Control of High Efficiency PEM Fuel Cells for Long Life, Low Power Applications

Part I

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Outline

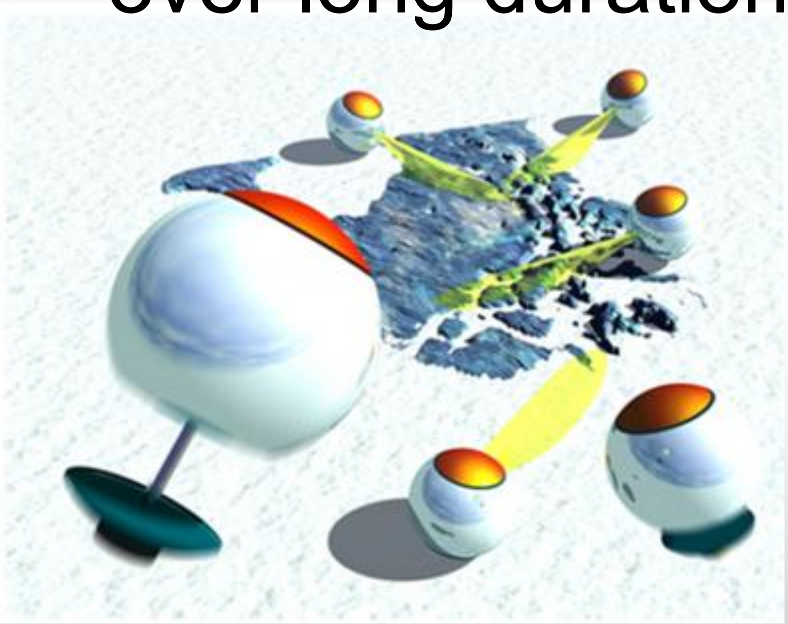
- Motivation
- Conventional Power Technology
- Fuel Cells
- PEM Fuel Cells and How They Work
- Performance & Efficiency
- Case Study
- Challenges with PEMs

Motivation: Present

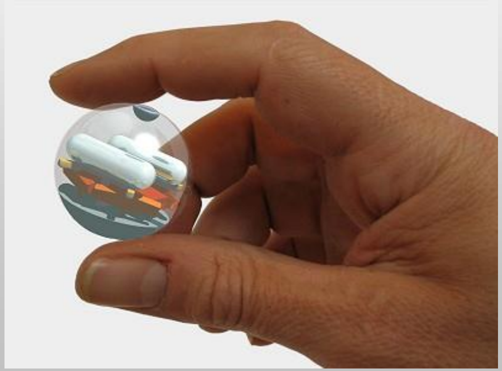
- Mobile electronic devices are energy hungry, battery have limited energy density could benefit from backup or alternative power sources.

Motivation: Future

- Mobile sensor networks can be an important tools to monitor the environment over long durations…



Intel



eKo

Motivation

- Distributed sensors network for monitoring environment
  - Climate Change, air pollution, radiation, rainfall
  - Disasters – earthquakes, volcanoes, tsunamis, forest fires, hurricanes.

Motivation

- Observe environmental trends, better predict and manage these events.
- Significant impact on society – saving lives, property and other valuable resources

Sensor Network Module Concept

Deploy Ball sized mobile sensor modules to monitor environment

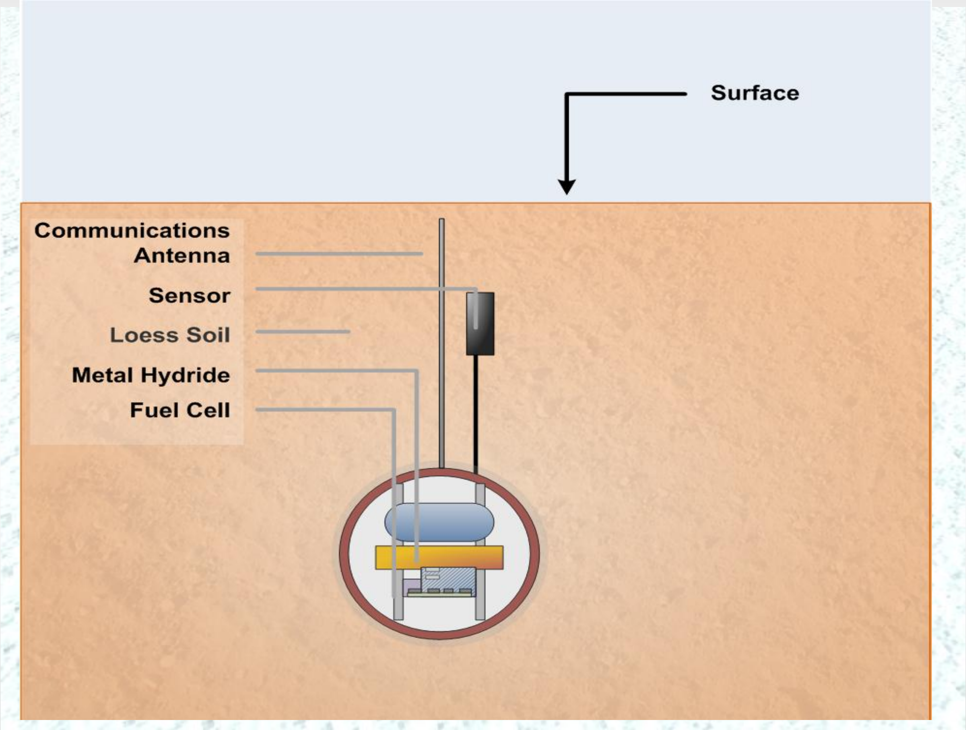
Initial Deployment:
- Personnel, Vehicle
  Air drop

Location:
- Above or below ground

Mass and Volume:
- 0.1 - 0.5 kg, ≤ 525 cm^3

Power and Life:
- 50-500 mW avg., 3-5 years

Optional Mobility:
- Hopping, Rolling, Bouncing



Low Cost and Sacrificial – Deploy 10 or 100 or even 1000’s

Battery Technologies

Battery	Rechargeability	Self-Discharge	Specific Energy	Energy Density
Nickel Metal Hydride	Rechargeable	20 %/ month	80 Wh/kg	300 Wh/L
Lithium Ion	Rechargeable	5 %/month	140 Wh/kg	500 Wh/L
Lithium Polymer	Rechargeable	1 %/month	200 Wh/kg	500 Wh/L
Alkaline	Non-rechargeable	0.5 %/month	110 Wh/kg	320 Wh/L
Lithium Manganese Dioxide	Non-rechargeable	0.17 %/month	280 Wh/kg	580 Wh/L
Lithium Thionyl Chloride	Non-rechargeable	0.08 %/month	500 Wh/kg	1200 Wh/L

Batteries

- Current power technology use lithium ion or polymer batteries
  - Low energy density, bulky
  - High power
  - Rechargeable
- Limits the mobile device:
  - Duration
  - Range
  - Functionality

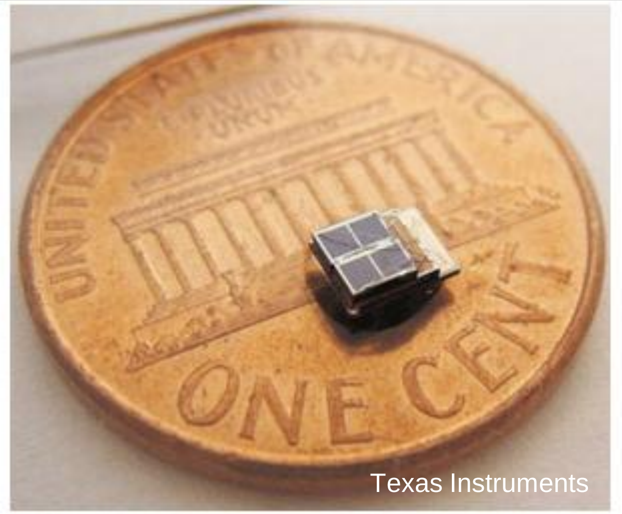

PcMag

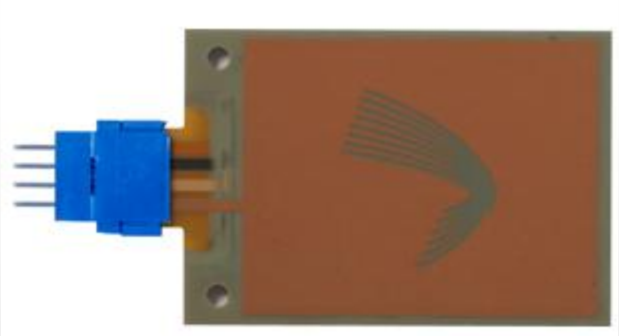
Photovoltaics

- Photovoltaics offer an alternate source of power for small mobile devices.
- Photovoltaic prices have dropped, relatively cheap, durable
- Dependent on varying solar insolation, big and bulky.
- Typically requires a hybrid system combining a battery to provide continuous power.

Kinetic Energy Harvesting

- Kinetic energy harvesting a possible alternative for specialized applications.
  - Where there is regular vibration
  - Power demand 1 mW or less.


Texas Instruments

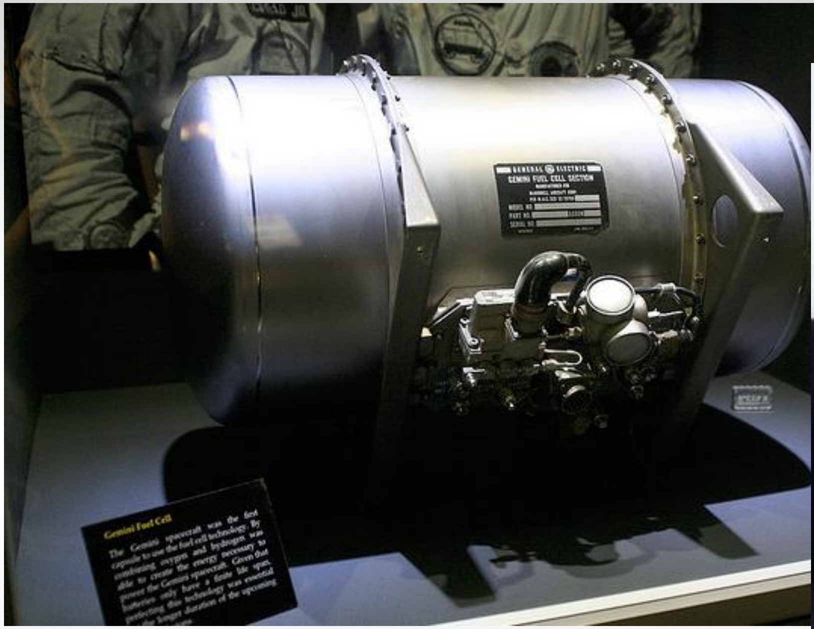


Fuel Cells

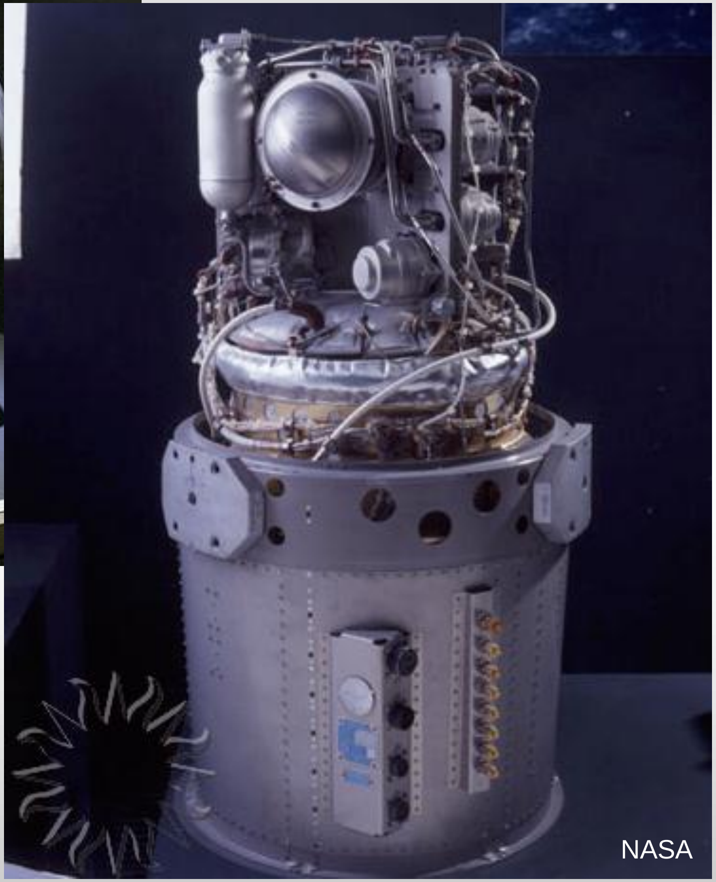
Fuel Cell	Electrolyte	Fuel & Oxidizer	Efficiency	Operating Temp
Alkaline	Potassium Hydroxide	H_2 and O_2 (pure)	40 - 60 %	90 – 100 ^oC
PEM	Polymer Membranes (typically Nafion®)	H_2 and O_2	40 - 70 %	5 – 100 ^oC
Direct Methanol	Polymer Membranes	CH_3OH and O_2	20 - 40 %	15 – 100 ^oC
Phosphoric Acid	Phosphoric Acid	H_2 and O_2	40 %	150 - 200 ^oC
Solid Oxide*	Oxide ion conducting ceramic	F: Methane, Propane, Butane, H_2 O_2	40 - 70 %	700 – 1000 ^oC

* No need for catalyst.

Fuel Cells in Space



NASA



NASA

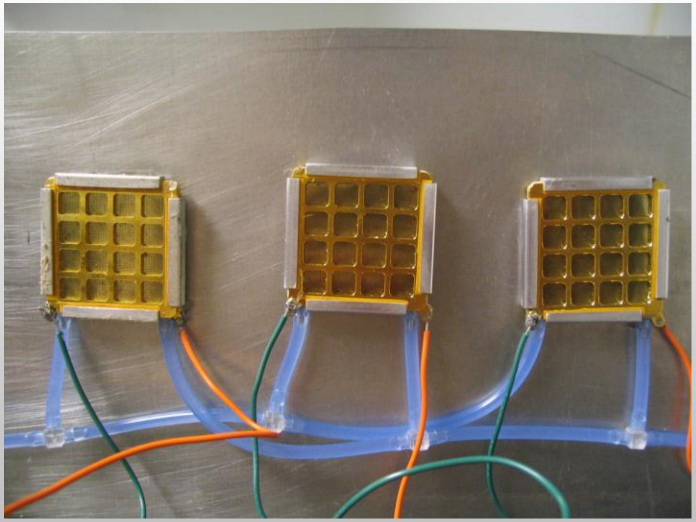
Fuel Cell Applications

Solid Oxide Fuel Cells

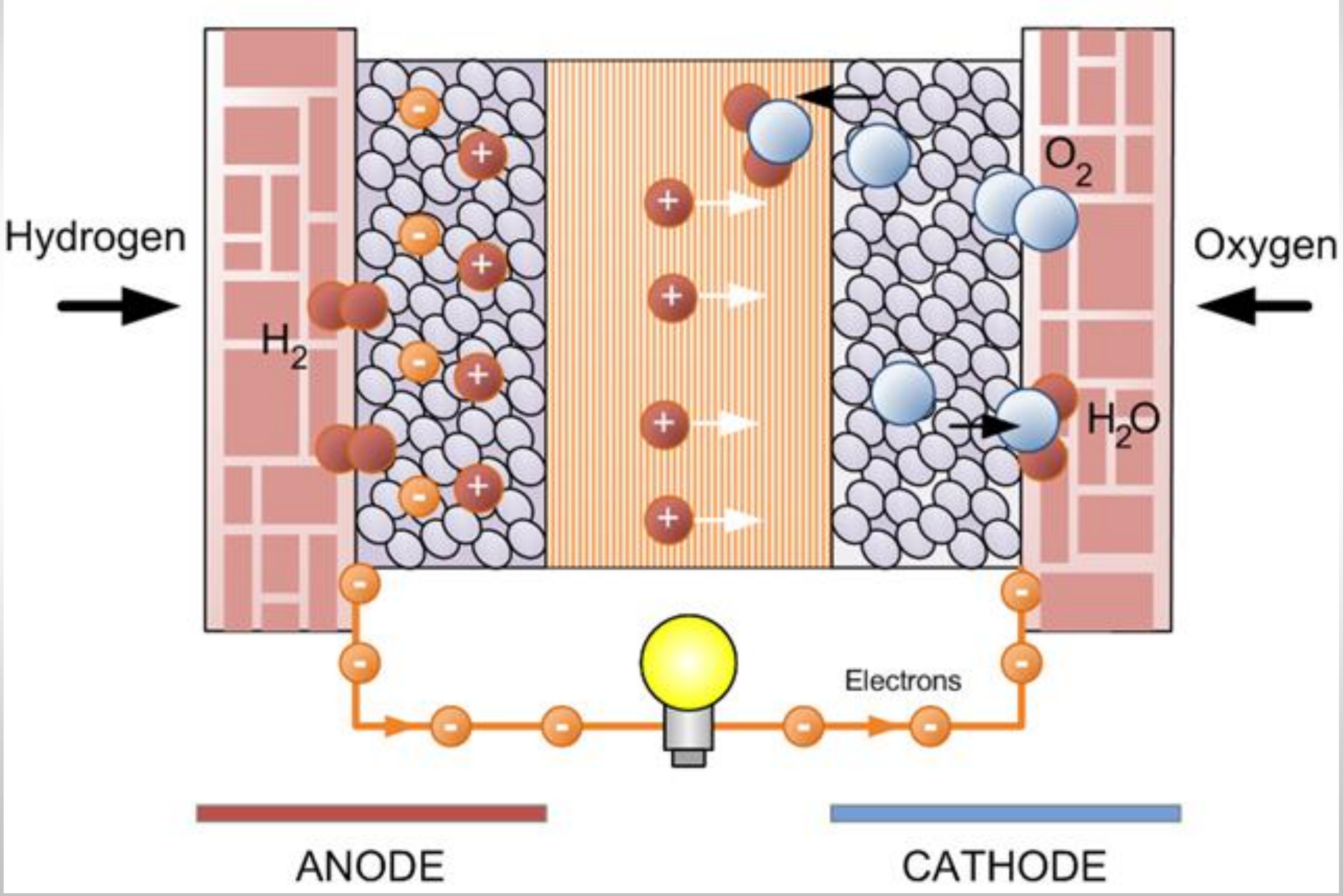
- Lilliputian Technologies has worked on a cigarette lighter sized SOFC for 10 years.
  - Provides backup power for mobile electronics.
  - Use butane fuel, cool to the touch.
  - Expected to be available commercially in late 2012.

Fuel Cell Power Supply

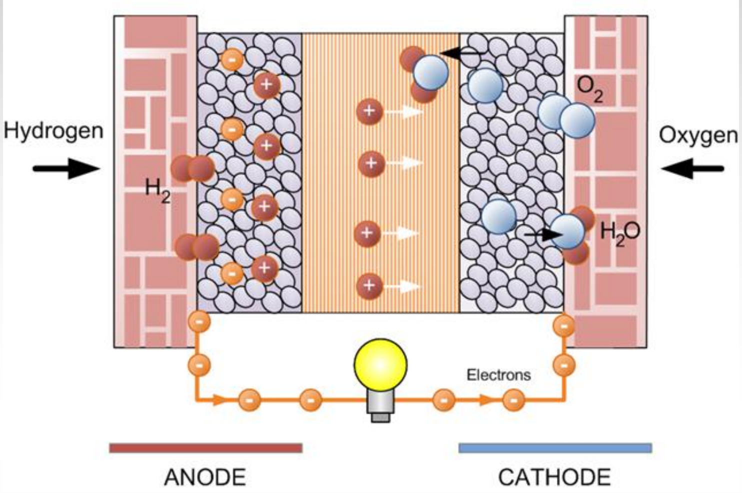
- Need for high energy density, high efficiency power source.
- PEM fuel cells are a promising solution.
  - Converts chemical energy directly to electrical energy.
  - High efficiency, 40 – 65 %
  - High energy density, quiet, clean, operate at STP.



PEM Fuel Cell



PEM Fuel Cell: How It Works



Anode:

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

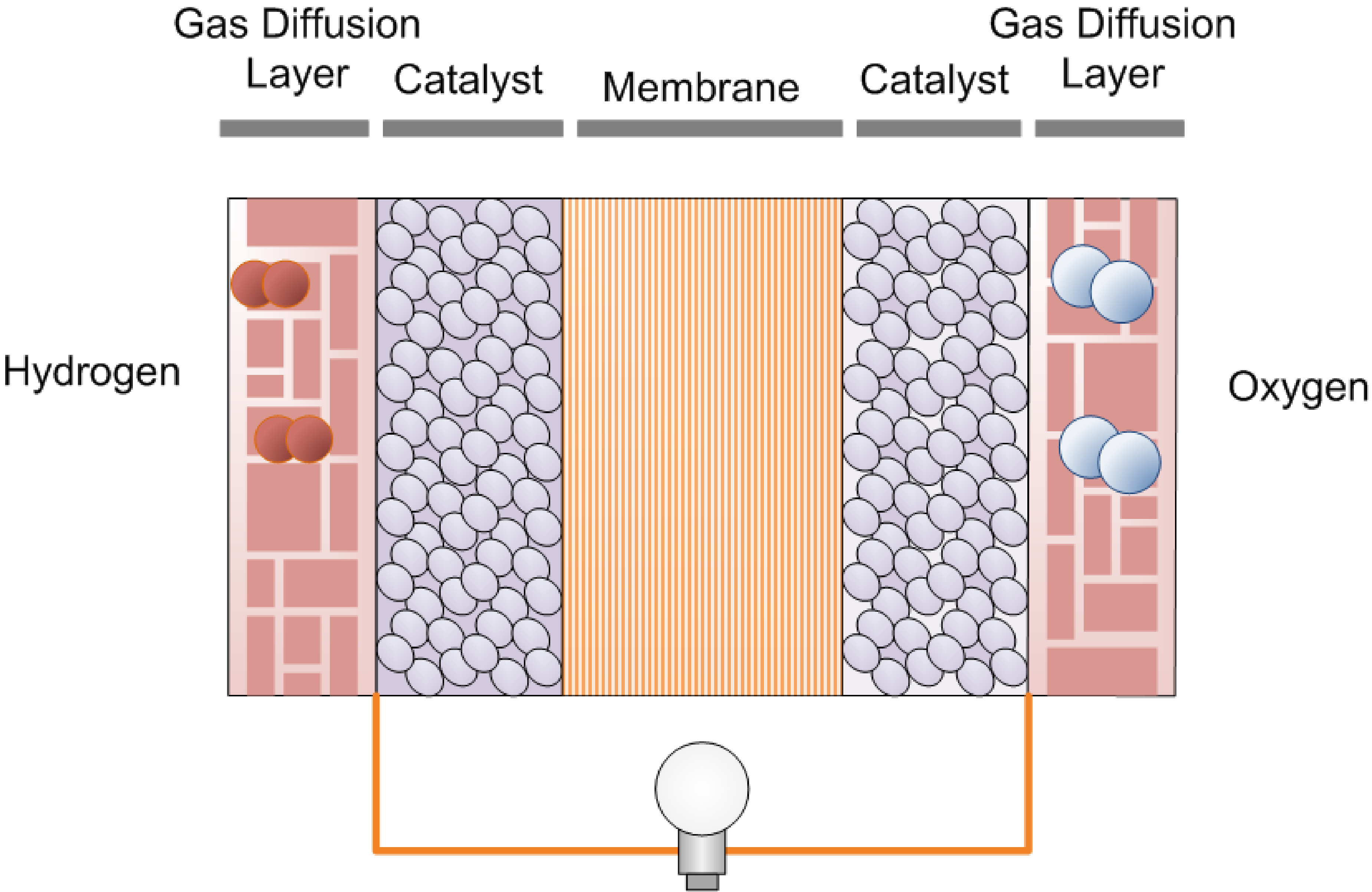
Cathode:

$$4H^+ + 4e^- + O_2 \longrightarrow 2H_2O$$

Overall:

$$2H_2 + O_2 \longrightarrow 2H_2O$$

How a Fuel Cell Works



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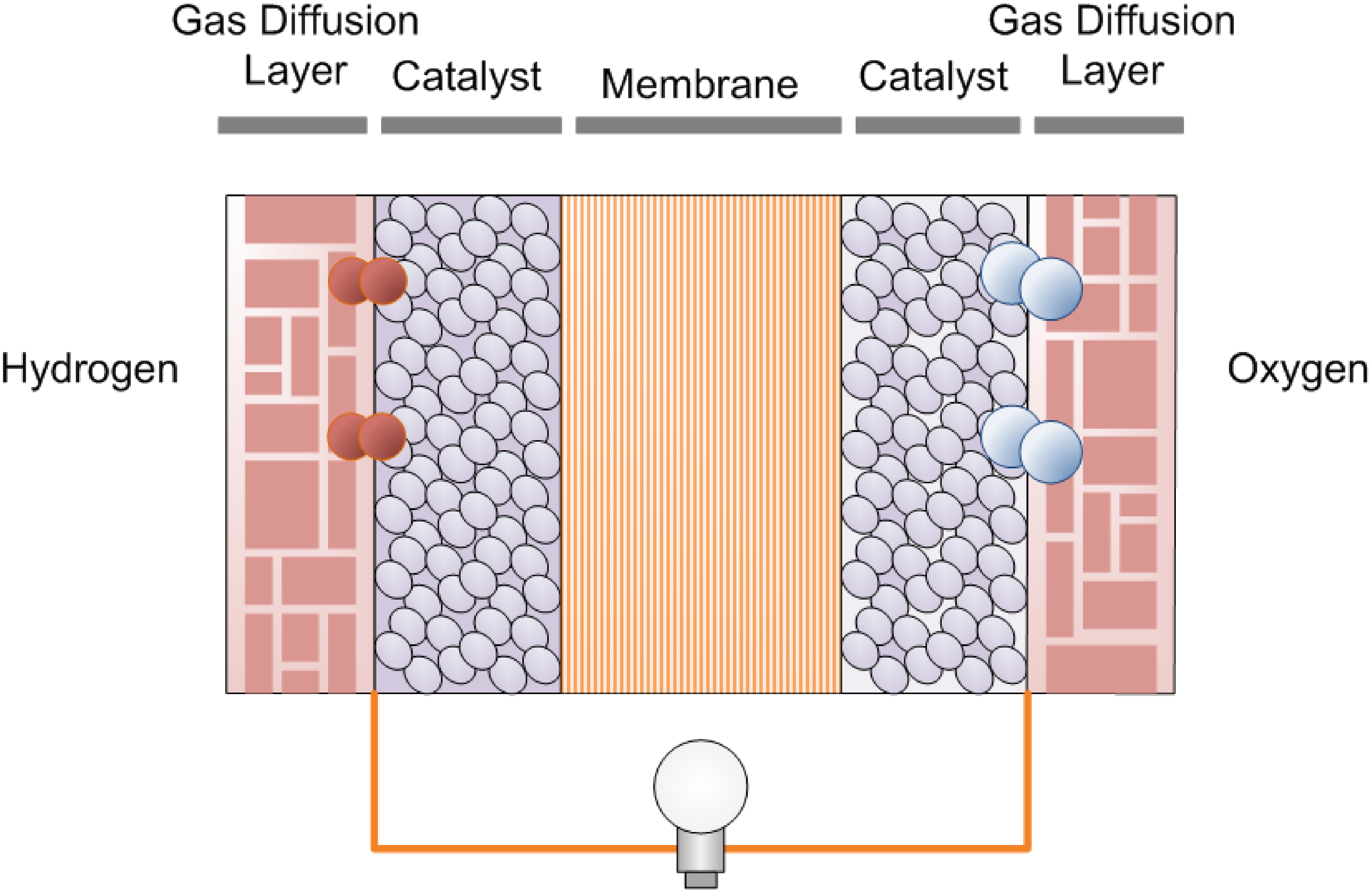


Gas Diffusion Layer

Catalyst

Membrane

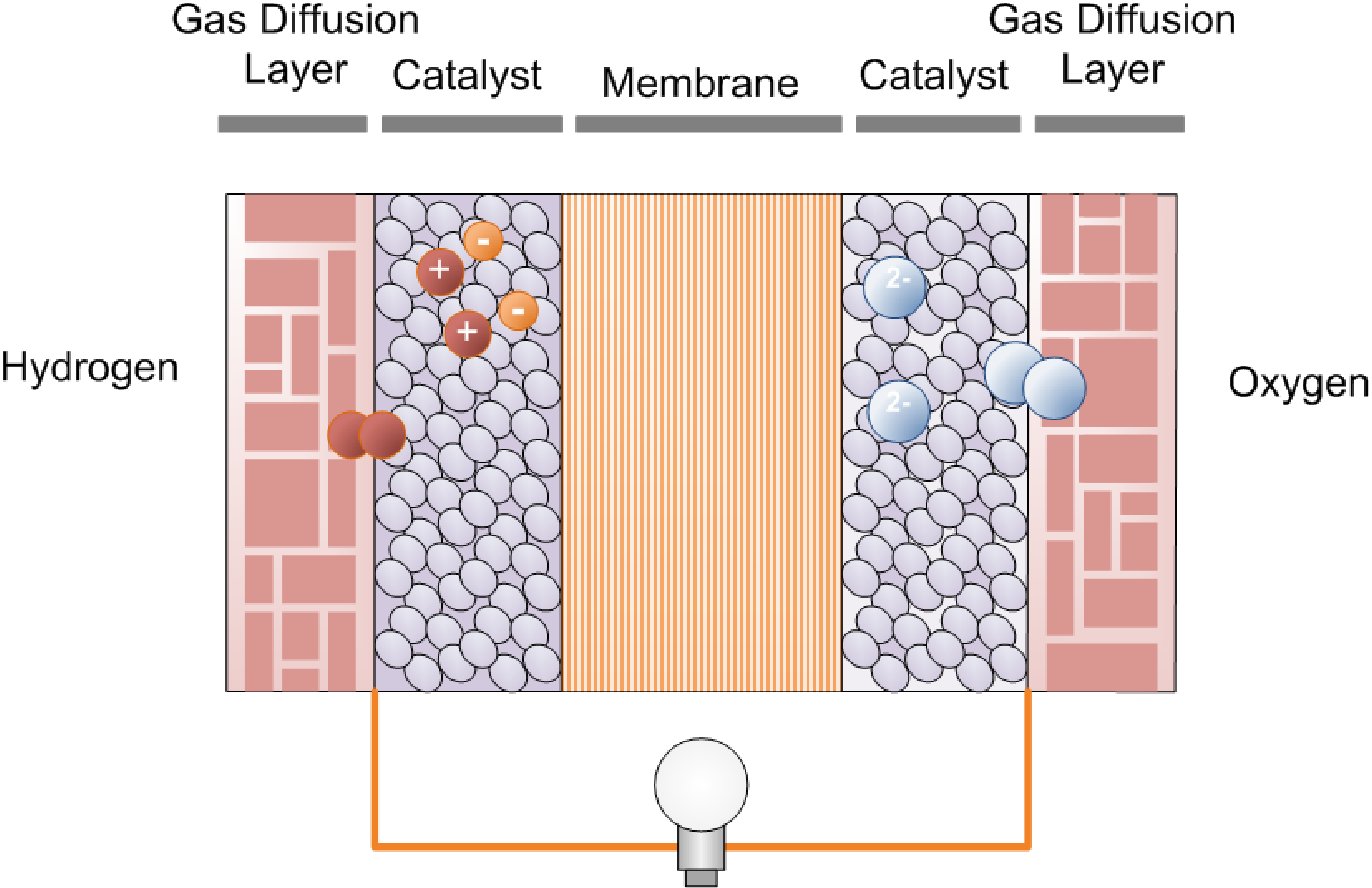
Catalyst

Gas Diffusion Layer

Hydrogen

Oxygen

How a Fuel Cell Works



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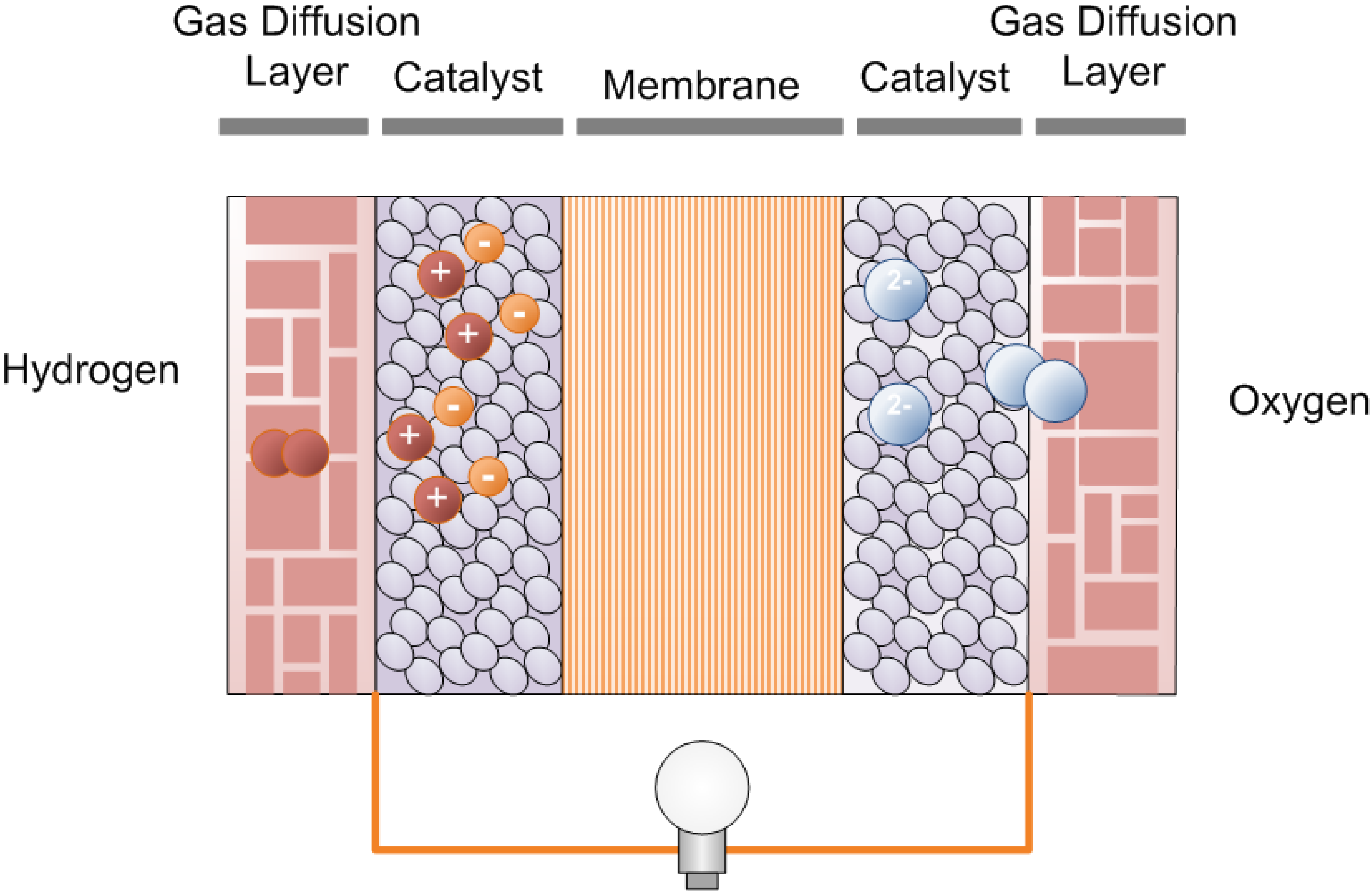

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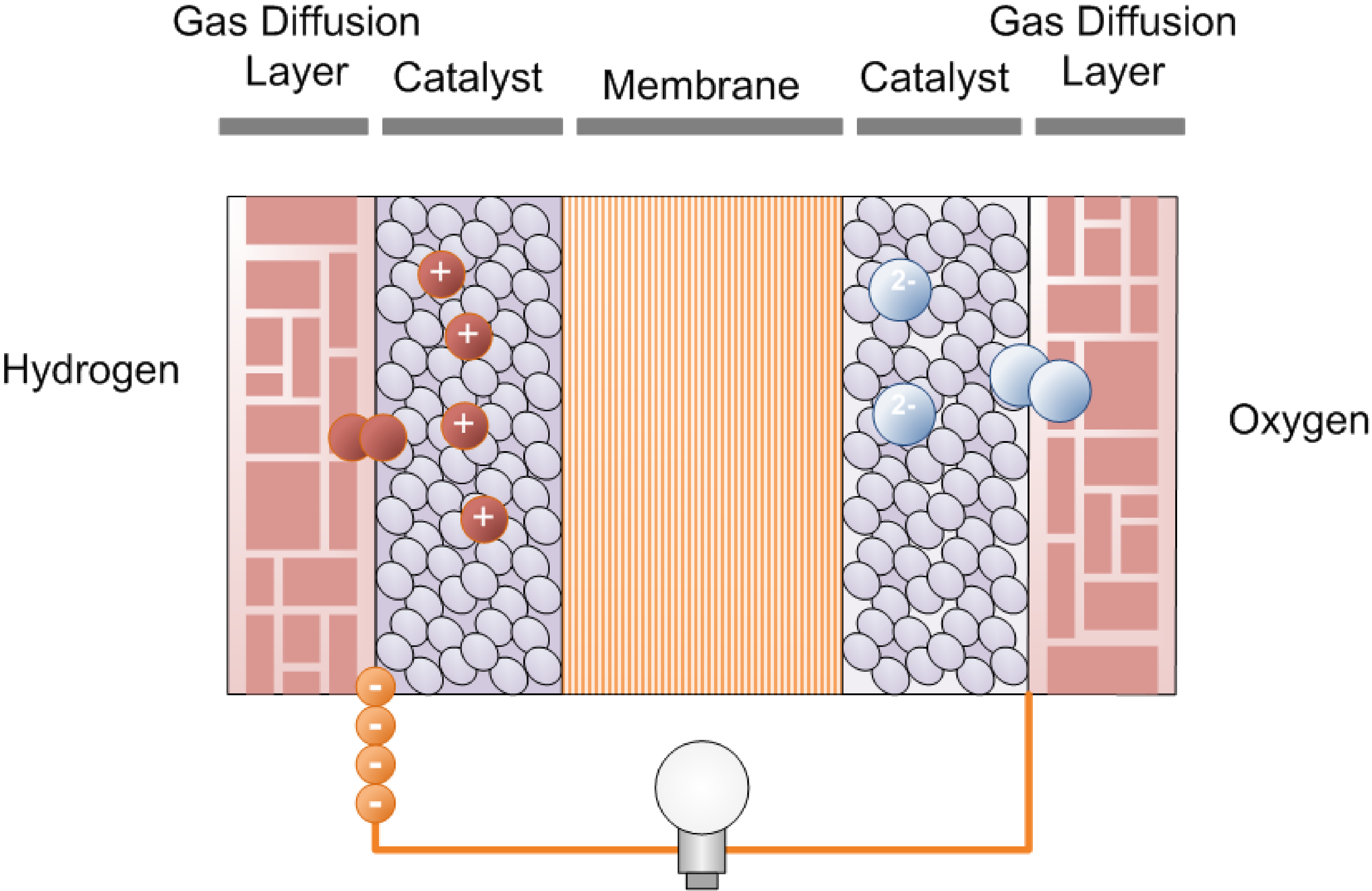

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Gas Diffusion Layer

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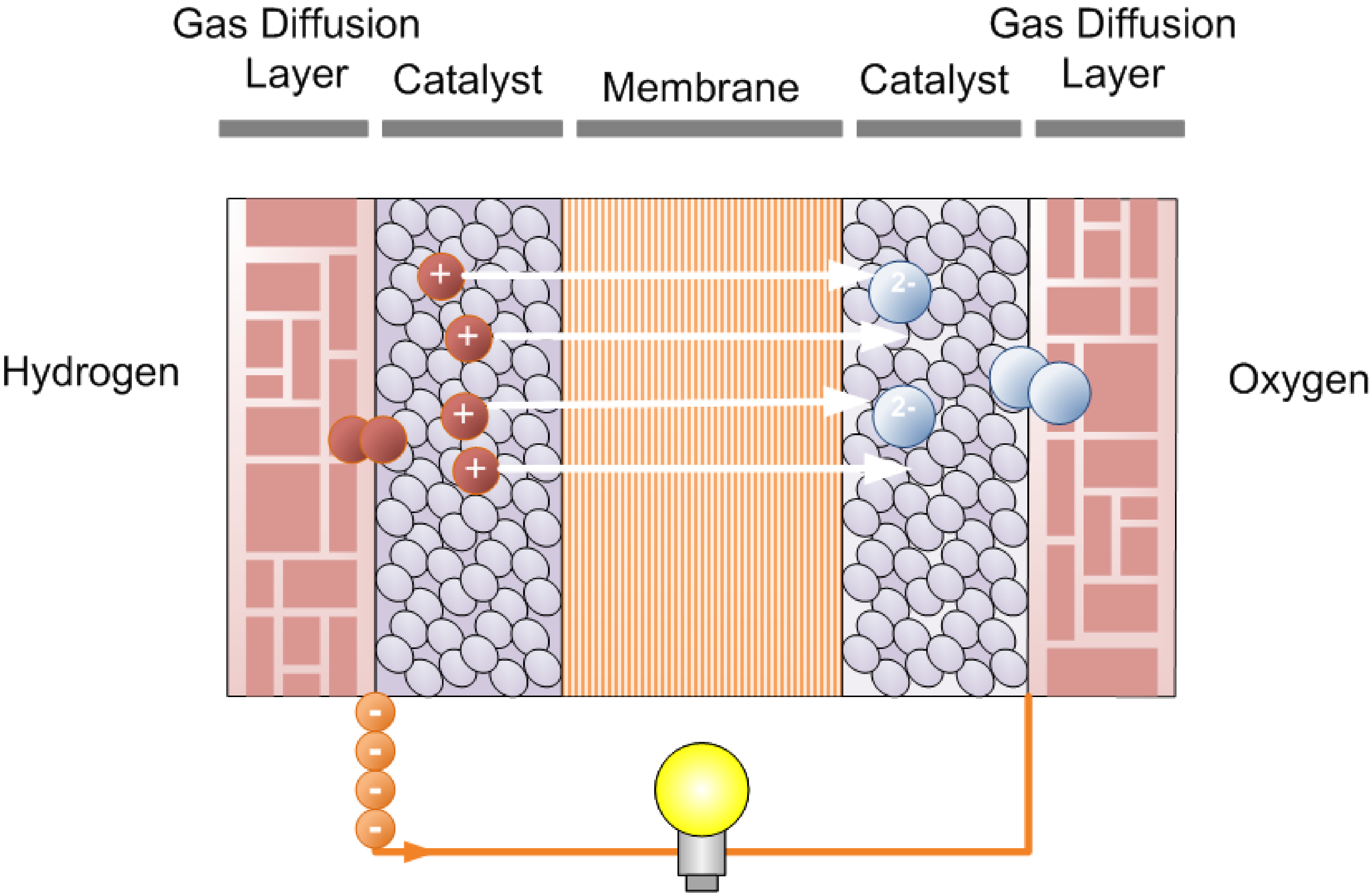

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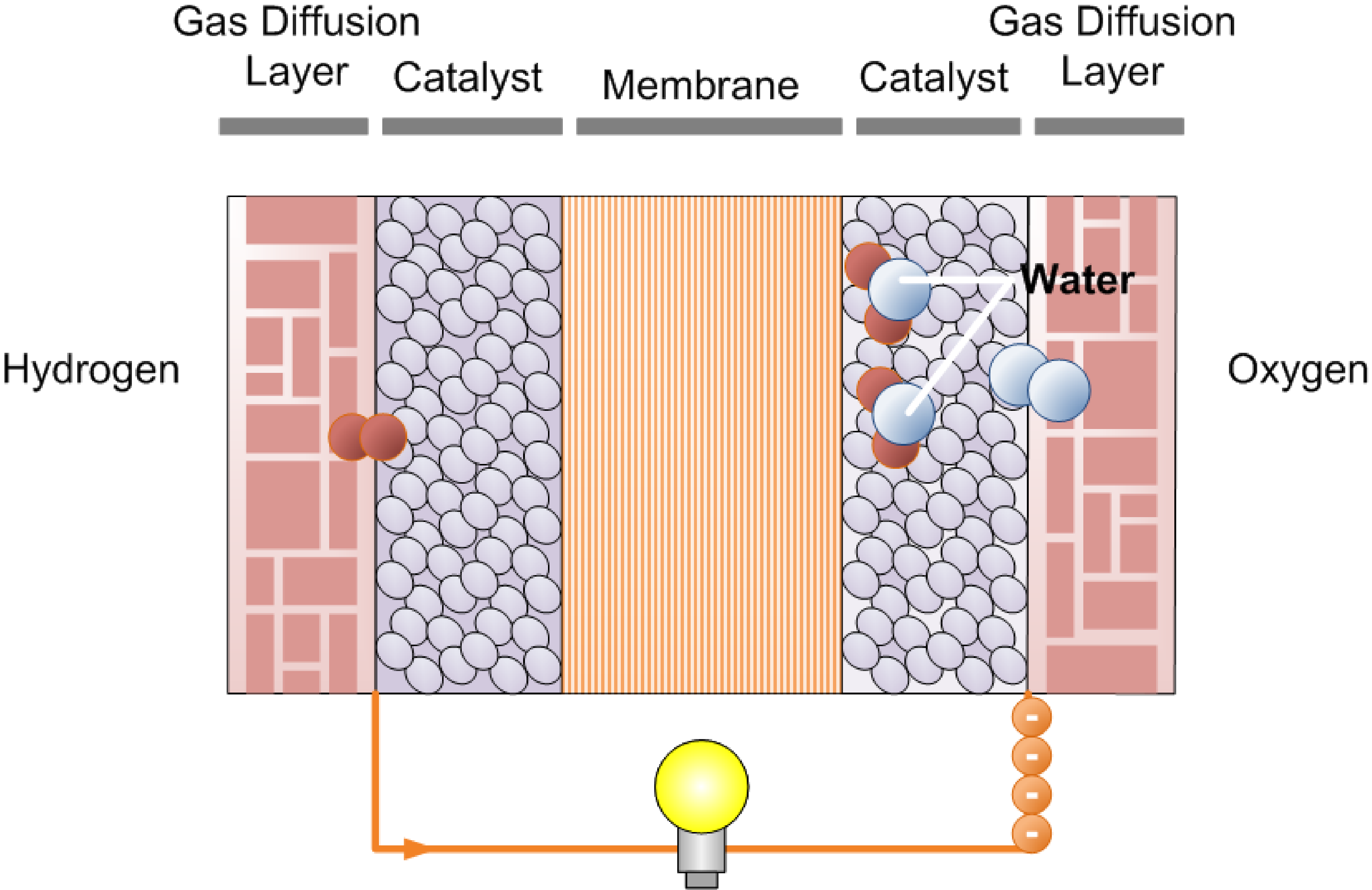
How a Fuel Cell Works



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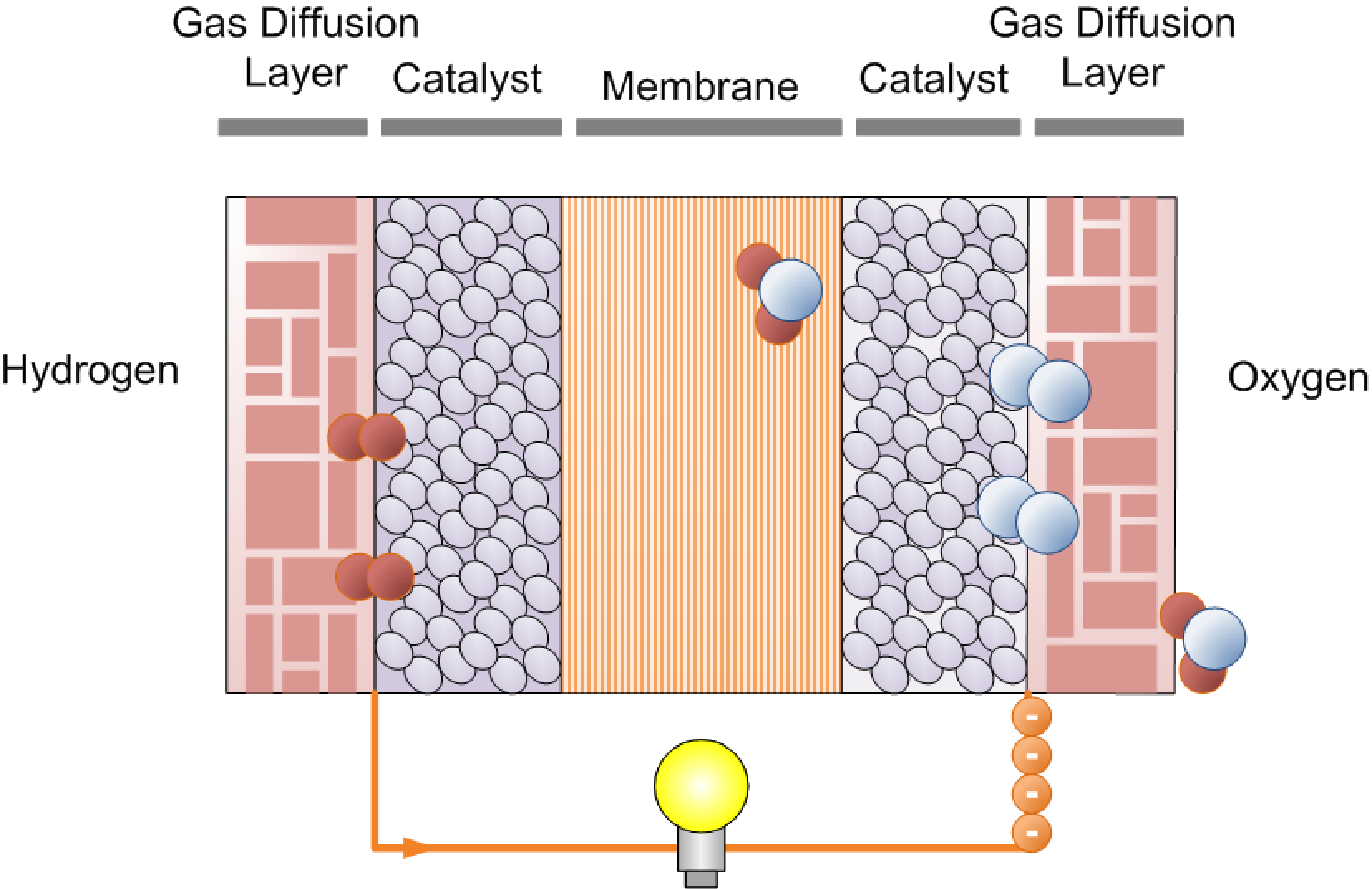
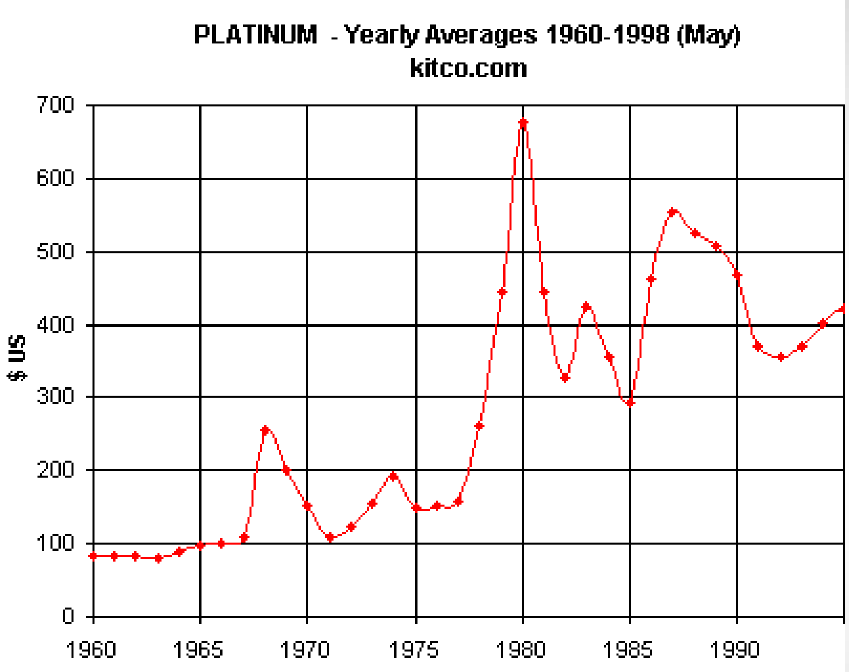


Challenges

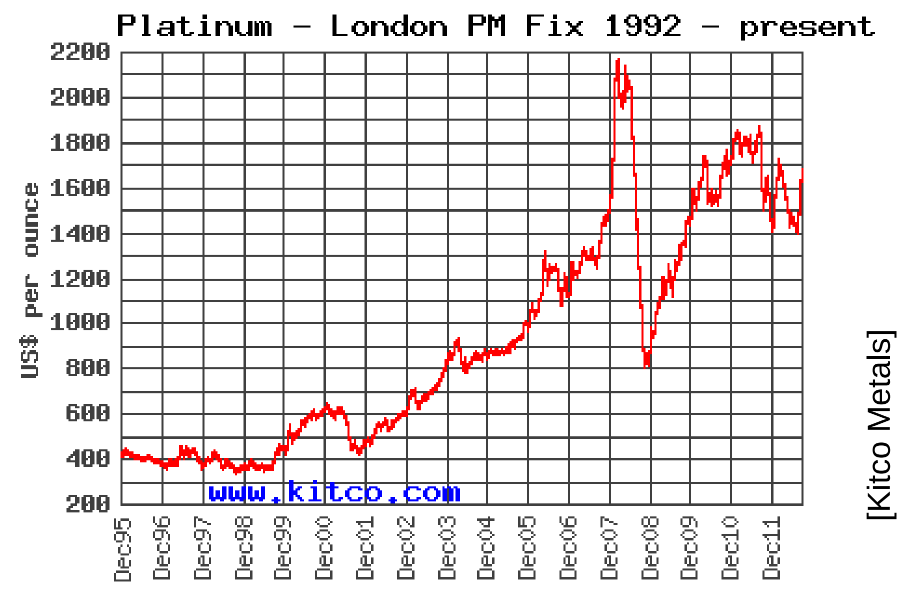
- PEM Fuel cells face 4 major problems:
  - Unreliable – due to degradation [Shao-Horn et al., 2007], [Rubio et al., 2004], [Wu et al., 2008], [Borup et al., 2009], [Madden et al., 2010]
  - Inefficient fuel storage [Schlapbach & Zuettel, 2001]
  - Low power density [Barbir, 2005], [O’Hayre et al., 2005]
  - High cost [Barbir, 2005]

- Significant progress being made in all these areas.

Platinum



PLATINUM - Yearly Averages 1960-1998 (May)
kitco.com



Platinum – London PM Fix 1992 – present

[Kitco Metals]

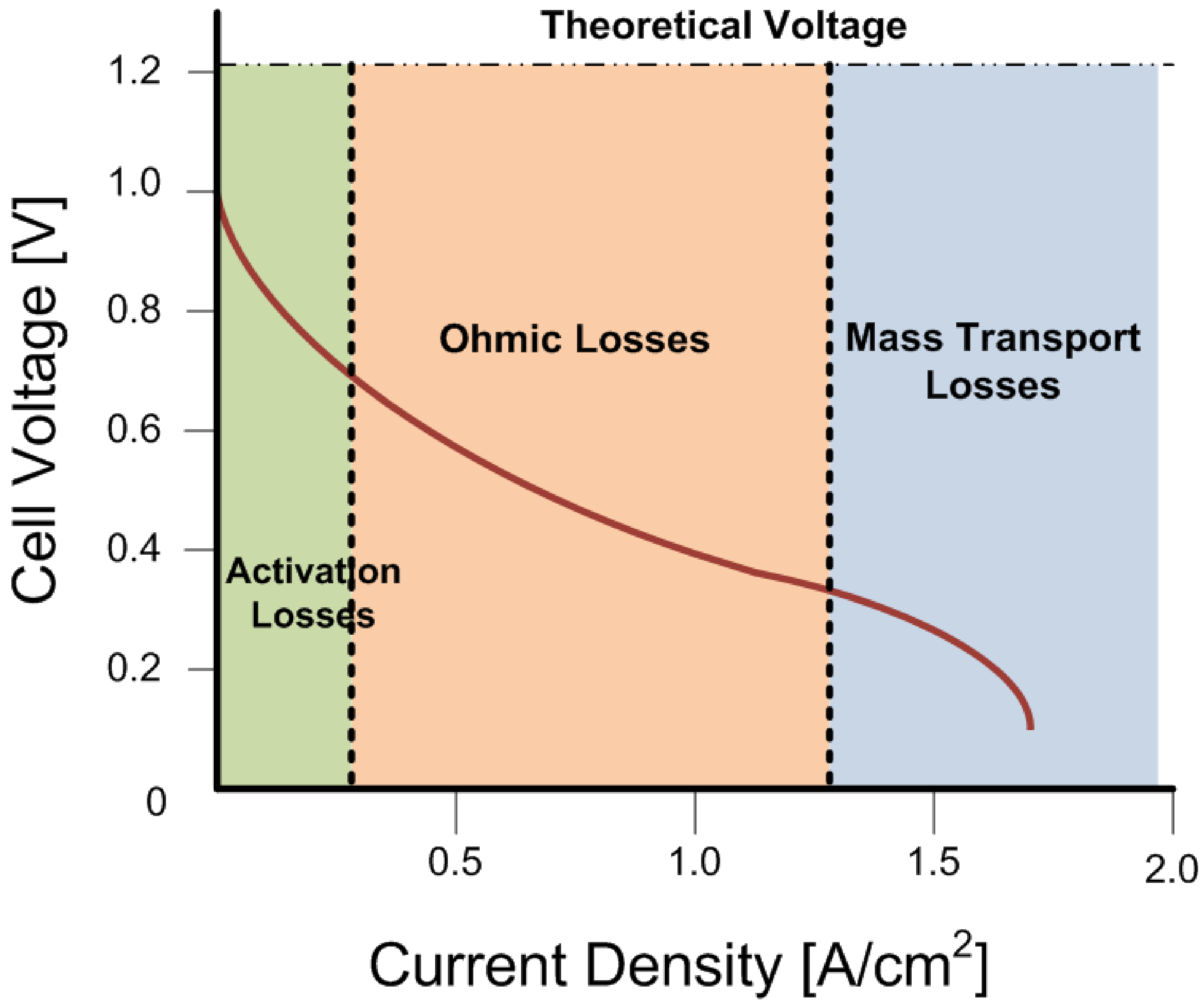
1960 -1995

1995 -

PEM Fuel Cells

- Operation and performance of PEM fuel cells.
  - Fuel Cell Polarization Curve
  - Losses
  - Efficiency

Fuel Cell Polarization Curve



Fuel Cell Voltage

$$V_{FC} = V_t - \Delta V_{act} - \Delta V_{ohm} - \Delta V_{trans}$$

Theoretical

Activation Losses

Ohmic Losses

Mass Transport Losses

Theoretical Voltage: Nernst Potential

$$V_t = \frac{-\Delta G}{nF}$$

ΔG	Gibbs Free Energy for the reaction
F	Faraday Constant
n	Number of electrons transferred per mole

$$O_{2\,(g)} + 4H^+ + 4e^- \rightleftarrows 2H_2O$$

$$V_t = 1.23\ \mathrm{V}$$

Activation Losses

$$\Delta V_{act} = \overbrace{\frac{RT}{\alpha_{O_2} n_{O_2} F} \ln i}^{\text{Anode loss}} - \overbrace{\frac{RT}{\alpha_{O_2} n_{O_2} F} \ln i_0}^{\text{Cathode loss}}$$

[Bard & Faulkner, 1980]

T	Temperature
R	Universal Gas Constant
α_{O_2}	Electron Transfer Coefficient
n_{O_2}	Electron Transfer Number
F	Faraday Constant
i	Current Density
i_0	Exchange Current Density

Ohmic Losses

$$\Delta V_{ohm} = iR_{FC}$$

$$R_{FC} = \sum_j R_j$$

R_{FC} Cell Resistance
R_j Resistance of component
i Current Density

Membrane Resistance

$$R_{mem} = \frac{t_{mem}}{\sigma}$$

$$\sigma = \left(k_1\lambda - k_2\right)\exp\left[k_3\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$$

$$\lambda = C_0 + C_1 h + C_2 h^2 + C_3 h^3$$

[Spiegel, 2008]

t_{mem}	Membrane Thickness
T	Cell Temperature
h	Relative Humidity

Mass Transport Losses

$$\Delta V_{trans} = \underbrace{\frac{RT}{nF}\ln\left(1-\frac{i}{i_{l,a}}\right)}_{\text{Anode loss}} + \underbrace{\frac{RT}{nF}\ln\left(1-\frac{i}{i_{l,c}}\right)}_{\text{Cathode loss}}$$

R	Cell Ohmic Resistance
i_l	Limiting Current Density
T	Temperature
R	Universal Gas Constant
F	Faraday Constant

Current and Mass Flow Rates

$$\dot{m}_{H_2} = \frac{iM_{H_2}}{2F}$$

$$\dot{m}_{O_2} = \frac{iM_{O_2}}{4F}$$

$$\dot{m}_{H_2O\ gen} = \frac{iM_{H_2O}}{2F}$$

Maximum Theoretical Efficiency

- Energy in is the total energy obtained from combustion which is the enthalpy, ΔH
- Energy out is the total electricity which is the Gibbs free energy, ΔG_f

$$\eta_{\max} = \frac{\Delta G_f^{\ 0}}{\Delta H^0}$$

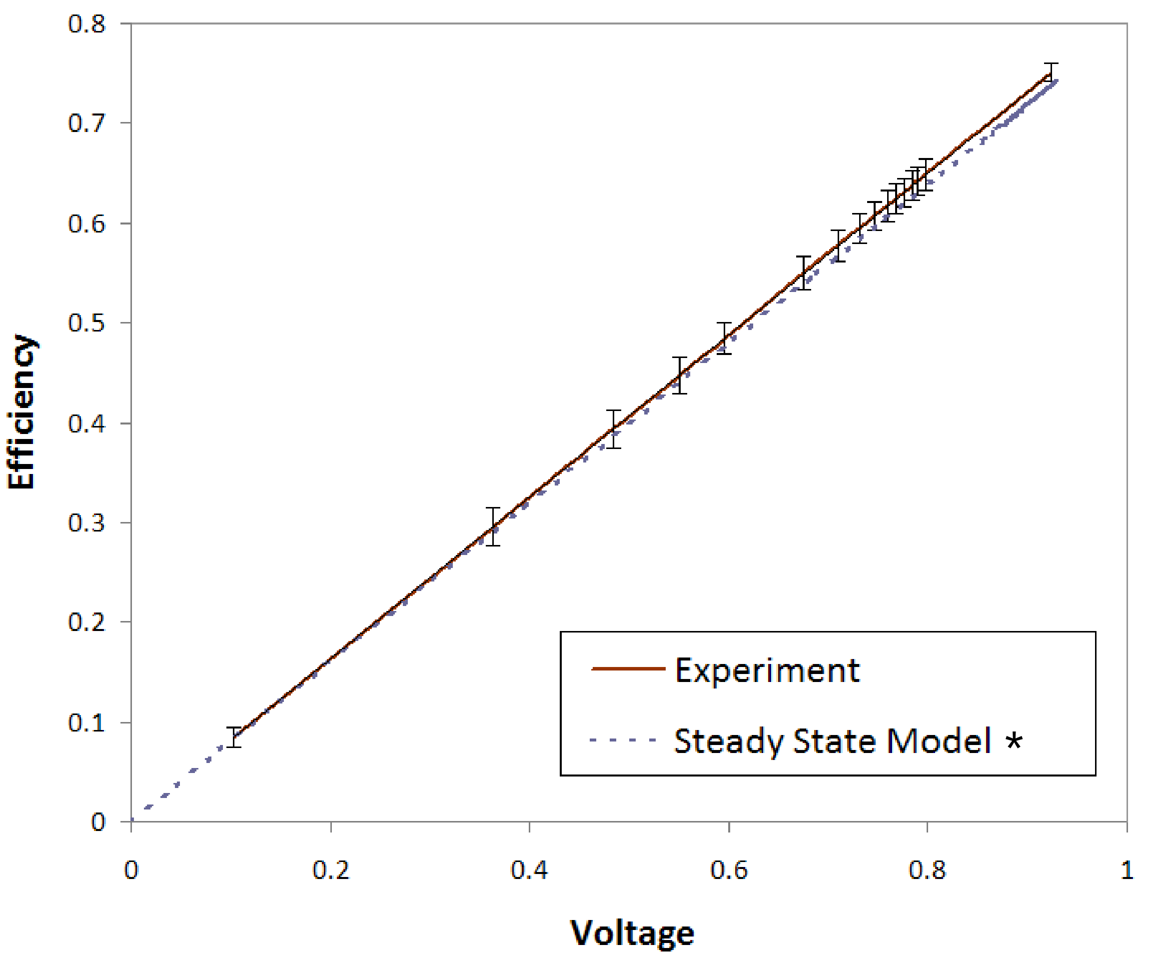
$$\eta_{\max} = \frac{237.1 \text{ kj/mol}}{286.0 \text{ kj/mol}}$$

$$\eta_{\max} = 83\%$$

Operating Efficiency [LHV]

$$V_{FC} = \frac{V_t - \Delta V_{act} - \Delta V_{ohm} - \Delta V_{trans}}{V_t}$$

Experiment vs. Theory



* Manyapu, K., Chapter 3: PEM Fuel Cell Steady State Model SM Thesis, 2010

Review

- Fuel Cell Performance impacted by:
  - Electrical Load
  - Mass flow of reactants
  - Temperature
  - Humidity

Case Study: Fuel Cell Power Supply for Sensor Network Module

Power System Design Study

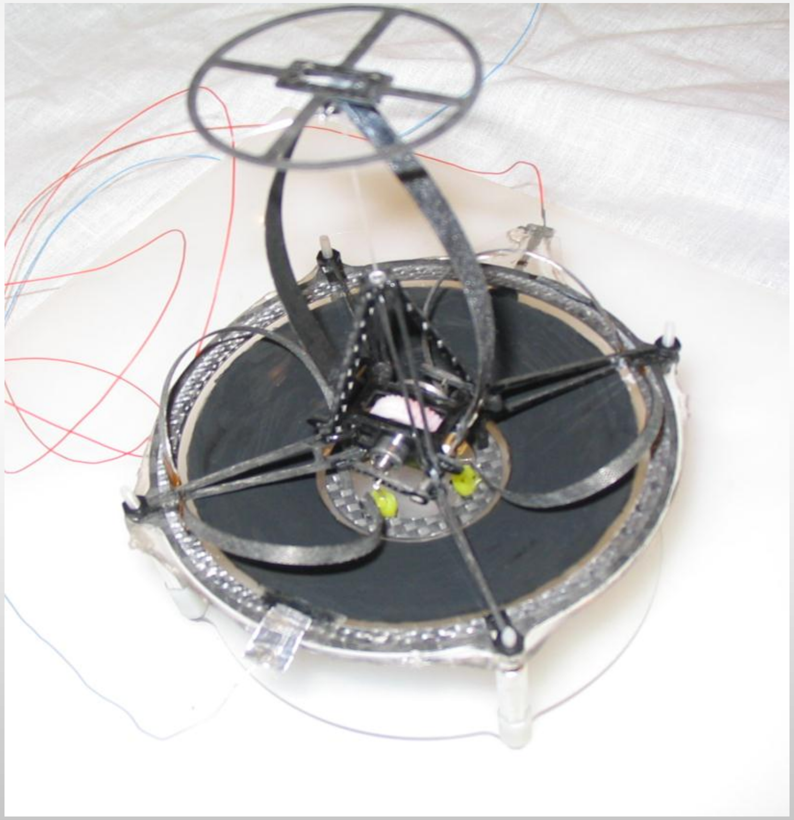
- Baseball sized sensor module
- Mass: Mobility + Payload: 0.1 kg
- Power: 50 mW avg., 100 mW Peak
  - 50 % power for mobility
- Life: 3 years
- Sensors: Camera, Temperature, Humidity, Accelerometer
- Mobility: Hopping, rolling, bouncing using DEA actuators

[Plante & Dubowsky, 2007]

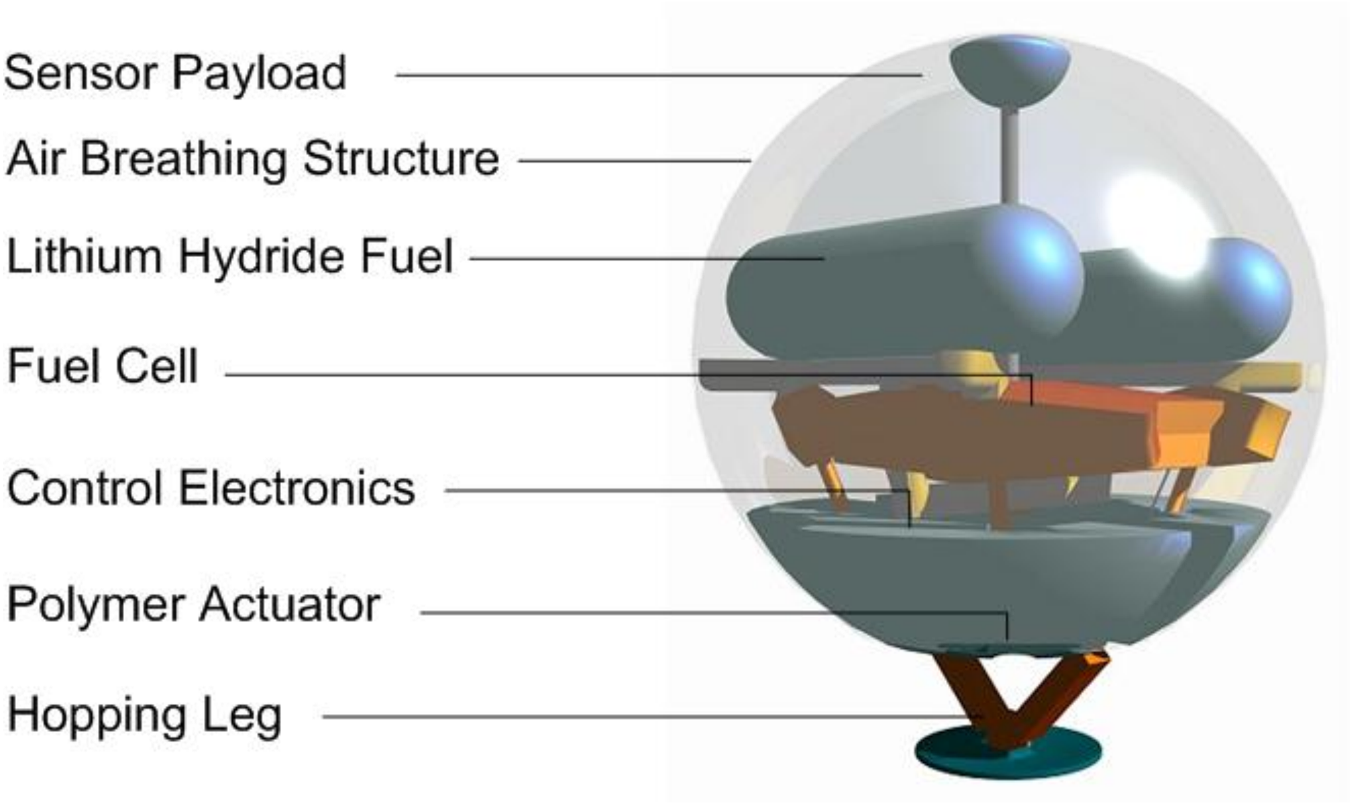
DEA Actuation and Mobility System

[Plante & Dubowsky, 2007]

- Extensive use of carbon fiber
- 18 grams



Mobile Sensor Module



Power Supply Mass Breakdown

Component	**Mass**
Fuel Cell	10g
Lithium Hydride + Fuel Storage	360 g
Electronics	10 g
Other Components	20 g
Total	400 g

Power System Comparison

Power Technology	**Energy Density (Wh/kg)**	**Self Discharge Rate (%/month)**	**Mass (3 Years Life)**
Alkaline	110	0.5	15.6 kg
Lithium Ion	140	5	33 kg
Lithium CR	270	0.17	6 kg
Lithium Thionyl Chloride	500	0.08	3 kg
Lithium Hydride PEM Fuel Cell Hybrid*	**4,950***	**1.2**	**0.4 kg**

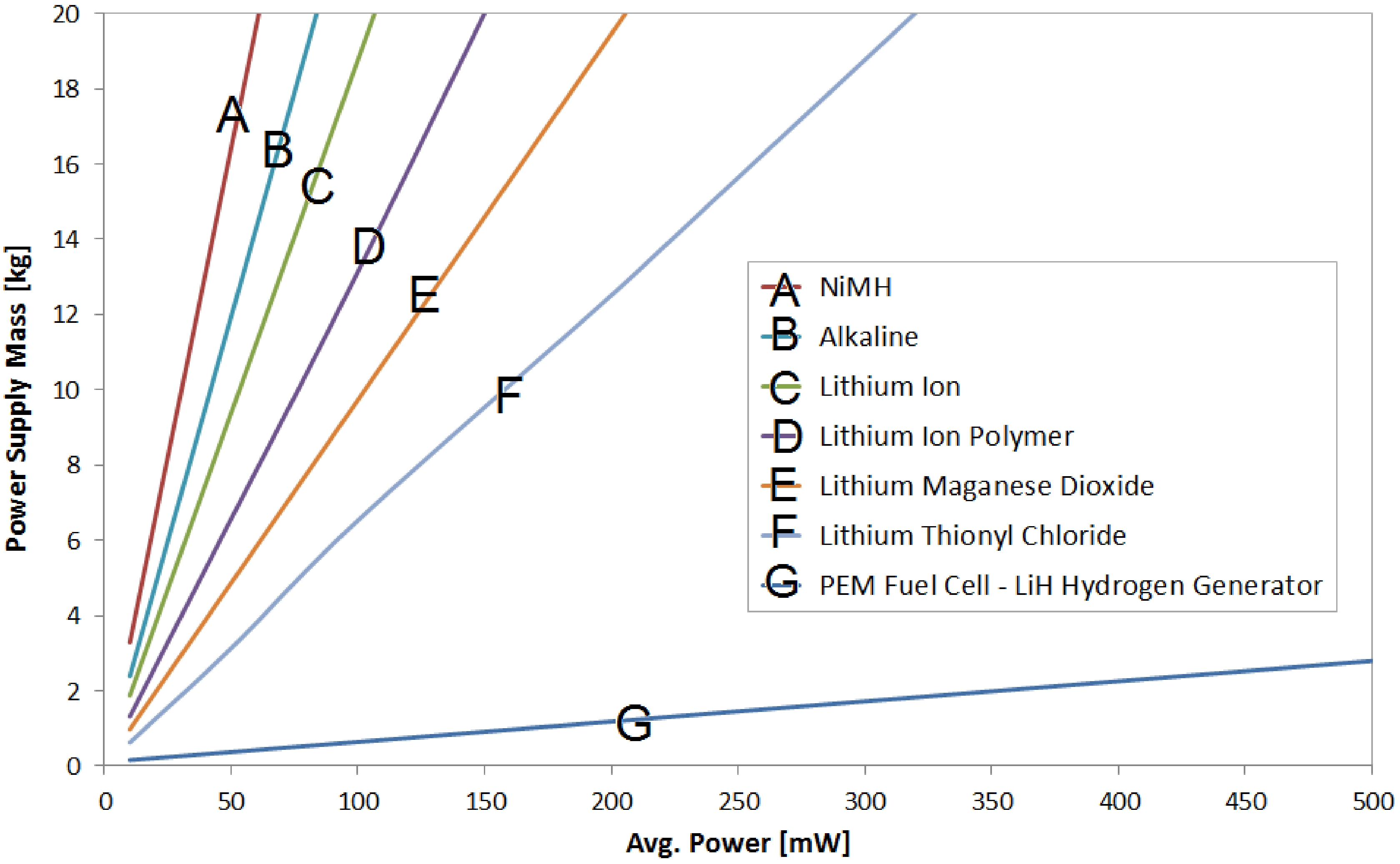
* Thangavelautham, J., Strawser, D., Cheun, M., Dubowsky, S. "Lithium Hydride Powered PEM Fuel Cells for Long-Duration Small Mobile Robotic Missions," *IEEE International Conference on Robotics and Automation (ICRA), 2012.*

Power System Comparison

Power Technology	**Mass (3 Years Life)**	**Number of Hops**	**Max Range [km]**
Alkalines	15.6 kg	6,600	2.7
Lithium Ion	33 kg	3,100	1.3
Lithium CR	6 kg	17,000	7.1
Lithium Thionyl Chloride	3 kg	27,000	11
Lithium Hydride PEM Fuel Cell Hybrid*	**0.4 kg**	**260,000**	**104**

* Thangavelautham, J., Strawser, D., Cheun, M., Dubowsky, S. "Lithium Hydride Powered PEM Fuel Cells for Long-Duration Small Mobile Robotic Missions," *IEEE International Conference on Robotics and Automation (ICRA), 2012.*

Power Supply Mass for 3 Years



Major Challenges

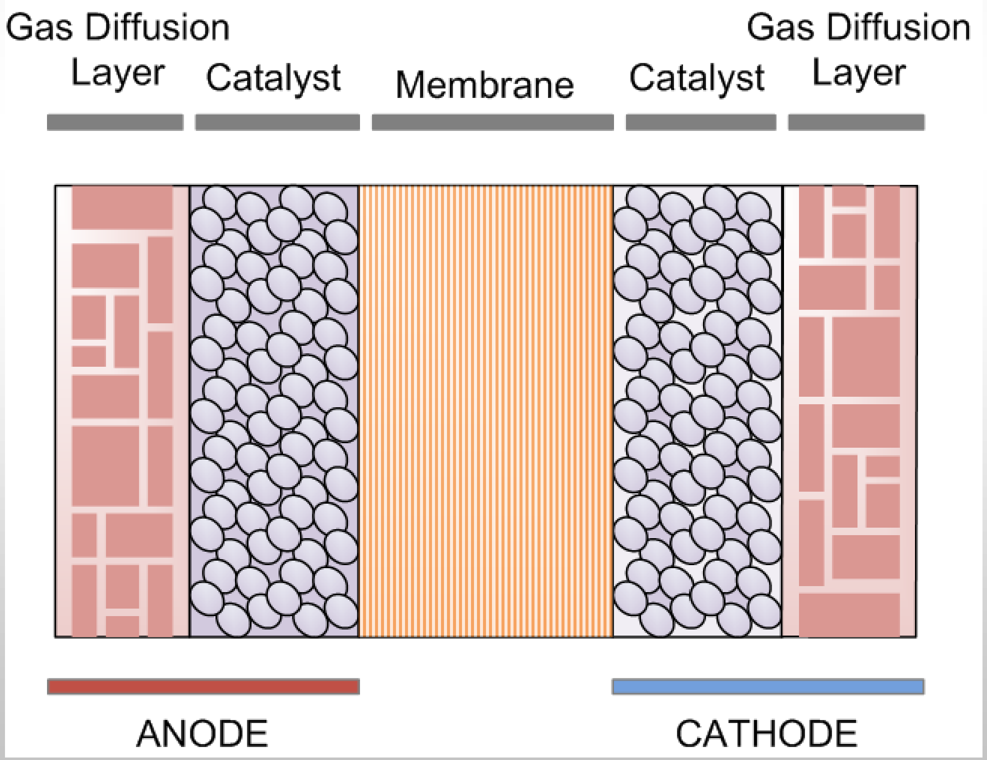
- Maximizing life by limiting effects of degradation
  - Steady state conditions
  - Varying load and environmental conditions
  - Startup and shutdown
  - Freezing Conditions

- Maximizing Performance
  - Minimizing utilization losses
  - Minimizing operating losses through proper operation

Fuel Cell Degradation

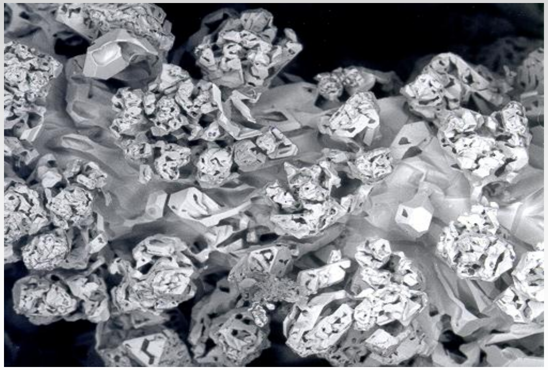
Key components that can degrade

- Catalyst Layer
- Membrane
- Gas Diffusion Layer



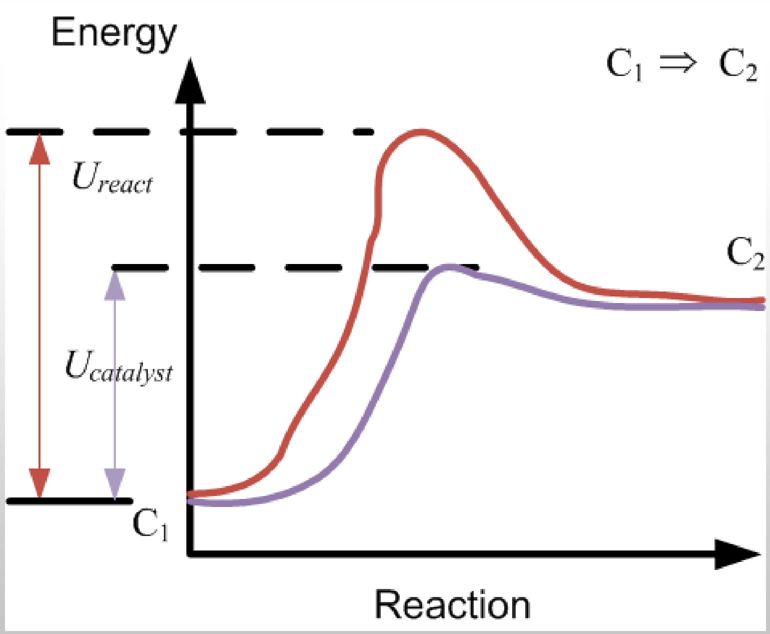
Role of Platinum Catalyst

- Speeds up and lower energy required for reactions
- Site for ionizing protons
- Site for assembly of water in the cathode



- Key metric – platinum surface area

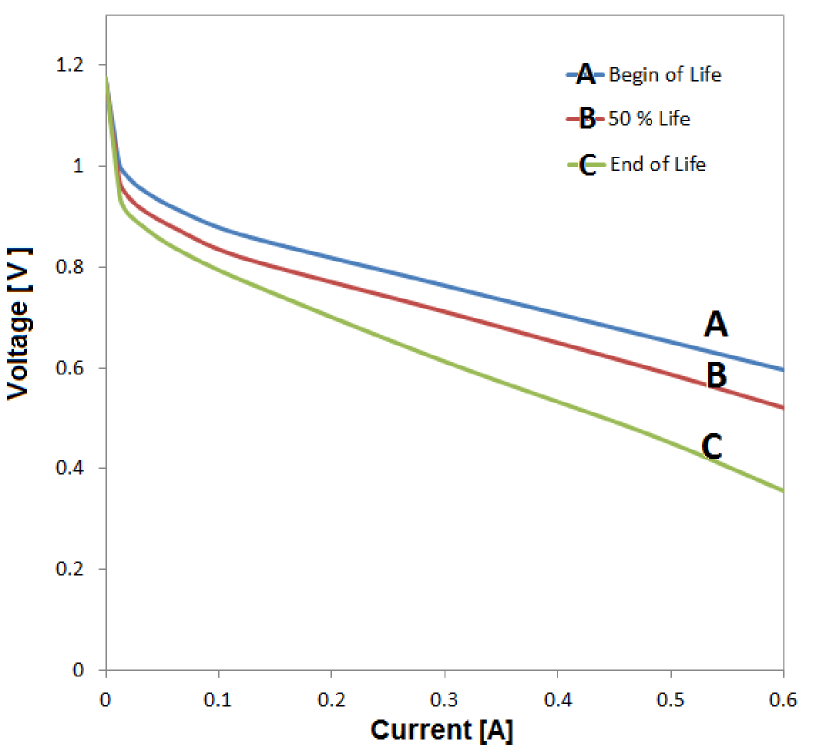
$$S = \sum_{x} \sum_{i=S,L} N_{x,i} 4\pi R_{x,i}^{2}$$



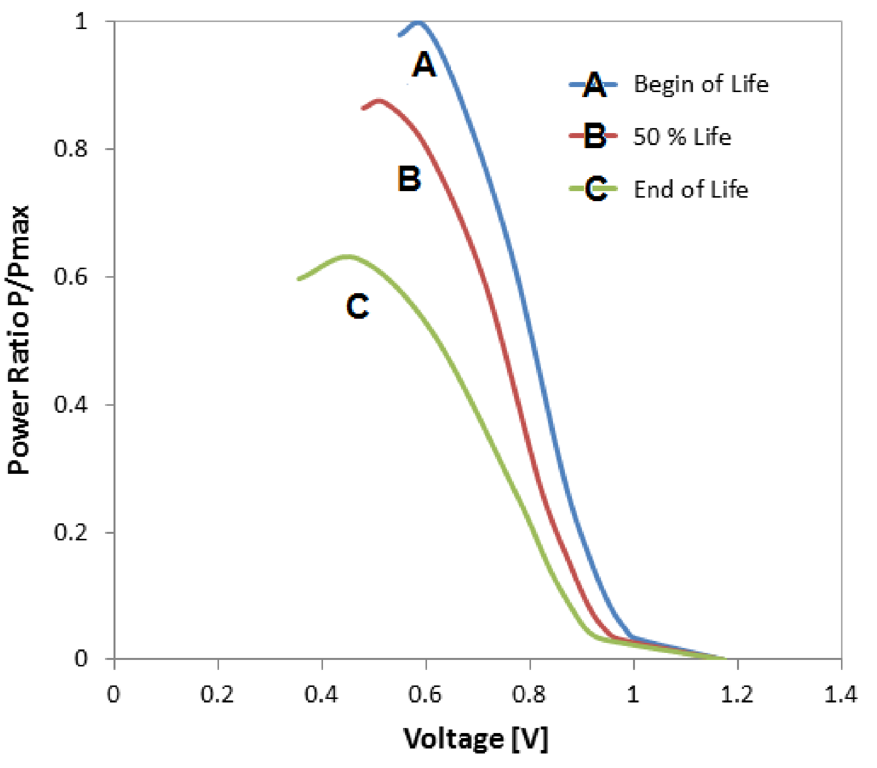
Platinum Loss

- Loss of platinum is irreversible
- Starts as slow-steady degradation of FC power performance
- Accelerates membrane structure degradation leading to catastrophic loss [Wu et al., 2008]

Effect of Platinum Loss



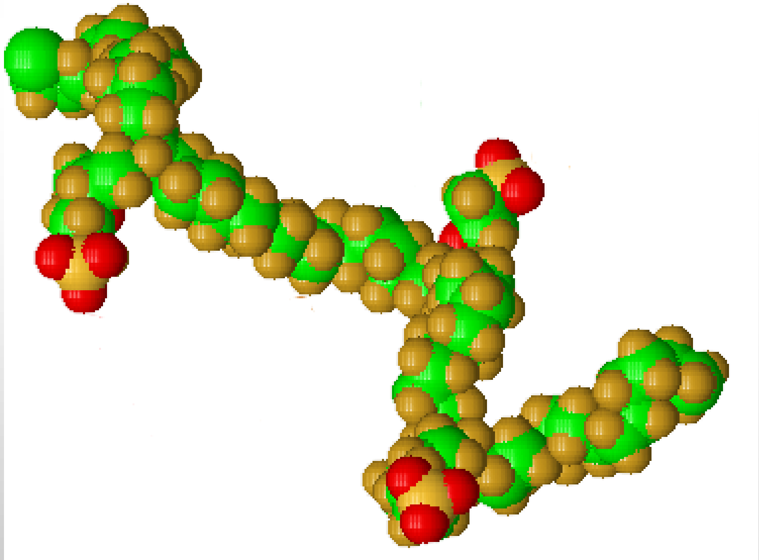
Polarization Curve

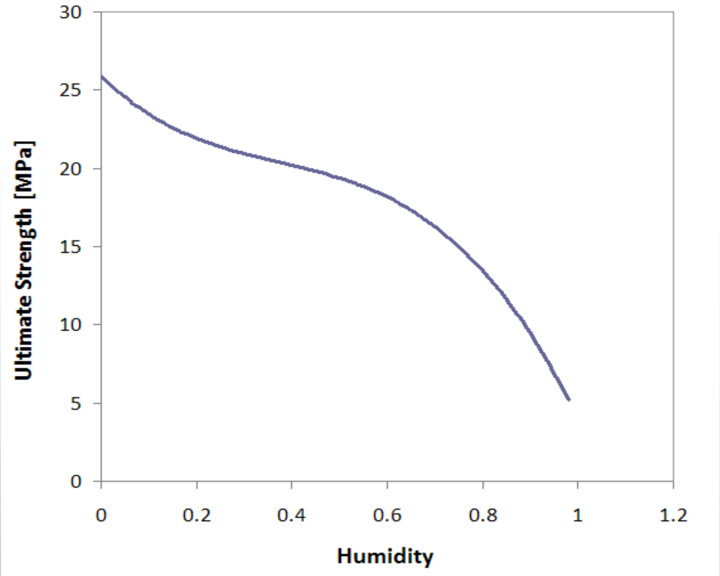


Peak Power

PEM Membranes

- Are Commonly composed of DuPont Nafion® polymer.
- The Shape of Nafion® changes with water content.
- Nafion’s ultimate strength decreases with increased humidity
- Membrane is vulnerable under these conditions

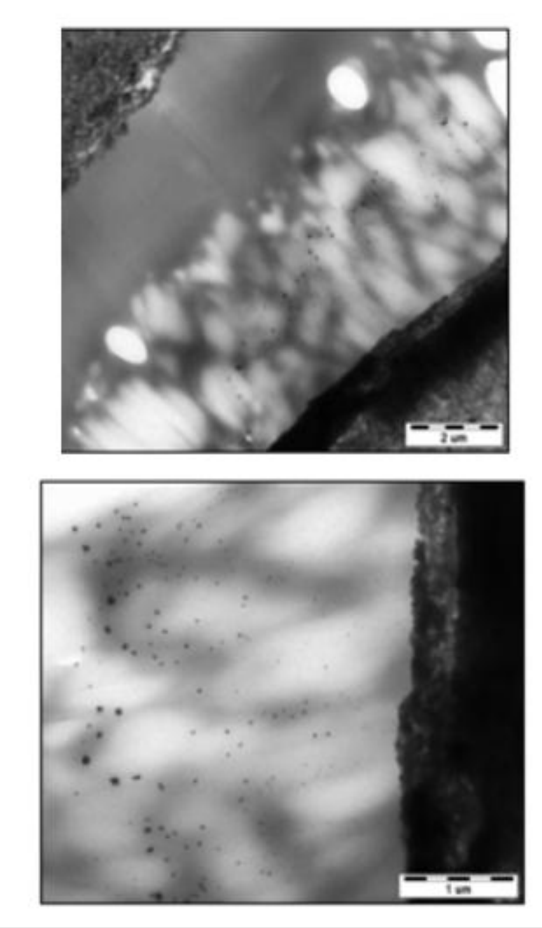




[Satterfield et al., 2006]

Membrane Degradation

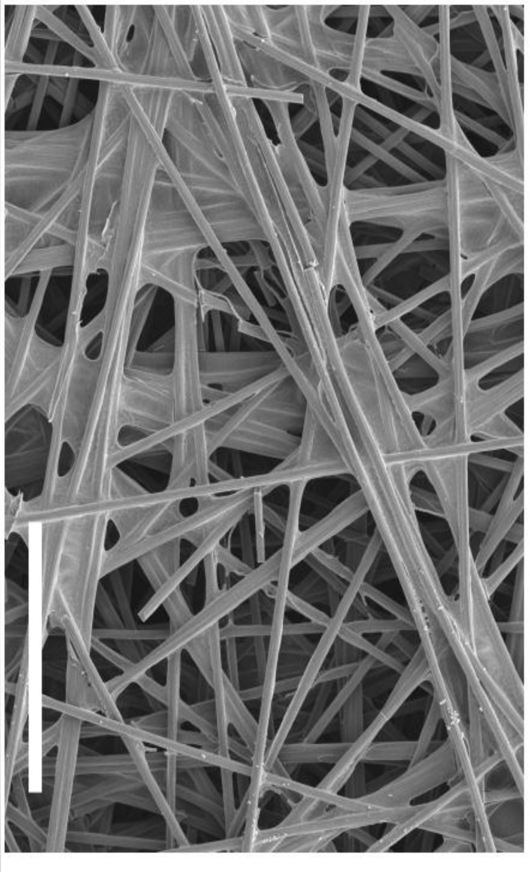
- Structural degradation
  - Fatigue stress caused by humidity/temperature cycling, high humidity operation [Zhou et al., 2009]
  - Change of membrane structure due to impurities such as dissolved platinum [Wu et al., 2008]
- Chemical degradation
  - Hydrogen peroxide attack due to thinning membranes from structural degradation
- Results in cracks, tears that break up membrane leads to catastrophic loss.



[Kim et al., 2009]

Gas Diffusion Layer Degradation

- Damaged by starvation, flooding, freezing, start-stop cycles
- Cathode layer corrodes at high temperatures [Wu et al., 2008]
- All issues preventable with proper control



[Baylak et al., 2009]

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מדינת ישראל

משרד הביטחון

Questions ?