Micro DMFC/Lithium-Ion Power Source for Low Power Applications

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212th Meeting of the Electrochemical Society
October 11, 2007

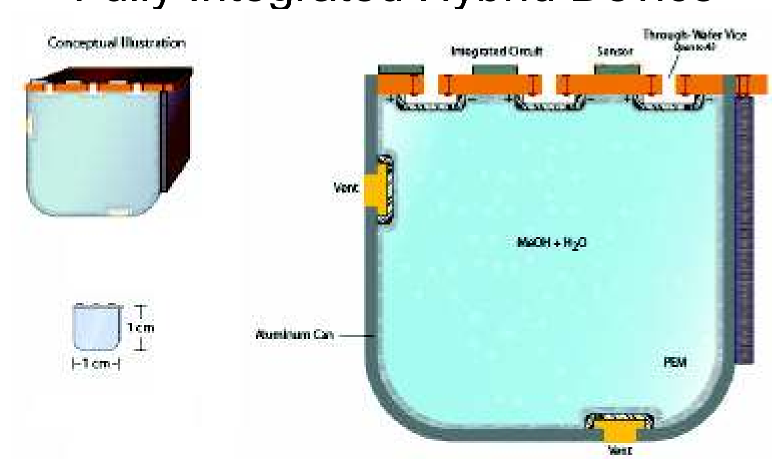
Motivation

- Explosive Growth in Wireless Devices
  - Sensing
  - Monitoring
  - Active RFID
  - Communication
- Next Generation Devices Micro-Scale
  - Stand Alone Post-Deployment (No Refueling)
  - Long life (> 1 yr)
  - Non Intrusive: 1-10 cm^3
    - These requirements dictate low average power density (1-1000 μW)

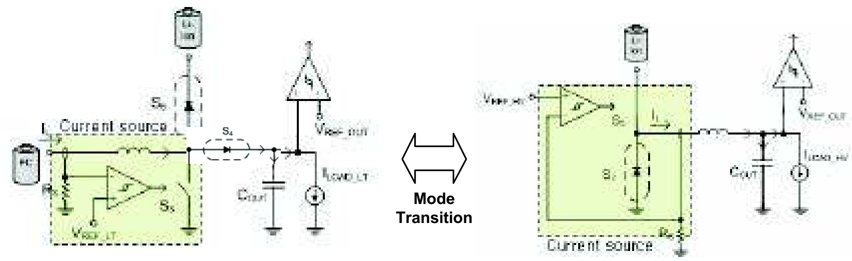
Device Requirements for Low Power Hybrid Micro DMFC

- Include component for sensing and data telemetry
  - State of the Art Sensing and Telemetry Requires Higher Power (1 mW → 100 mW)
- Propose Hybrid Solution
  - Fuel Cell Operates in Steady State 1 μW → 1 mW
    - Provide “sleep” current; Send excess to power storage device
  - Li-Ion Battery Provides Moderate Burst Power: 1 mW → 100 mW
    - Low Duty Cycle
- High energy density Fuel (12 M methanol)
- Fully Integrated
- Goal: High Total System Efficiency (> 75 %)

Fully Integrated Hybrid Device



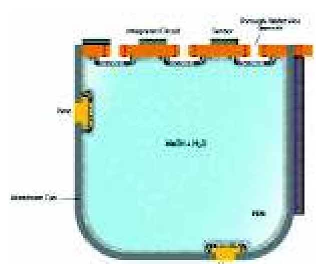
Operational Modes



Light-Load (Sleep): FC → Load, Li Ion

Heavy-Load (Event): Li Ion, FC → Load

What needs to be invented?



- CO_2 Vent
- Low-loss membrane
- Compatible electrode structure
- Passive fuel delivery system
- Power management electronics

- Choose appropriate energy storage solution
- Do all this with focus on maximizing efficiency

Fuel Cell Energy Efficiency, ε

- Minimize methanol fuel lost to evaporation and crossover
- Reduce ionic resistance
- Increase the cell operating and open circuit voltages

- Total fuel consumption:
    - Fuel consumed for generating electrons (energy)
    - Fuel lost through cross over through the membrane
    - Fuel lost through the carbon dioxide vent
    - Electrical loss due to the high resistance of the membrane
    - Fuel tightly bound to the wicking material

Novel System Components

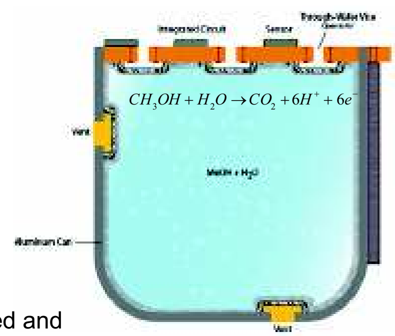
- CO_2 Vent
- Low-loss membrane
- Compatible electrode structure
- Passive fuel delivery system
- Power management electronics

- Choose appropriate energy storage solution

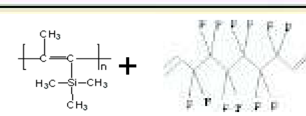
Fuel Tank: CO_2 Accumulation

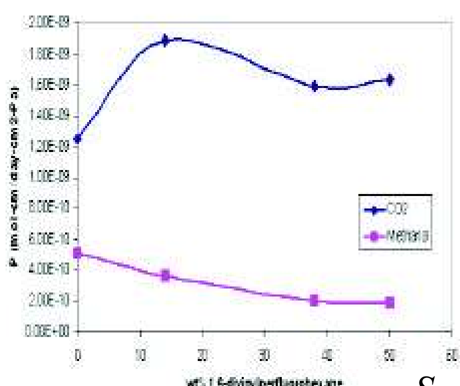
Problem:

- CO_2 build up in fuel tank
    - Pressure built: ~1 PSI /day
    - Rupture of device
    - Intensify MeOH crossover
- Solution:
    - Design of a CO_2 Release Mechanism:
        - Methanol barrier
            - Mechanical Valve: complicated and bulky
            - Membrane window: easy to fabricate

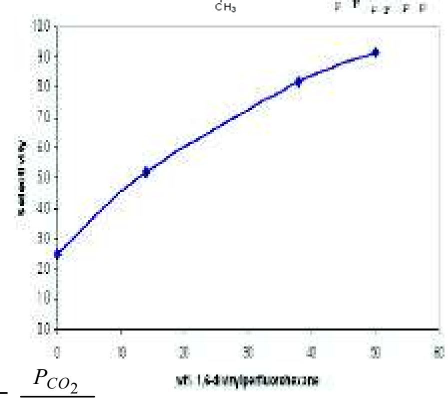


CO_2 and Methanol Permeabilities for PTMSP with 1,6-divinylperfluorohexane





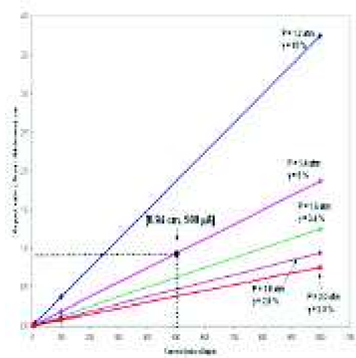
$$S = \frac{P_{CO_2}}{P_{MeOH}}$$



System Design and Component Life Time

Design Parameters

- Required I = 500 μA
  Allowed P =1.4 atm
- Vent Aspect ratio = 0.94 cm
- **5% of the consumed fuel will be lost through the vent**
- **Fuel cell life time ~ 1 year**



Novel System Components

- CO_2 Vent
- Low-loss membrane
- Compatible electrode structure
- Passive fuel delivery system
- Power management electronics

- Choose appropriate energy storage solution

Conductivity is NOT the Most Important!

- Low Current
- No support infrastructure
- Passive Operation

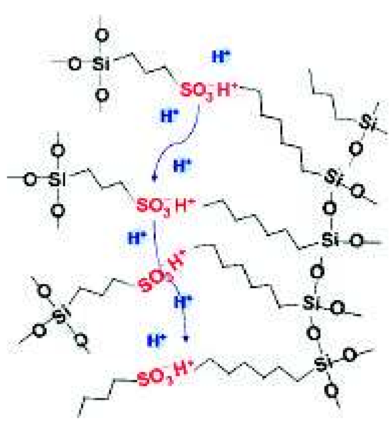
Issue : **What is important in the low power device?**

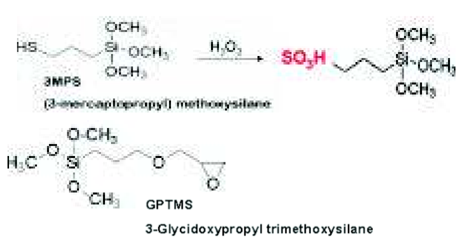
→ **Balance between**
Conductivity and MeOH permeability

(Example) Nafion 117 : Conductivity ~ 10^{-1} S/cm

Permeability Coefficient : $2.672 \times 10^{-6} \frac{\text{Mol cm}}{\text{cm}^2 \text{ day Pa}}$

3MPS-GPTMS Composite Glass





- Conductivity is $>10^{-3}$S/cm
- MeOH permeability Coefficient

$\sim 10^{-10} \frac{\text{Mol cm}}{\text{cm}^2 \text{ day Pa}}$

(cf.) Nafion : $2.672 \times 10^{-6} \frac{\text{Mol cm}}{\text{cm}^2 \text{ day Pa}}$

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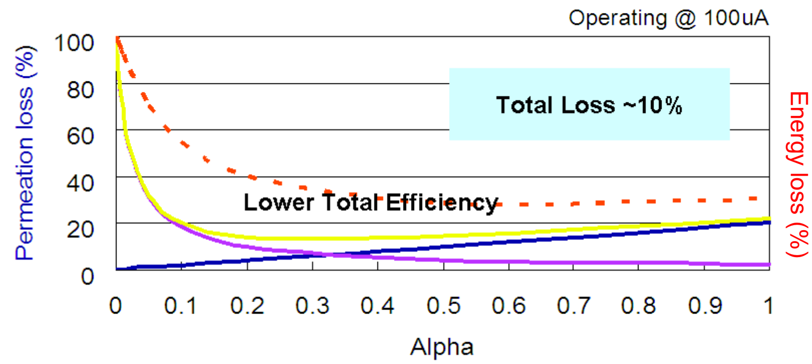
School of Chemical & Biomolecular Engineering

Fuel Efficiency of Glass Electrolyte



Fuel Cell efficiency with Nafion <<1 % ➡ **Fuel Cell efficiency with Glass ~ 90%**

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Novel System Components

- CO_2 Vent
- Low-loss membrane
- Compatible electrode structure
- Passive fuel delivery system
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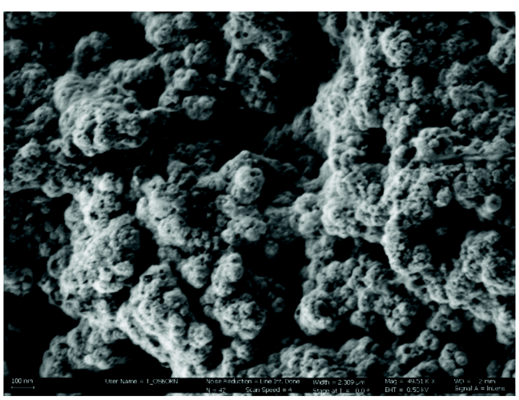
- Choose appropriate energy storage solution

Our Approach*

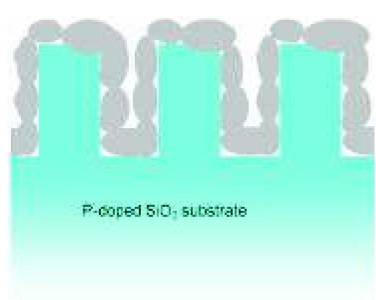
- Trouble with Nafion-based ink
  - CTE mismatch with SiO_2-based electrolyte
  - Performance is strong function of environment
- Nafion-free catalyst "ink"
  - Sol-gel glass with incorporated Pt/C particles
    - Reduced methanol crossover (~10^{-10} Barrers)
    - Acceptable Ionic Conductivity (2.5 x 10^{-4} S/cm)
    - No CTE mismatch with glass proton exchange membrane
    - Excellent adhesion and stability
  - Electroless Pt deposition after glass formation step
    - Pt as catalyst and current collector

* W.E. Mustain et. al, Electrochemical and Solid State Letters, In Press.

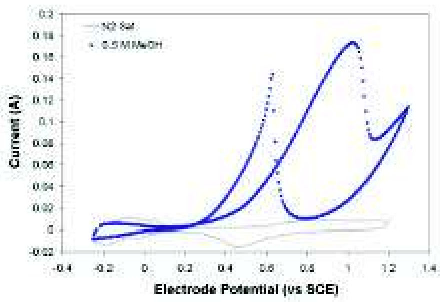
Scanning Electron Micrograph of Composite Catalyst Layer

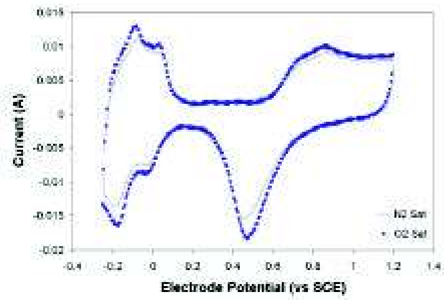


1 μm



Cyclic Voltammograms for Composite Pt/C-SiO_2 Electrode, 0.5 M H_2SO_4, 23°C, 50 mV/s, 1 cm^2





Pt/C-SiO_2 Composite Electrode Summary

- Successfully made glass electrodes
  - No CTE mismatch with the electrolyte
  - Easy fabrication
- Improved performance compared to nafion electrodes
  - Higher voltage
  - Higher current densities
- Need to demonstrate PtRu/C-SiO_2 Anodes
- Need to improve catalyst utilization

Novel System Components

- CO_2 Vent
- Low-loss membrane
- Compatible electrode structure
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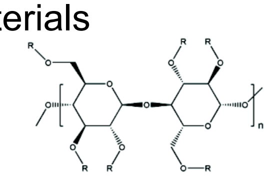
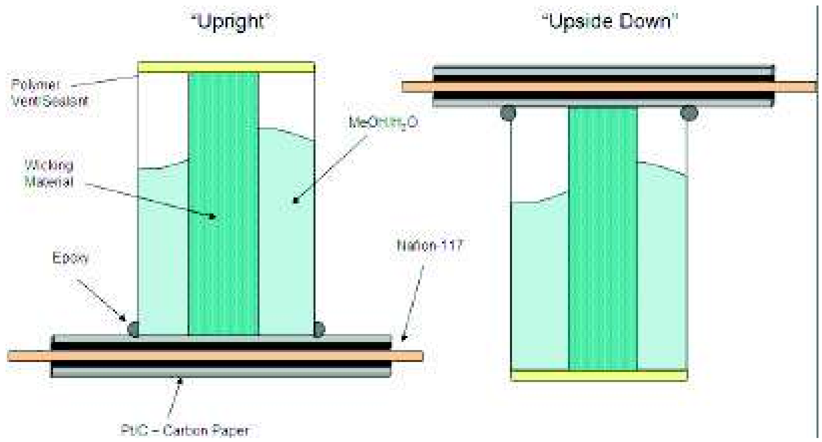
Passive Fuel Delivery

- Orientation Independent Operation
  - Upright and upside down
- Look for steady fuel delivery
  - Chronoamperometric experiments
- Identified Several Wicking Materials
  - Hydroxy Methyl Cellulose Foam

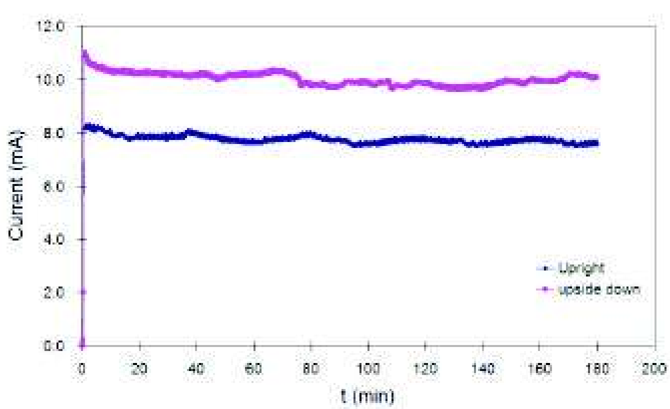


Cellulose: R = H
Methyl cellulose: R = CH_3 (40-90%) or H

Wicking Experimental Setup



Chronoamperometric Voltammograms for Upright and Upside Down Configurations, 0.3 V, 23 C



Wicking Summary

- Wicking material shows promising performance
  - Stable performance
  - Orientation independent
- Presence of cellulose foam reduces methanol crossover through membrane
  - Reduced "pooling" at the electrolyte interface
- Need to find a way to integrate into the device
  - Chemical attachment for long-life stability

Novel System Components

- CO_2 Vent
- Low-loss membrane
- Compatible electrode structure
- Passive fuel delivery system
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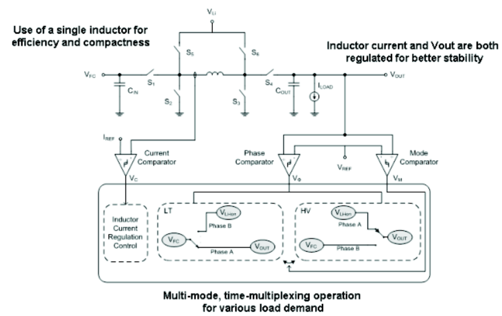
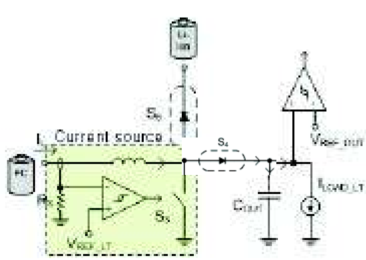
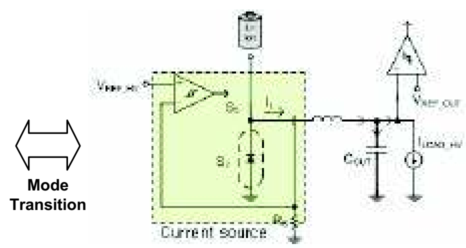
Design Considerations

- Ultra-Low Current (μA)
  - Typically low efficiency
    - Inductor-based system
- Loads (telemetry + sensors) require higher current (mA)
- Non-Continuous System
  - Two Operational Modes
    - Low Load
      - FC charges battery and "sleep" current
    - Heavy Load
      - Battery provides power to load



Operational Modes





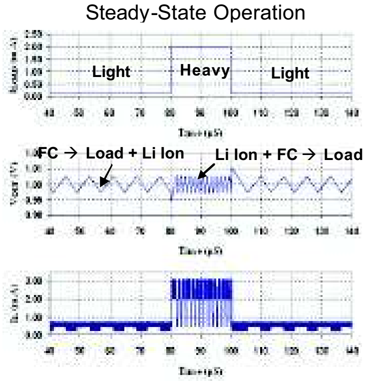
Light-Load: FC → Load, Li Ion

Heavy-Load: Li Ion, FC → Load

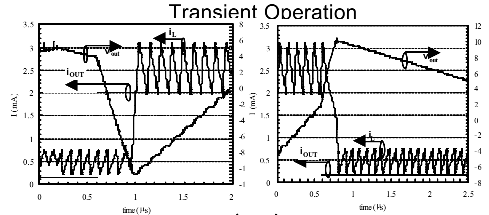
Simulation Results

AMI 0.6 m Process

Steady-State Operation



Transient Operation



Light to Heavy ⟺ **Heavy to Light**

Power Efficiency

Power Efficiency (?)	Sim.
Light : FC → Load	51%
Light : FC → Li Ion	44%
Heavy : Li Ion → Load	82%
Heavy : FC → Load	89%

Power Management Summary

- Designed multi-mode power management system
  - “Low” sleep/low load current (50 µA)
- Simulation results promising and awaiting fabricated chip
  - Test and evaluation

- We must reduce the low-load mode current below 10 µA

Novel System Components

- CO_2 Vent
- Low-loss membrane
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- Choose appropriate energy storage solution

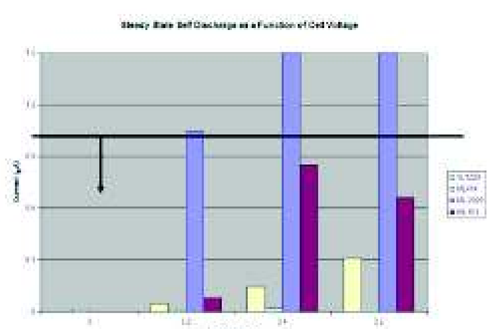
Battery Operation

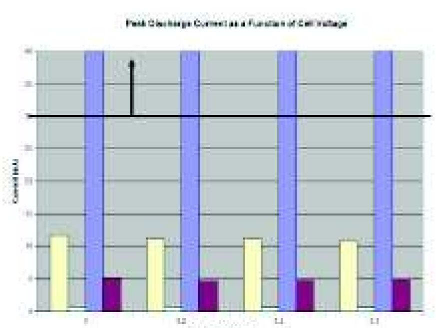
- Fuel Cell Operates Under Constant Load
  - During "event" current comes from battery
    - Battery must provide short bursts of power at near constant potential: > 30 mA
      - Battery always near fully charged
      - Fuel Cell current is low (10-1000μA)
        - » Ultra Low Self Discharge: < 1 μA
- Critical Battery Parameters
  - Self Discharge
  - Peak discharge current

Batteries Tested

Name	VL1220	ML414	ML2020	ML614
Manufacturer	Panasonic	Panasonic	Panasonic	Panasonic
Electrolyte	V_2O_5	MnO_2	MnO_2	MnO_2
Nominal Voltage (V)	3	3	3	3
Nominal Capacity (mAh)	7	1.2	45	3.4

Steady State Self Discharge and Peak Discharge Current for Selected Cells





Section Conclusions

- Vanadium oxide batteries show better performance
  - Lower Self Discharge
    - 0.05 – 0.3 μA
  - Higher peak discharge rate
    - > 1.5 C
- Issues Remain
  - No button cell had low enough self discharge and high enough discharge rate (higher capacity vanadium oxide cells)
- One possible solution is thin-film Li-ion
  - Oak Ridge Micro Energy, Excellatron, Cymbet

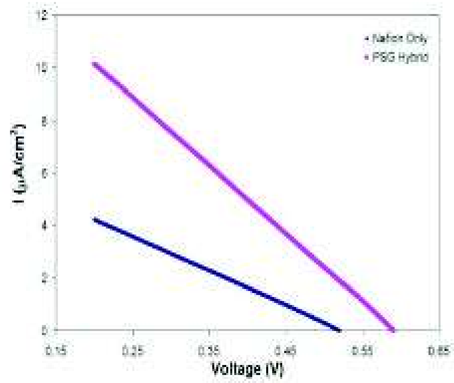
Acknowledgements

- Suhwan Kim, Tyler Osborn, Johanna Stark
- Kohl Group
- The authors would like to thank the Test Resource Management Center (TRMC) Test and Evaluation/Science and Technology (T&E/S&T) Program for their support. This work is funded by the T&E/S&T Program through the Naval Undersea Warfare Center, Newport, RI, contract number N66604-06-C-2330.
- The authors would also like to thank WiSPI.net and the Georgia Research Alliance for their financial contributions.

Questions?

Technology Comparison

Storage Device	Capacity, Ahr	Voltage, V	Energy density, kJ/cm^3
Energizer e^2 Lithium	2.9	1.5	1.95
(e^2 in rectangular case)	2.9	1.5	1.53
Li-thionyl chloride			
ER3VP	1.0	3.6	1.77
ER17500	2.7	3.6	2.37 (lower in square case)
Li secondary			
ML1220	0.012	3.0	0.540
ML2016	0.090	3.0	0.688
Li-cobalt oxide	1.350	3.6	1.06
Methanol (8M)	1.29/cm^3	0.5 - 0.7	2.3
Methanol (12M)	1.94/cm^3	0.5	3.5


12
10
8
6
4
2
0
I (μA/cm²)
0.15
0.25
0.35
0.45
0.55
0.65
Voltage (V)
Nafion Only
PSG Hybrid