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

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

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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 technical obstacles to the implementation of our electrochemical membrane approach, together with the current state of 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.

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14. ABSTRACT

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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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Electrochemical self-assembly of alumina nanocapillary arrays

- *Provides segregated high pressure vessel (30,000 psi = 2x DoE H₂ 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*
      - $G_c = 1.8 \text{ kWh/kg}$ (5.5 wt% hydrogen)
      - $V_c = 1.3 \text{ kWh/L}$ (40 g-hydrogen/L)
  - Oxygen – Gravimetric Energy Storage
    - Mobile, personal oxygen supply
      - Aerospace, SCUBA, First Responders

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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

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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

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

Exceeds Conventional Gas Cylinders 3-fold
Templated Nanocapillary Fabrication

1. Electrochemical Anodization
2. CVD CNT Growth
3. Integrate Membrane &
   Fill with Hydrogen
4. Complete Gas Storage Material

- Shaped Al
- Aluminum Oxide Nanocapillary Array
- CNT Coated Pore Wall
- Nafion® Membrane
- AAO Nanocapillary Pores
- Carbon Nanotube (CNT)
AAO Growth and CNT CVD

Electrochemical self-assembly of AAO nanocapillaries

Integration of CNT as current carrier

Electrochemical Pumping

Hydrogen Pumping

\[ H_2 \xrightleftharpoons[Pt]{Pt} 2H^+ + 2e^- \]

Oxygen Pumping

\[ 2H_2O \xrightleftharpoons[Pt]{IrO_2} O_2 + 4H^+ + 4e^- \]
Assembly of the MEA/Cap

(A) Grow CNTs in Nanocapillaries

(B) Cast Oxygen Electrode into Pores

Cast Hydrogen Electrode on Membrane
Colloidal Nanoparticle Catalyst Ligands

-0.3
-0.2
-0.1
0
0.1
0.2
0.3
0 0.3 0.6 0.9 1.2 1.5
I (mA/cm$^2$)
E (V vs SHE)
1st Cycle
2nd Cycle
Q$_{CO}$

H$_2$ Desorption

Pt-Citrate
MW = 189
Pt-PVP
polypyrrolidone
MW = 40,000
Pt-PDDA
polydiallyltrimethylammonium chloride
MW < 100,000
Performance of Inner/Outer Electrode

MEC Electrode Reaction

\[ \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \]

MEC Electrode Reaction

\[ 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \]

MEC Electrode Reforms Well & Dissociates Poorly

10x Pt Loading
Gas evolution forces the removal of excess ligands improving catalytic performance
H₂ Pumping Characterization

Humidifier

5% H₂ in Ar

Fuel Cell Reference Side

Mainstream Nano-H₂ Storage Device

Fuel Cell Measurement Side

Graph showing time vs. downstream sensor voltage (mV), time vs. template current (Amps), and time vs. applied template voltage (V) with labels for pumping in and out of pores.
H₂ Pumping/Holding Characterization

Humidifier

Fuel Cell Reference Side

Fuel Cell Measurement Side

Mainstream Nano-H₂ Storage Device

5% H₂ in Ar

Chart showing downstream sensor voltage (mV) over time (s), template current (Amps) over time (s), and applied template voltage (V) over time (s).

H₂ Pumped Out of Pores
H₂ Pumped Into Pores
Pumping In
Hold Open Circuit
Pumping Out

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Summary

- Nanocapillaries are capable of volumetric and gravimetric gas storage densities exceeding current state-of-the-art technologies and DOE’s ultimate H₂ storage targets.
- Nafion® PEM can be used to both cap the nanocapillaries as well as electrochemically pump gases.
- H₂ and O₂ 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.

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Mainstream’s Focus Areas

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

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

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

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

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

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
Theoretical Gas Storage Densities

Hydrogen

Gravimetric Storage Density (kg/kg)

Volumetric Storage Density (g/L)

CNT Wall Thickness (nm)
(65 nm Pore)

DoE Ultimate Target
DoE 2020 Target

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

Oxygen

Gravimetric Storage Density (kg/kg)

Volumetric Storage Density (g/L)

CNT Wall Thickness (nm)
(100 nm Pore)

Gas Cylinder $G_c$
Gas Cylinder $V_c$

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

\[ f_{ad} = \pi \alpha \left( \gamma_{pore} \right) d_p l \]
Rinsing Catalyst Improves H₂ Release

Acid flush process removes citrate and increases catalytic H₂ dissociation
Gas Evolution Processing of Catalyst

![Graph showing cell current vs. applied voltage](image)

- Oxidizing at Template
- Hydrogen production in template

- Cell current (mA)
  - Loop 1
  - Loop 3
  - Loop 6
  - Loop 9
  - Loop 12
  - Loop 15

- Applied Voltage (V)
Hard Anodization

Current Density at 140 V (mA/cm²)

- Thermal Dosing: 100 µm/h
- Thermal Dosing: 45 µm/h
- Thermal Dosing: 33 µm/h
- Steady State: 20 µm/h

Current Density (mA)

Fit (i = 35.1t^{0.381})

Time (h)

0 50 100 150 200
Mainstream Engineering Corporation

- Small business incorporated in 1986
- 100+ employees
- Mechanical, chemical, electrical, materials and aerospace engineers
- 85,000 ft² 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

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.