A Novel Concept for Energy Storage

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GE Global Research

Trans-Atlantic Workshop on Storage Technologies for Power Grids
Washington, DC, October 19-20, 2010

This work supported as part of the Center for Electrocatalysis, Transport Phenomena, and Materials for Innovative Energy Storage, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001055

imagination at work

Acknowledgements

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T. Miebach
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Yale team
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Stanford team
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A. Hosseini

DOE - BES
J. Vetrano
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LBL/Berkeley team
J. Kerr
J. Arnold
T. Devine
R. Fish
K. Clark
D. Kellenberger
S. Rozenel

Megatrends … fuel cost, emission reduction & digitization

Intermittent renewables, smart grid deployment

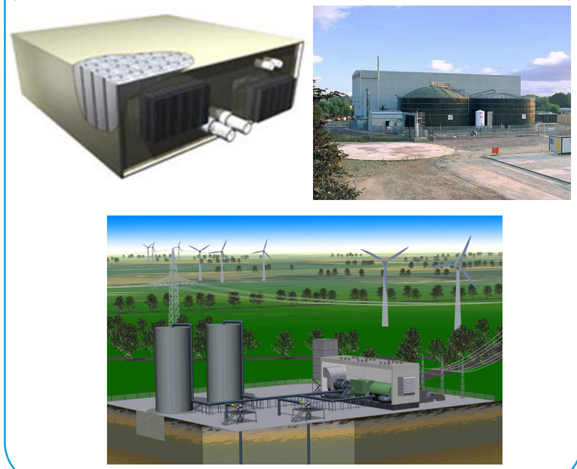
Opportunities for an advanced energy storage

Grid

Renewable Integration, Power Qality, Smart Grid, T&D Management

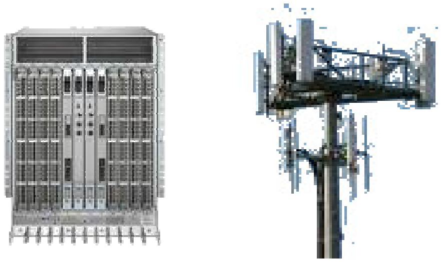
Energy Storage

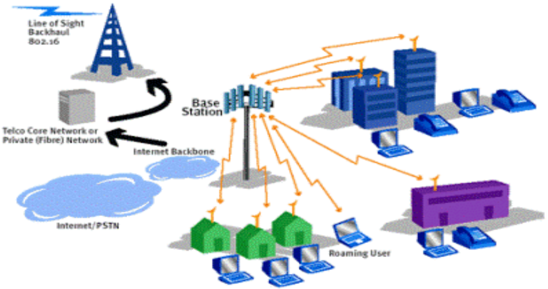
Mechanical, Chemical, Electrical, Electrochemical



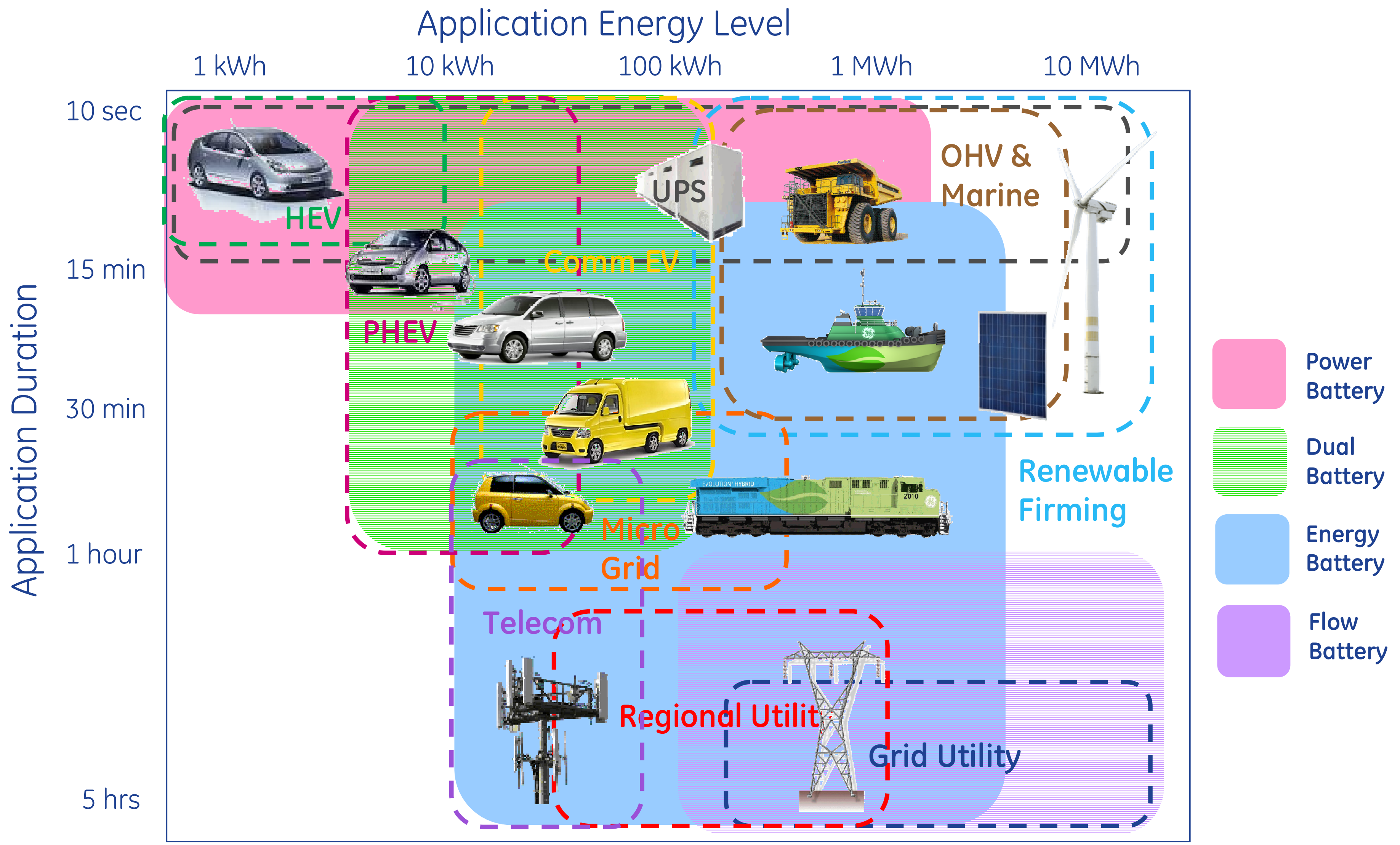
Backup Power

Telecom, UPS, Stand Alone Systems





Application Energy Storage Requirements



Energy battery: NaMx now…organic flow battery in future

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Energy Storage Market

- **Global investment in electric power ancillary services systems will reach $6.6 billion by 2019**
- **Deployment of renewables and smart grid is the strongest driver to push the grid storage market 3 – 5 times by 2016**
- **The global stationary energy storage business $35 billion by 2020**
  - ➢ 11 competing technologies
  - ➢ Li ion batteries may be ¼ of revenue
  - ➢ Compressed air, flywheel and sodium-sulfur batteries follow
- **Stationary fuel cells revenue $0.7 – 1.2 billion in 2013**
- **Stationary energy storage got a boost from transportation energy storage development (market size $19.9 billion in 2012)**

Sources: http://www.pikeresearch.com/category/research/energy-storage

http://www.luxresearchinc.com/press/RELEASE_41B_Energy_Storage_Market.pdf

http://www.netl.doe.gov/energy-analyses/

Electrochemical Energy Storage Options

Secondary batteries

- Stationary electrode materials
- Mature technology (lead acid, NiCd, NiNH, NaS)
- Emerging technologies ($NaMCl_2$, Li-ion)
- New chemistries (Li-air, Li-S, Zn-air)

NGK 34 MW NAS alongside 51 MW Wind Farm

Source:http://www.ngk.co.jp/english/products/power/nas/

Redox flow batteries

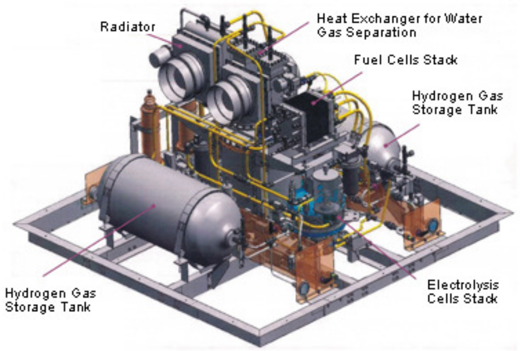
- Flowing electrode materials
- Mature technology (zinc-bromine, all-vanadium)
- Emerging technologies (cerium-zinc, iron-chromium)
- New chemistries (vanadium-bromine, soluble lead)

VRB (Prudent Energy) PacifiCorp (Moab, Utah) 2 MWh VRB-ESS

Source: http://www.pdenergy.com/

Regenerative fuel cells

- Gaseous electrode materials
- Emerging technologies (H_2-O_2 conventional and unitized)
- New chemistries (H_2-Br_2 , H_2-H_2O_2 , $NaBH_4$-H_2O_2)

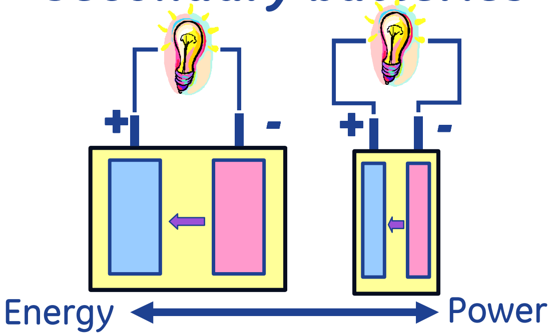


1kW-prototype Regenerative Fuel Cell System

Source: www.apg.jaxa.jp

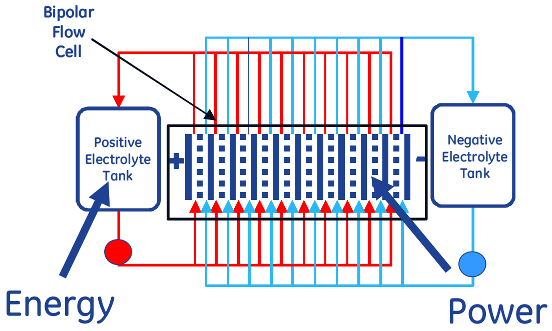
Electrochemical Energy Storage Comparison

Secondary batteries



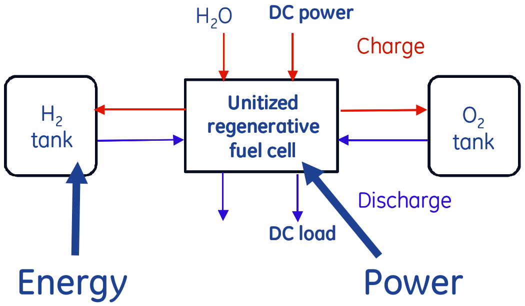
- No power-energy separation
- Moderate energy density (50 – 240 Wh/kg)
- High energy efficiency (65 – 90 %)
- Degradation mode – electrode
- Linear scalability (small cells)
- Moderate cost
- Mature technology

Redox flow batteries



- Power and energy separated
- Low energy density (10 – 50 Wh/kg)
- High energy efficiency (65 – 78 %)
- Degradation mode – membrane
- Non-linear scalability (cell stacks)
- Low cost
- Emerging technology

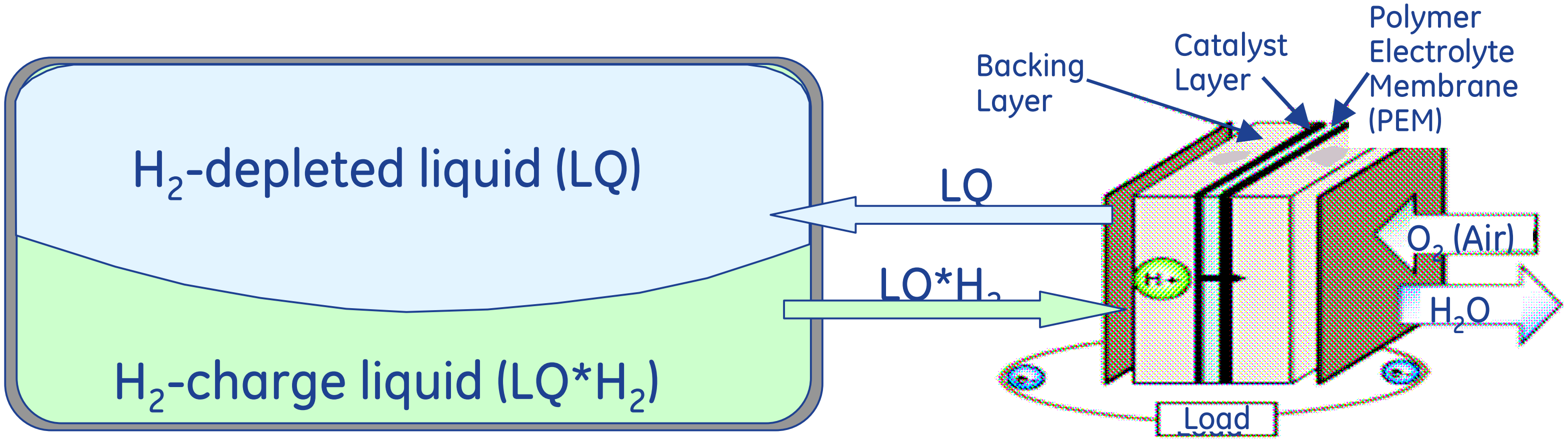
Regenerative fuel cells



- Power and energy separated
- High energy density (450 – 500 Wh/kg)
- Low energy efficiency (35 – 50 %)
- Degradation mode – catalyst
- Non-linear scalability (cell stacks)
- High cost
- New technology

- Combination of high energy density and efficiency, long cycle life, high DOD, low cost, fire and environmental safety desirable
- Main focus on transportation, more efforts on stationary storage needed
- New concepts wanted

Direct organic fuel cell/flow battery concept



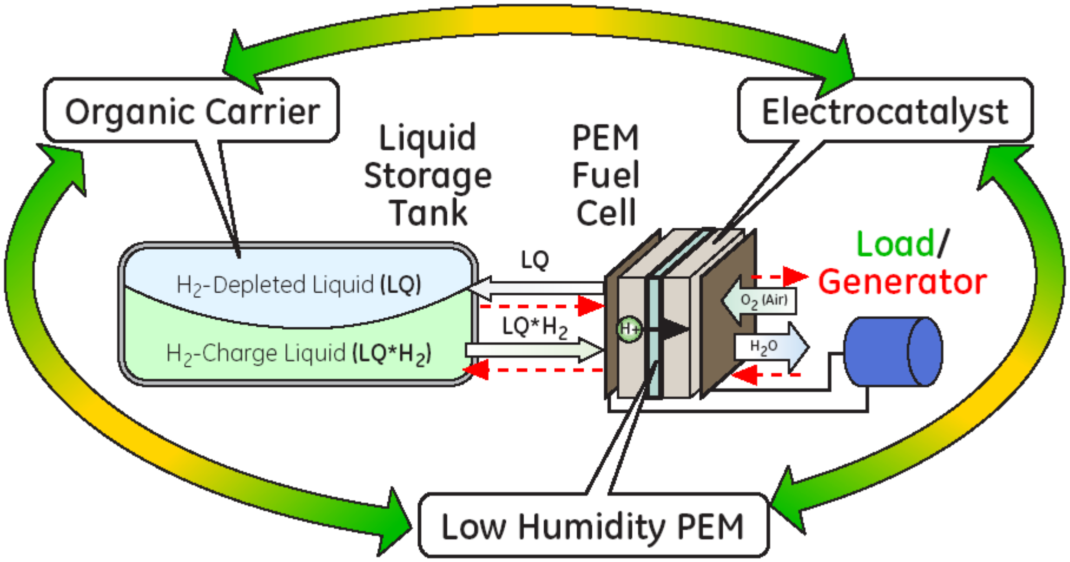
- Feed the hydrogenated organic liquid carrier directly into the fuel cell where it will be electrochemically dehydrogenated to a stable, hydrogen depleted organic compound without ever generating gaseous H_2 to produce power
- The spent organic carrier may be replenished either mechanically or electrochemically from water splitting
- Minimize the balance of plant by excluding a catalytic reactor and a heat exchanger

- **High theoretical energy density (up to 1350 Wh/kg)**
- **Low membrane crossover – high efficiency**
- **Energy conversion and storage separated - low packaging**
- **Reversibility (fuel cell ↔ flow battery)**
- **Excellent safety, zero carbon emission**

U.S. DEPARTMENT OF ENERGY

Center for Electrocatalysis, Transport Phenomena, and Materials for Innovative Energy Storage
Dr. Grigorii Soloveichik (GE Global Research)

Electrocatalysis, transport phenomena and membrane materials basic research aimed to three novel components of an entirely new high-density energy storage system combining the best properties of a fuel cell and a flow battery: organic carriers, electro(de)hydrogenation catalysts, and compatible PEM



Focus areas:
- C-H bond catalysis/
- Electro(de)hydrogenation catalyst
- Organic fuel
- Low humidity proton exchange membrane

Award DE-SC0001055

Yale University

STANFORD University

an Office of Basic Energy Sciences
Energy Frontier Research Center

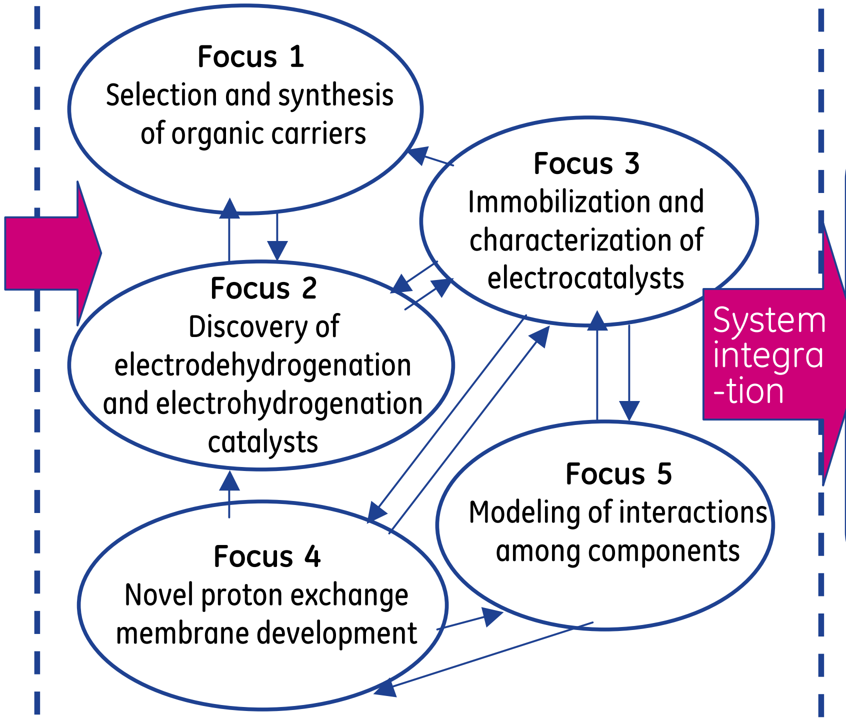
Task interactions and program vision

Challenges and needs

- Electron level material processes
- Atom- and energy efficient synthesis
- Far from equilibrium processes control
- Electrical energy storage
- Catalysis for energy
- Hydrogen economy
- Solar energy utilization

Fundamental research

EFRC



Focus 1
Selection and synthesis of organic carriers

Focus 2
Discovery of electrodehydrogenation and electrohydrogenation catalysts

Focus 3
Immobilization and characterization of electrocatalysts

Focus 4
Novel proton exchange membrane development

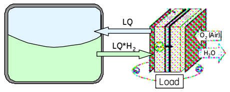
Focus 5
Modeling of interactions among components

System integra-tion

Program management

Technology

High density energy storage organic fuel cell/flow battery



Applications

Solar energy

Plug-in hybrids

Wind energy

Load leveling

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Fuel (organic carrier) focus

Traditional approach

$LQH_n \Leftrightarrow LQ + n/2\ H_2$

ΔH to be minimized

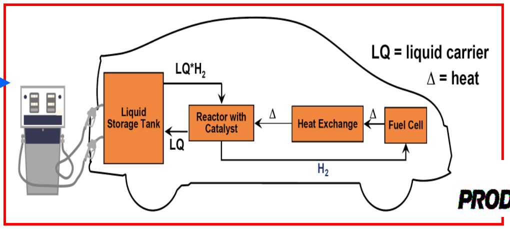
EFRC approach

$LQH_n + n/4\ O_2 \Leftrightarrow LQ + n/2\ H_2O$

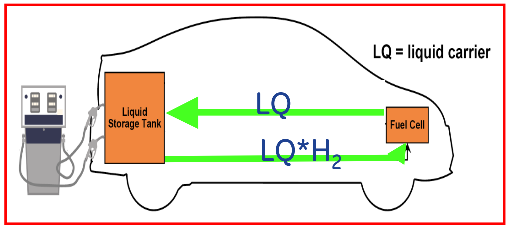
$\Delta(G_{LQHn} - G_{LQ})$ to be minimized to maximize cell voltage

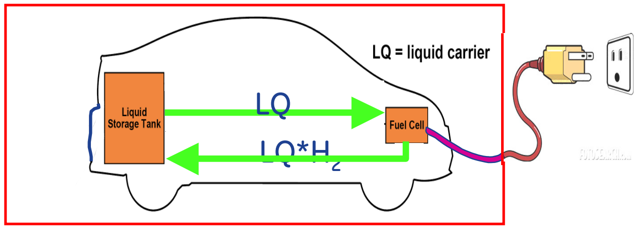
Theoretical cell voltage 0.95 – 1.1 V

(depends on organic hydrogen carrier)



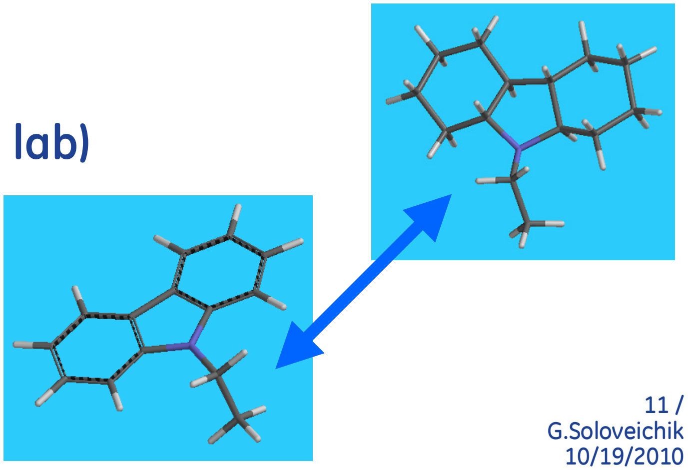
AIR PRODUCTS





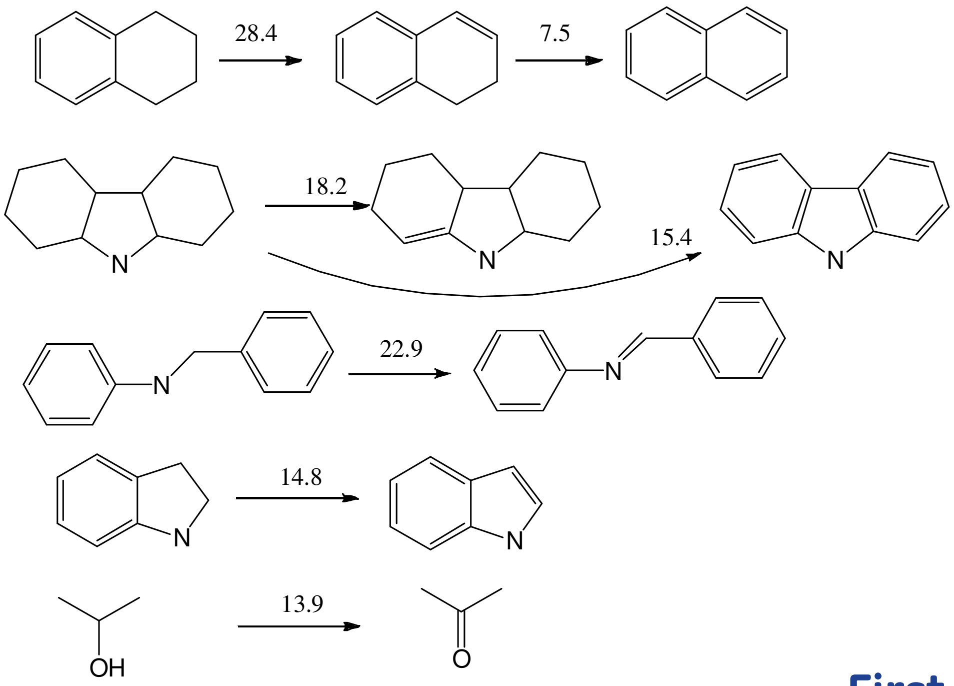
Organic fuel requirements

- **Minimal ΔG dehydrogenation of organic carriers via molecular modeling guidance**
- **Scalable synthesis of aromatic precursors and hydrogenation to saturated carriers (high pressure lab)**
- **Liquid at ambient conditions, low vapor pressure**

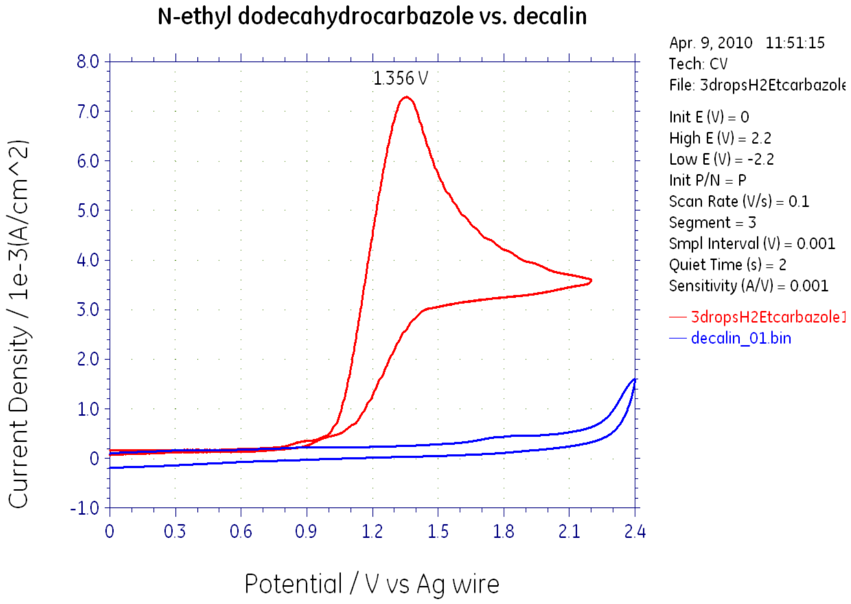


Organic fuels molecular modeling

Comparison of dehydrogenation energies for model and promising fuels in kcal/mol H_2 by DFT calculation (method B3LYp, basis set 6-311++G**)



Electrooxidation of model fuels on Pt electrode



Apr. 9, 2010 11:51:15
Tech: CV
File: 3dropsH2Etcarbazole

Init E (V) = 0
High E (V) = 2.2
Low E (V) = -2.2
Init P/N = P
Scan Rate (V/s) = 0.1
Segment = 3
Smpl Interval (V) = 0.001
Quiet Time (s) = 2
Sensitivity (A/V) = 0.001

First dehydrogenation step most critical

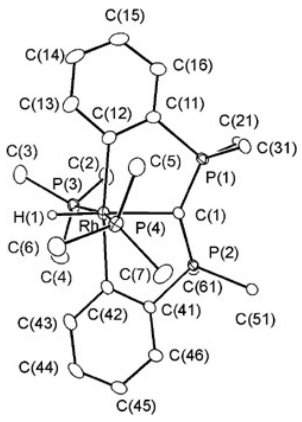
Single-bond and multiple-bond model and promising fuels selected based on computational modeling

C-H bond catalysis focus

Homogenous C-H bond activation **and** electron transfer

$$LH_n - n e^- \overset{\text{catalyst}}{\Leftrightarrow} L + n H^+$$

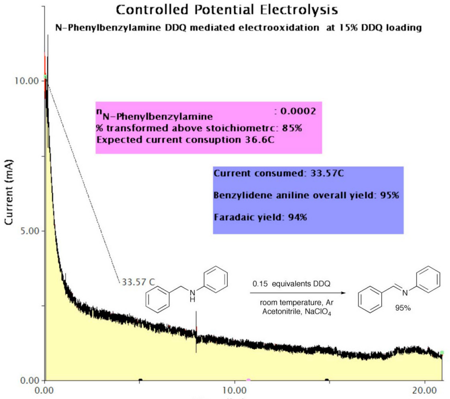
Utilize defined metal centers for catalysis understanding



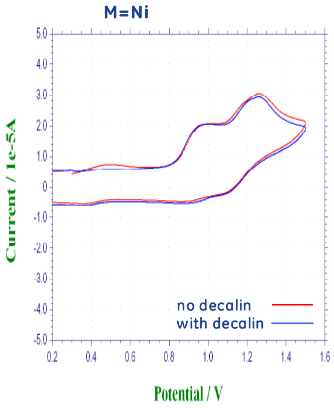
Rh-based
pincer complex

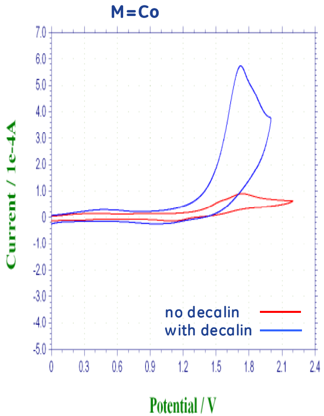
Catalyst requirements

- Catalytic activity in the C-H bond activation and further dehydrogenation of saturated hydrocarbons
- Redox activity in target electrochemical potential windows
- Microscopic reversibility (dehydrogenation/hydrogenation)
- Ability to transfer multiple electrons and protons
- Tunable redox potentials to selected organic fuels



Organic catalyst for electrodehydrogenation

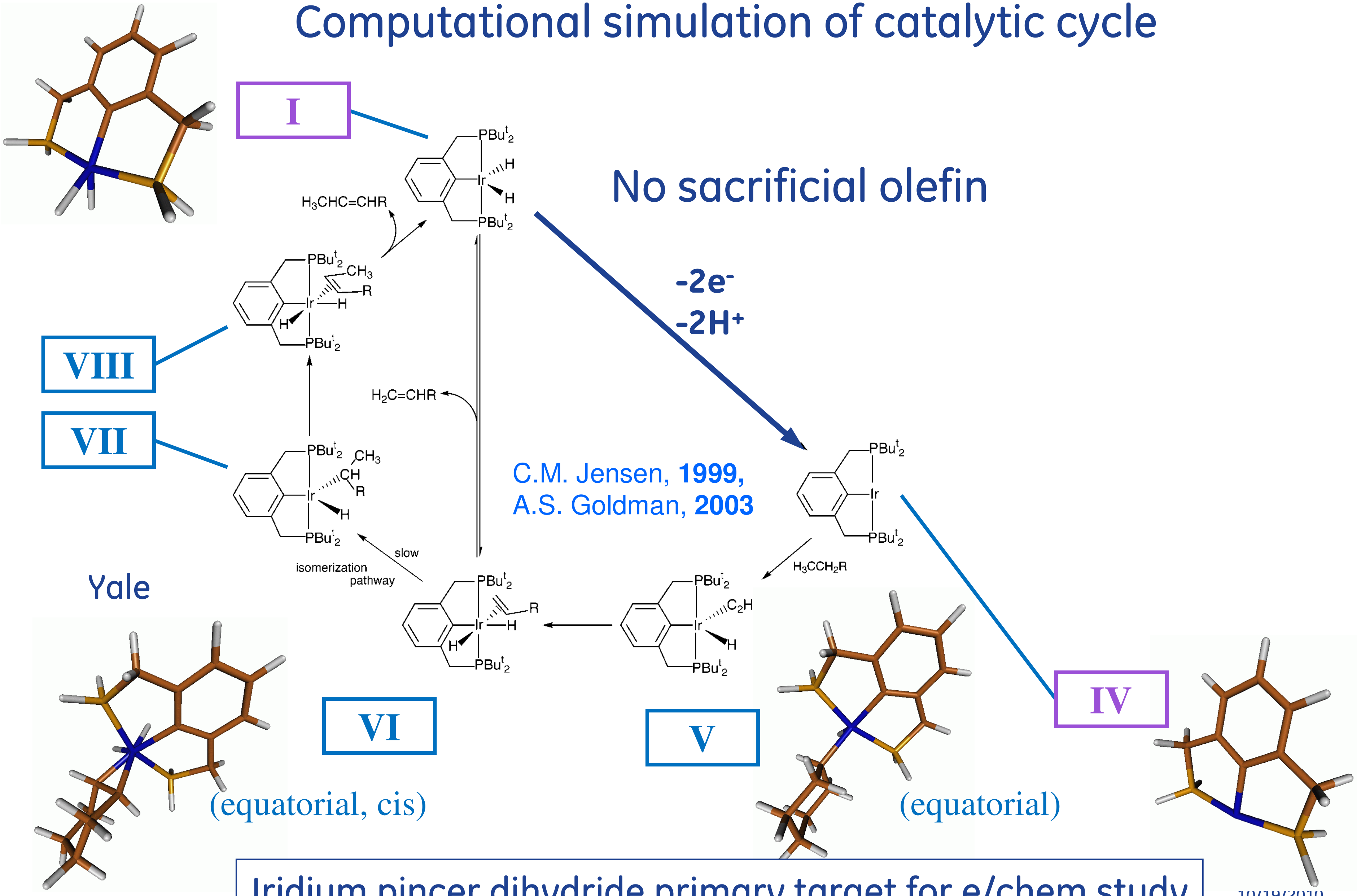




First electrocatalytic oxidation of cycloalkane on a metal complex

Alkane dehydrogenation mechanism

Computational simulation of catalytic cycle



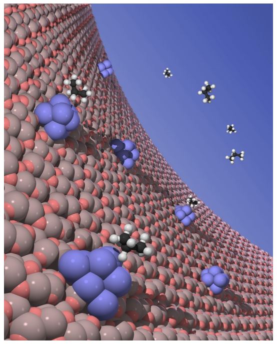
No sacrificial olefin

C.M. Jensen, **1999,**
A.S. Goldman, **2003**

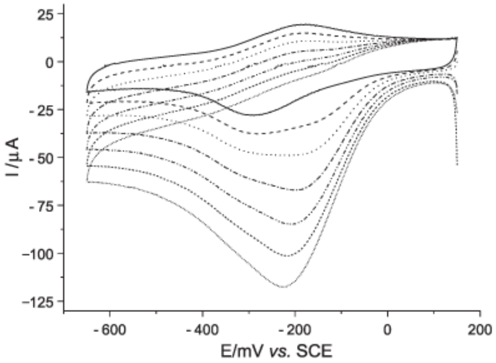
Iridium pincer dihydride primary target for e/chem study

Electrocatalysis focus

Electrocatalysis for dehydrogenation and hydrogenation

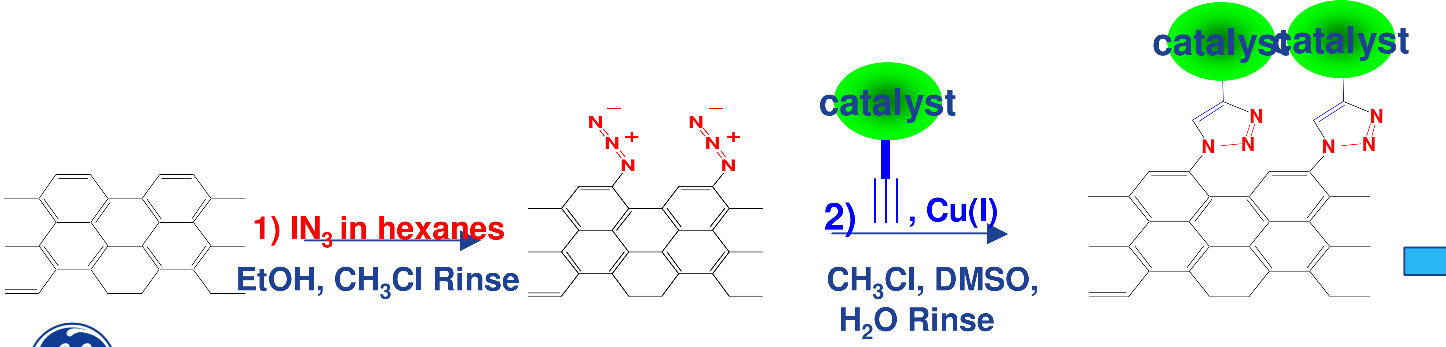


$$LH_n - n e^- \overset{\text{electrode}}{\Leftrightarrow} L + n H^+$$

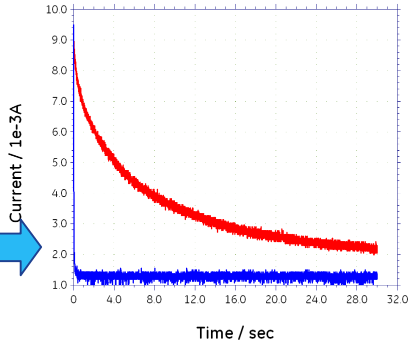


Electrocatalyst requirements

- **Fast electron transfer from metal centers through a linker to electrode via study of the transport mechanism and determination of controlling factors**
- **Fast proton transport to PEM via structured catalyst/support**
- **Robust catalyst that tolerant to impurities/reaction products**
  - **design catalyst ligand environment for selectivity**
  - **use nanosized metal alloys catalysts supported on carbon**

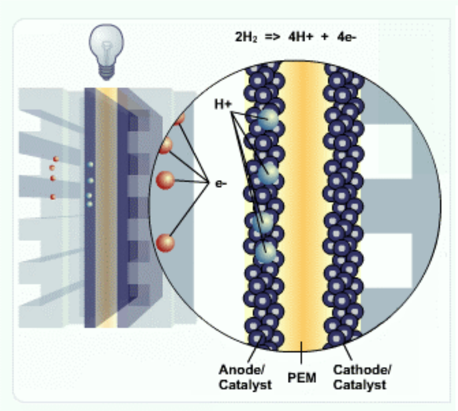


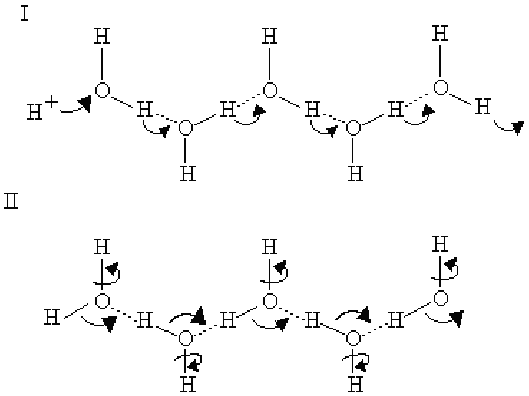
Chronoamperometry of baseline RVC (blue) and functionalized RVC (red)



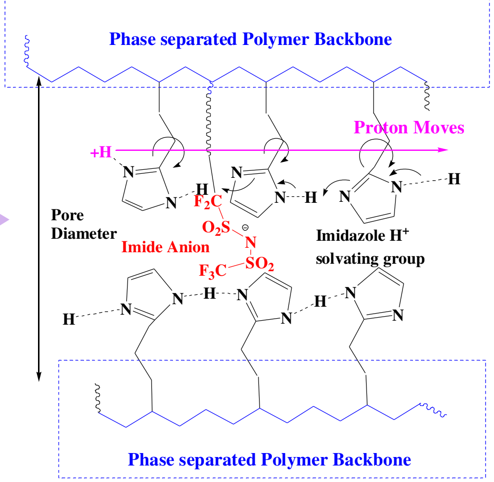
Proton exchange membrane focus

Traditional approach



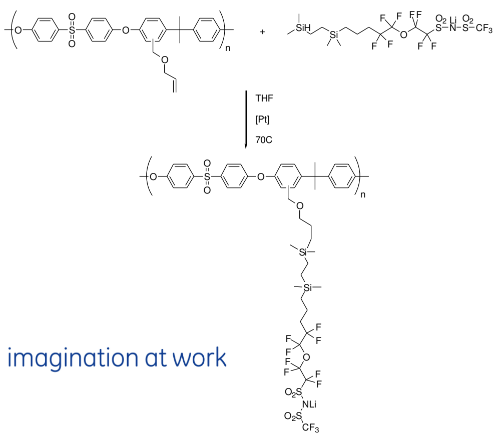


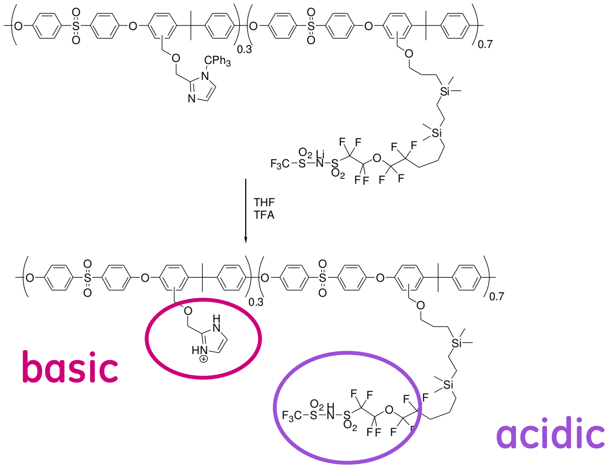
EFRC approach



Membrane requirements

- Water free PEM (H_2O detrimental to anode chemistry)
- Low fuel and products solubility – mechanical integrity
- Proton conductivity 10^{-3} S/cm @ 120 °C
- High oxidative stability at 120 °C
- Thermal stability (> 150 °C)



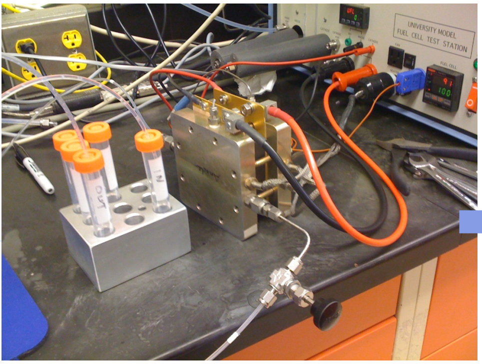


Direct organic hydride fuel cell testing

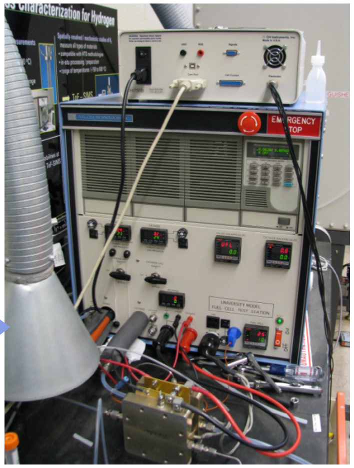
Membrane Electrode Assembly (MEA)

- 5 cm^2 active area
- Anode: 4mg/cm^2 60% PtRu/C, C-cloth anode GDL
- Cathode: 2 mg/cm^2 40% Pt/C
- 115 Nafion® membrane

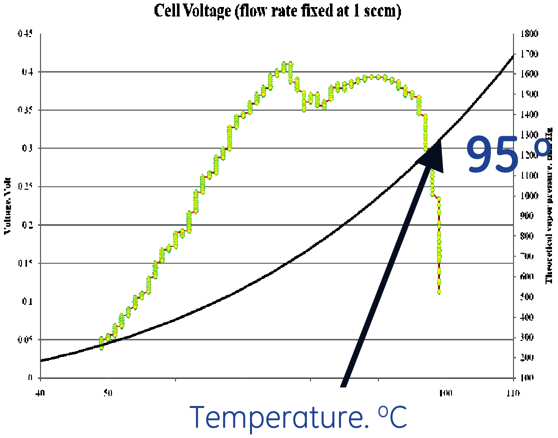
Fuel Cell Assembly



Fuel Cell Testing Station

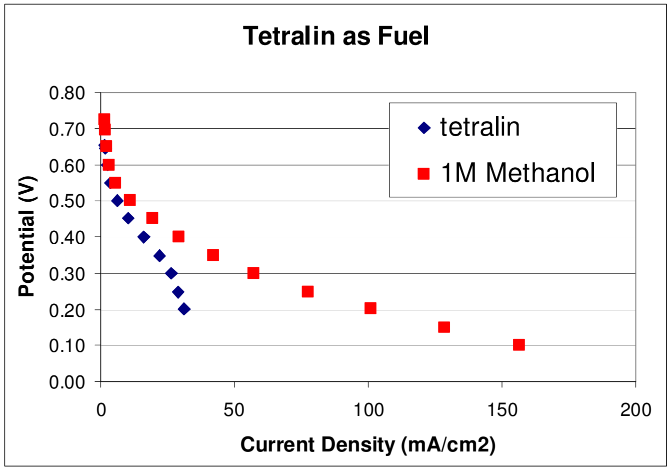


Cyclohexane/air cell



Membrane dehydration, new membranes needed

Tetralin/air cell



Significant current observed for tetralin

Liquid fuel cells OCV, V

Fuel	Theory	Exp.
MeOH	1.21	0.73
Decalin	1.10	0.55
Tetralin	1.08	0.66

Use of liquid hydrocarbon fuel in fuel cell demonstrated

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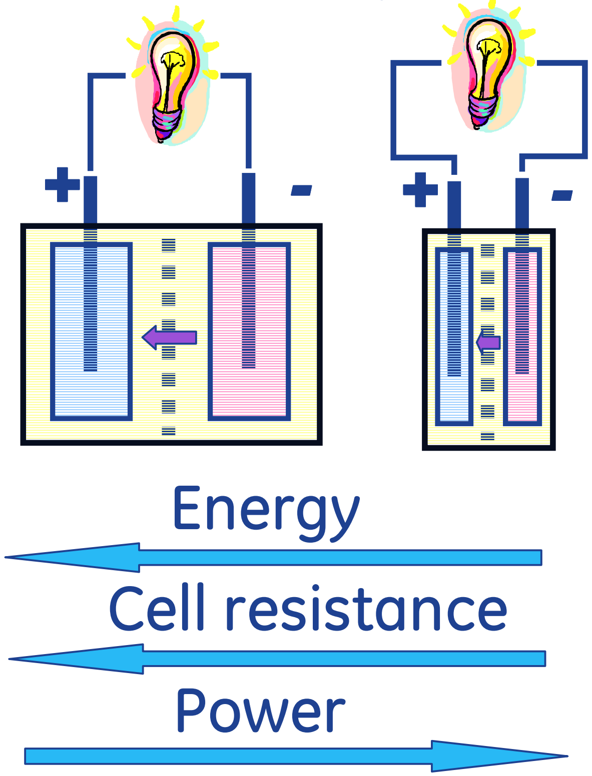
Conclusions

- Smart grid development and deployment of intermittent renewables require performance and cost effective energy storage
- New concept of high energy density storage system combining a PEM fuel cell and a flow battery suggested
- Energy Frontier Research Center targets major components of this system: organic fuel, electrocatalyst and low humidity PEM

Backup slides

Secondary batteries



Type	Cell voltage, V	Energy density, Wh/kg	Demo scale, MW	Major players
Lead acid	2.04	30 - 50	20	C&D Battery, Exide Technologies, Hagen Batterie AG, Storage Battery Systems
NiCd	1.29	50 - 75	27	Saft Batteries, Storage Battery Systems
NaS	1.78 – 2.07	150 - 240	34	NGK Insulators Ltd.
Li-ion	3.3 – 4.2	75 - 200	20	A123, Ener1, Altair Nanotechnologies, Saft Batteries
$NaNiCl_2$	2.58	135	-	FZ Sonick SA, GE
LiS	2.2	350	-	SION Power, PolyPlus

Advantages:

- Mature technology
- High round trip efficiency
- High power or high energy
- Modular design

Major technical challenges:

- High cost for advanced batteries
- Linear scalability (kW to MW)
- No deep cycling
- Electrode degradation, short lifetime
- Corrosion (high temperature batteries)
- Safety

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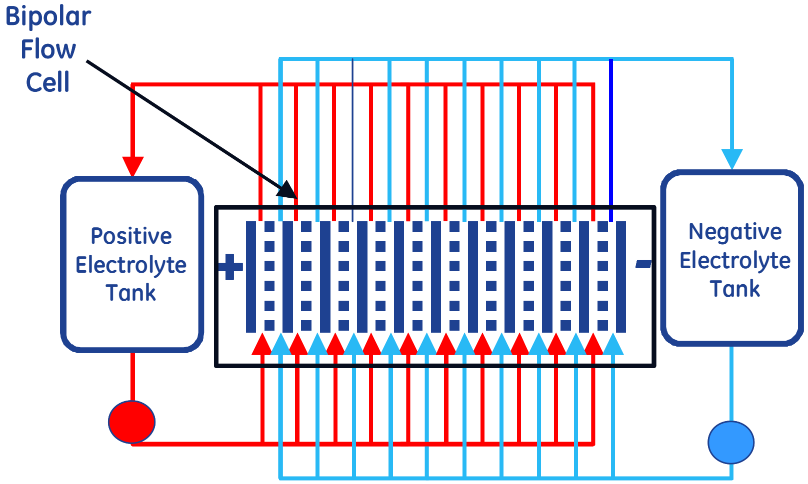
Flow batteries



Type	Cell voltage, V	Membrane	Energy efficiency, %	Major players
All-vanadium	**1.26**	**PEM**	**78**	**Prudent Energy, Sumitomo, VFuel Pt**
Polysulfide-bromine	**1.36**	**Ion-selective**	**77**	**Prudent Energy (IP holder)**
Zinc-bromine	**1.85**	**Porous diaphragm**	**73**	**ZBB Energy, Premium Power, Primus Power**
Cerium-zinc	**2.48**	**PEM**		**Plurion**
Iron-chromium	**1.18**	**Ion-selective**	**66**	**Deeya Energy**
Soluble lead acid	**2.04**	**No membrane**	**65**	**General Atomics**

Advantages:

- Separation of energy and power
- Non-linear scalability (kW to MW)
- High round trip efficiency
- Modular design
- Long lifetime
- Low cost

Major technical challenges:

- Low energy density (25 – 70 Wh/kg)
- Corrosion, expensive plumbing
- Environmental issues

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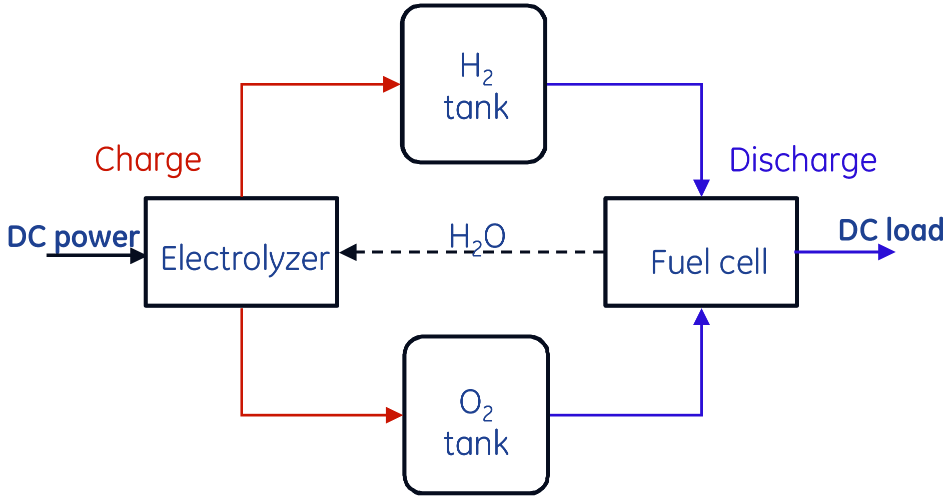
Regenerative H_2/O_2 fuel cells

Conventional design



D. Bents et al., NASA Glenn Research Center, 2008
http://gltrs.grc.nasa.gov

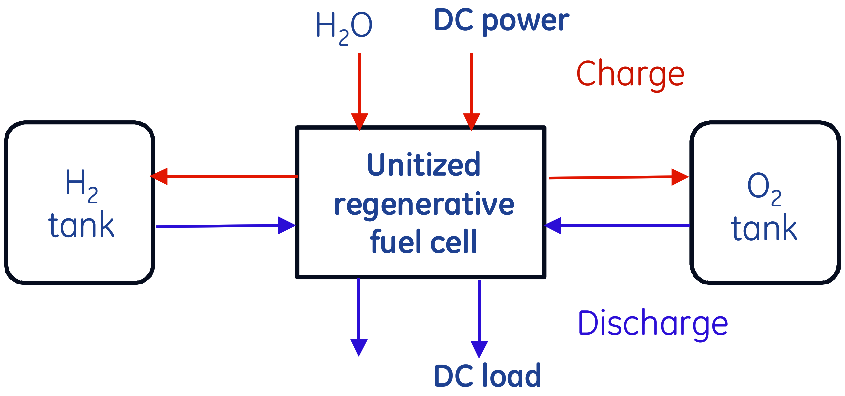
Major players:

Giner, Proton Energy Systems

Advantages:

- High energy density (500 Wh/kg)
- Separation of energy and power
- Long lifetime
- No environmental issues

Unitized design



F. Mitlitsky et al., LLNL https://www.llnl.gov/str/Mitlit.html
F. Barbir et al., IEEE A&E Systems Magazine, 2005
500 Wh/kg with roundtrip efficiency of 34%.

Major players:

EnStorage URFC

Major technical challenges:

- Dual function oxygen electrode (unitized FC)
- Low roundtrip energy efficiency
- Low energy density storage system
- Cost

Electrochemical energy storage systems

System	Energy density, Wh/kg	Round trip efficiency, %	Cost, $/kWh	Cycle life	Deep cycling	Scale	Response time	EHS issues
Lead acid	41	78	150	short	no	kWh	+	Toxic, corrosive
Na/S	120	72	450	long	no	MWh		Thermal runaway
Na/MCl2	135	75	400	moderate	no	kWh		Molten Na
Li-ion	130	60 - 80	1300	moderate	no	kWh	+	Thermal runaway
VRB	35	78	800	long	yes	MWh	+	Corrosive, toxic
ZBB	70	73	500	long	yes	MWh		Toxic, corrosive
RFC	450	35 - 50	?	long	yes	kWh	+	Flammable

- **Solid electrodes – degradation, liquid electrodes – low energy density**

imagination at work