NAVSEA NEWPORT Undersea Warfare Center Division

The Development of a Magnesium-Hydrogen Peroxide Semi-Fuel Cell

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Contents

The Development of a Magnesium-Hydrogen Peroxide Semi-Fuel Cell

Objective

Characterize and evaluate the electrochemical performance of a magnesium solution-phase catholyte semi fuel cell for low current density,long endurance Propulsion applications.

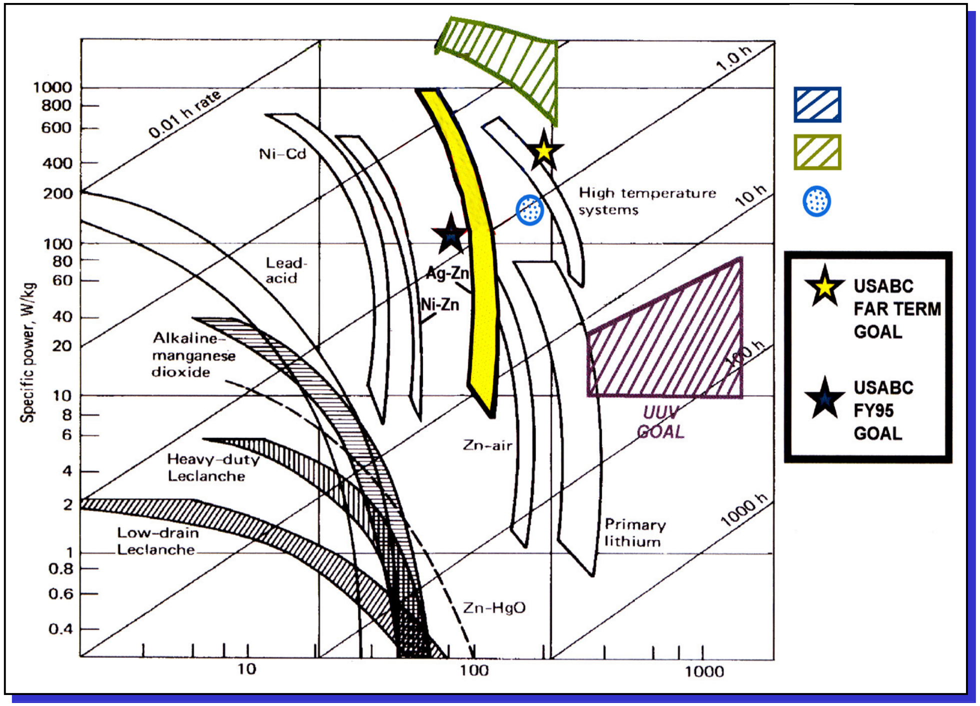
Approach

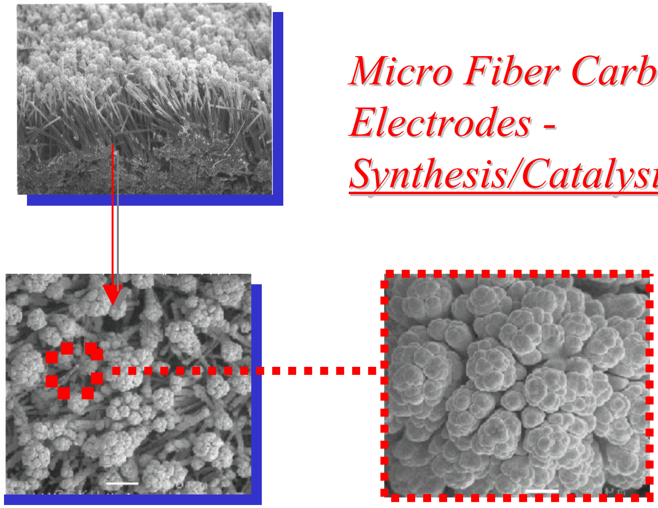
Experimentally Optimize the Critical parameters

- Cell Configuration
- Electrode Synthesis & Catalysis

Contents

NUWC Electric Propulsion
High Energy Density Mg-Semi-Fuel Cell Development





Micro Fiber Carbon Electrodes - Synthesis/Catalysis

The *Combined* Power Density and Energy Density Requirements for future UUV's Exceed most current Naval and Commercial electrochemistries

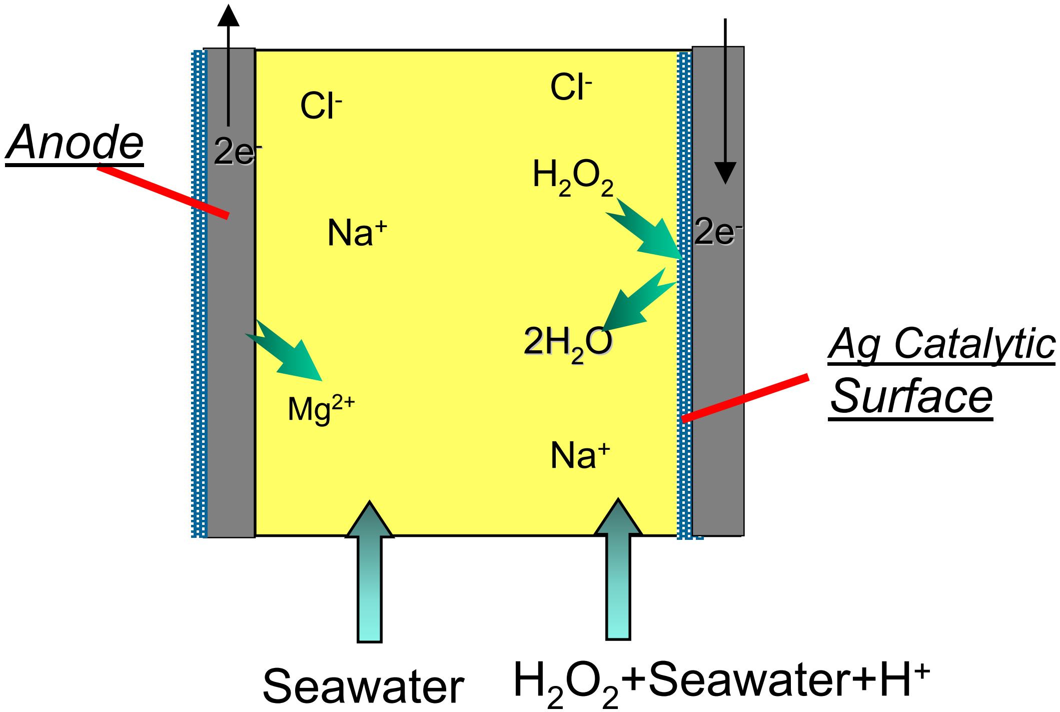
Mg-SFC Background

Anode: $Mg \rightarrow Mg^{2+} + 2e^-$ $E^o = 2.37\ V$

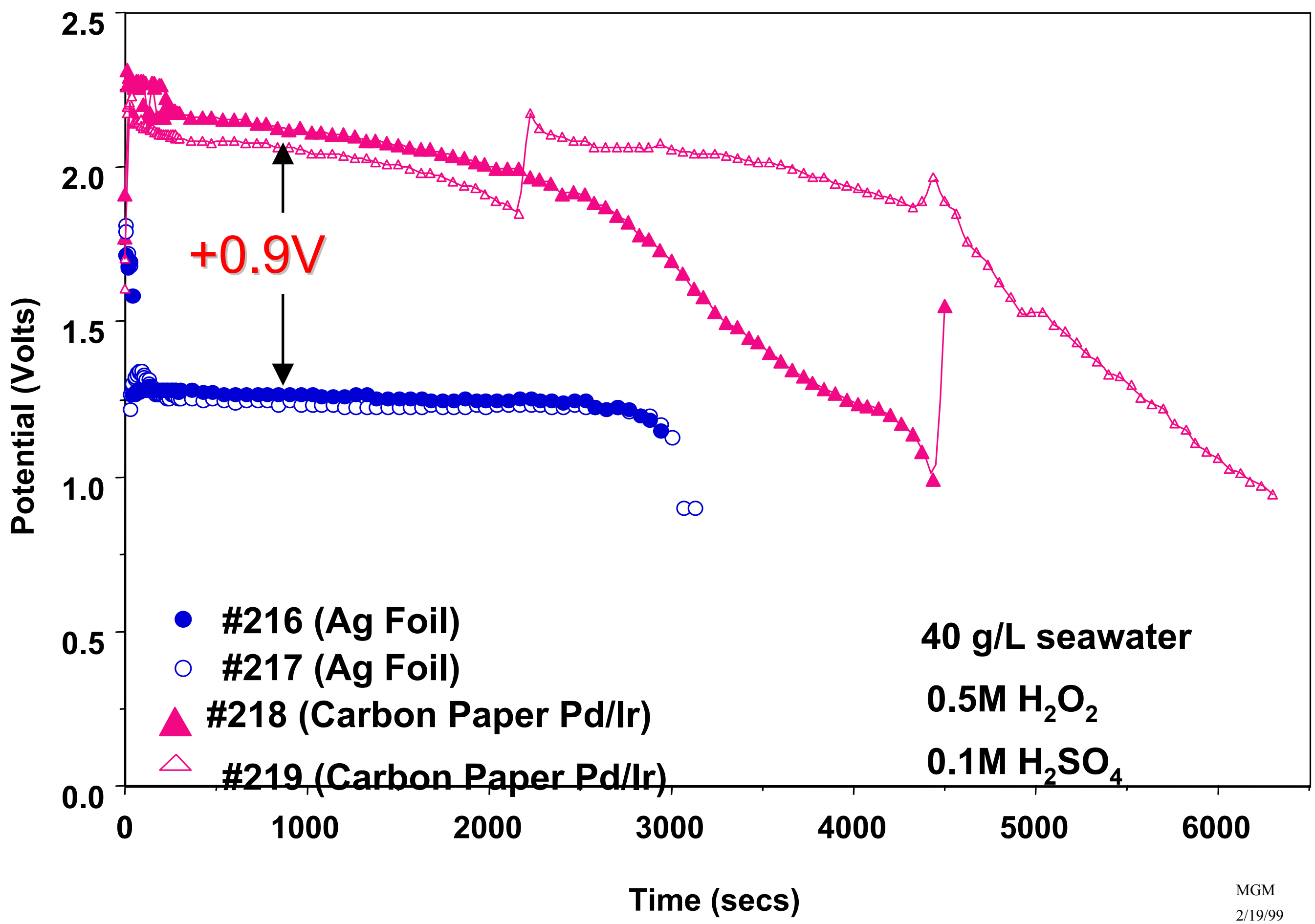
Cathode: $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ $E^o = 1.77\ V$

Cell Rxn: $Mg + H_2O_2 + 2H^+ \rightarrow Mg^{2+} + 2H_2O$ $E_{cell} = 4.14\ V$

E_{cell}=1.2V (measured)

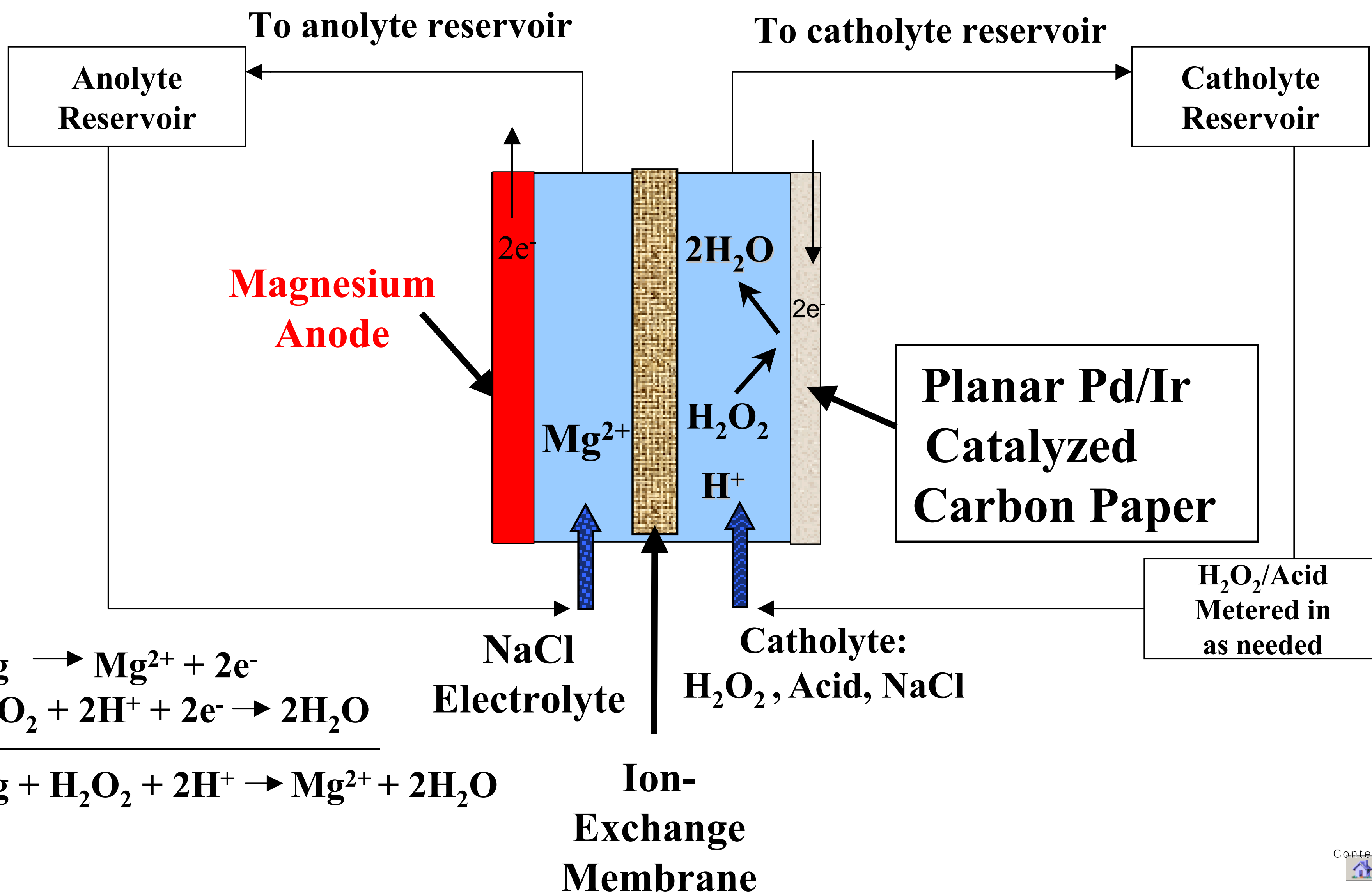


$Mg-H_2O_2/H_2SO_4$
Ag vs. Carbon Paper Pd/Ir Catalyst



- *Constant Current @ 25mA/cm^2*
- *Seawater Electrolyte – Unseparated Cell*
- *Pd/IR enables 70% Voltage Increase, but **Efficiency is < 25% due to direct Rx***

Mg Semi Fuel Cell Schematic Diagram With Planar Carbon Paper



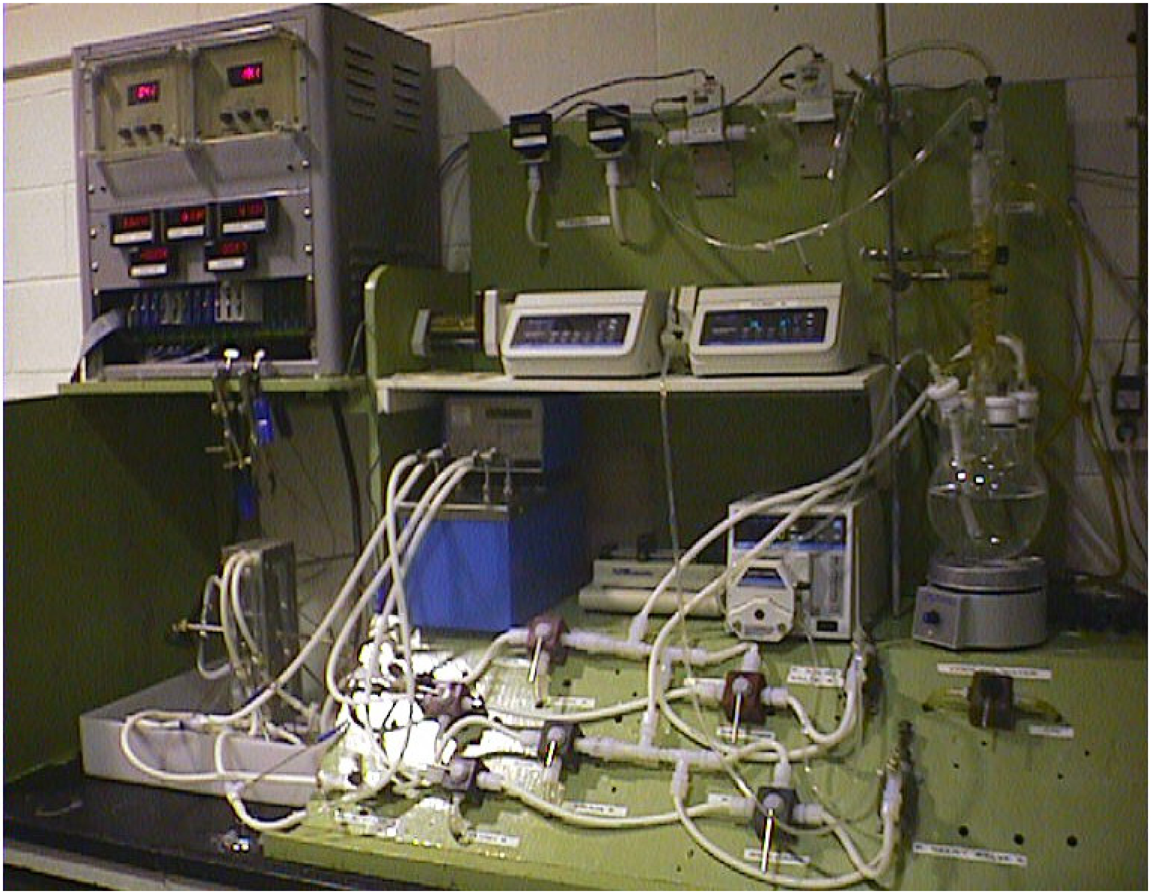
$Mg \rightarrow Mg^{2+} + 2e^-$

$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$

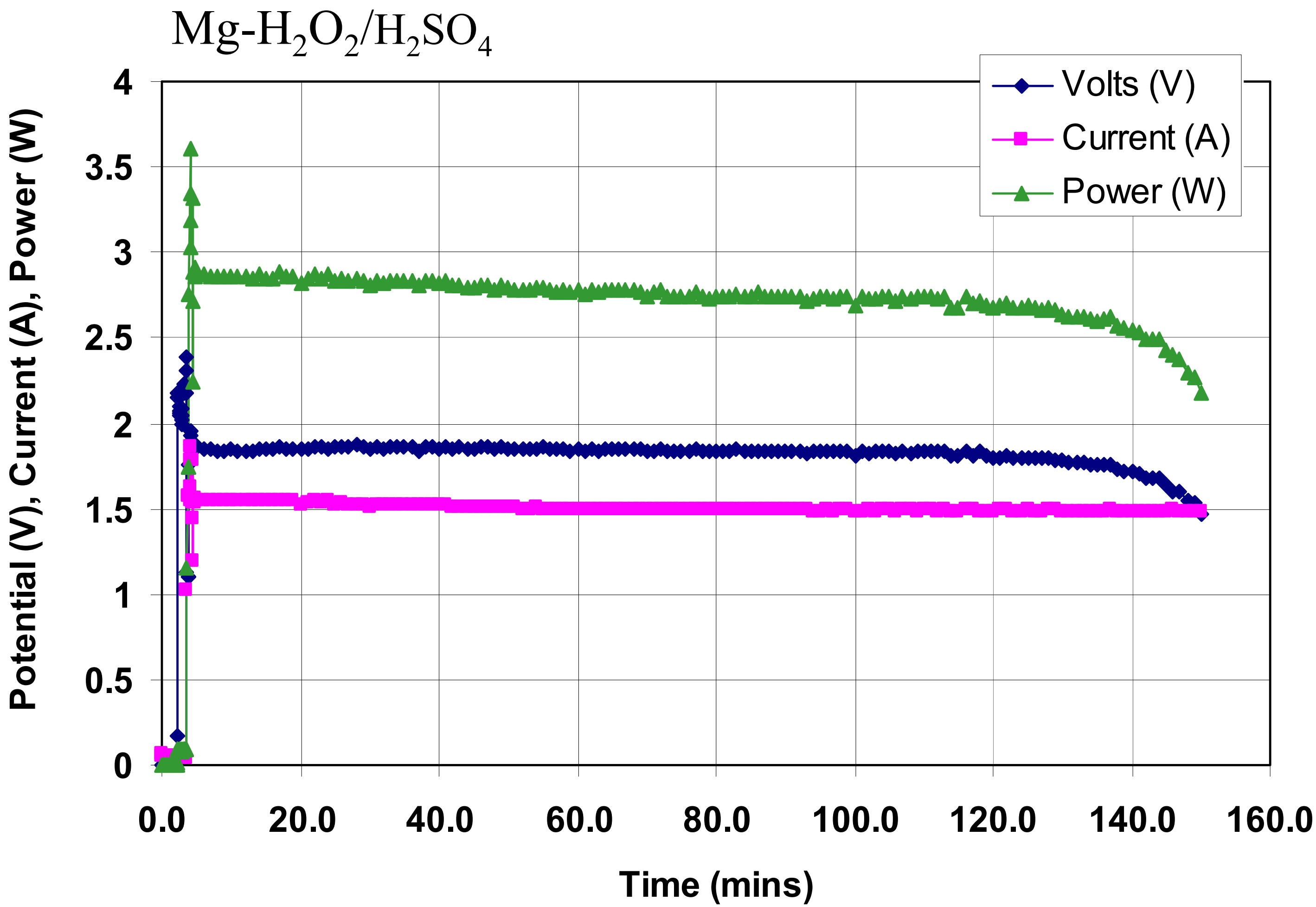
$Mg + H_2O_2 + 2H^+ \rightarrow Mg^{2+} + 2H_2O$

Contents

Mg-SFC Separated Cell Experimental Apparatus

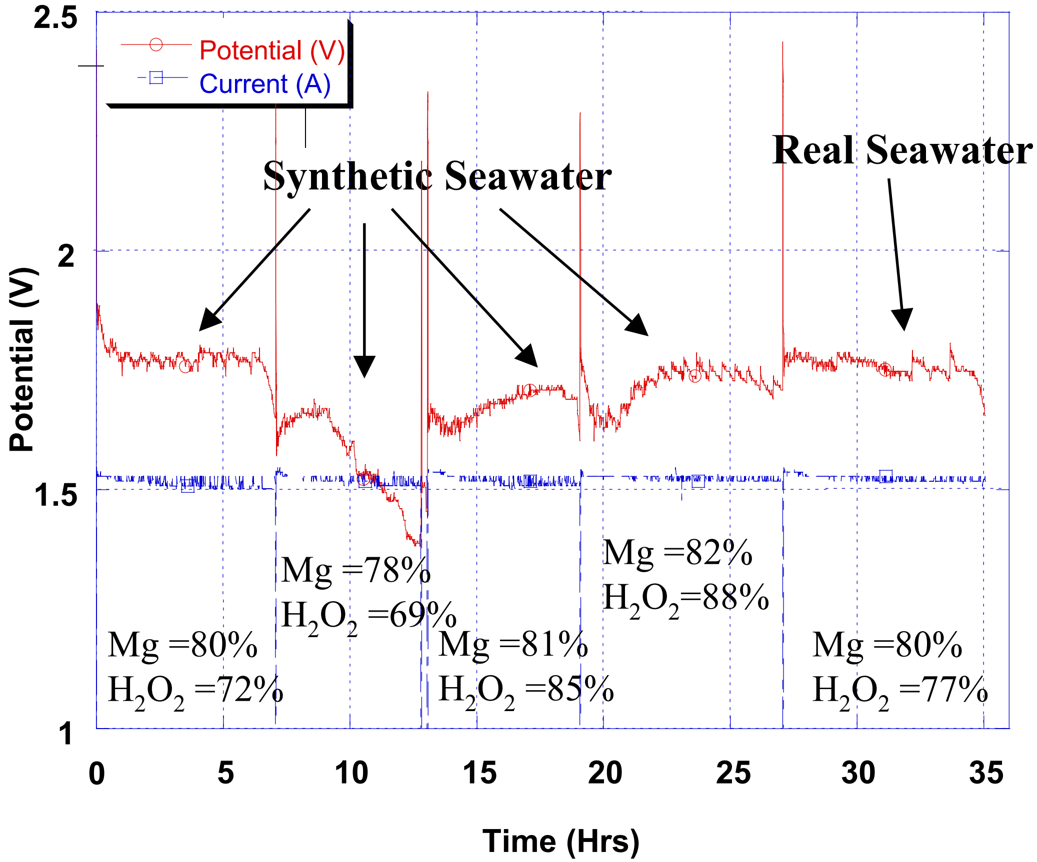


Pd:Ir Carbon Paper Continuous Operation



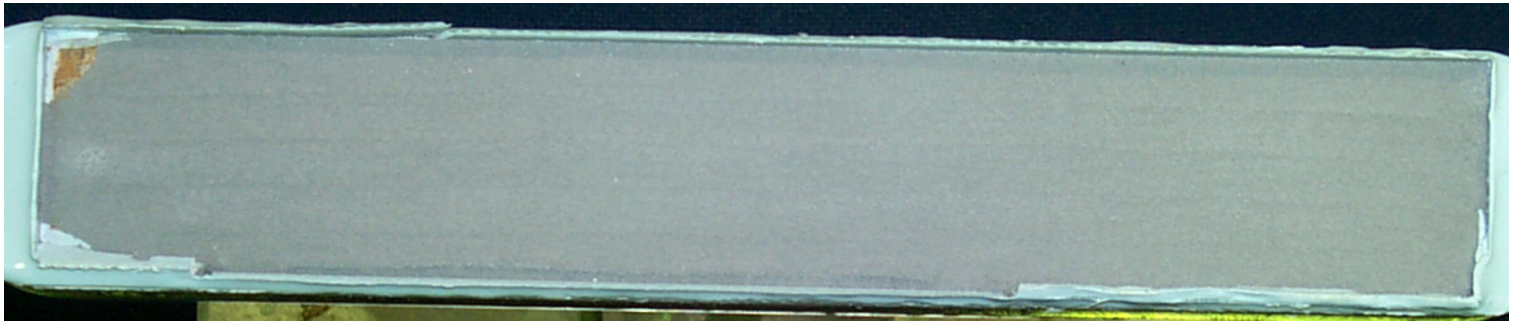
- *Separated Flow w/Nafion 115, Constant current of 25mA/cm²*
- *Anode* ***Efficiency is 75% – 85% (vice 20% w/o membrane)***
- ***Voltage 1.85 Volts***

Mg-SFC 'Thin-Electrode' Data



- Mg Efficiencies 80%, Voltages +1.75V
- Electrode thickness (Mg 40mils) limit duration to 8 hours
- "Real" Seawater tested and exceeds expectations
- Demonstrated Start-Restart Capabilities

$Mg-H_2O_2$ /H_2SO_4 SFC 50-Hour Test Anode and Membrane Analyses



Mg Anode after 50 hours

- Uniform oxidation of Mg anode
- Efficiency above 80%

Nafion Membrane after 50 hours

• Excellent Performance Observed from Anode and Membrane

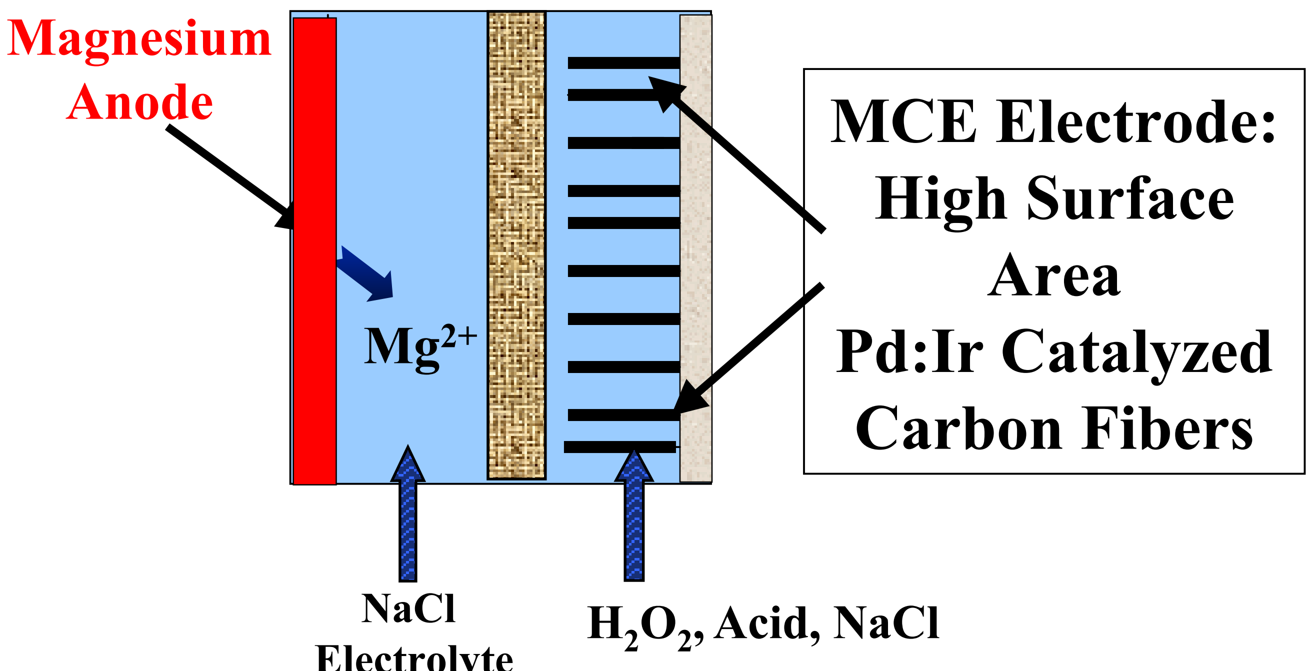
High Surface Area Cathode

Increased cell voltage at high current

High surface area results in lower current density and reduced effects of concentration polarization.

Higher peroxide efficiency

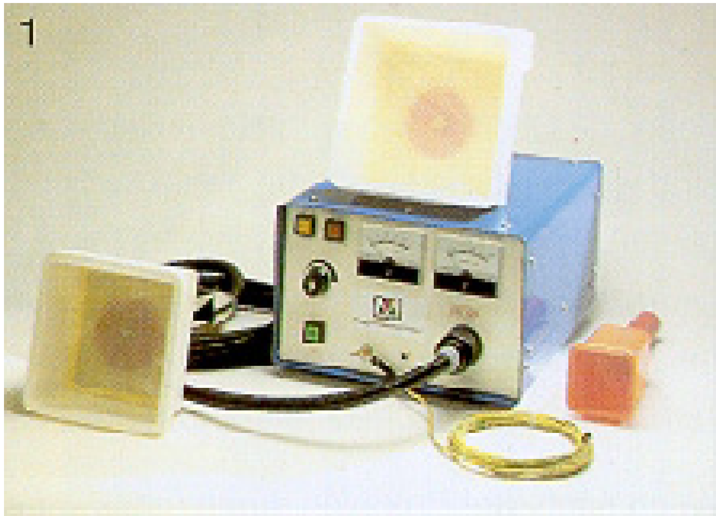
Turbulent mixing achieved by fibers.
Lower H_2O_2 concentration needed.



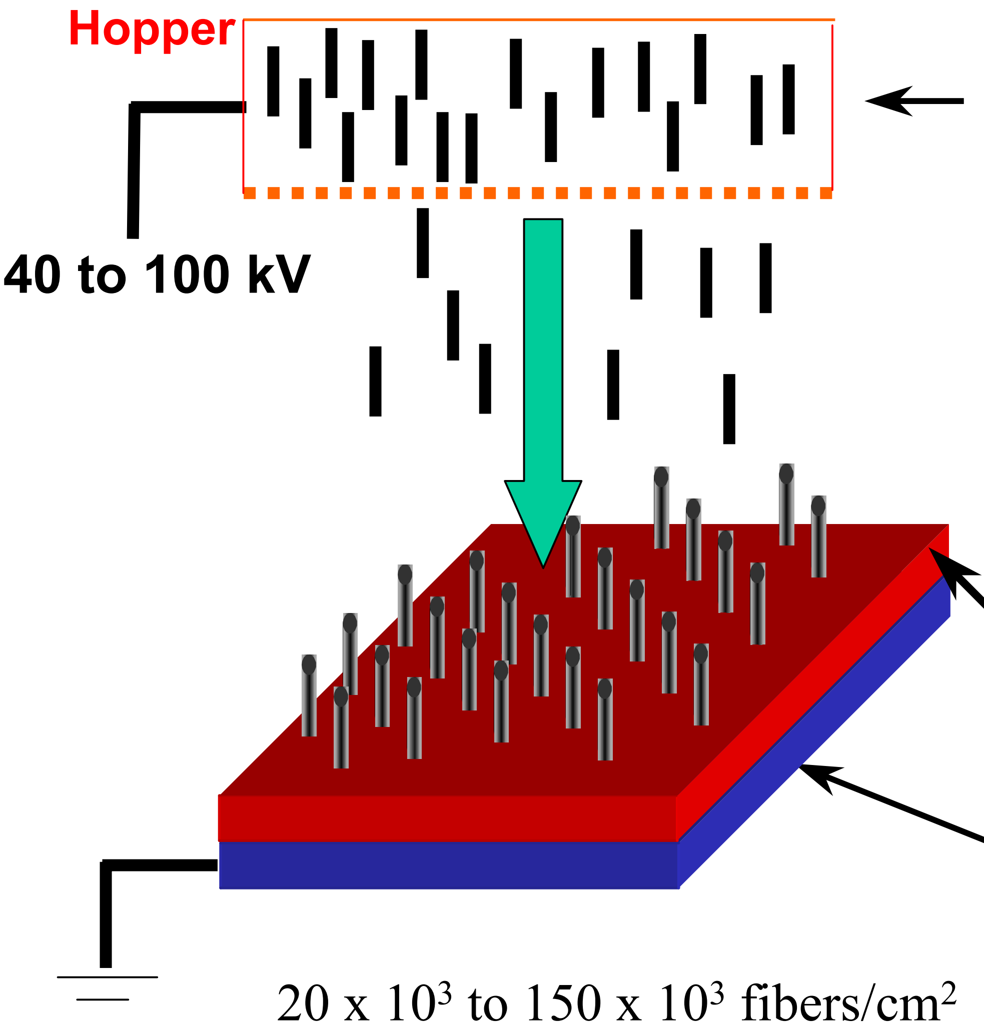
Microfiber Carbon Electrode (MCE) Fabrication via Electrostatic Flocking

Flocking Apparatus

Applied Voltage: 40kV - 100kV
Electrode to substrate distance:
9cm to 30 cm
Flocking time: 12 s to 300 s



Preparation of MCE via Electrostatic Flocking



<u>1) Charge the carbon fibers in hopper</u>

Pitch based
0.2mm to 1.5mm length
1.0µm to 30µm diameter

2) Shake hopper so that fibers fall through the screen and are embedded in wet conductive ink.

<u>Conductive adhesive</u>
(Carbon Ink)

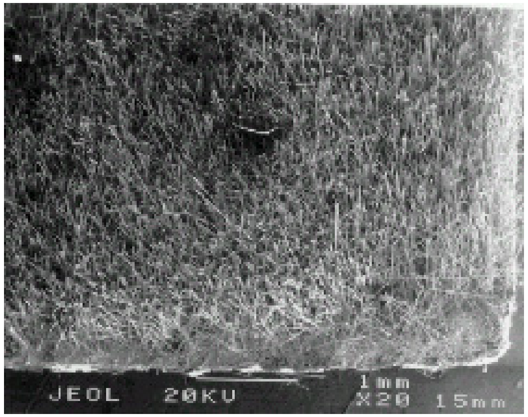
<u>Conductive support</u>
(Carbon paper, 0.25mm thick)

20×10^3 to 150×10^3 fibers/cm^2

Effect Of Flocking Parameters On Fiber Density

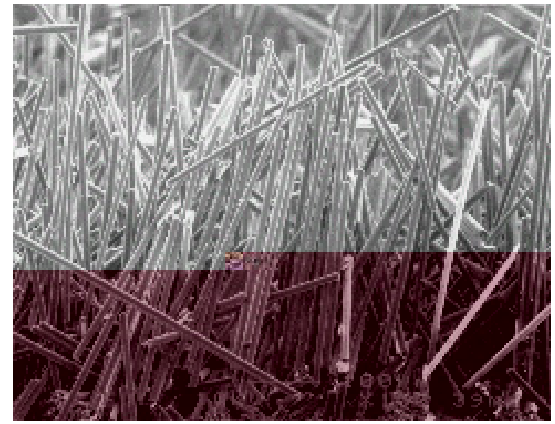
Top Views

Cross Section Views

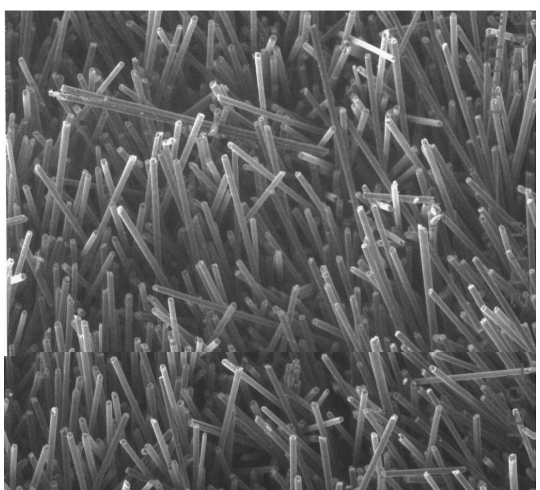


1 mm

55,700 fibers/cm^2



100 µm



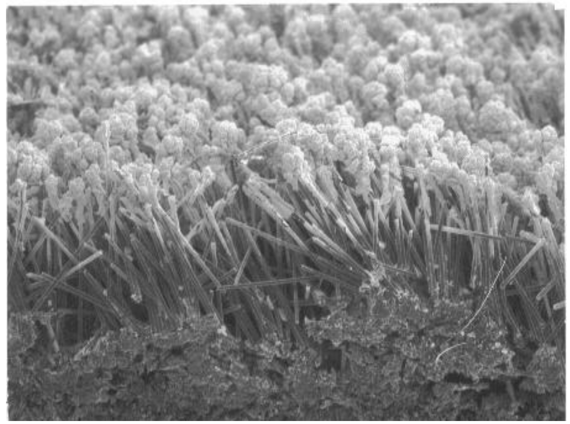
100 µm

100,344 fibers/cm^2

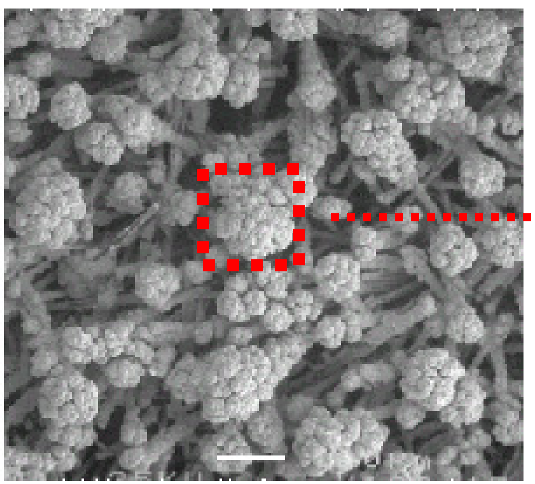
100 µm

Pd:Ir Catalyzed Microfiber Carbon Electrode (MCE)

Cross-section

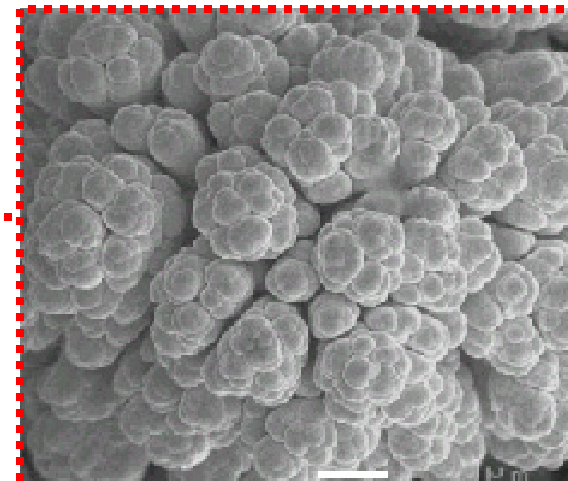


100 µm



100 µm

Top Views

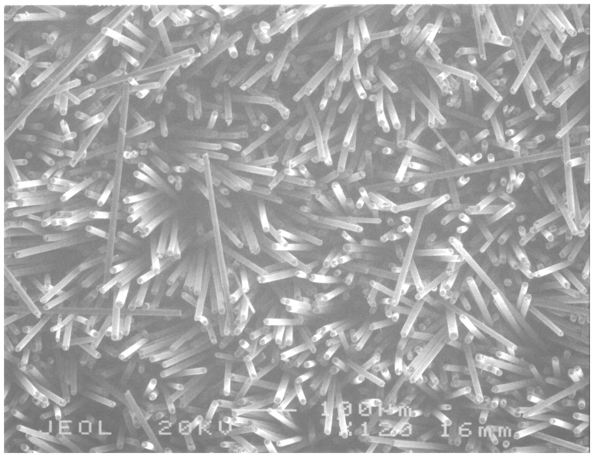


10 µm

<u>Deposition Conditions</u>: Cyclic Voltammetry, -0.10 to -0.30V vs. Ag/AgCl, 1 mV/s, 25 cycles, 2.0 mM $PdCl_2$ and Na_2IrCl_6

Contents

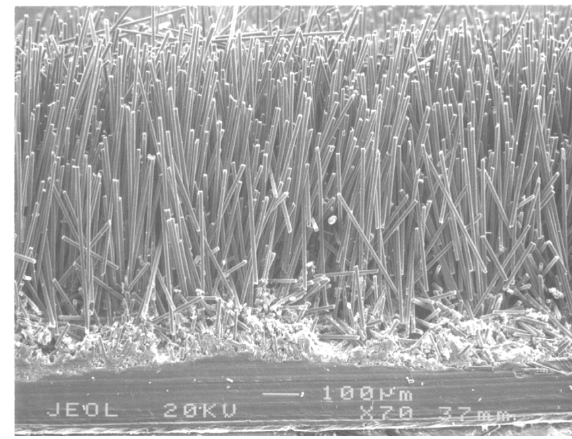
Carbon Microfiber Array
Prepared By Electrostatic Flocking



← Carbon Microfibers →

Conductive Carbon Adhesive →

Flexible Carbon Foil →



— 100 µm

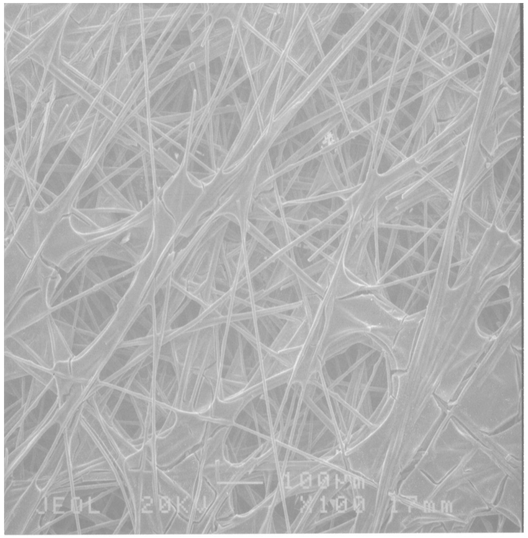
— 100 µm

Overhead View

Cross section View

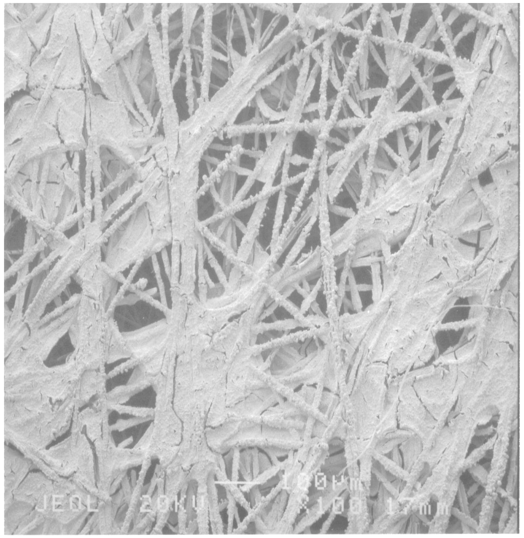
Contents

Planar Carbon Paper (Control) Electrode



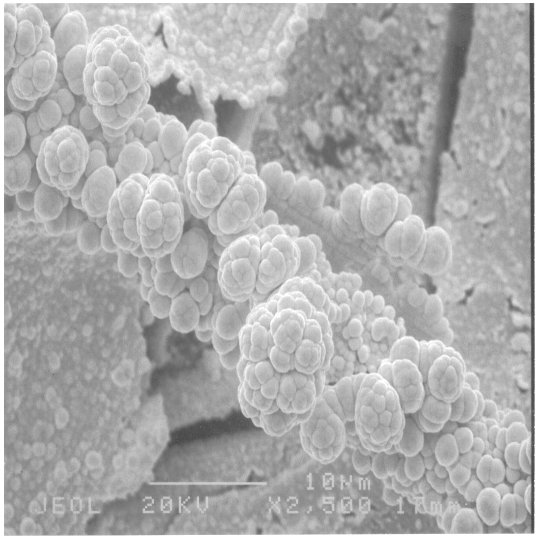
— 100 µm

Uncatalyzed



— 100 µm

Pd:Ir Catalyzed

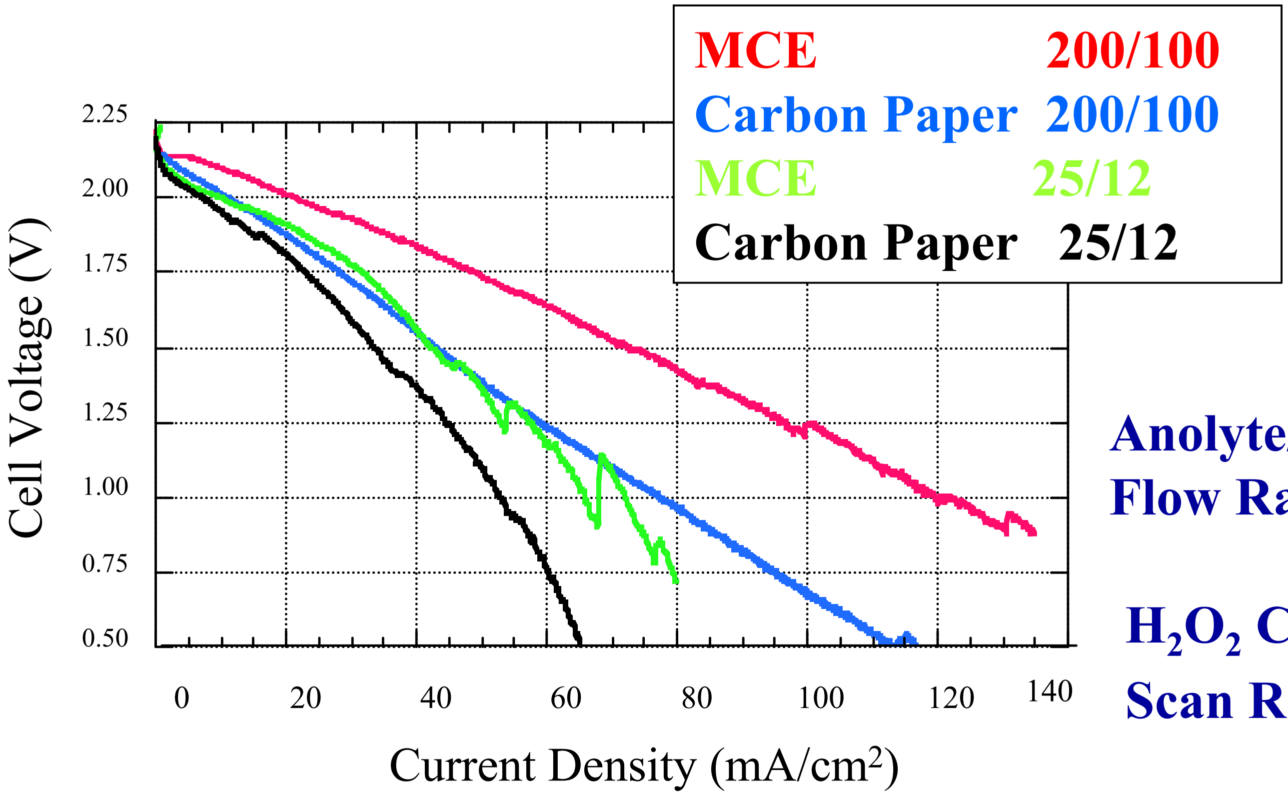


— 10 µm

Pd:Ir Nodules

Contents

Effect of Electrode Surface Area and Anolyte/Catholyte Flow rate on Rate Capability

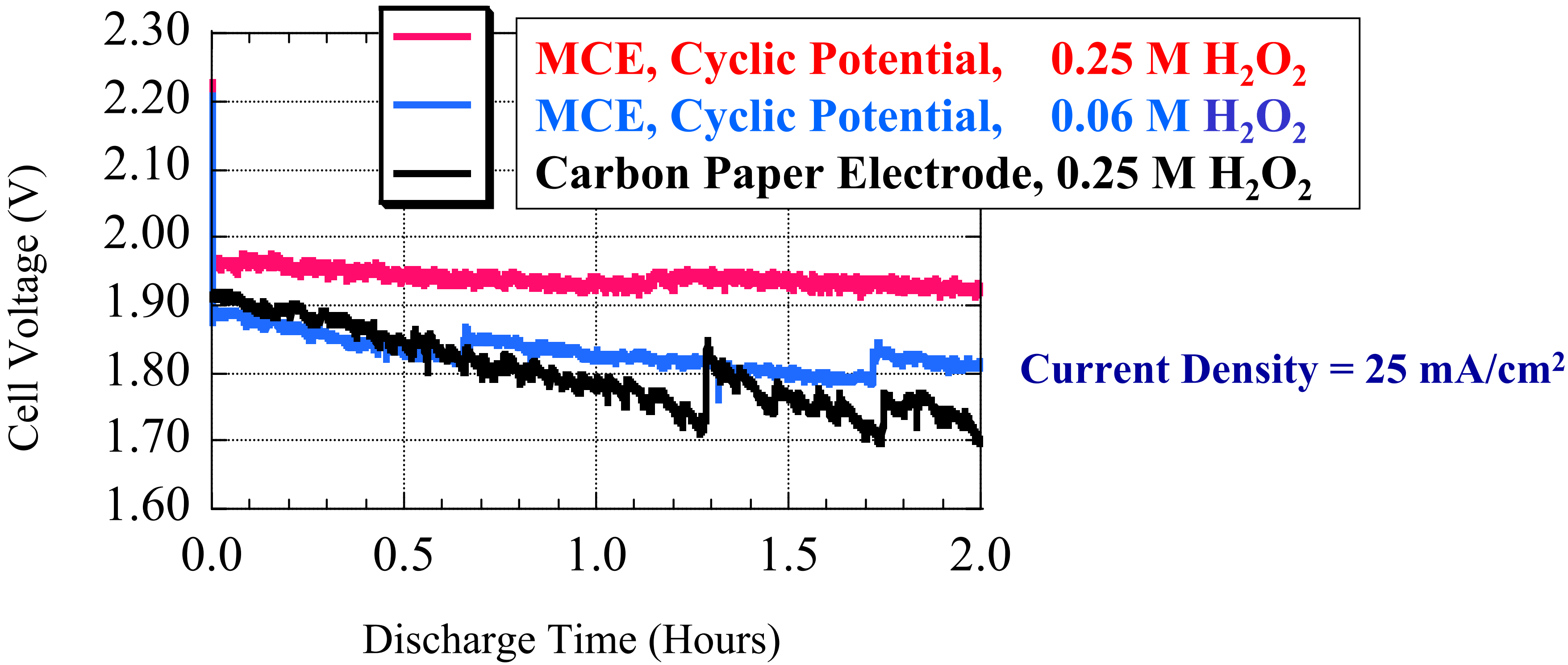


Anolyte/Catholyte Flow Rates (mL/min)

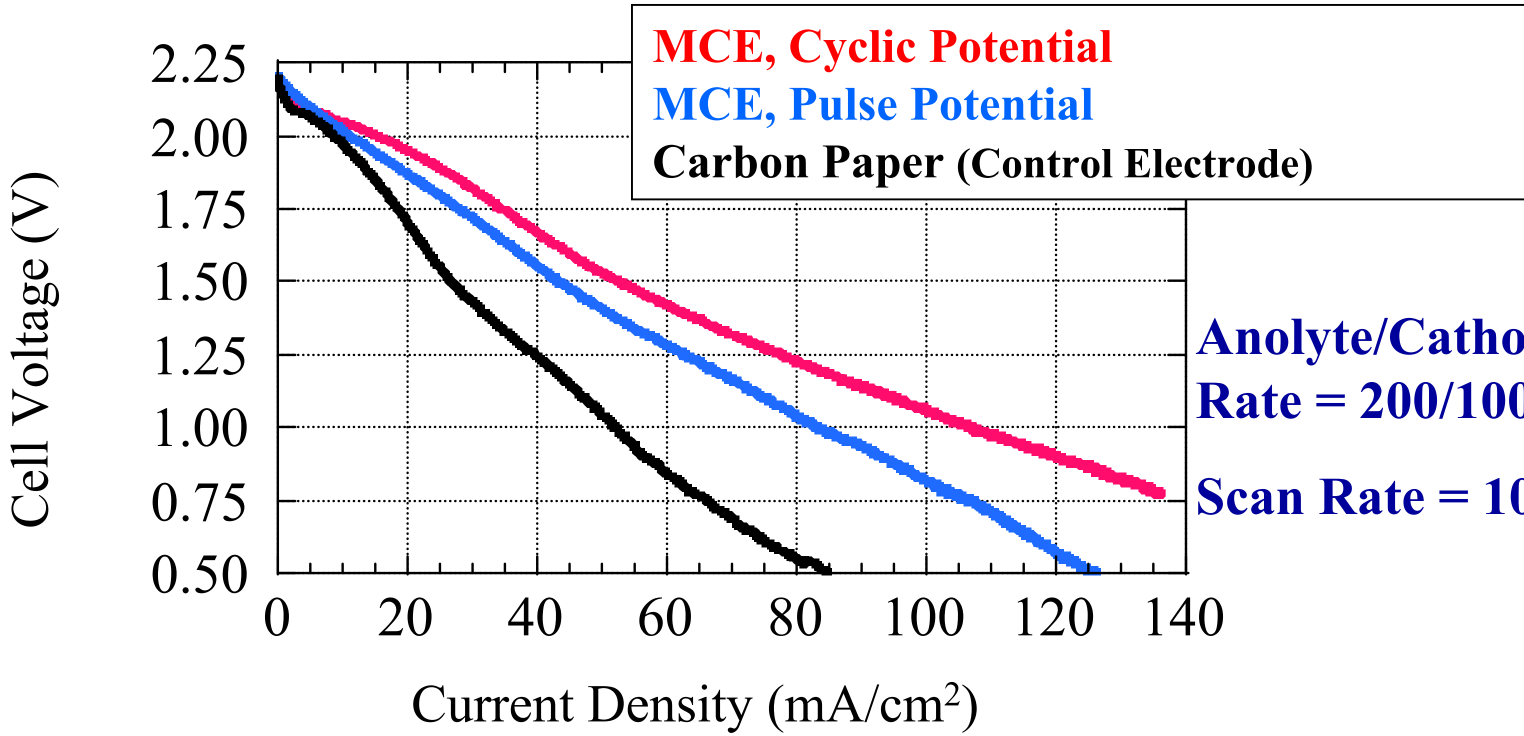
H_2O_2 Concentration = 0.25M

Scan Rate = 10 mA/s

Constant Current Performance of Mg–SFC with MCE and Carbon Paper Cathodes



Polarization Performance at Reduced H_2O_2 Concentration 0.060M H_2O_2

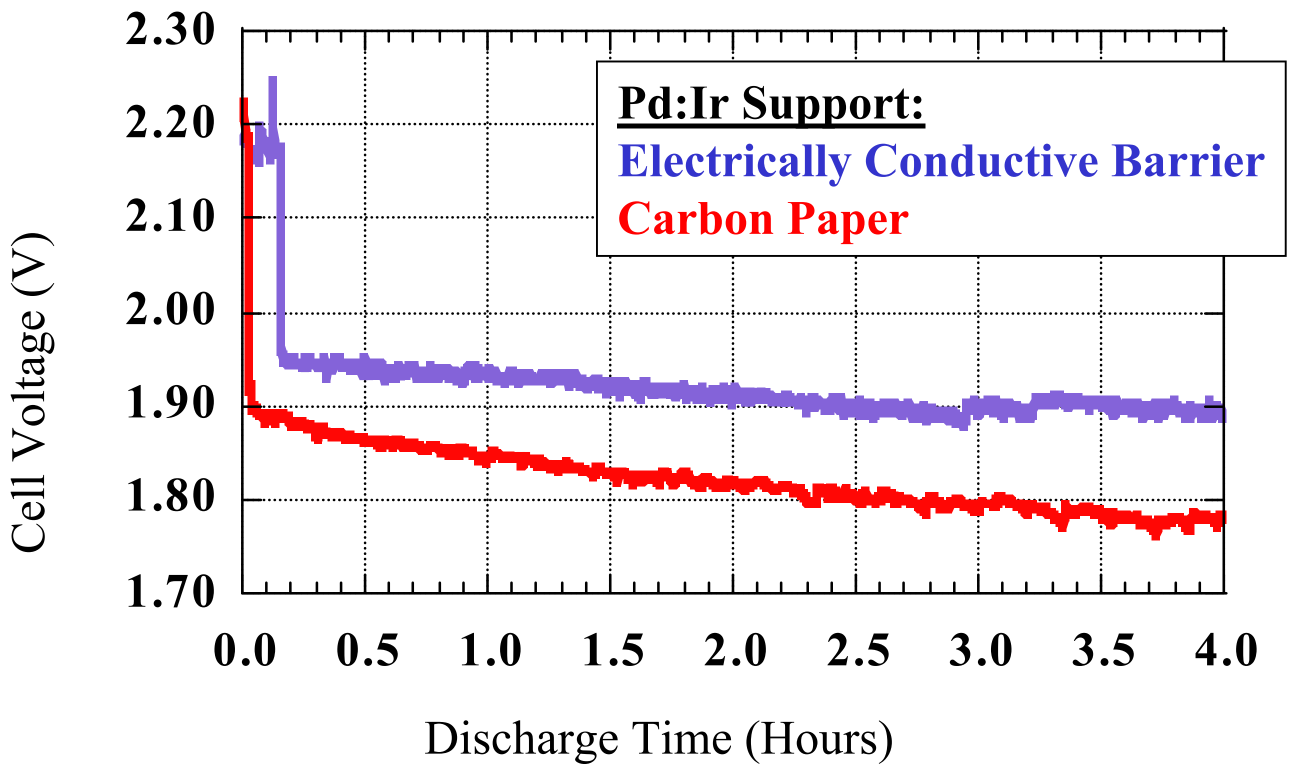


Anolyte/Catholyte Flow Rate = 200/100 mL/min

Scan Rate = 10 mA/s

MCE Electrically Conductive Barrier vs. Carbon Paper

Mg SFC Electrode Dimensions: 1 x 1.5"
Current Density: 25 mA/cm^2
Catholyte: 0.25 M H_2O_2, 0.20 M H_2SO_4, 40 g/L NaCl



Contents

Summary

- Demonstrated Full Duration (60+ hours) Nafion Membrane

- Demonstrated Full Thickness (200 mils) Mg electrodes for 50 hrs, Expect 60+ hours with this electrode

- Established consistent voltages of 1.9V/cell

- Polarization and constant current results show that the MCE electrode significantly improves the rate capability of the Mg/H_2O_2 SFC.

- At equivalent H_2O_2 concentrations, the MCE SFCs have significantly better rate capability.

- The MCE developed a higher cell voltage at 0.25 M H_2O_2 and nearly the same cell voltage at 0.06M H_2O_2 concentration as the carbon paper SFC.

- Bi-Polar Mg/Carbon viable for Series Stack Configuration

Acknowledgments

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- Drs. Yong Kim and Armand Lewis
  University of Massachusetts Dartmouth
  Textile Science Department

- Mitsubishi Chemical Co.

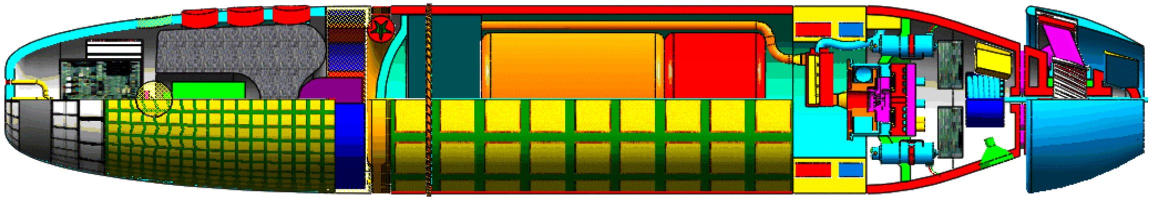
- Engineered Fibers Technology, LLC

Contents

Thank you

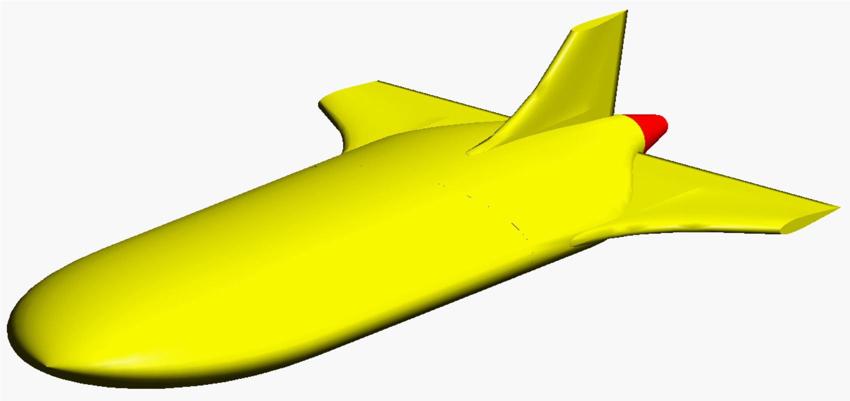
Nature of Current Work: What We Do

New Generation Torpedo
(500+ kW)



21" UUV
(2-5 kW)

MRUUV
(1-10 kW)



Develop Advanced Energy Systems (6.1, 6.2 & 6.3) to meet a Full Power & Energy Spectrum for Future Undersea Tactical Scale Vehicles :Torpedoes, Targets & UUVs

New Semi Fuel Cell Concept

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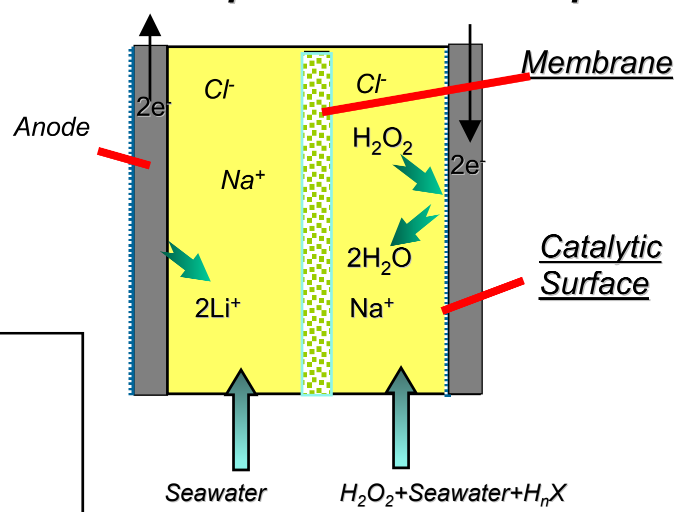
Li (stabilized) -SFC Separated Flow Concept

$2Li+H_2O_2+2H^+ \rightarrow H_2O + 2Li^+$, E^o=4.82 Volts

Mg - H_2O_2 (acidic)	4.14 V	0.89 Ah/g	3.68 Wh/g[1]	600 Wh/kg[2]
Li - H_2O_2 (acidic)	4.82 V	1.07 Ah/g	5.18 Wh/g[1]	>700 Wh/kg[2]

1-THEORETICAL (per mass of reactants (grams))
2-PROJECTED System

Li-SFC w/Separated flow Concept



Membrane Requirements

1. Block H_2O_2 from anode
2. Exchange Na^+, X^{n-} , and Cl^- for electroneutrality

High Voltage Li-SFC w/Separated Flow Concept Yields Potential High Energy SFC (25% above Mg-SFC): +700 Wh/kg

Life Cycle Costs

110 kWh Mission

- Based on Material for Five (5) 110 kWh Missions

- Higher Quantities will Reduce Al Cost 25-50%

Non-Consumables (Bladders, Valves, Meters, Controller, Pumps)

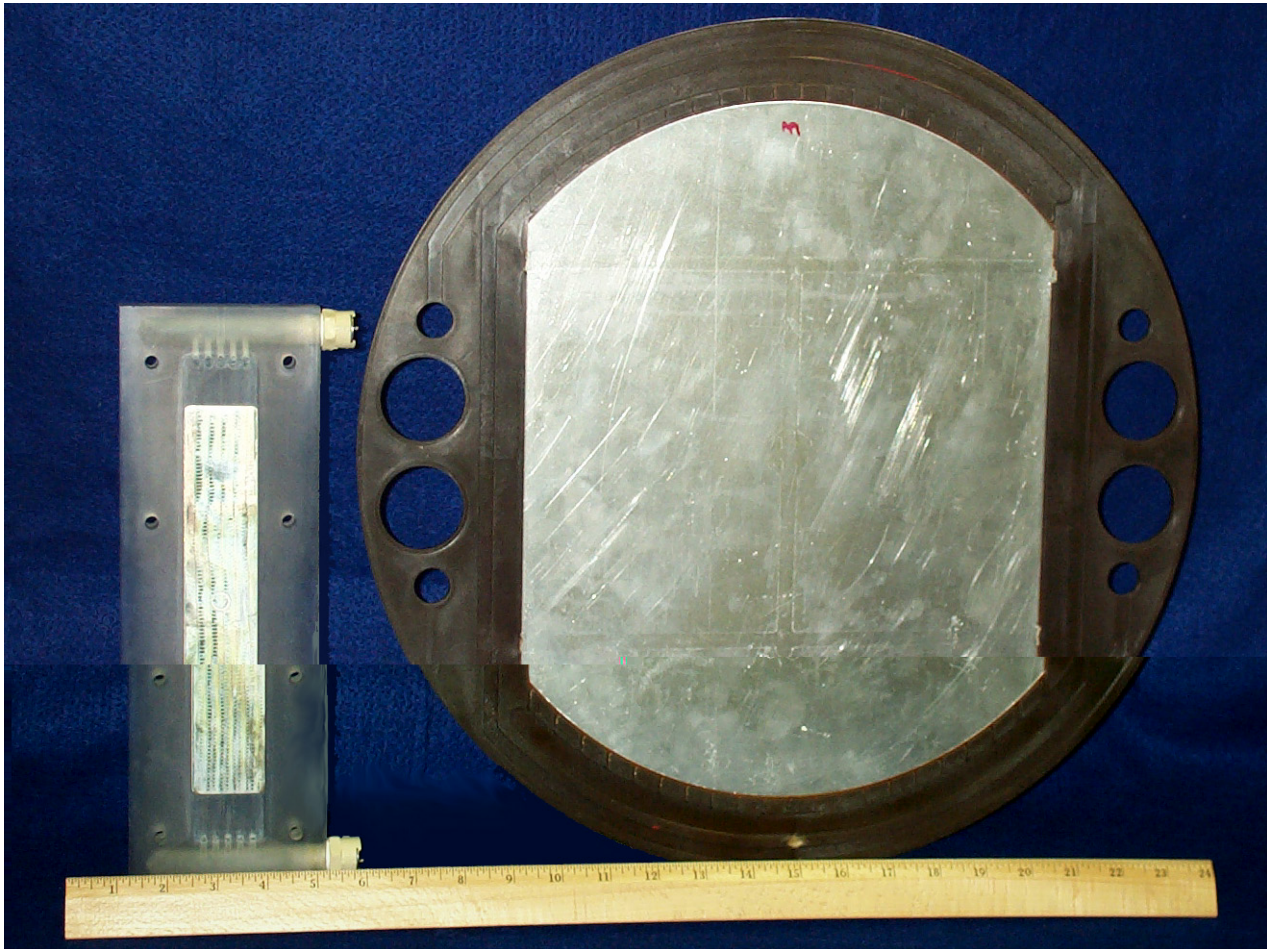
UPC Estimate ~ $50 -$75k

10 Runs (Life Cycle) - Goal of 20 Runs

$5k/run Amortized non-consumables

Net LCC (Mg-SFC) = $14.5 k/run, (135-140 $/kWh) - Based on quantities for 5 runs or less

Prototype Experimental Hardware



1.5 x 8 cell(77 cm2)--> 21″ Prototype(1100 cm2)