University of Chester Thornton Science Park

Second Generation PEM Fuel Cells and the Indirect Reduction of Oxygen

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FCH2 2015, 21st May 2015

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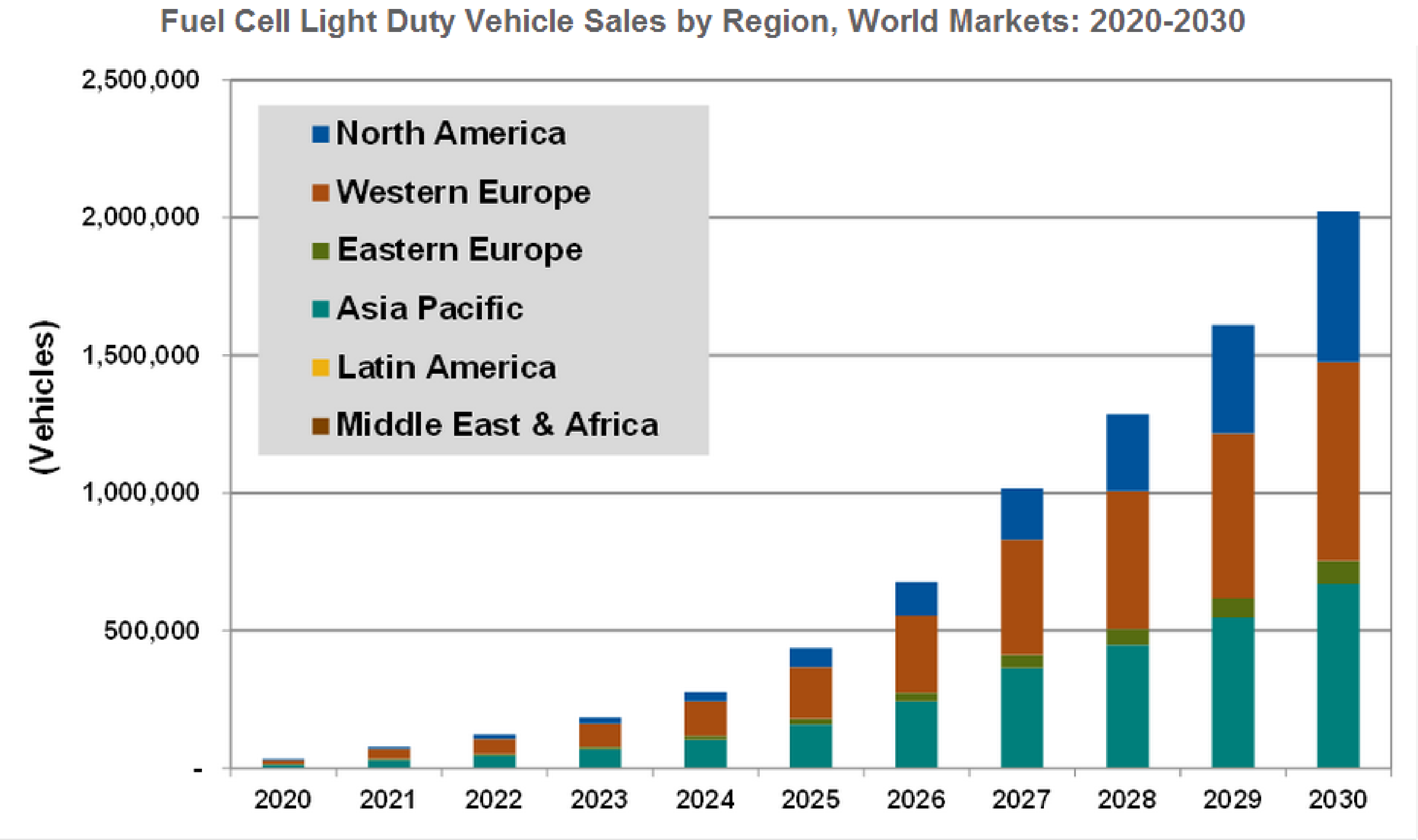
Science & Engineering

University of Chester

PEM Fuel Cell Market Predictions



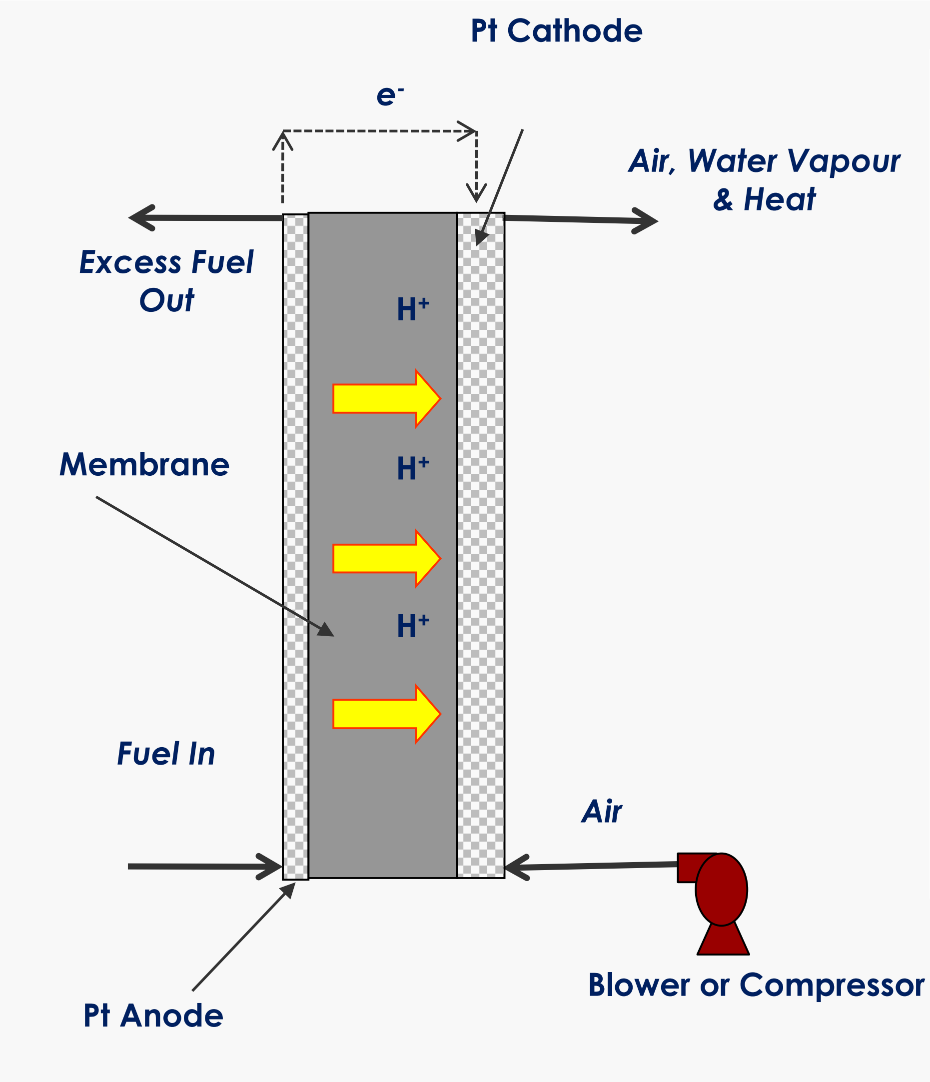
(Source: Navigant Research)

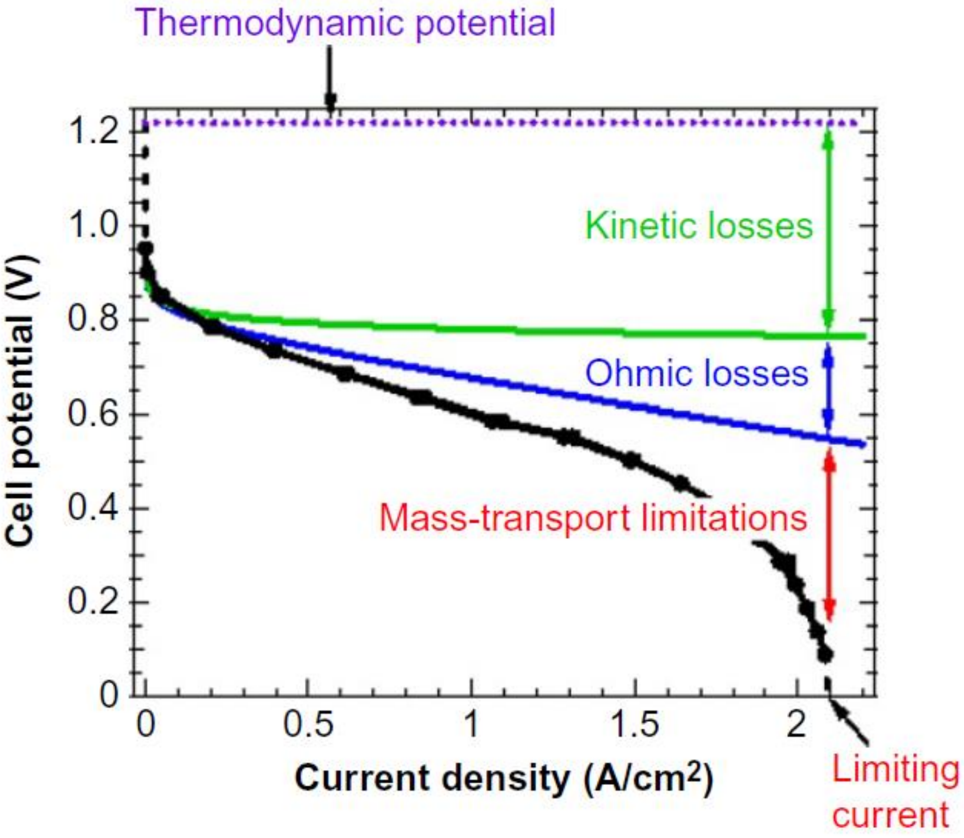
Outline

- Conventional PEM fuel cells
  - Challenges
  - Direct reduction of O_2
- Redox Flow Batteries
  - H_2-Br_2
- Regenerative PEM fuel cells
  - In-direct reduction of O_2
  - Low cost
  - Durable

Conventional PEM Fuel Cells

Conventional PEM Fuel Cell

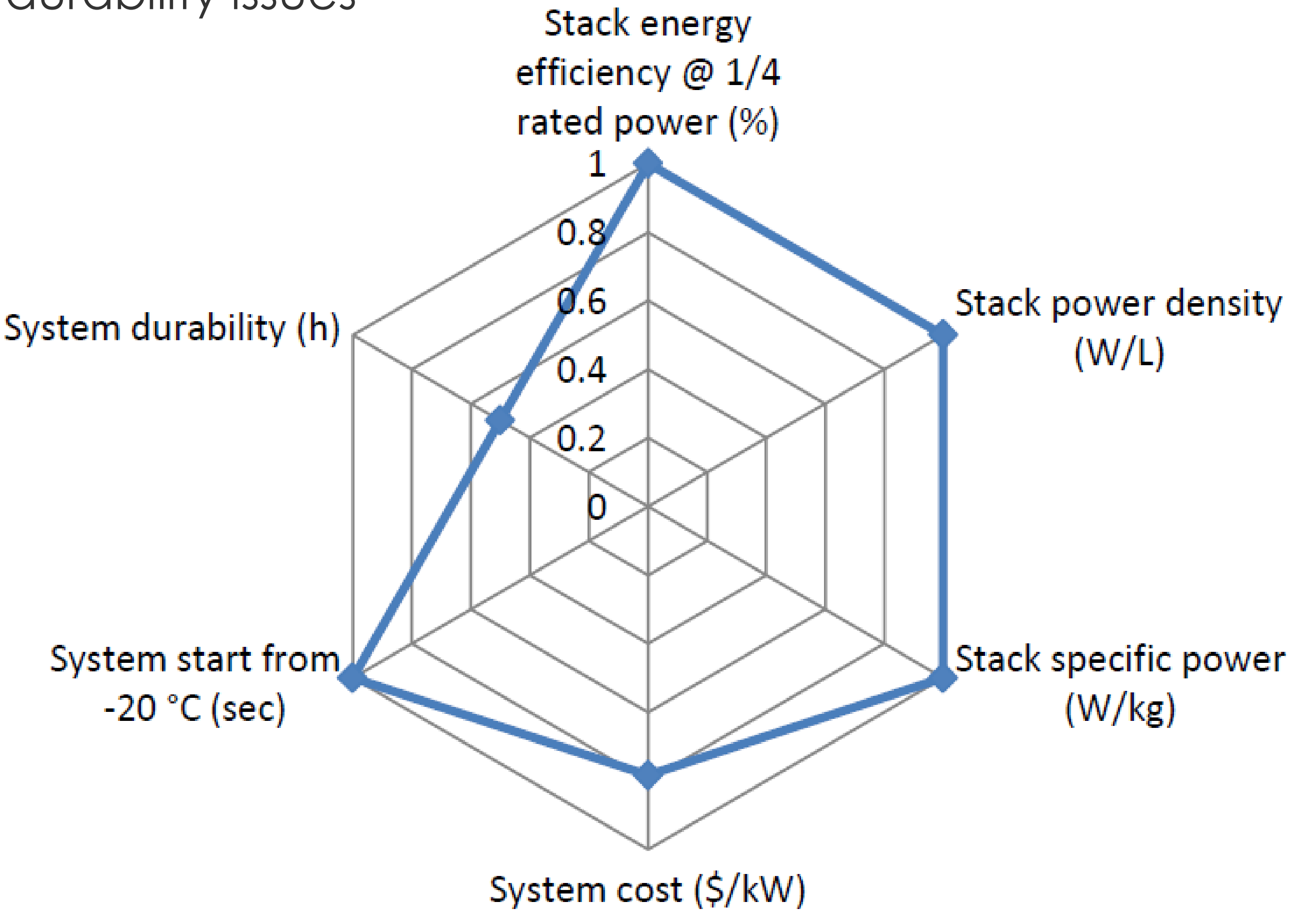




Advances in Chemical Engineering, 41, 2012, 65

The Problem

- Direct reduction of oxygen
  - Difficult reaction – requires “high” Pt loading
  - Causes durability issues

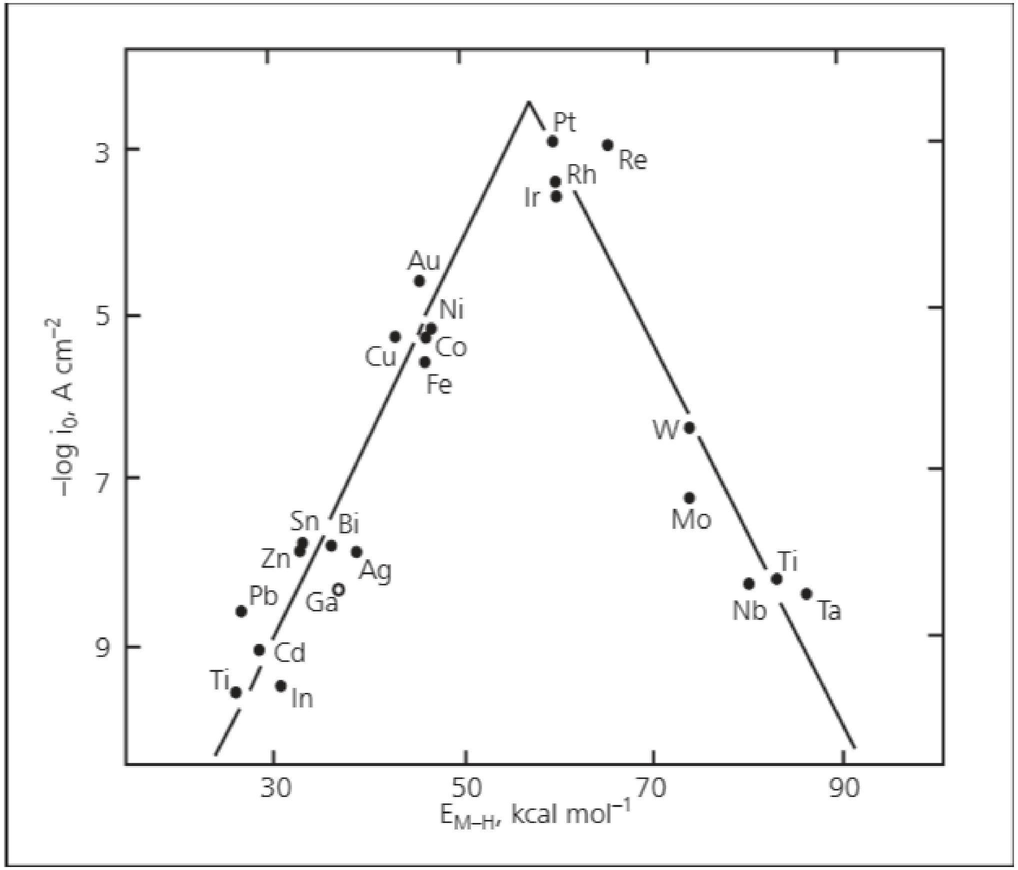


US Drive: Fuel Cell Technical Team Roadmap, June 2013

Platinum

- Recent US DoE analysis:
  - Pt contributes ~17% of total cost of 80 kW PEMFC system
  - 2012 technology + mass production
- Toyota PEMFC vehicle launch:
  - €66,000 + VAT per car (Germany)
  - 30 g Pt loading
  - >3% of car cost

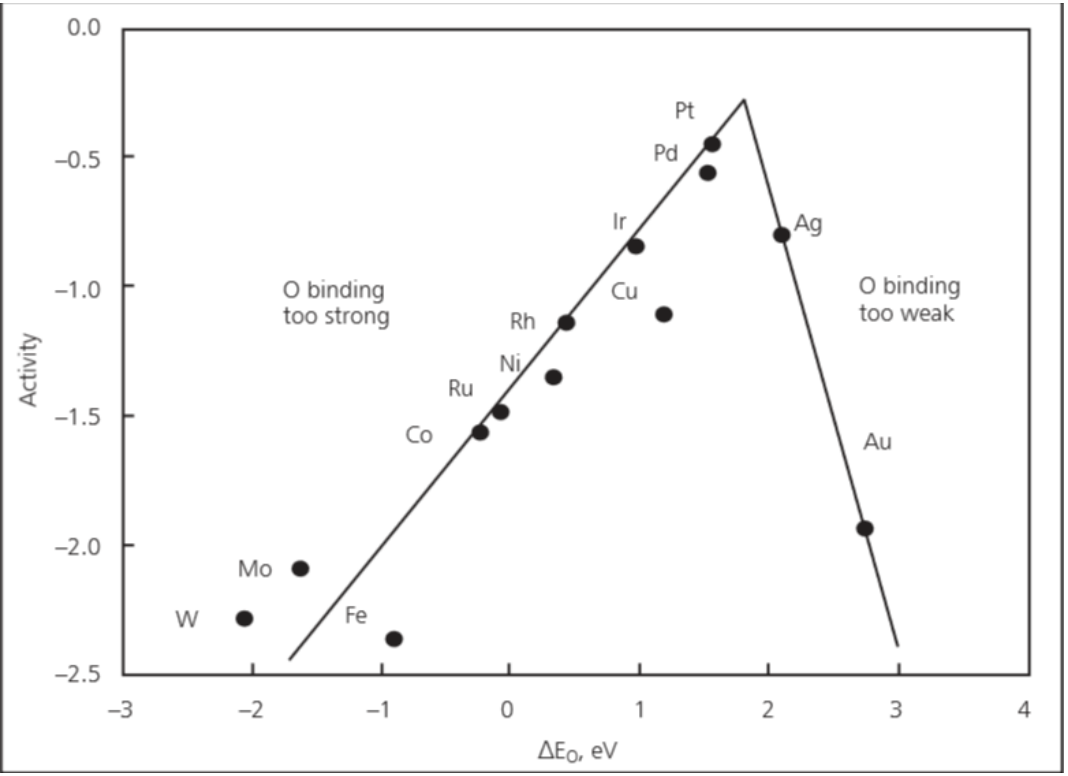
Platinum – HOR



- Pt best metal for HOR
- Kinetics are very fast
- “simple” reaction
- Voltage losses are very small
  - <5 mV for 0.05 mg cm^{-2} *

* *J. Electrochem. Soc.*, 157 (2007) B631

Platinum - ORR



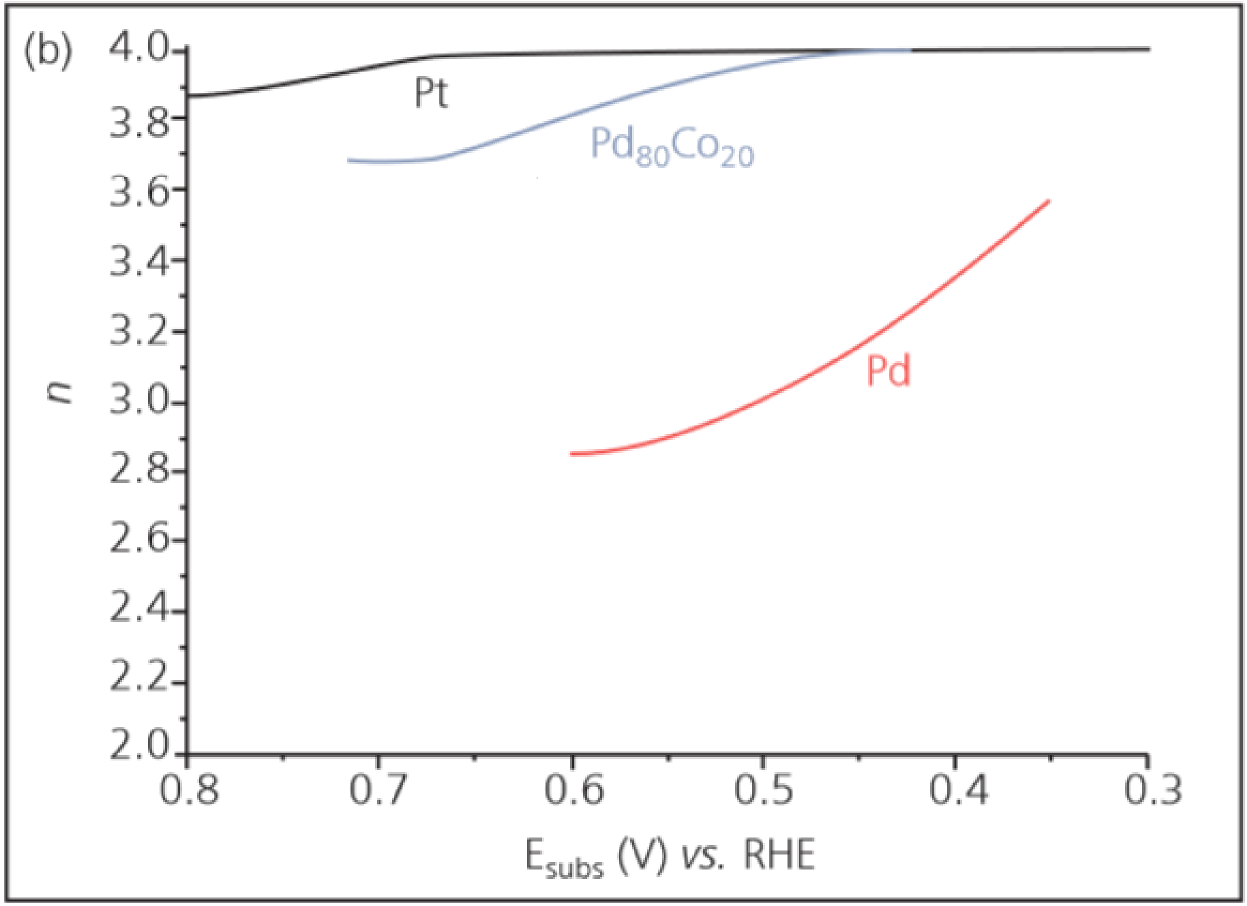
- Pt is the best metal for the OOR
- Kinetics are slow
- More Pt required for ORR
- Complicated reaction with numerous pathways
- 2e vs. 4e
- Voltage losses are very large
- More than half of the voltage loss for PEMFC *

* *J. Electrochem. Soc.*, 157 (2010) B1529

Reduction Pathway

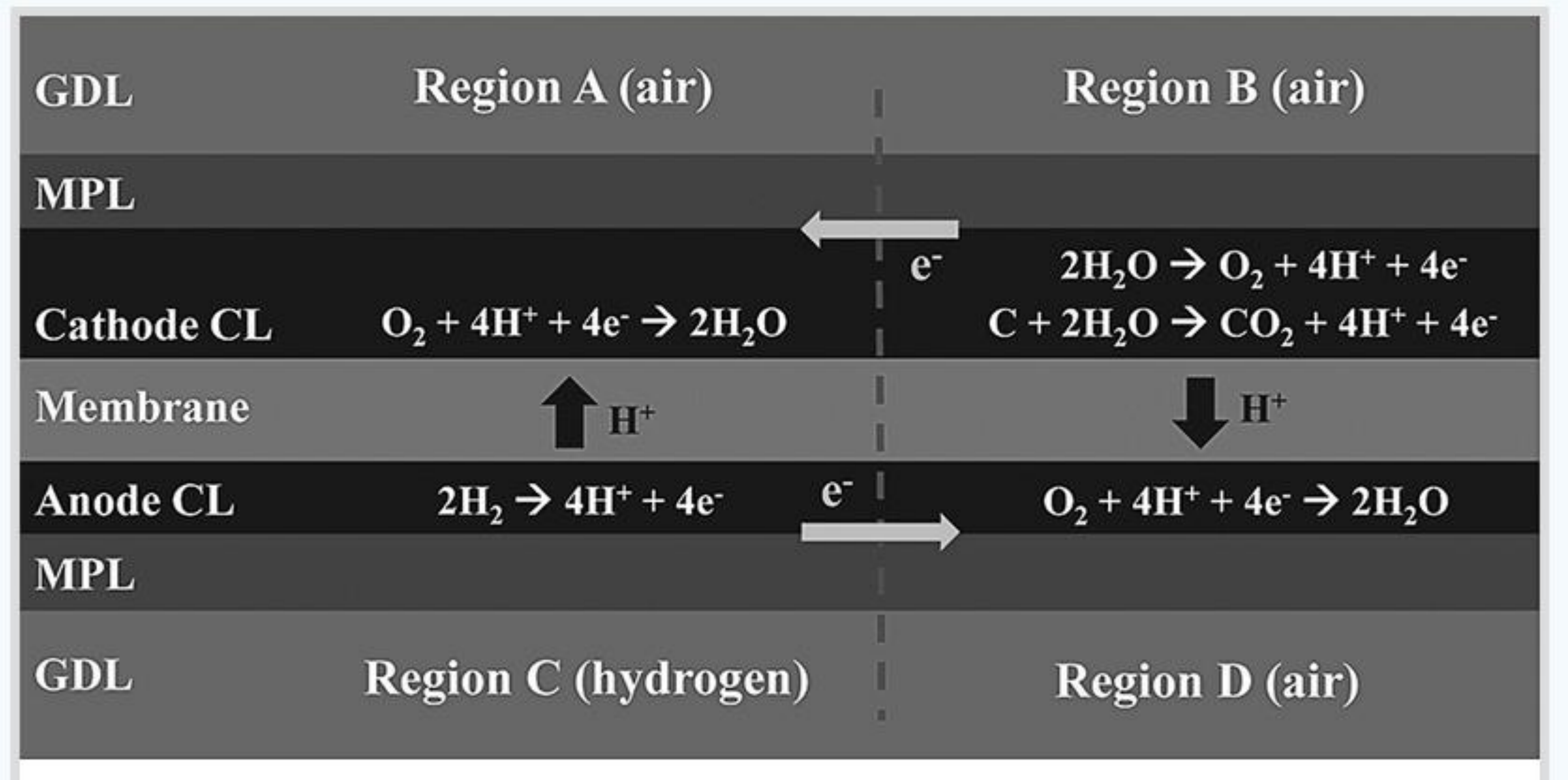
Oxygen Reduction Reaction	***E*°**
$O_2 + e^- + H^+ \rightarrow HO_2^\bullet$	-0.13 V
$HO_2^\bullet + e^- + H^+ \rightarrow H_2O_2$	+1.4 V
$H_2O_2 + e^- + H^+ \rightarrow HO^\bullet + H_2O$	+0.71 V
$HO^\bullet + e^- + H^+ \rightarrow H_2O$	+2.55 V
$O_2 + 2\,e^- + 2\,H^+ \rightarrow H_2O_2$	+0.68 V
$H_2O_2 + 2\,e^- + 2\,H^+ \rightarrow 2\,H_2O$	+1.77 V
$O_2 + 4\,e^- + 4\,H^+ \rightarrow 2\,H_2O$	**+1.23 V**

Pt Reaction Selectivity



- Undesirable side products cause durability issues
  - Presence of H_2O_2 is highly damaging

Start Up Durability Issues



Cooling

- Engineering challenge for conventional PEM fuel cells
- Limited to ~80°C – difficult to dissipate waste heat
- Need higher operating temperatures

Conventional PEMFC Technology

- Challenges
  - Direct reduction of oxygen
    - Slow kinetics cause large voltage drop
    - High Pt loading
    - Degradation via by-products
    - Start up issues
  - Cooling issues due to 80°C max temperature

Redox Flow Batteries

Recent Commercial VRB Systems and Installations

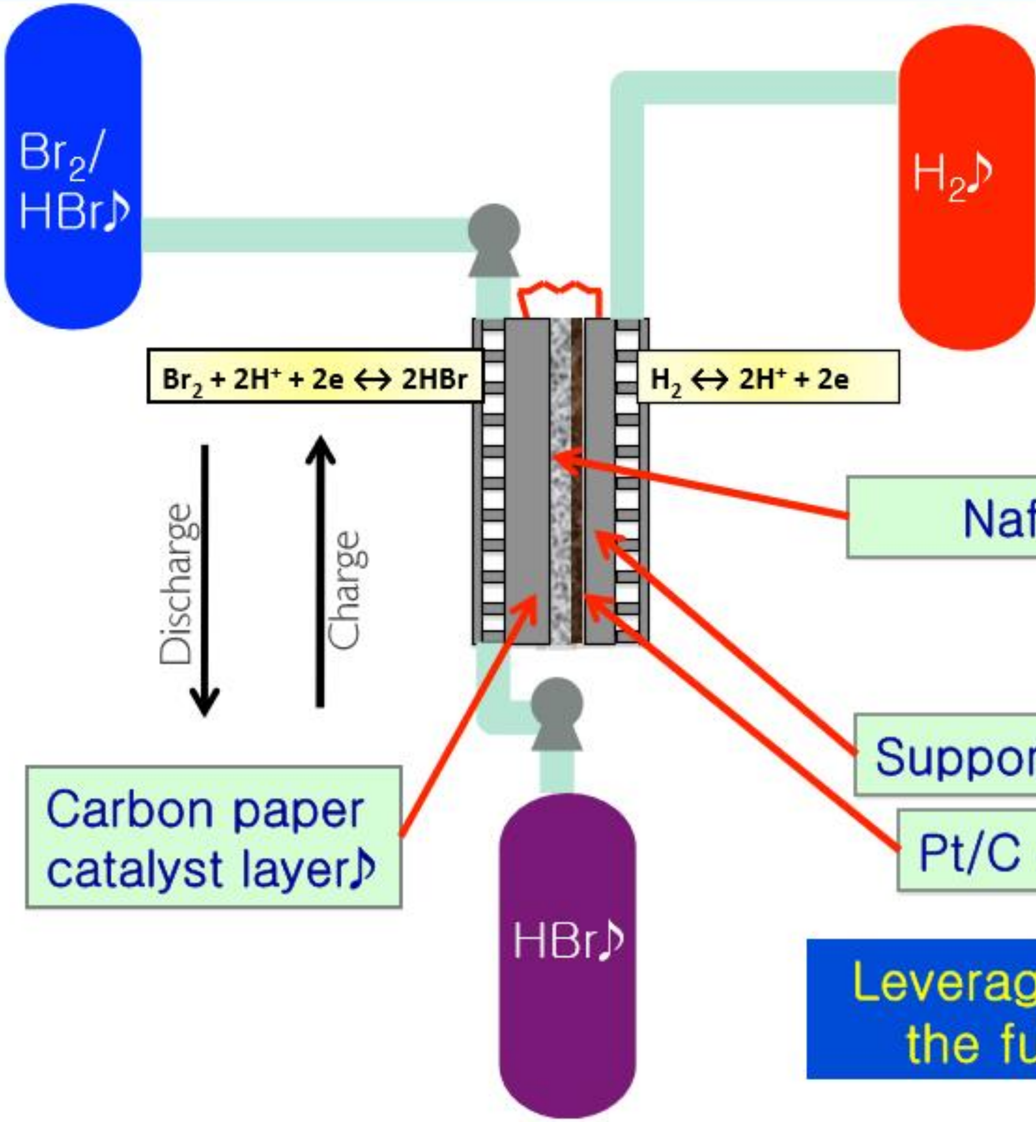
1 MW/5 MWh VRB - Sumitomo - Japan

5 MW/10 MWh Rongke

Gildemeister - Germany

300 kW/3.6 MW Prudent - California

Hydrogen/Bromine Flow Battery

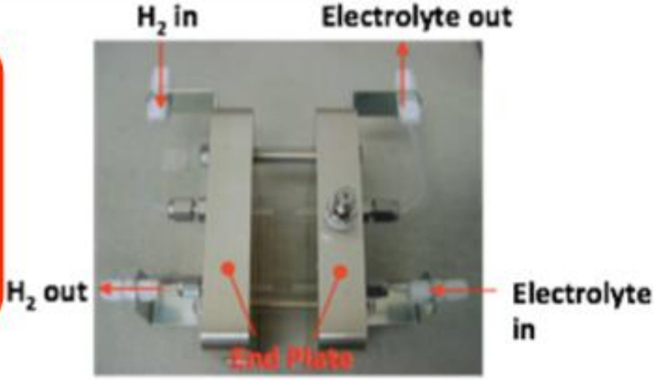


Nafion membrane♪

Support layer (GDL)♪

Pt/C catalyst layer♪

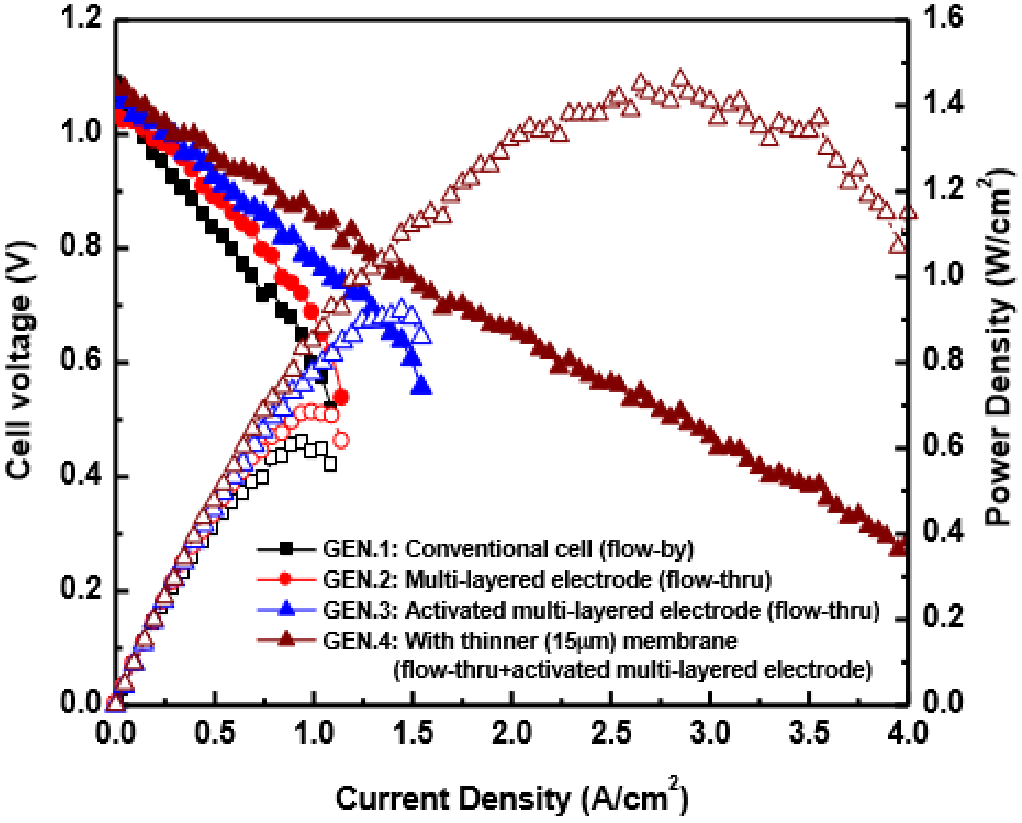
Carbon paper catalyst layer♪

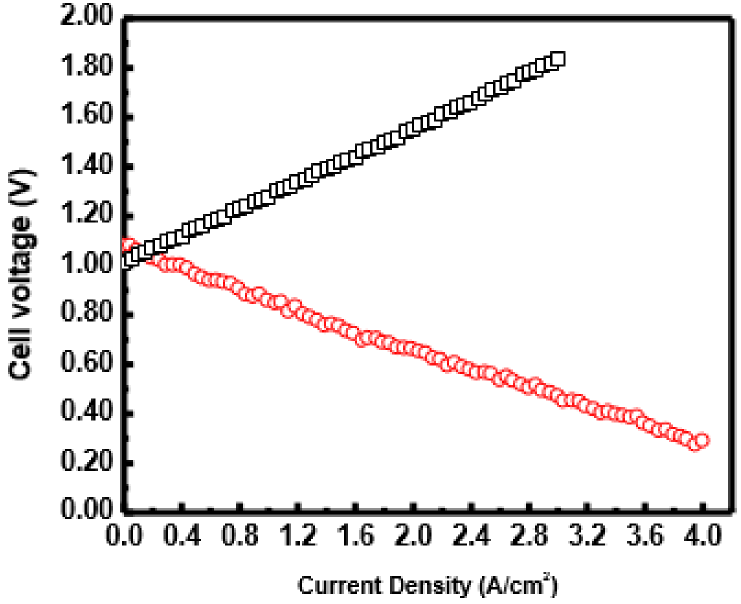


Leveraging designs developed in the fuel-cell field for the cell♪

Performance

Ambient temperature and pressure♪
0.9 M Br_2 / 1 M HBr♪





Voltaic efficiency	PD (W/cm²)
80 %♪	0.99♪
90 %♪	0.60♪

A. Weber, IFBF 2013, Dublin

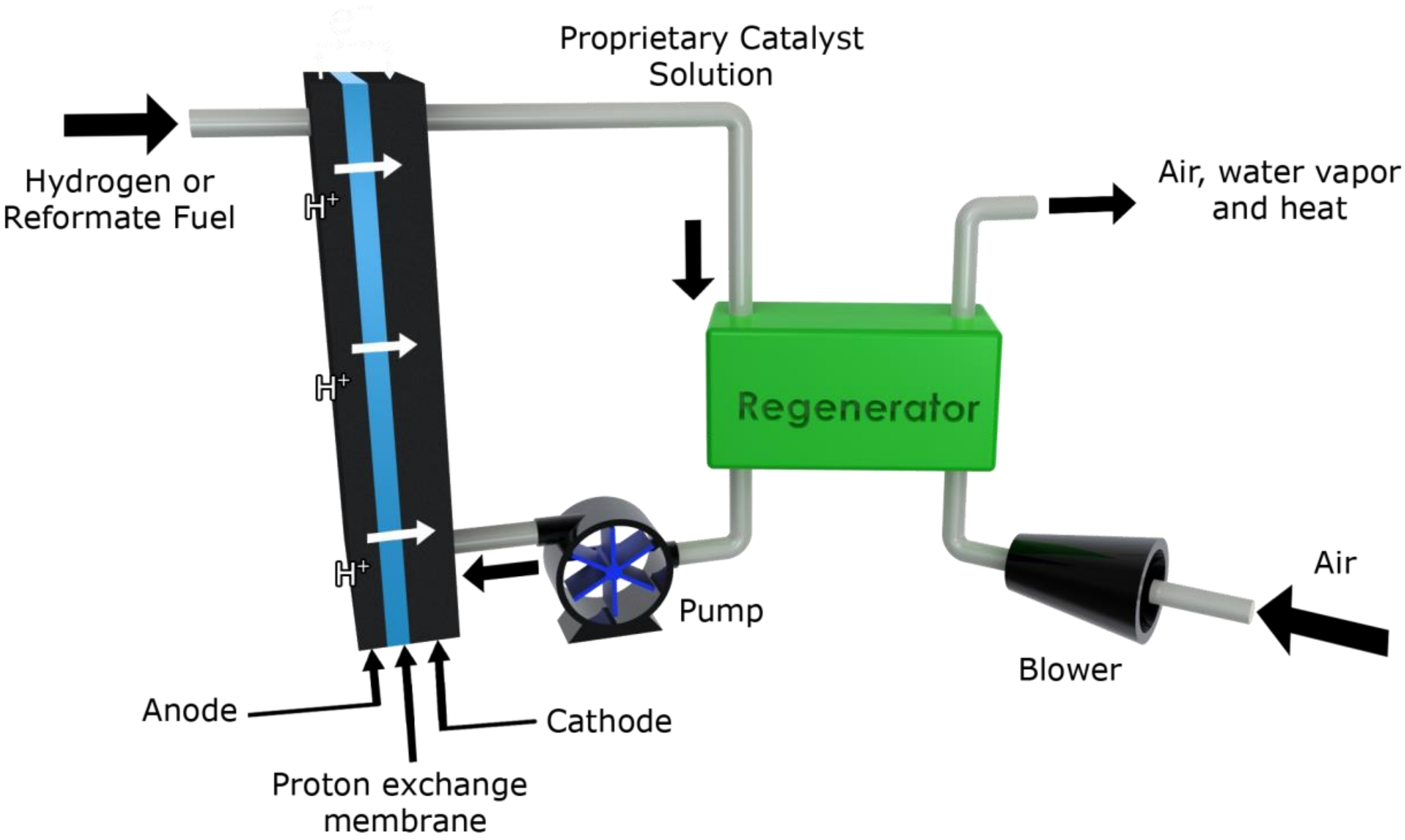
Regenerative PEM Fuel Cells
In-Direct O_2 Reduction

Regenerative PEMFC Technology

- Challenges
  - Direct reduction of oxygen
    - Slow kinetics cause large voltage drop
    - High Pt loading
    - Degradation via by-products
    - Start up issues
  - Cooling issues due to 80°C max temperature
- Solution
  - In-direct reduction of oxygen
    - No Pt required
    - Durability issues resolved

ACAL Energy Concept

Liquid Phase Catalyst/Mediator to Drive Fuel Cell



Proprietary Catalyst Solution

Hydrogen or Reformate Fuel

Air, water vapor and heat

Pump

Air

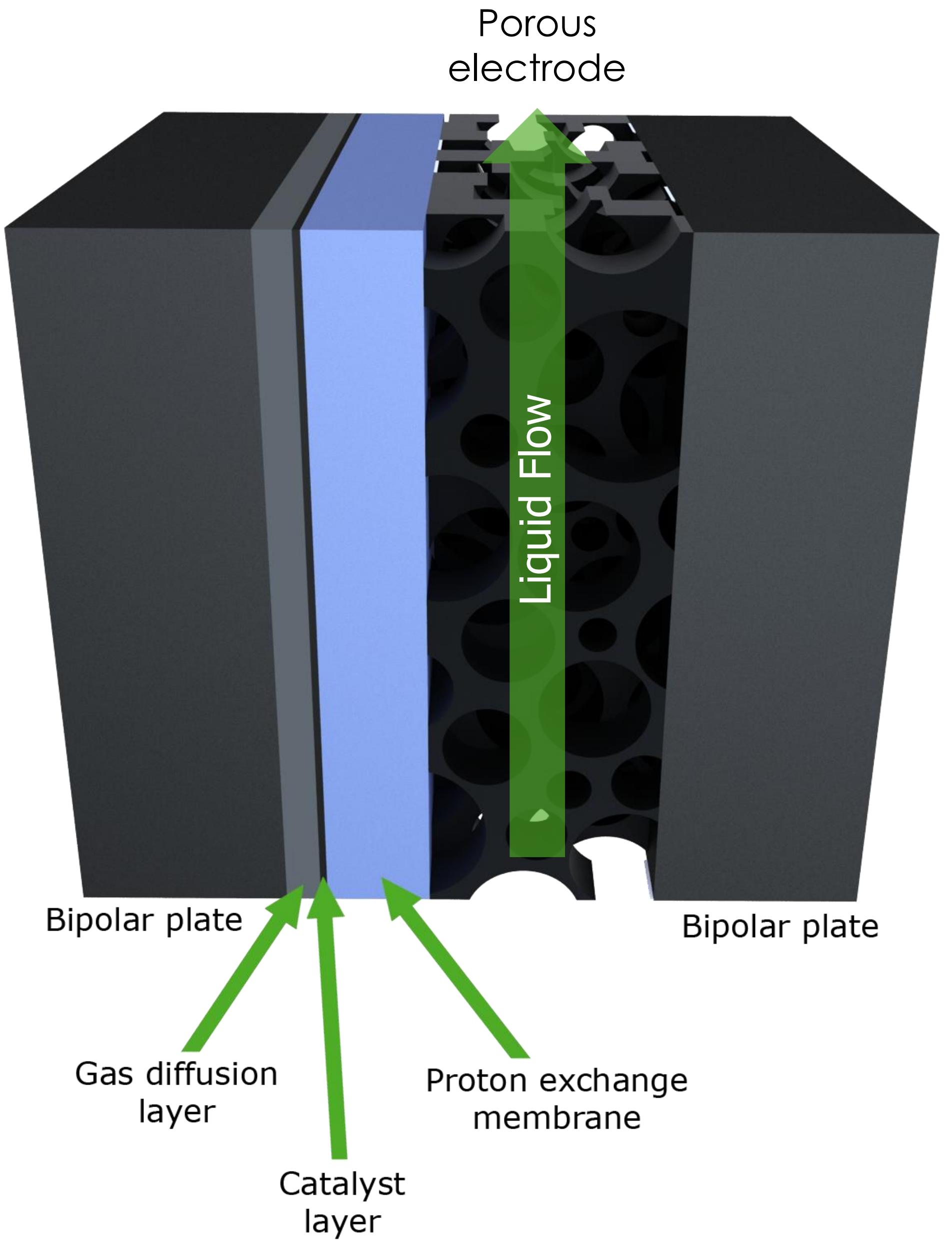
Blower

Anode

Cathode

Proton exchange membrane

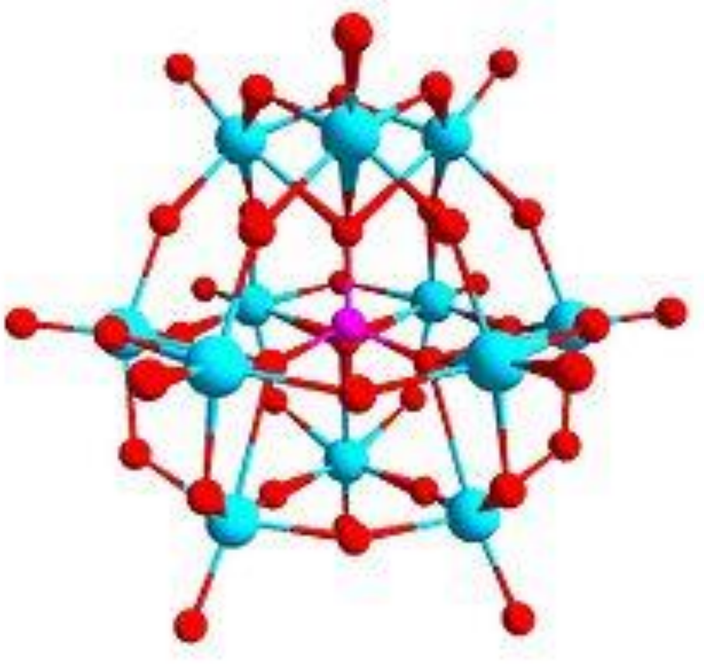
Basic Cell Architecture



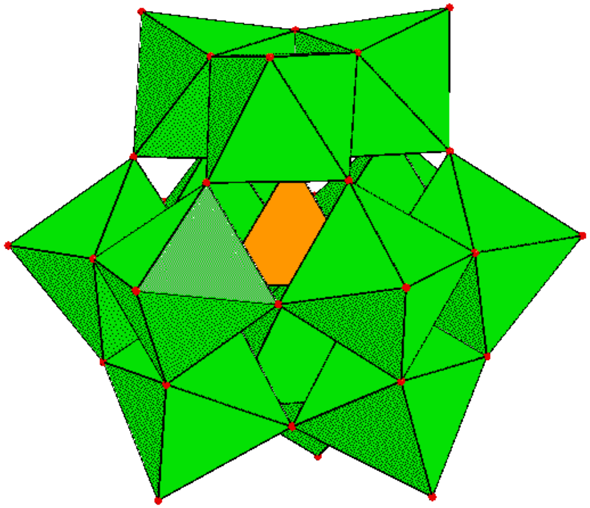
- Standard cell components
- Fuel cell – flow battery hybrid
  - Anode very similar to conventional PEMFC
  - Cathode similar to redox flow battery
- Optimization needed
- Same fuels as standard PEM
  - Hydrogen, reformate and methanol evaluated

Polyoxometallates (POMs)

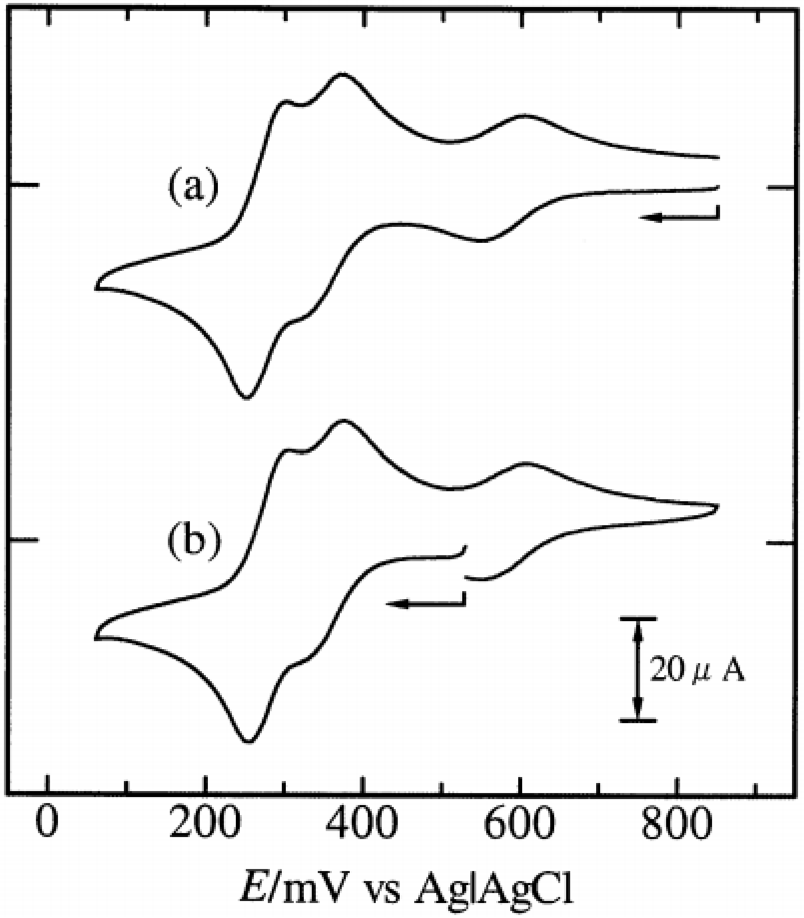
- Keggin structures form a category of POMs
  - Best known example is PMA (Aldrich)
- Inorganic complexes
  - Stable
  - Electrochemically reduced at carbon electrode
  - Reduced keggin reacts with oxygen



$[PMo_{12}O_{40}]^{3-}$

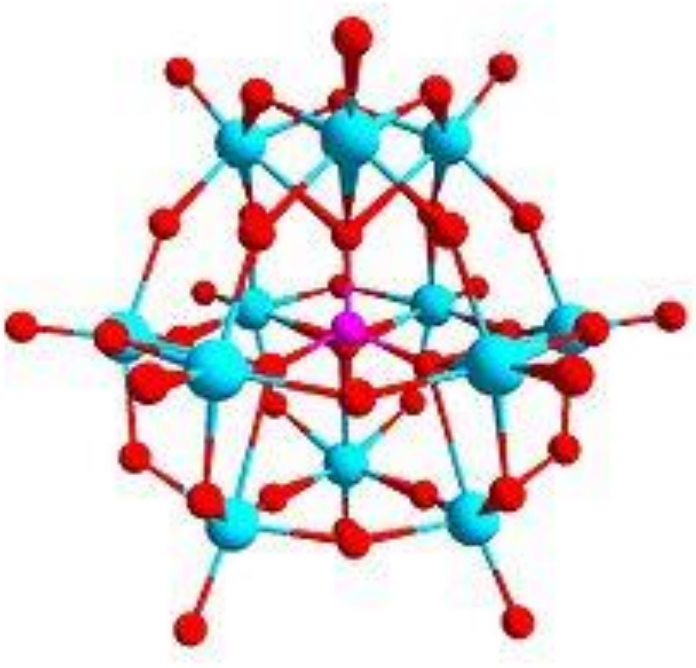


POM Electrochemistry



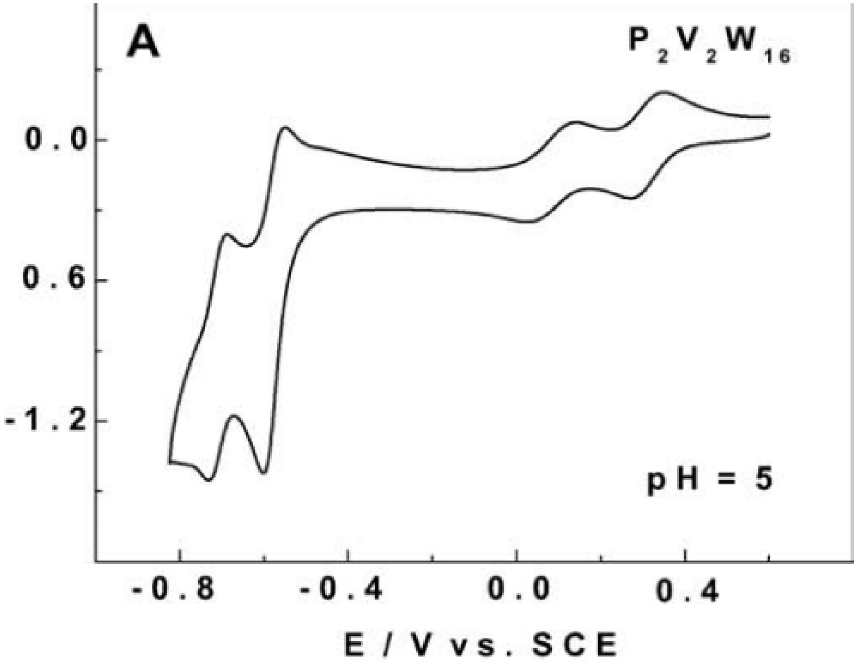
0.5 mM $(n\text{-Bu4N})_4[PVMo_{11}O_{40}]$ in
0.1 M $HClO_4$/MeCN/water
Glassy carbon working electrode

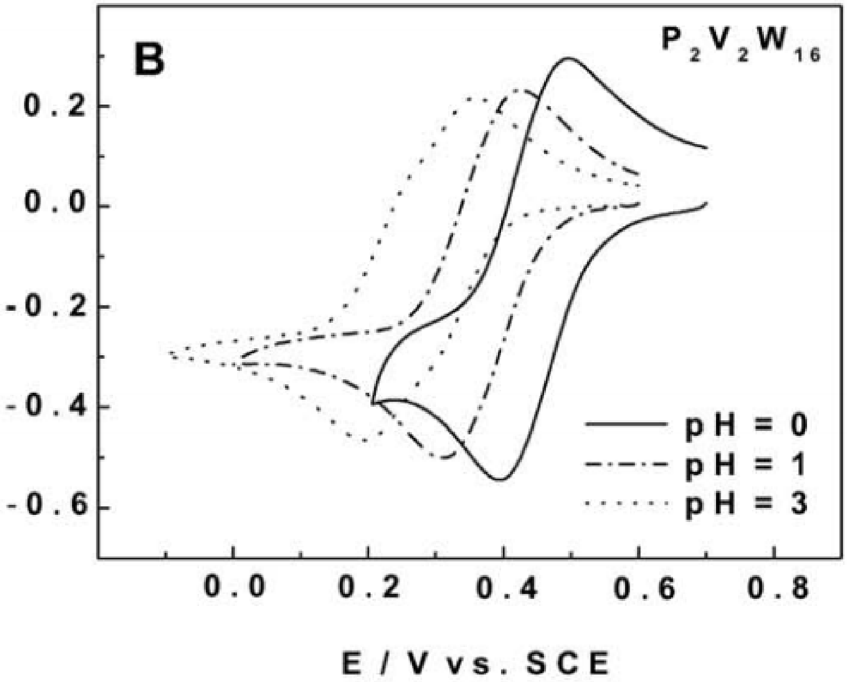
J. Electroanal. Chem. 451 (1998) 203

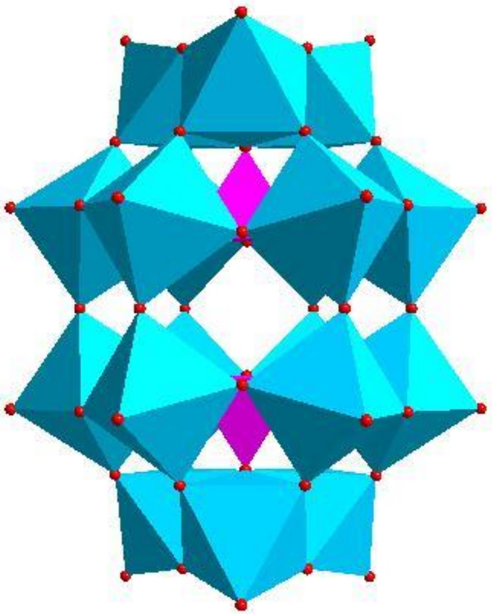


$[PVMo_{11}O_{40}]^{4-}$
Keggin

POM Electrochemistry







$[P_2V_2W_{16}O_{62}]^{8-}$
Dawson

0.2 mM $[P_2V_2W_{16}O_{62}]^{8-}$ in aqueous media
Glassy carbon working electrode

C. R. Chimie, 8 (2005) 1057

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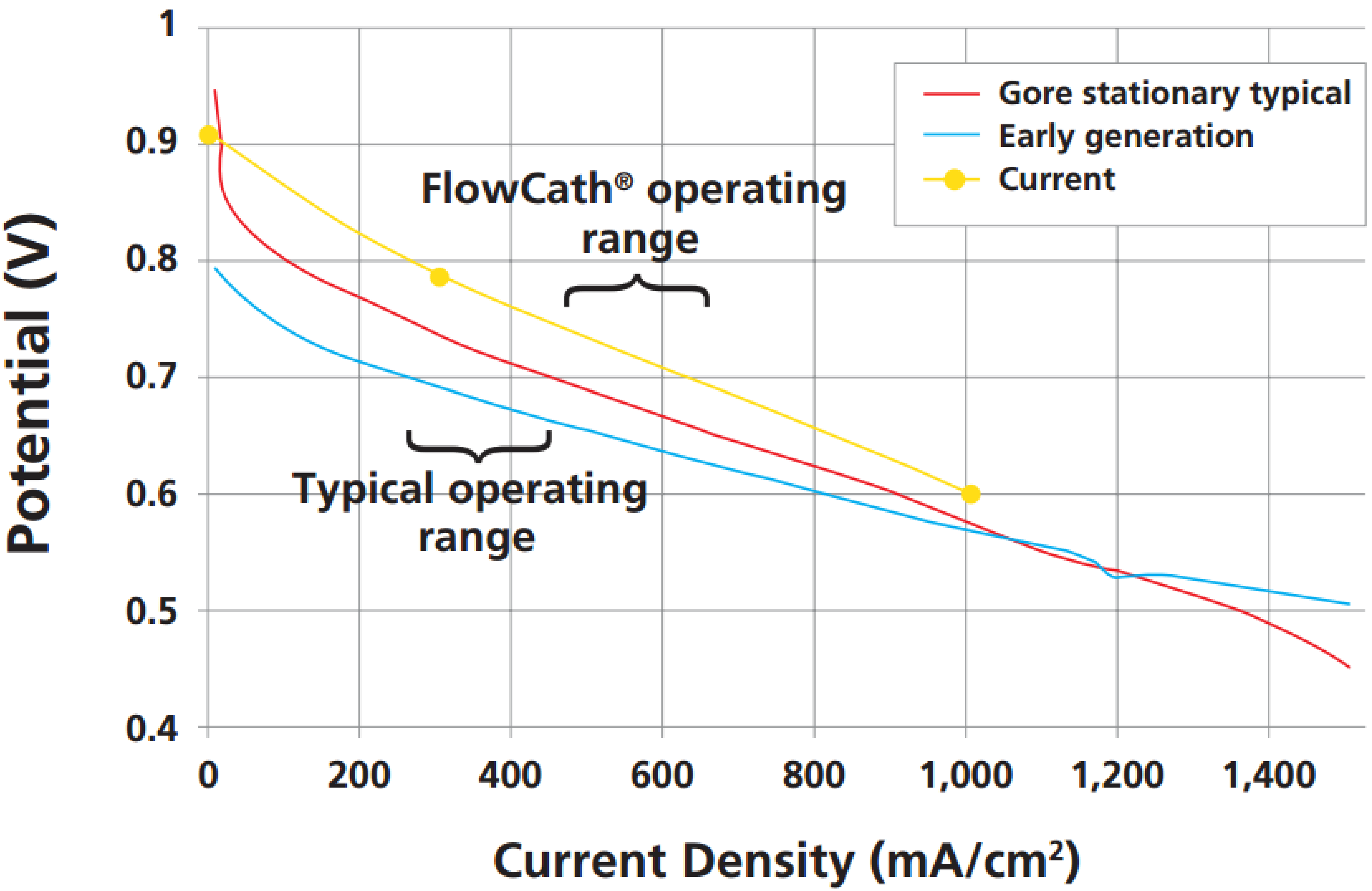
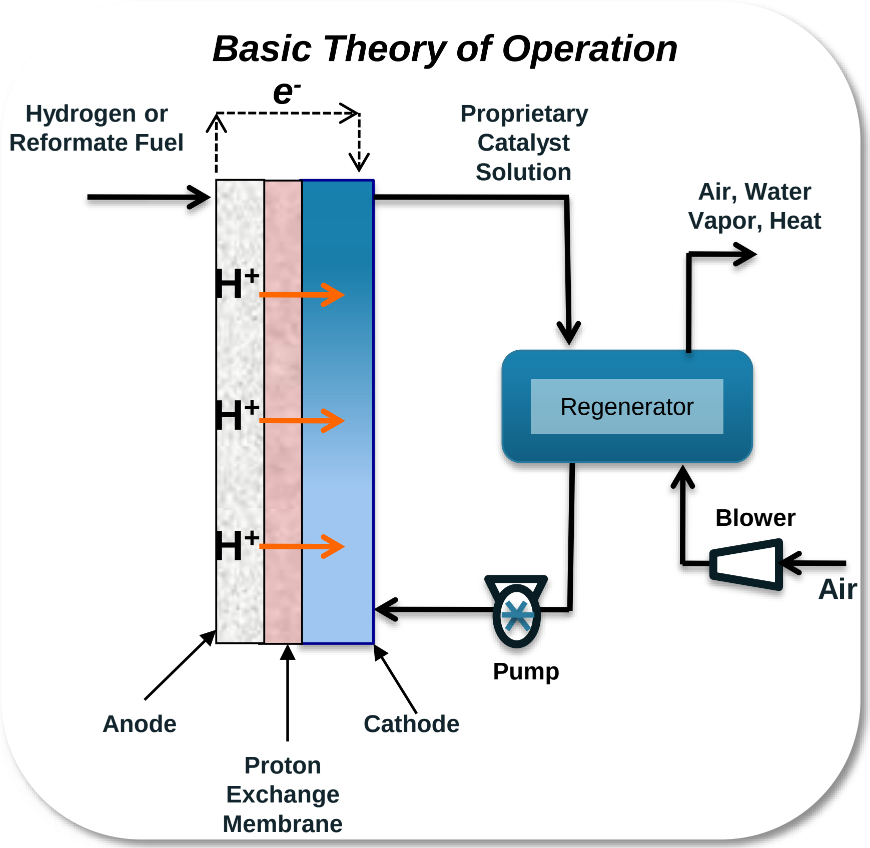
Comparison with Commercial MEA Data

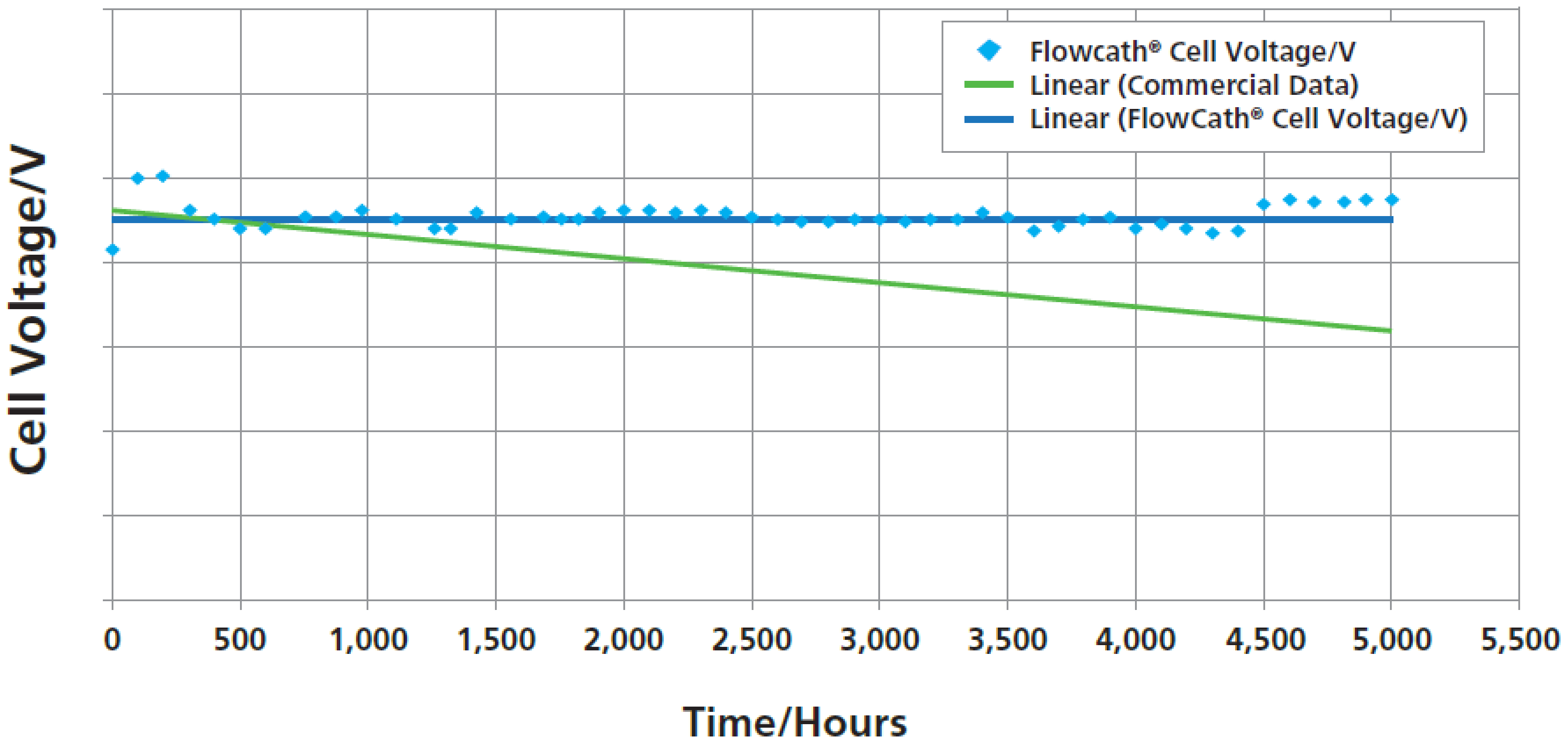


Fundamentally More Durable



- Catalyst system thermodynamically stable
  - High operational durability
- Reaction with oxygen occurs away from electrode
  - No oxygen or peroxide in contact with electrode or membrane to cause damage
- Membrane in contact with aqueous solution
  - Membrane always hydrated

Automotive Durability Protocol – FlowCath® v Commercial



Cooling

- Regenerative fuel cells can operate above 80°C
- Cathode side of membrane is always wet
  - Membrane drying can be avoided
- Big impact on cooling
  - Catholyte acts as a coolant

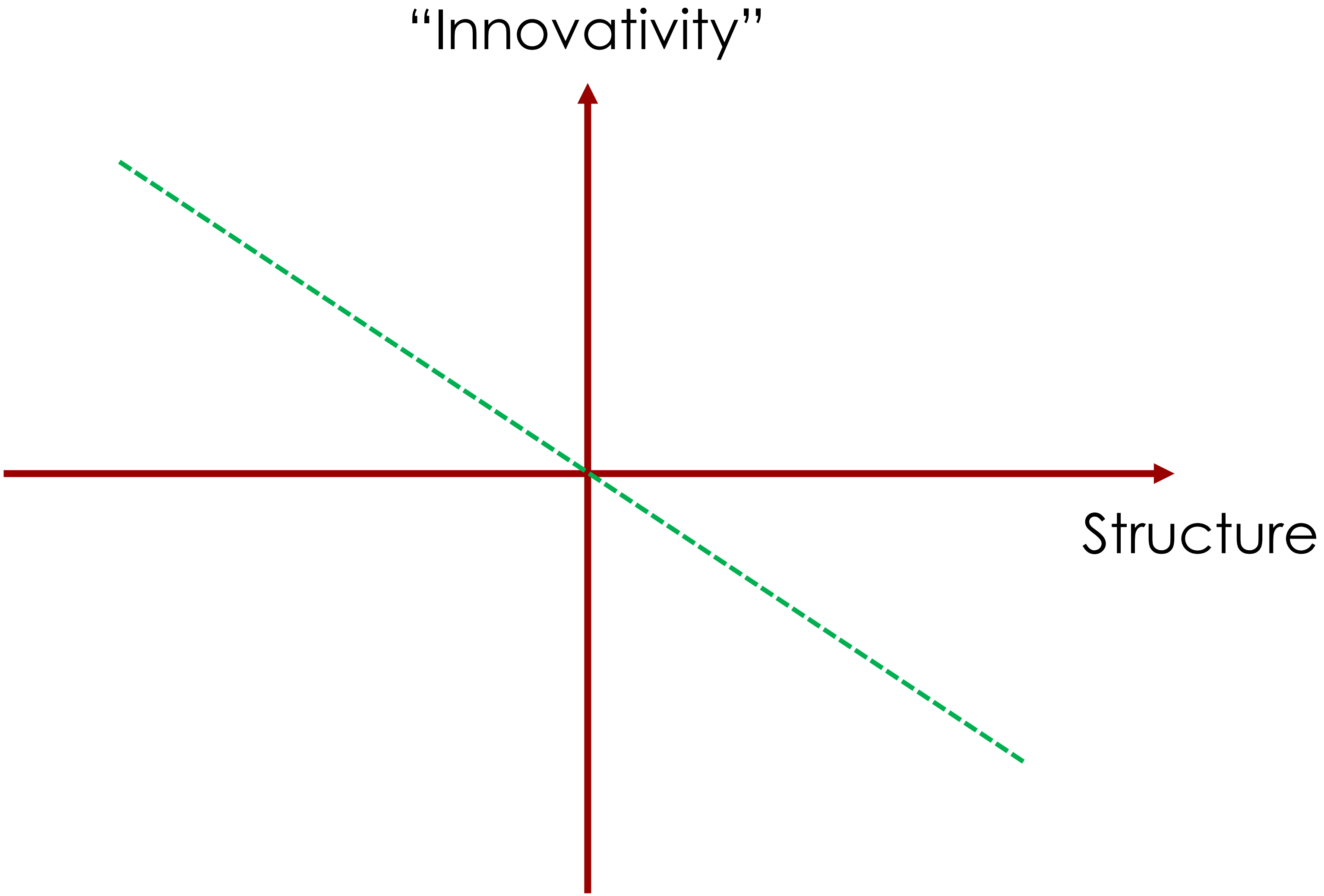
A New Set of Challenges

- Cell optimization, scale up and stack assembly
  - Flow battery vs. fuel cell architecture
- Liquid catalyst formulation
  - High electrode potential vs. fast regeneration reaction
- Bubble generation
  - High surface area bubbles vs. high efficiency bubbling
  - The bubbler performance and catalyst chemistry determine the volume of catholyte required
- >100°C operation
  - 10,000 hours durability achieved at 70-80°C
  - Oxygen concentration vs. regeneration kinetics

Innovation

- Ford invited (and patented) the regenerative fuel cell concept in the 1980s
- Despite a wealth of resources, Ford could not achieve adequate current densities
- Over the last 10 years major advances have been achieved by a small company on a limited budget
- Why?

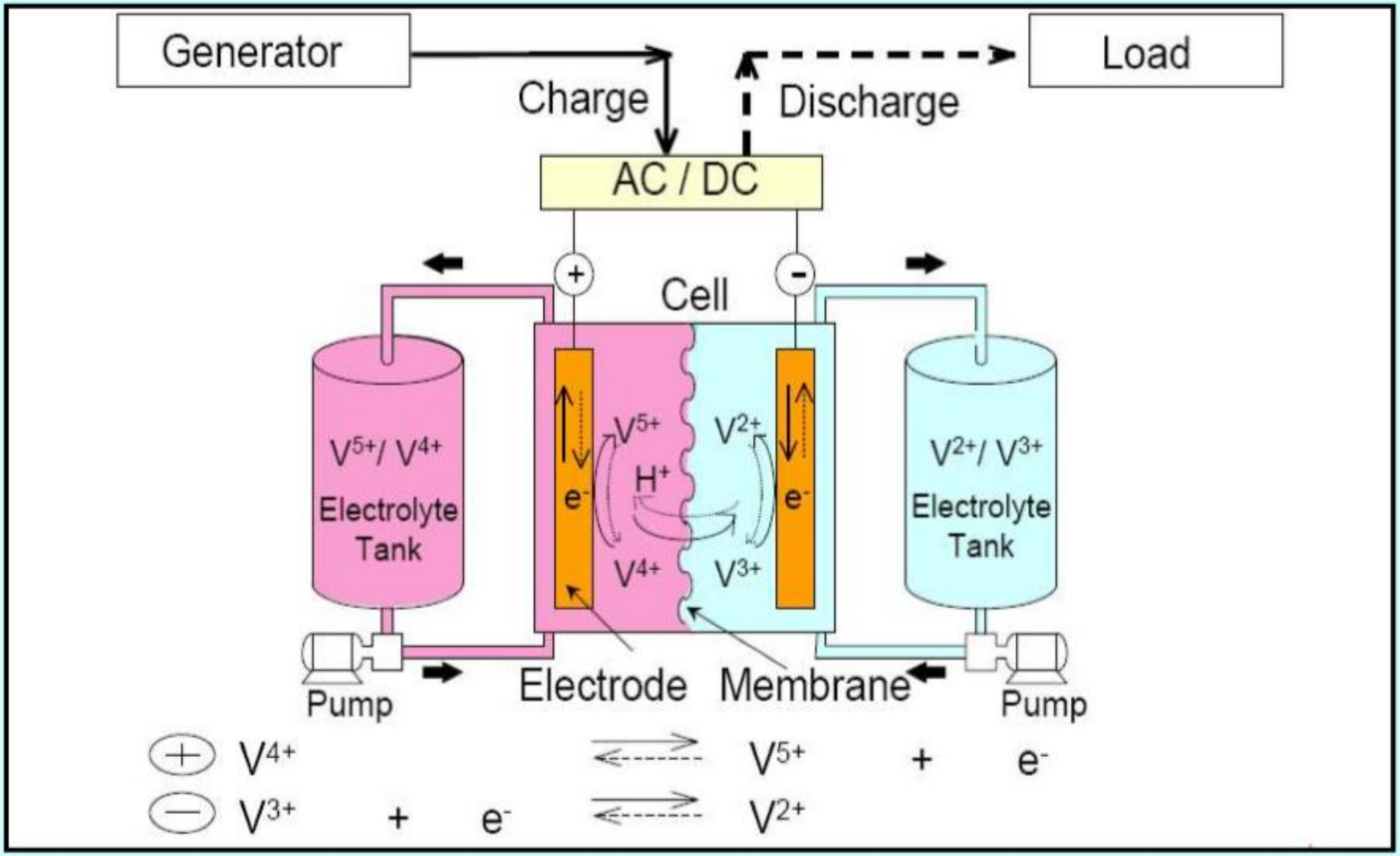
Innovation vs. Structure



Thank you

Backup Slides

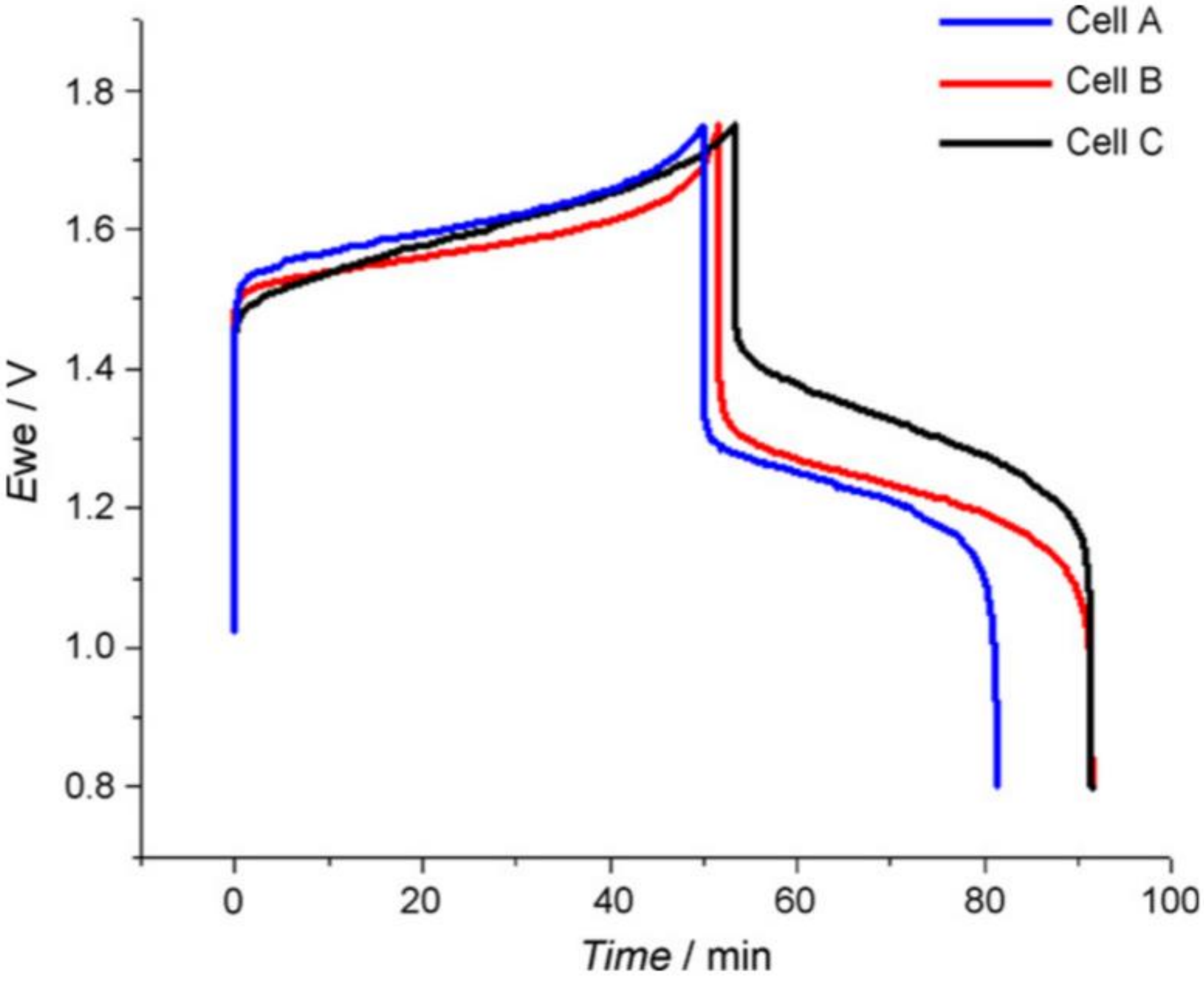
All-vanadium redox flow cell



$$\oplus \quad V^{4+} \rightleftharpoons V^{5+} + e^-$$

$$\ominus \quad V^{3+} + e^- \rightleftharpoons V^{2+}$$

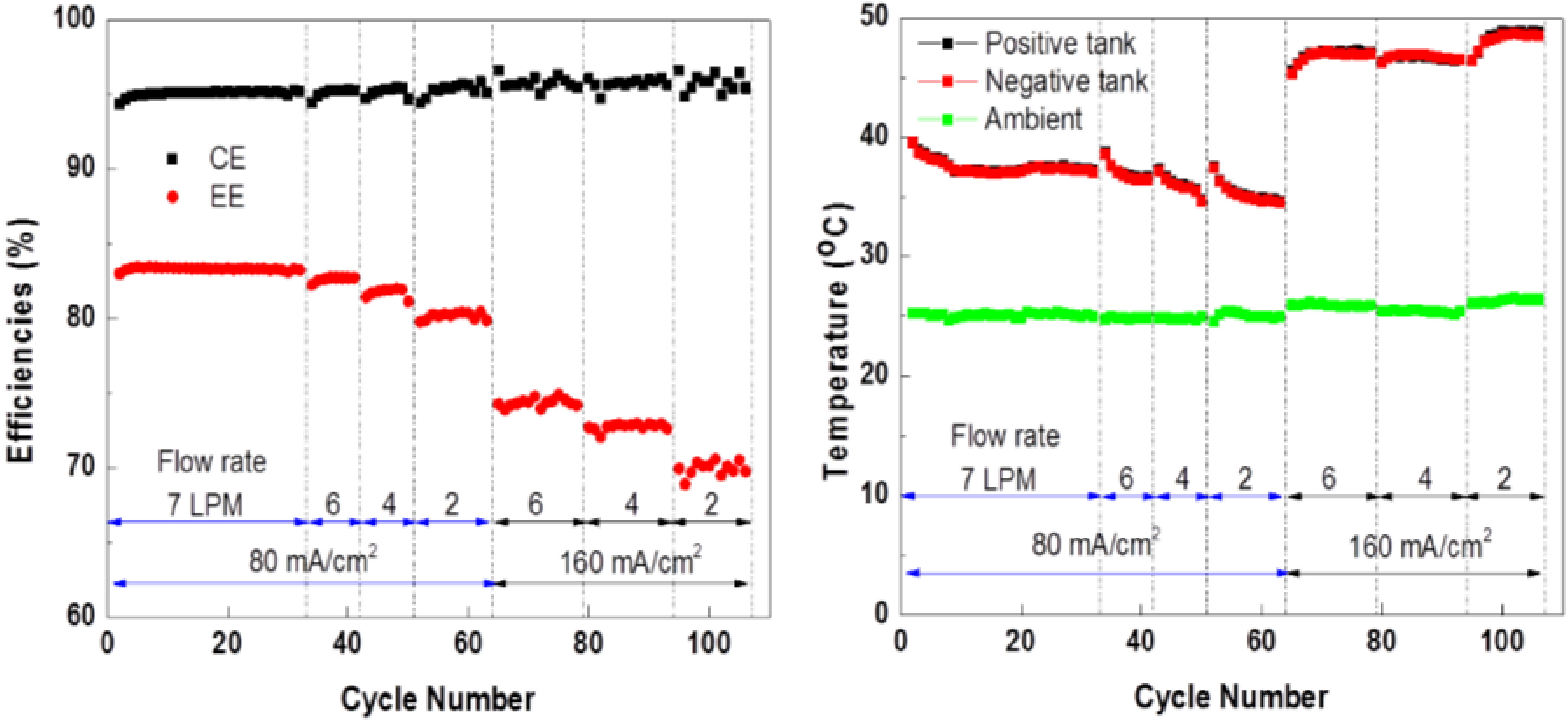
Performance



- Charge-discharge curves
- Coulombic efficiency
- Electrical efficiency

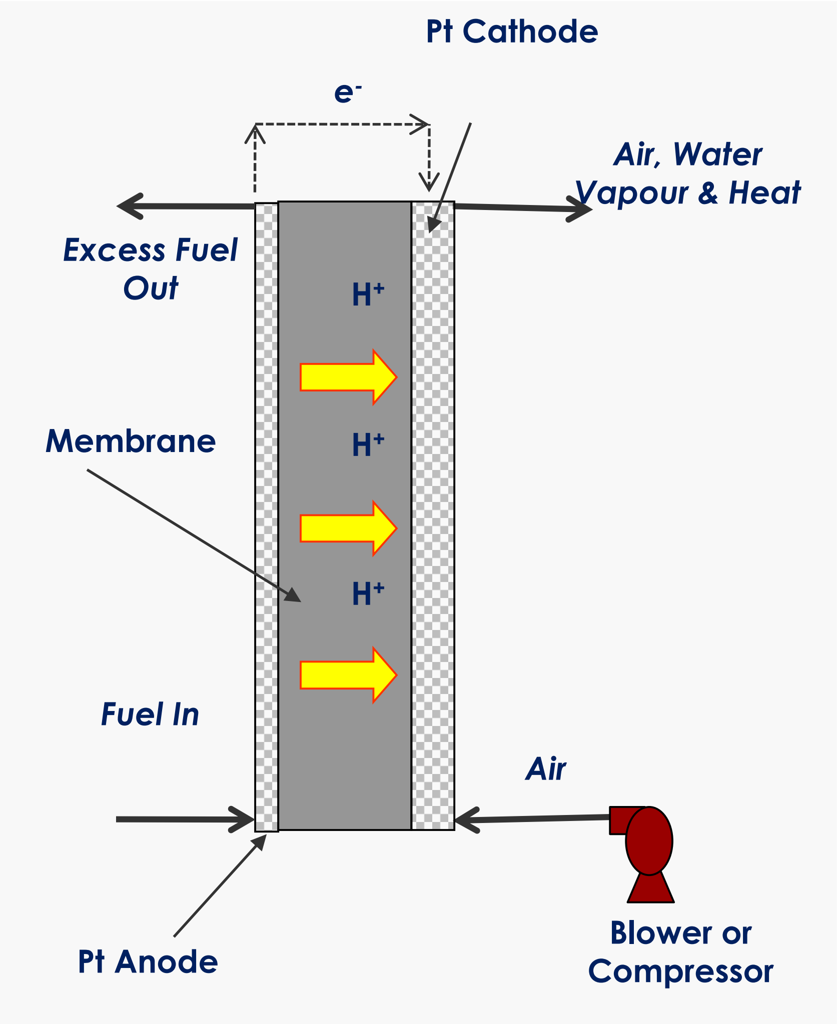
Performance

Performance depending on flow rate and °C



Successfully operated up to 160 mA.cm^{-2} at an energy efficiency ~75%

Conventional PEM Fuel Cell Weaknesses



Pt Cathode

e^-

Air, Water Vapour & Heat

Excess Fuel Out

H^+

Membrane

H^+

H^+

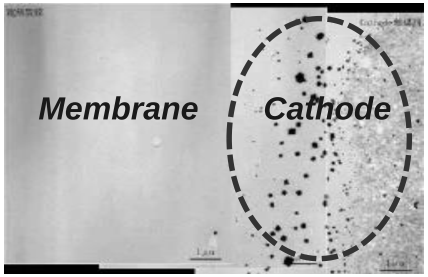
Fuel In

Air

Pt Anode

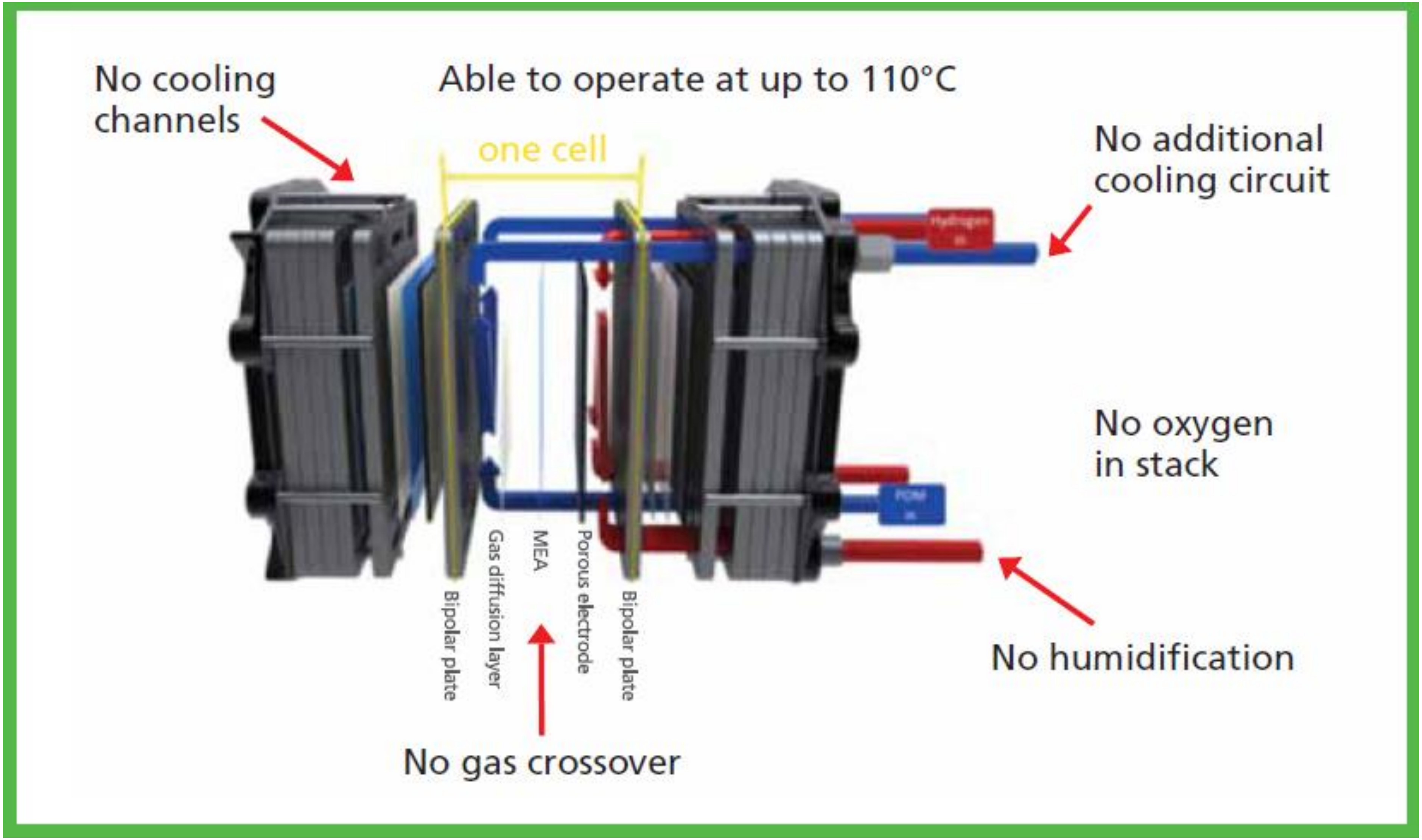
Blower or Compressor

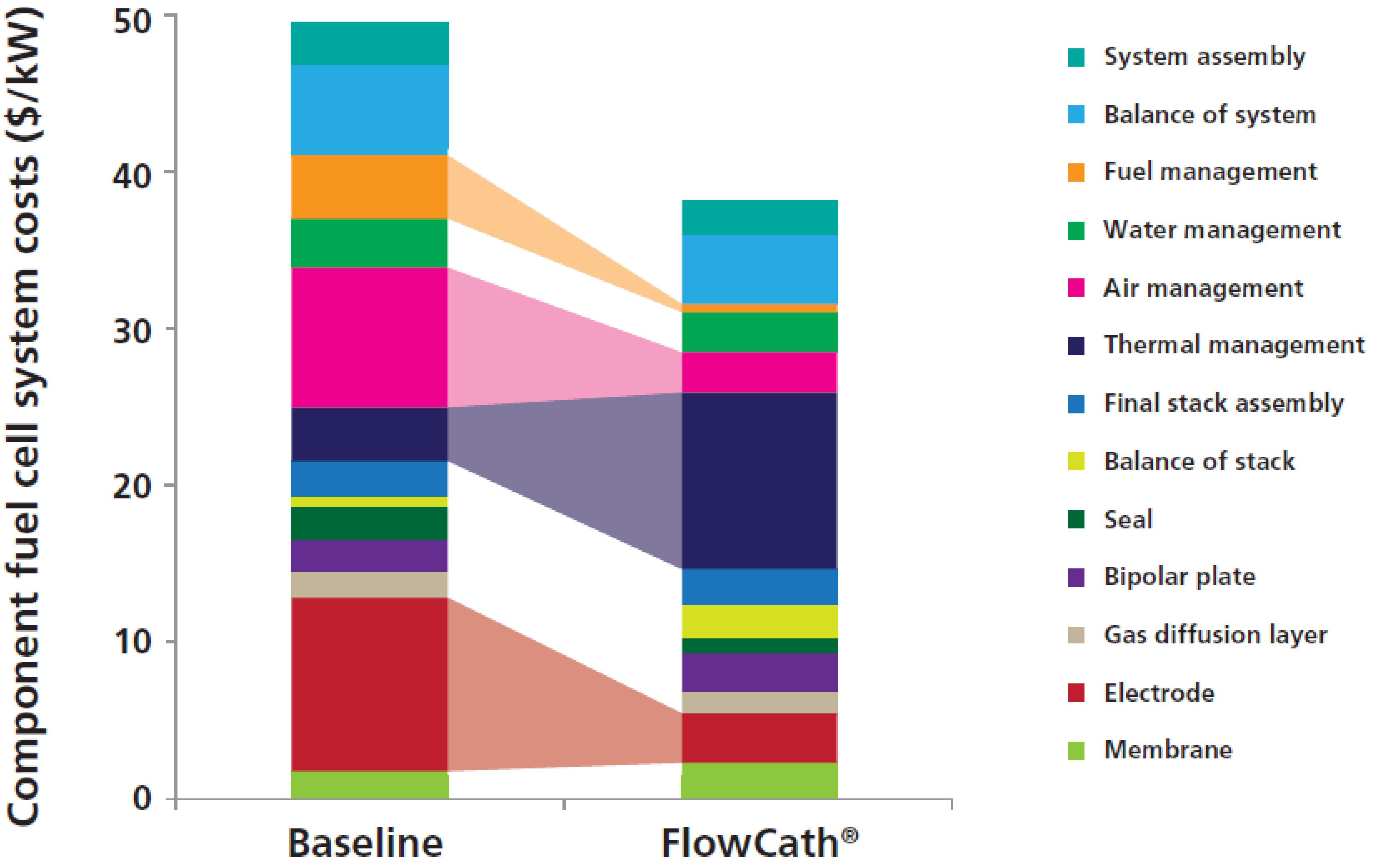
- Too Costly
  - High platinum content
  - Expensive balance of plant
- Poor durability
  - Membrane and catalyst suffer degradation
- Development cycle for catalyst requires durability effort to be repeated for each development
  - Large task for auto companies



'Platinum agglomeration is key reliability issue'

- Japanese Auto Maker


No cooling channels
Able to operate at up to 110°C
one cell
No additional cooling circuit
Hydrogen in
No oxygen in stack
Bipolar plate
Gas diffusion layer
MEA
Porous electrode
Bipolar plate
No humidification
No gas crossover


Component fuel cell system costs ($/kW)
50
40
30
20
10
0
Baseline
FlowCath®
System assembly
Balance of system
Fuel management
Water management
Air management
Thermal management
Final stack assembly
Balance of stack
Seal
Bipolar plate
Gas diffusion layer
Electrode
Membrane