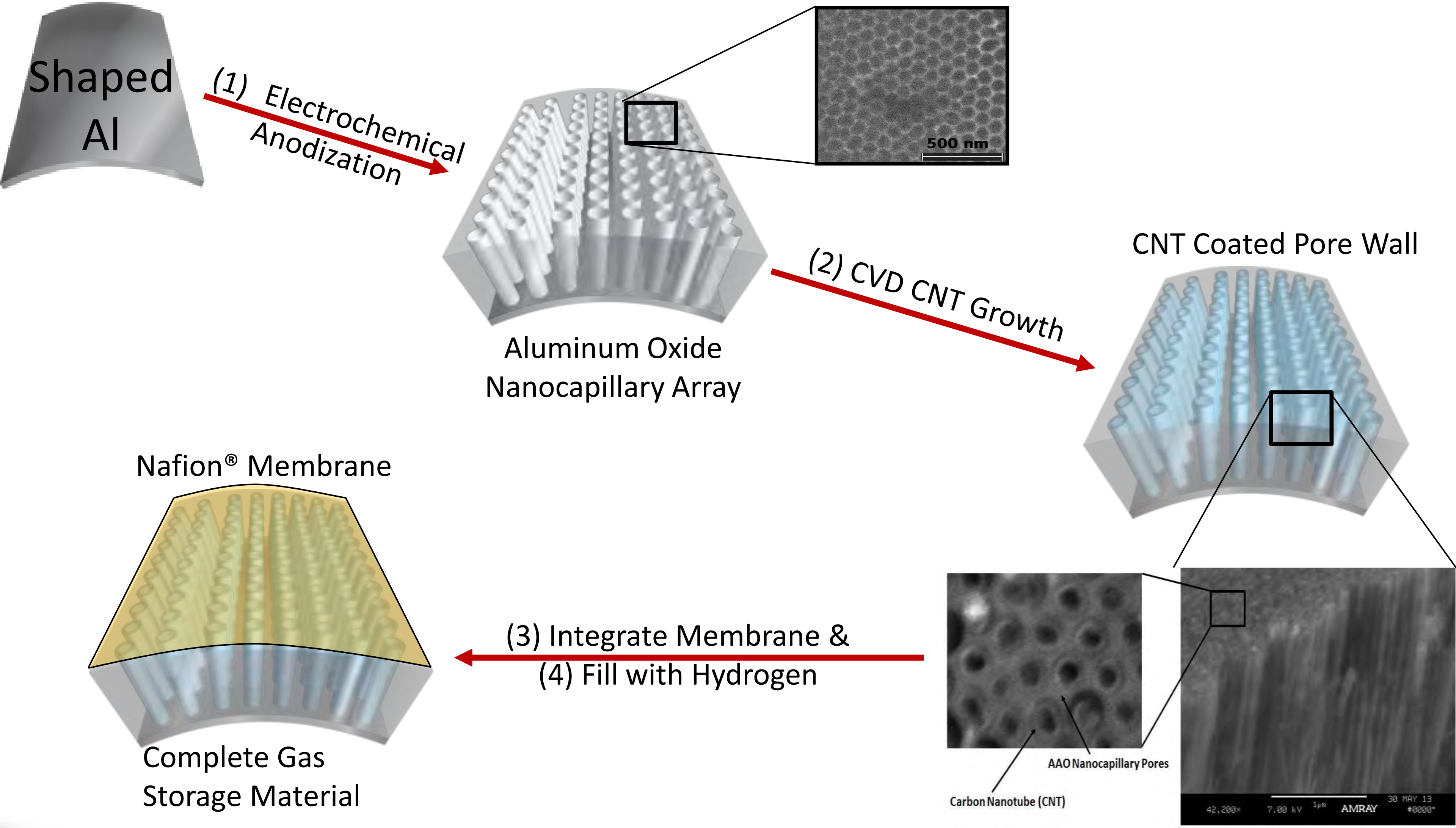
Oxygen



Exceeds Ultimate DOE Targets by 91% for V_c and 111% for G_c

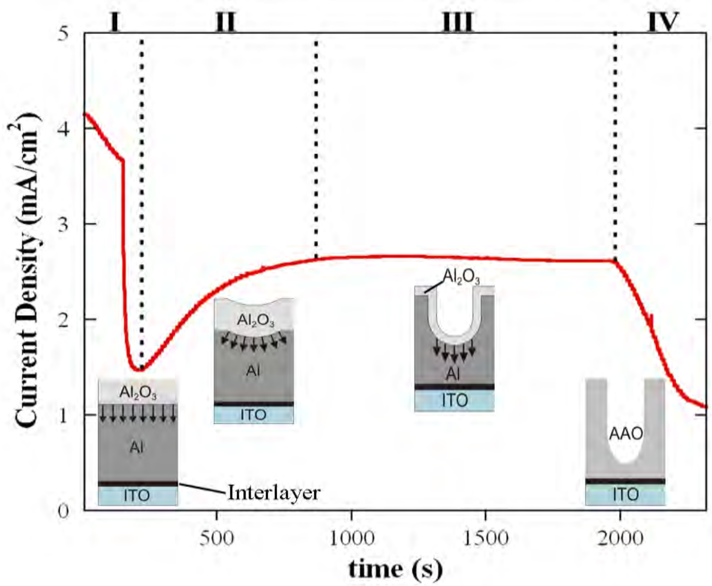
Exceeds Conventional Gas Cylinders 3-fold

Templated Nanocapillary Fabrication

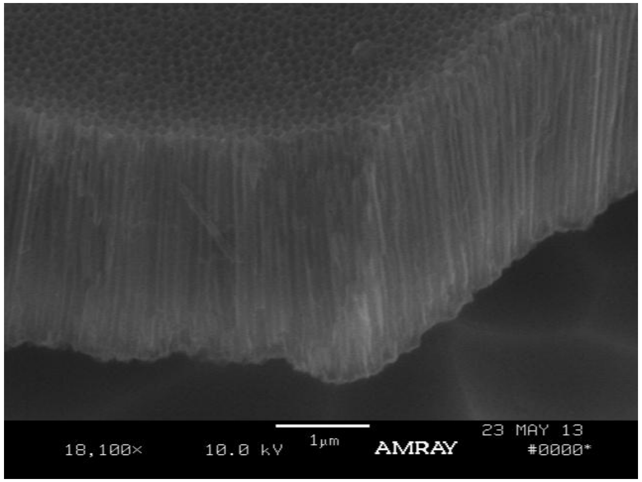


AAO Growth and CNT CVD

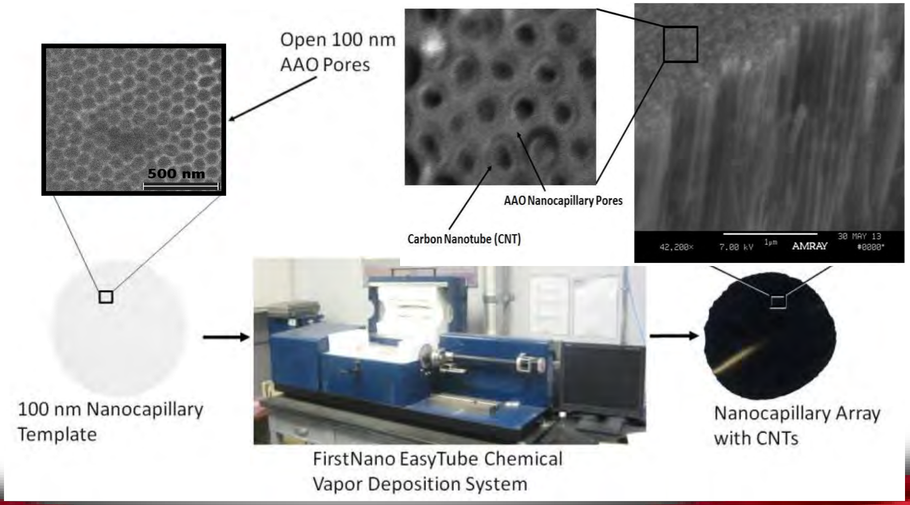
Electrochemical self-assembly of AAO nanocapillaries

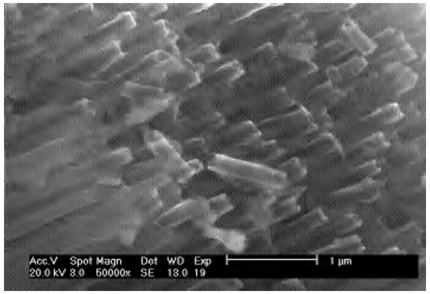


Hill, J.J. et. al., J. Electrochem. Soc. 2011

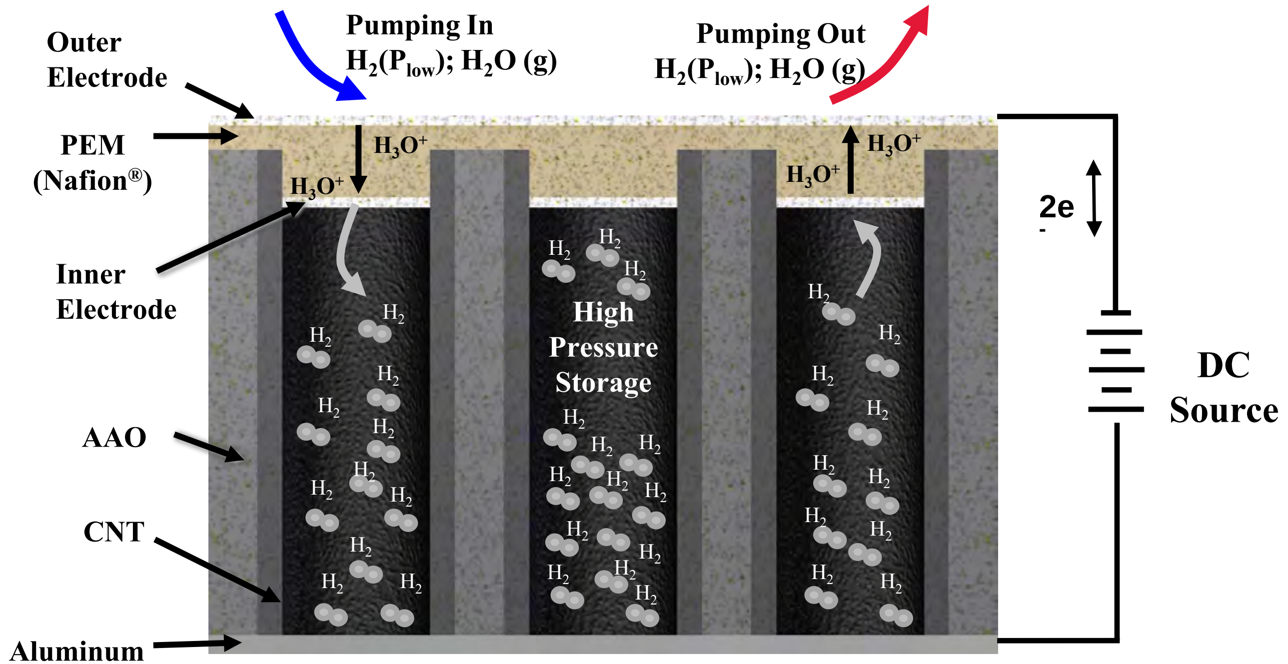


Integration of CNT as current carrier





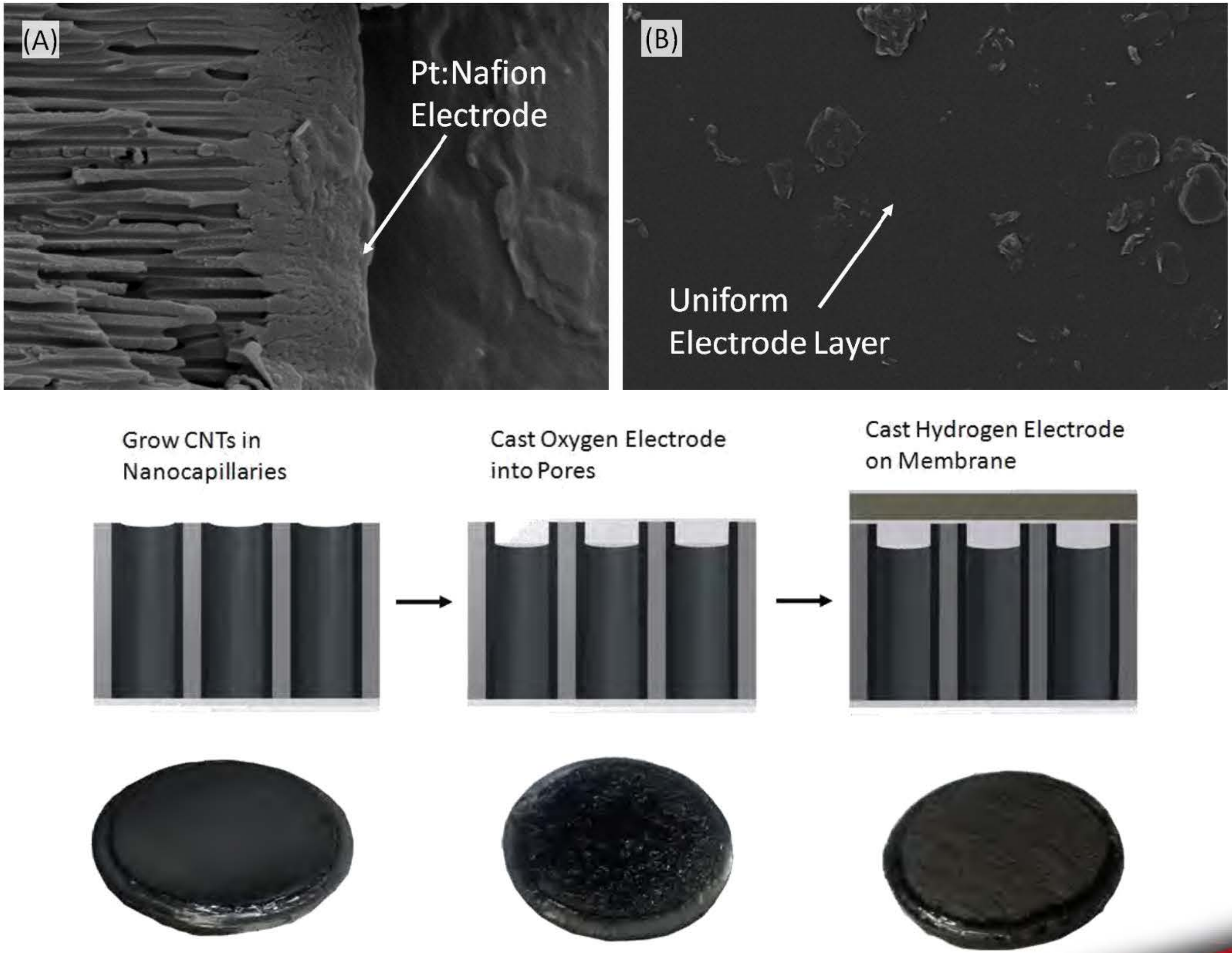
Electrochemical Pumping



Hydrogen Pumping $$H_2 \underset{Pt}{\overset{Pt}{\rightleftharpoons}} 2H^+ + 2e^-$$

Oxygen Pumping $$2H_2O \underset{Pt}{\overset{IrO_2}{\rightleftharpoons}} O_2 + 4H^+ + 4e^-$$

Assembly of the MEA/Cap



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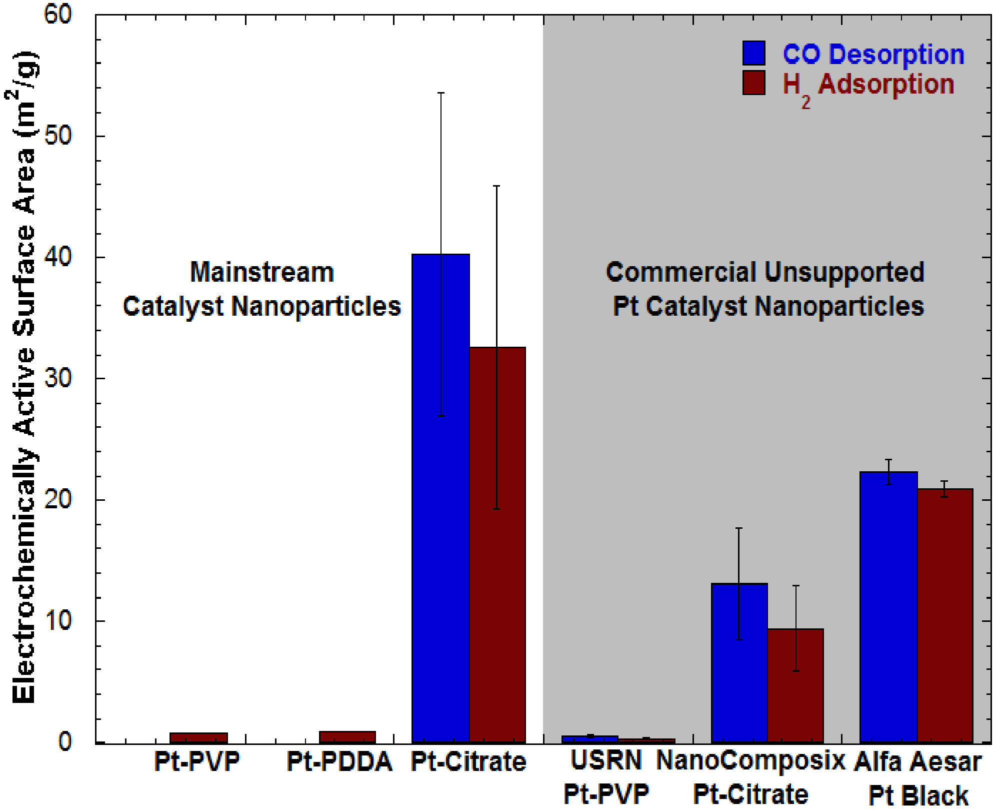
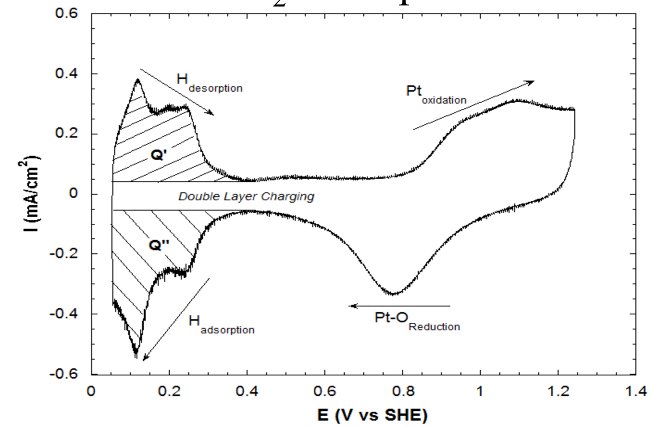
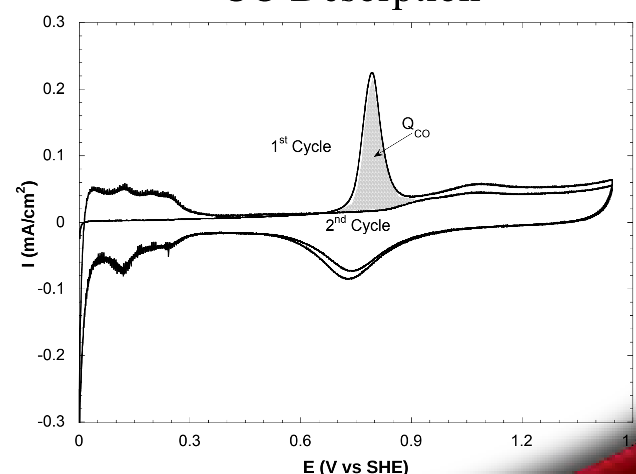
Colloidal Nanoparticle Catalyst Ligands

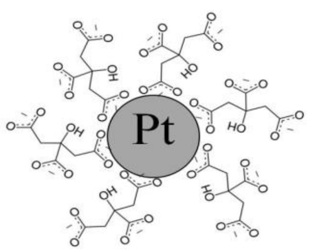


H_2 Desorption

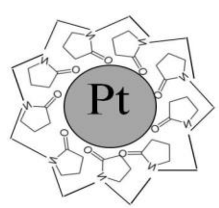


CO Desorption

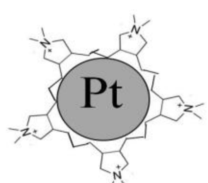




Pt-Citrate
MW= 189

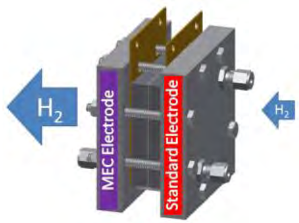


Pt-PVP
(polyvinylpyrrolidone)
MW = 40,000



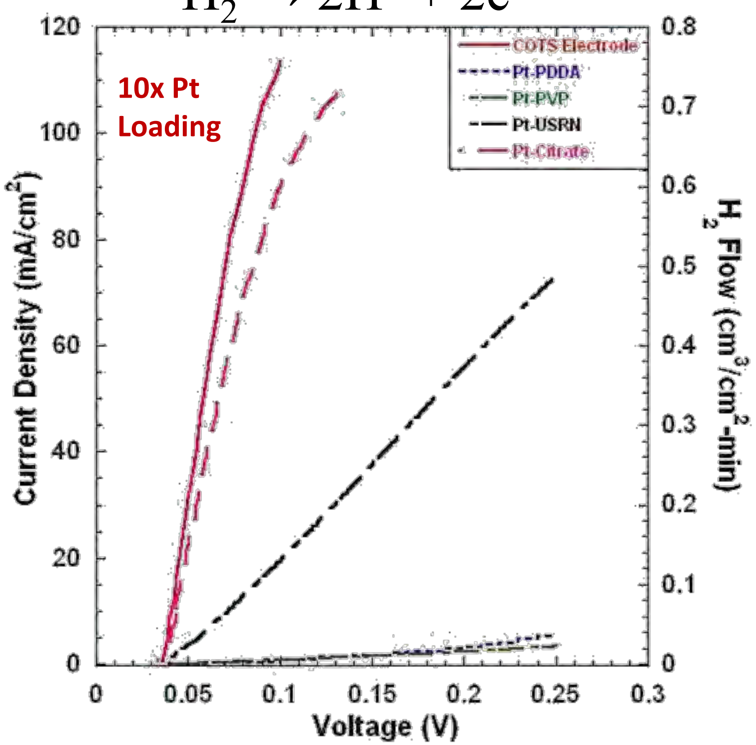
Pt-PDDA
(polydiallyldimethylammonium chloride)
MW < 100,000

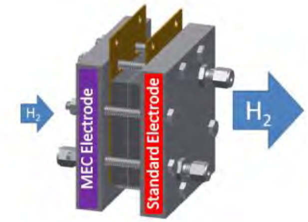
Performance of Inner/Outer Electrode



<u>MEC Electrode Reaction</u>

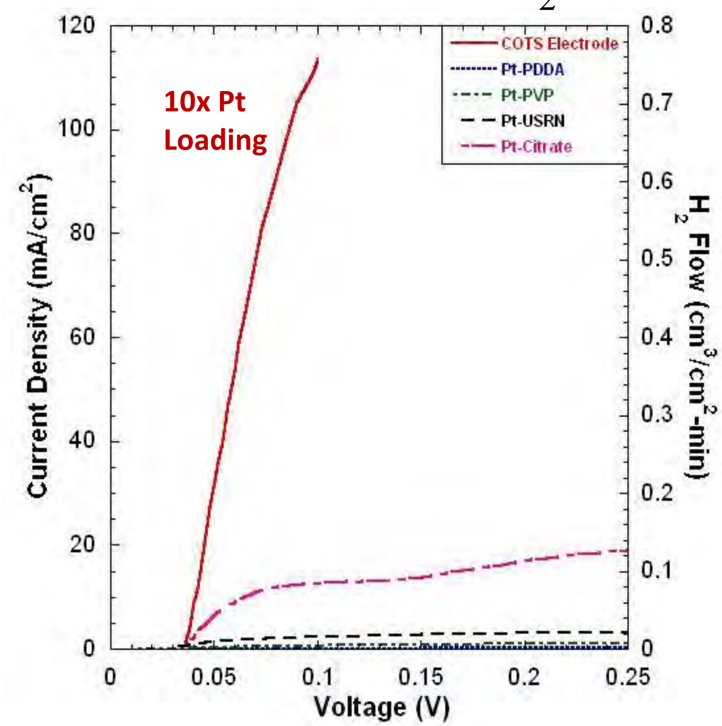
$H_2 \rightarrow 2H^+ + 2e^-$





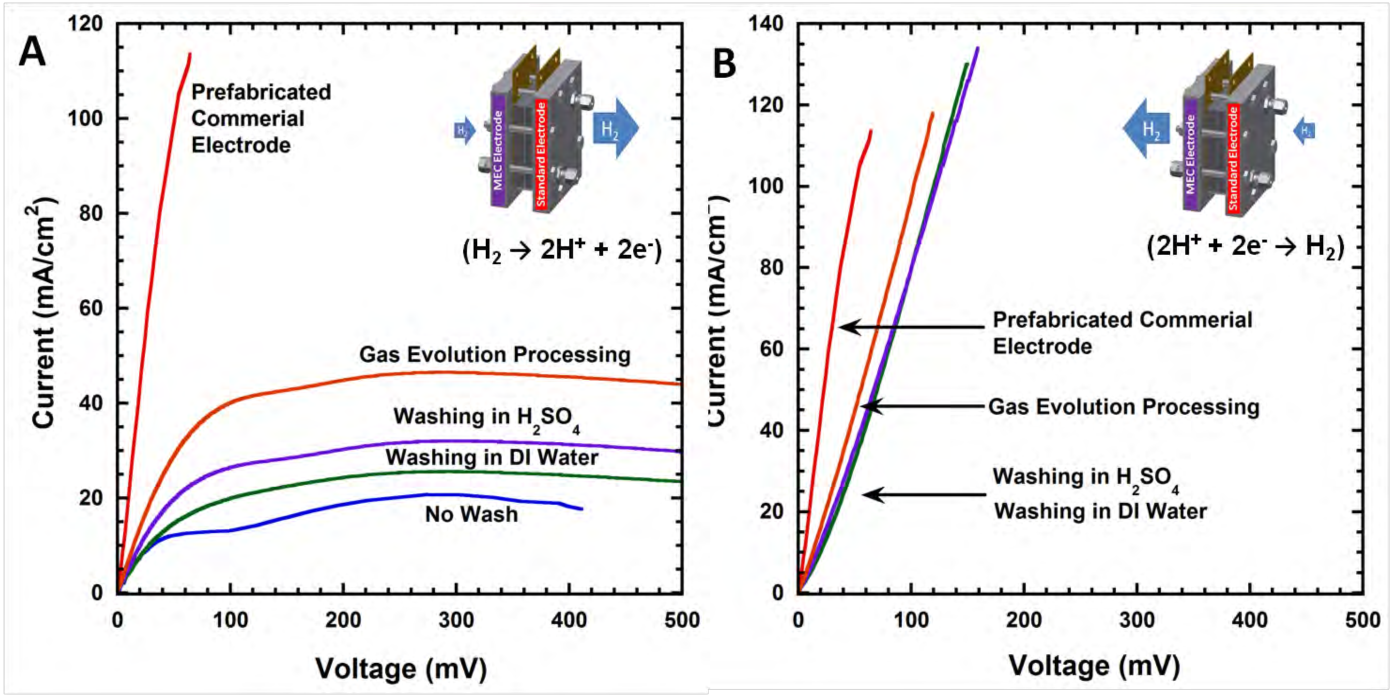
<u>MEC Electrode Reaction</u>

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



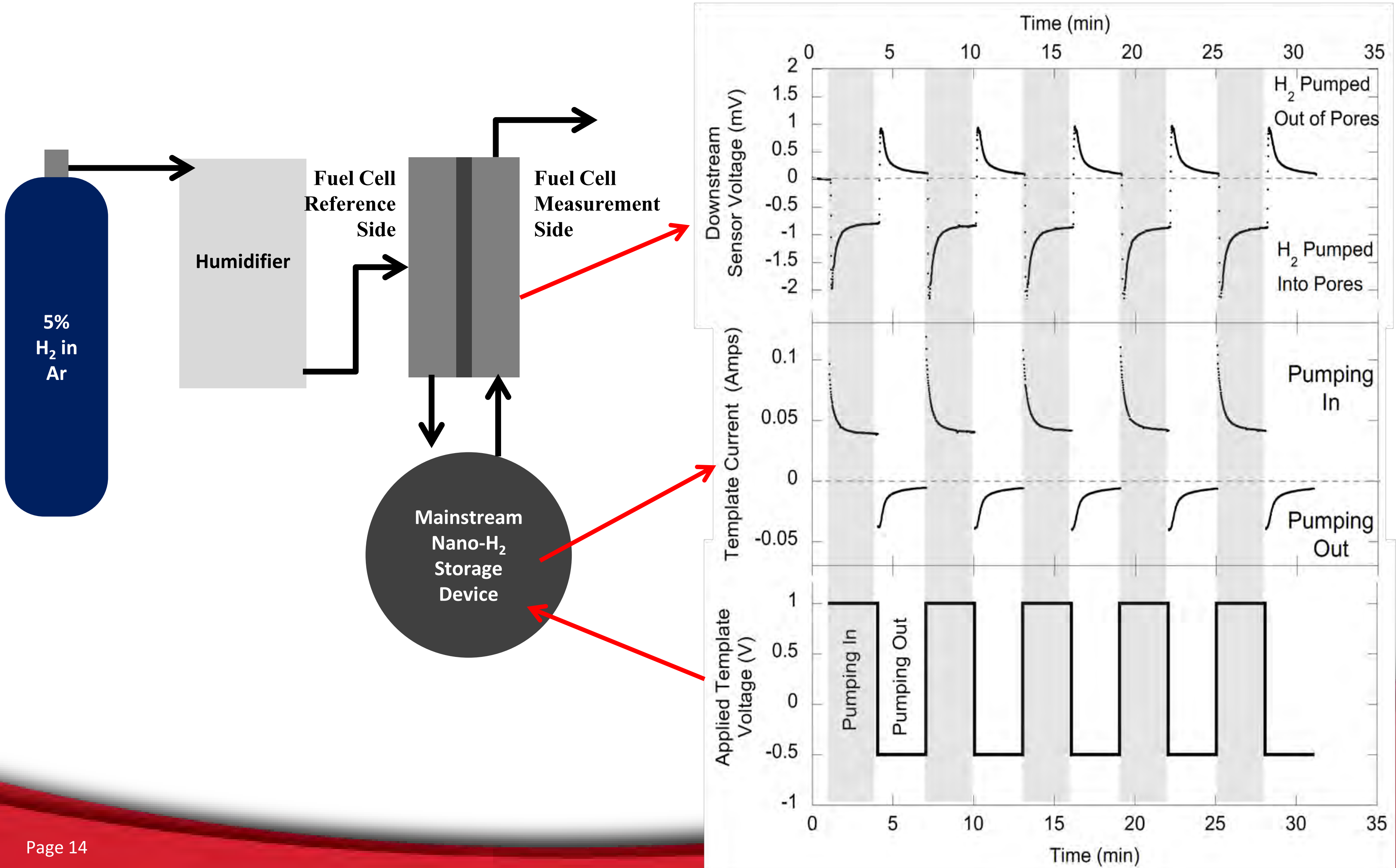
MEC Electrode Reforms Well & Dissociates Poorly

Catalyst Post-Processing

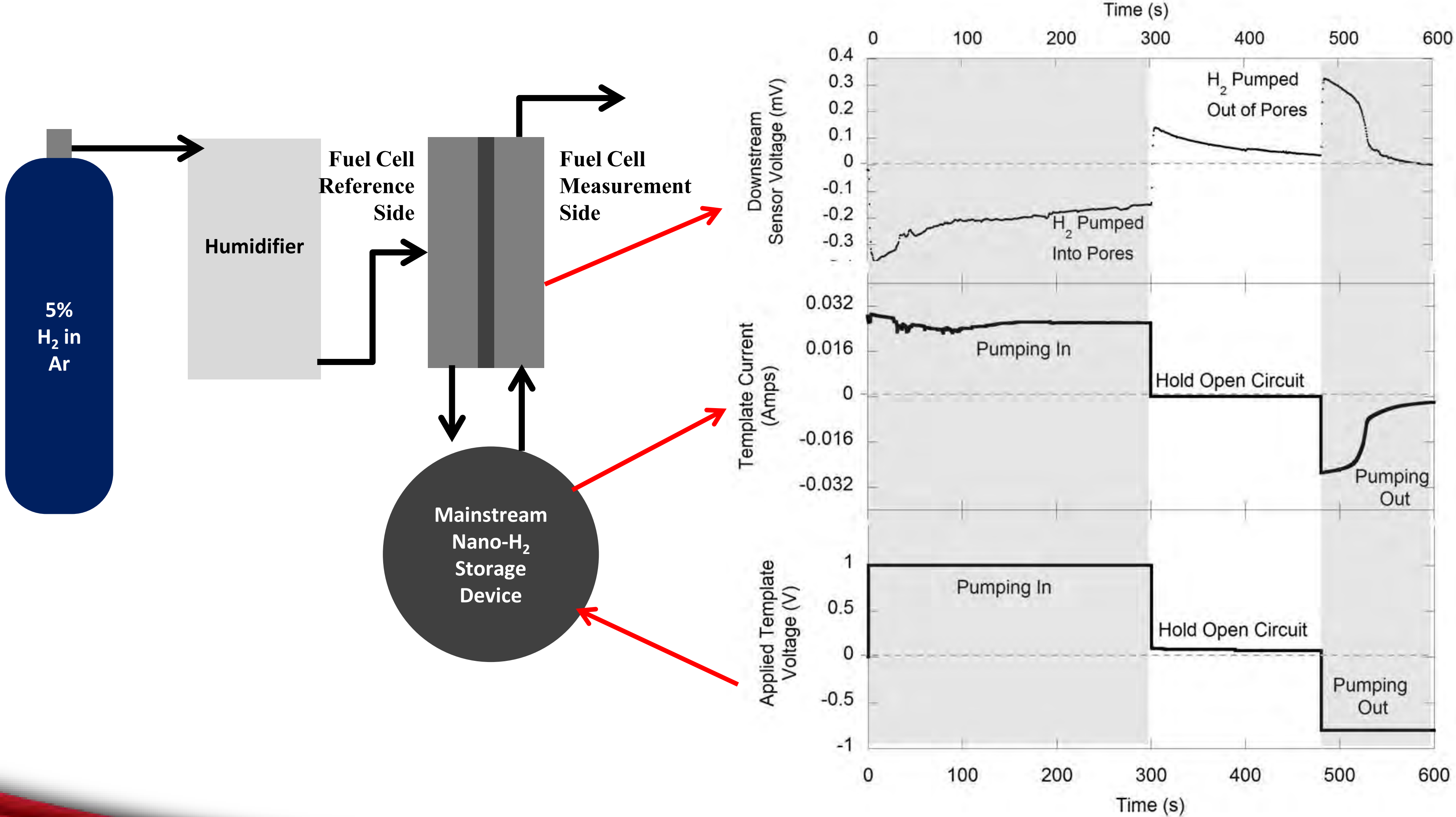


- Gas evolution forces the removal of excess ligands improving catalytic performance

H_2 Pumping Characterization



H_2 Pumping/Holding Characterization



Summary

- Nanocapillaries are capable of volumetric and gravimetric gas storage densities exceeding current state-of-the-art technologies and DOE 's ultimate H_2 storage targets.
- Nafion® PEM can be used to both cap the nanocapillaries as well as electrochemically pump gases.
- H_2 and O_2 was pumped into and out of nanocapillaries including after holding the device at open circuit.

- More research is needed to improve pumping rate, membrane sealing, and catalytic performance.

Funding

U.S. Air Force SBIR - Edwards AFB
(FA9302-13-C-0030)

Chemical and Biological Defense SBIR –
Edgewood Chemical Biological Center
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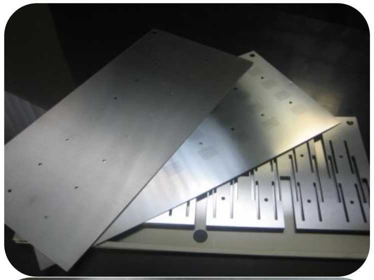
Mainstream's Focus Areas

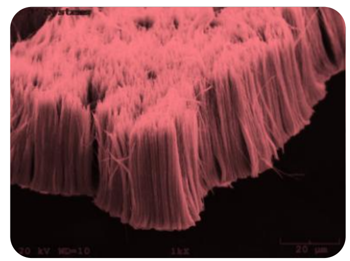


THERMAL CONTROL
- High Heat Flux Cooling
- Thermal Energy Storage
- Directed Energy Weapons
- Rugged Military Systems

Mainstream Bioenergy
Harvesting Power.

ENERGY CONVERSION
- Combustion
- Diesel/JP-8 Engines
- Biomass Conversion
- Alternative Fuels
- Fuel Cells

TURBOMACHINERY
- Compressors
- Turbines
- Bearings/Seals
- Airborne Power Systems



MATERIALS SCIENCE
- Thermoelectrics
- Batteries/Ultracapacitors
- Hydrogen Storage
- E-Beam Processing
- Nanostructured Materials

POWER ELECTRONICS
- High Speed Motor Drives
- Hybrid Power Systems
- Solar/Wind Electronics
- Pulse Power Supplies
- Battery Chargers

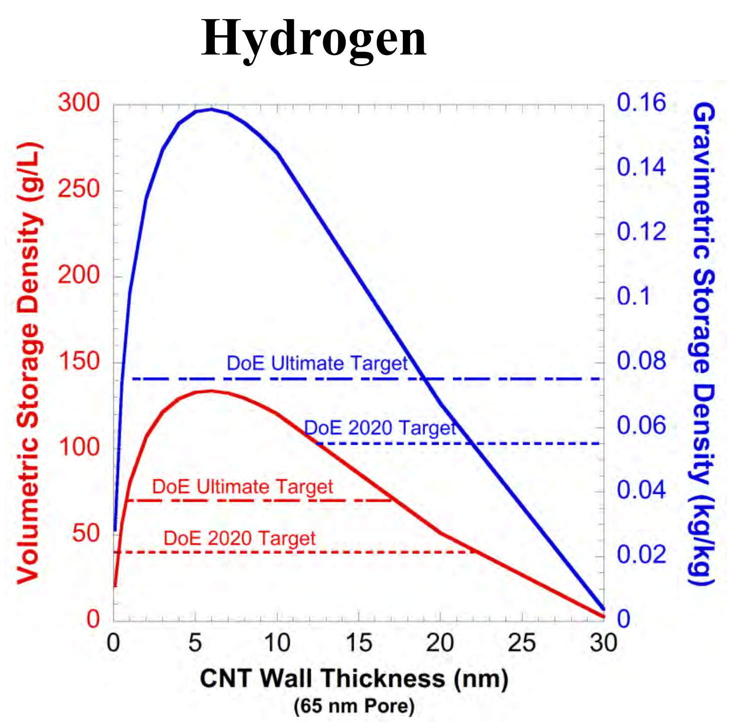
CHEMICAL TECHNOLOGIES
- Heat Transfer Fluids
- Catalysis
- Chemical Replacements
- Water Purification
- Chemical Sensors

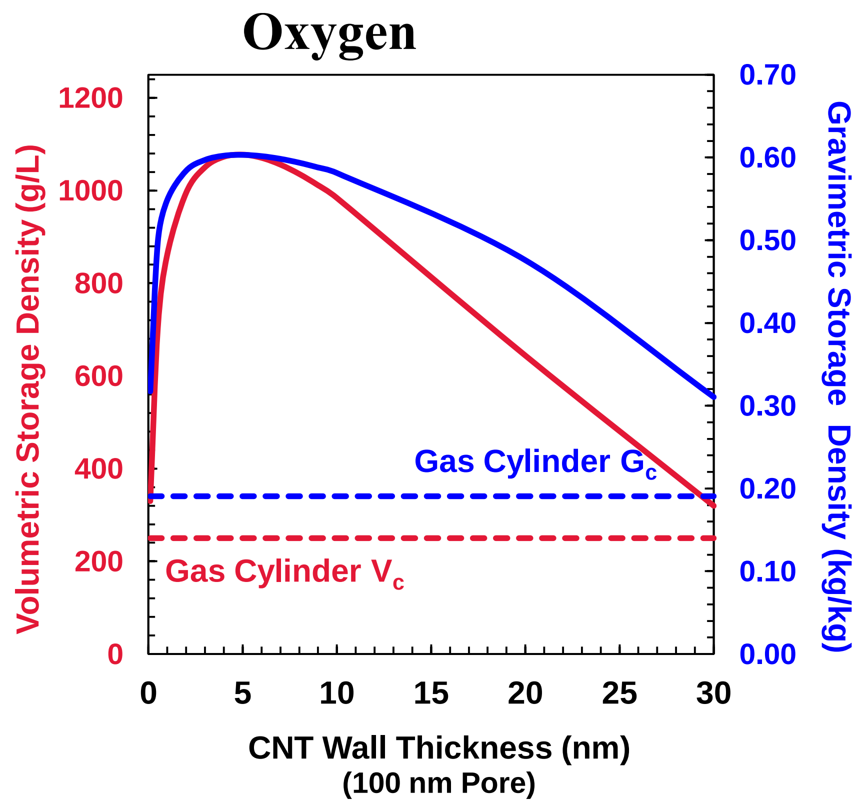
Mission Statement:
To research and develop emerging technologies.
To engineer these technologies into superior quality, military and private sector Products that provide a technological advantage.

QUESTIONS

SUPPLEMENTAL SLIDES

Theoretical Gas Storage Densities





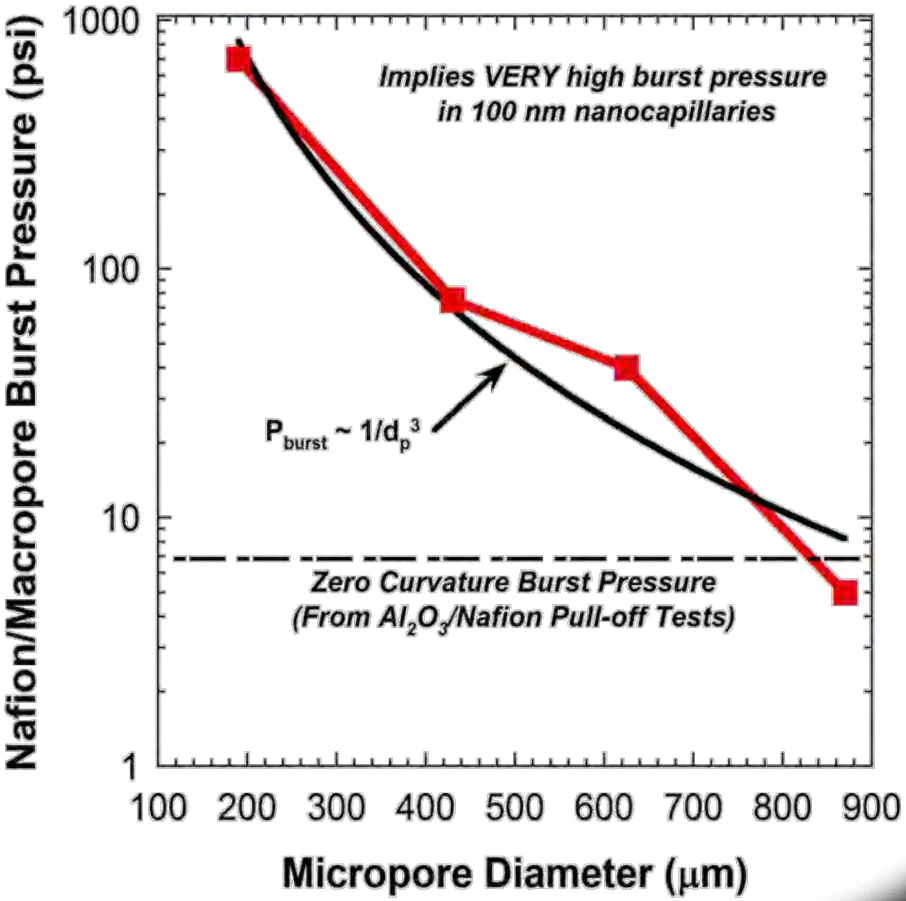
Exceeds Ultimate DOE Targets by 91% for V_c and 111% for G_c

Exceeds Conventional Gas Cylinders 3-fold

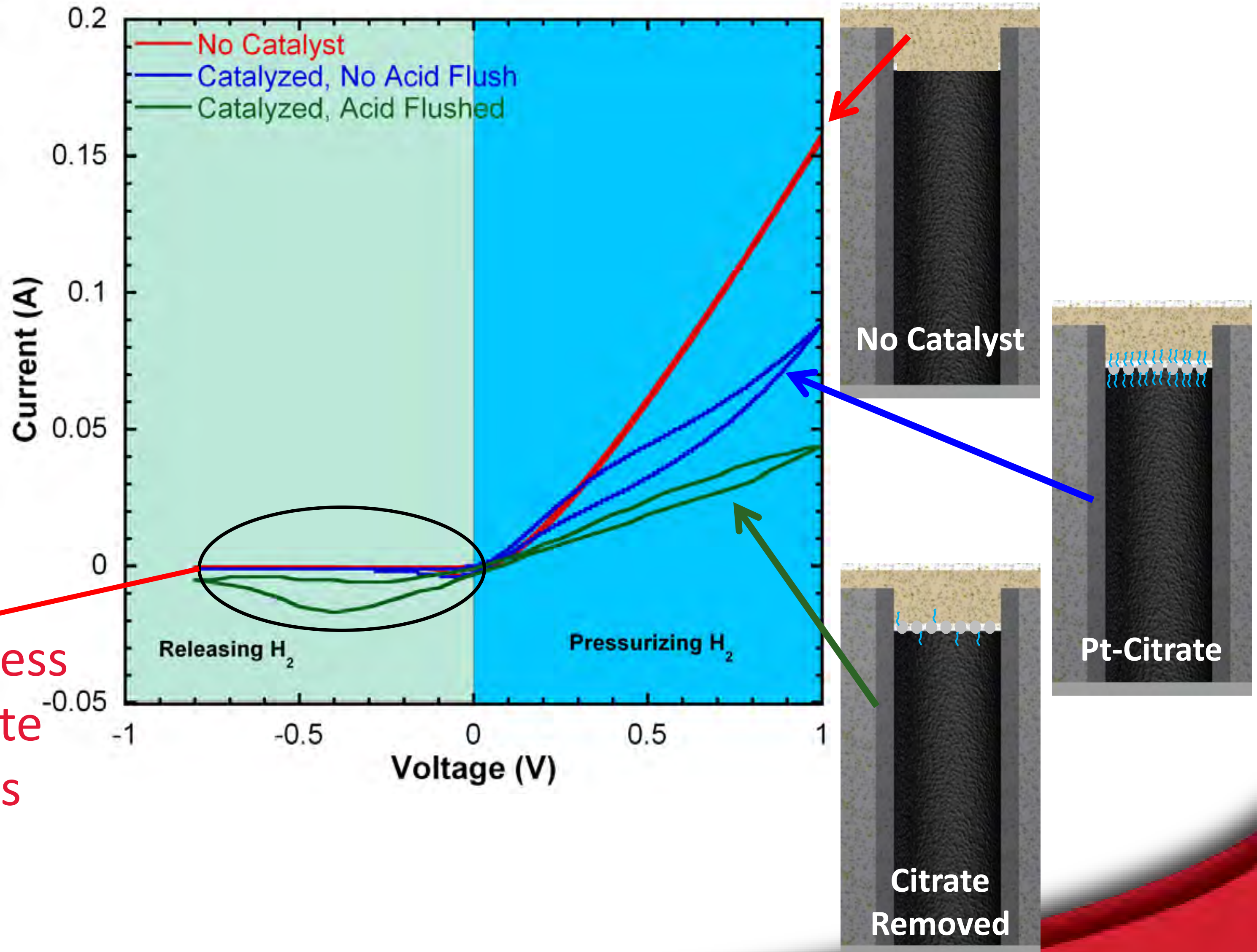
Electrochemical Compression of Gas into Nanocapillary Arrays

- Micro-pore cap & blowout pressure
- Measure adhesive properties (Nafion®)
- Extrapolate to nano-scale
- Predict required penetration depth

$$f_{ad} = \pi\alpha\left(\gamma_{\text{pore}}\right) d_p l$$

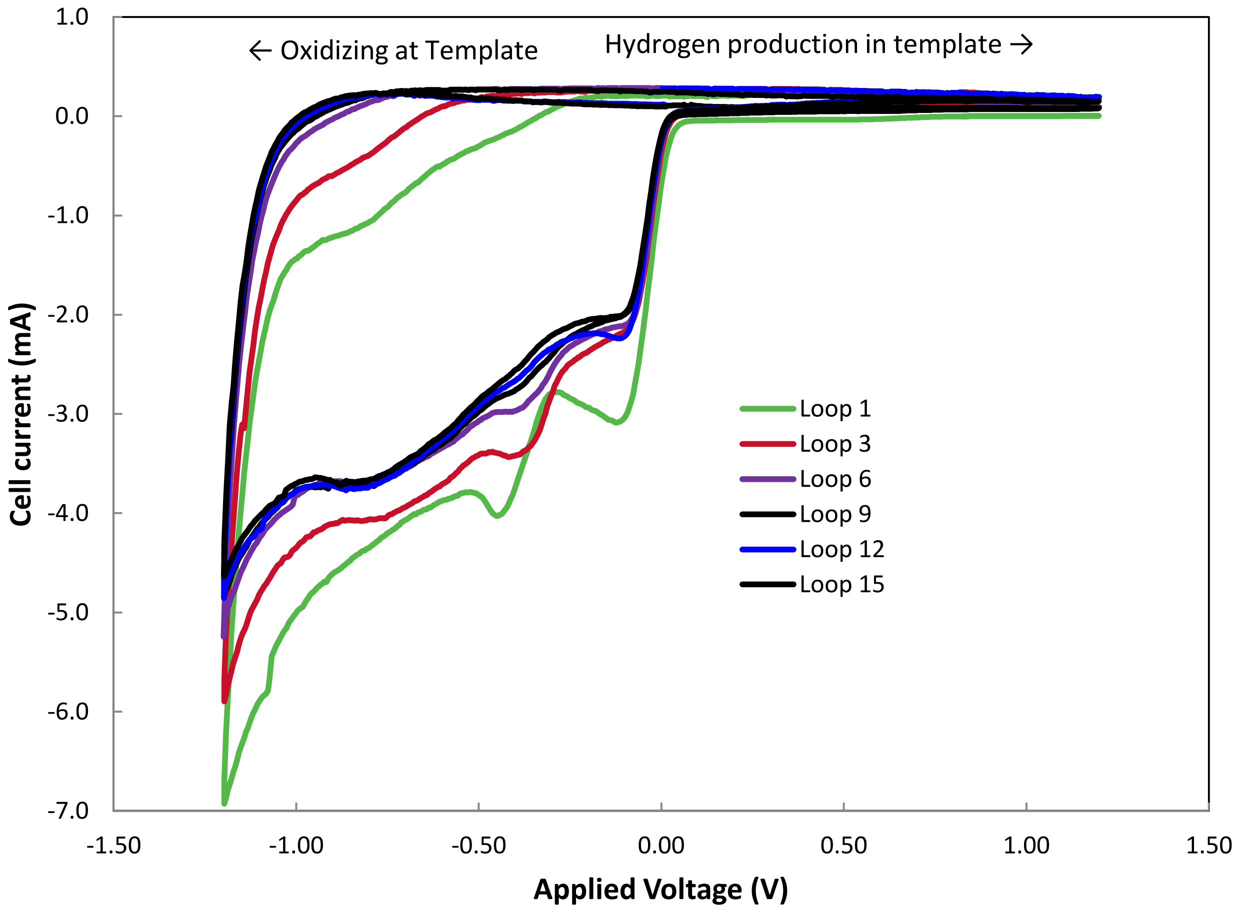


Rinsing Catalyst Improves H_2 Release

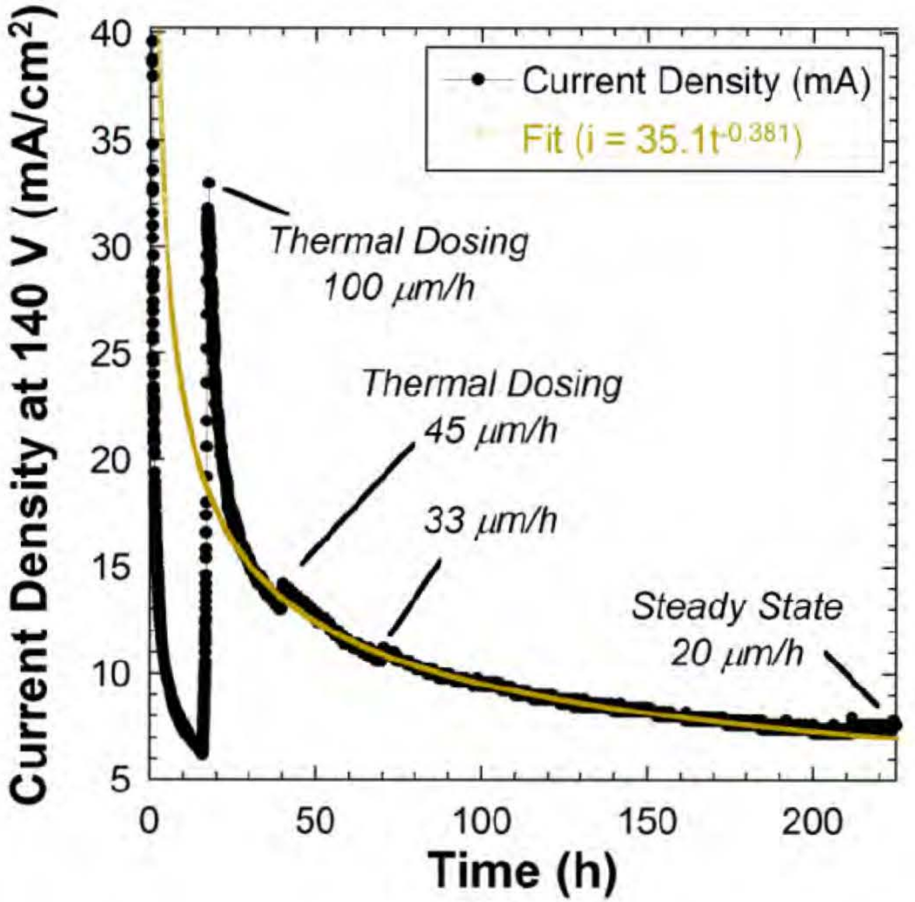


Acid flush process removes citrate and increases catalytic H_2 dissociation

Gas Evolution Processing of Catalyst



Hard Anodization



Mainstream Engineering Corporation

- Small business incorporated in 1986
- 100+ employees
- Mechanical, chemical, electrical, materials and aerospace engineers
- 85,000 ft^2 facility in Rockledge, FL
- Laboratories: electric power, electronics, materials, nanotube, physical and analytical chemistry, thermal, fuels, internal combustion engine
- Manufacturing: 3- and 5- axis CNC and manual mills, CNC and manual lathes, grinders, sheet metal, plastic injection molding, welding and painting

1-Administrative Offices **2-Research and Development** **3-Research and Development**
4-Production **5-Product Development**

Capabilities

- **Basic Research, Applied Research & Product Development**
- **Transition from Research to Production (Systems Solution)**
- **Manufacture Advanced Products**

Mission Statement

To research and develop emerging technologies.
To engineer these technologies into superior quality, military and private sector products that provide a technological advantage.