# Collaborative Fuel Cell R&D - IPHE

**Peter Devlin—U.S. Department of Energy**

*IPHE 2nd Implementation-Liaison Committee Meeting*
*Gunzburg, Germany*
*March 1-3, 2004*

# *Possible collaboration topics*

- **High-temperature polymer membranes**
- **Non-platinum electrocatalysts**
- **Alkaline fuel cells**
- **Fuel cell testing protocols and facilities**

# Issues for High Temperature Membrane Development

- Adequate conductivity and performance across the full expected operating range of humidity and temperature (-20°C to 150°C)
- Mechanical stability
- Chemical stability
- Cost

# *Areas for High Temperature Membrane R&D under IPHE*

**Possible Collaboration**

- **Identify and understand higher temperature (non-aqueous) proton conducting mechanisms**
- **Identify materials with high conductivity, thermal stability, and mechanical stability across all operating conditions**

**Materials of Interest**

- **<u>Near Term :</u> Composite materials comprised of Nafion or non-Nafion systems with additives to improve conductivity and/or water retention**
- **<u>Long Term:</u>**
  - **New polymers with alternative conduction mechanisms and improved thermal stability**
  - **Non-aqueous or inorganic proton conductors with or without additives**

# *Proposed* Milestones

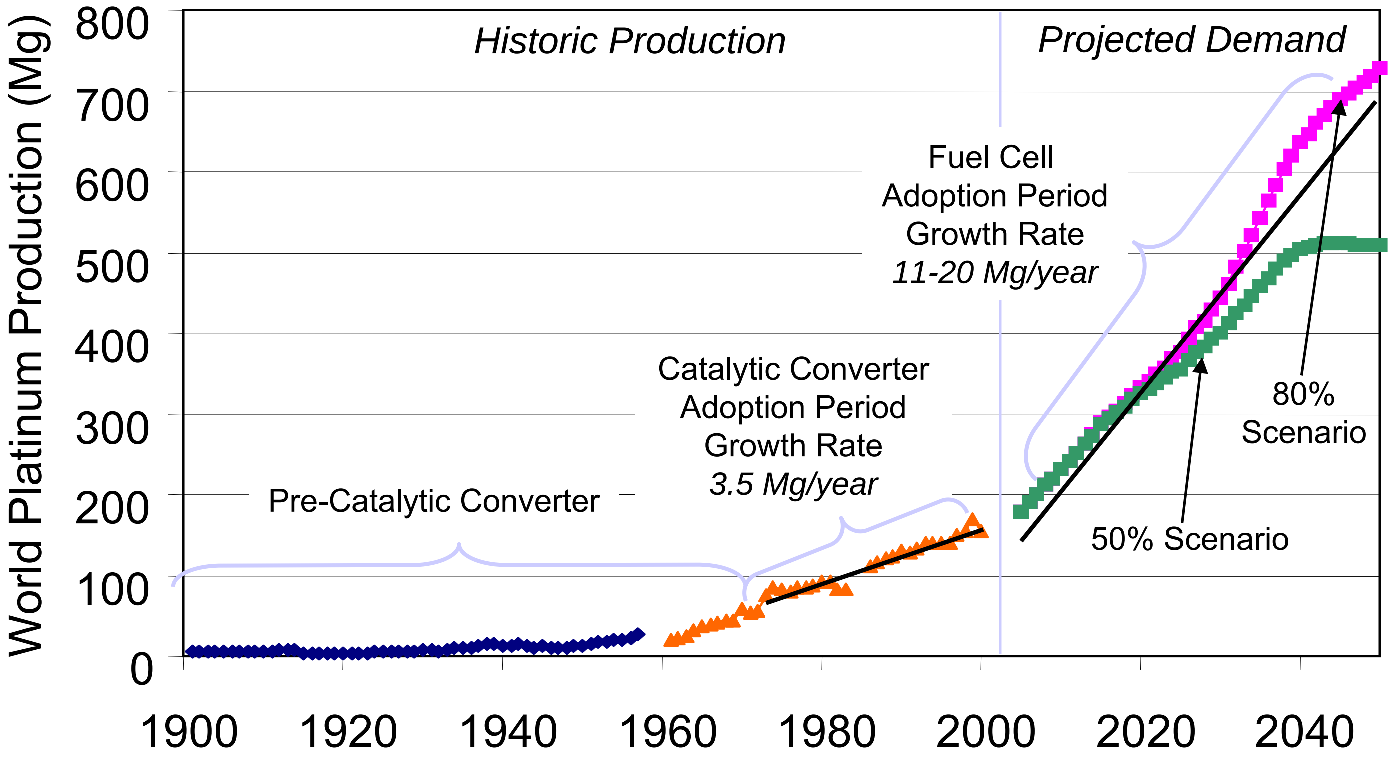
| |
|---|
| **By 2010, have an adequate understanding of high temperature proton conduction mechanisms in order to develop PEM membranes that can operate at 120°C** |
| **By 2015, develop PEM membranes that can operate at ≥150°C**<br>**•New polymers with improved thermal stability**<br>**•Non-aqueous proton conductors and additives**<br>**•Inorganic conductors** |

# *Pt loading Study Conclusions*

- **Demand** - Primary Pt demand is expected to grow at 3 to 6 times the rate of growth from 1960 to 2000 when FCVs are commercially viable.
- **Supply** - The Pt industry has the potential to meet a scenario where FCVs achieve 50% market penetration by 2050. Mining advances and significant recycling are needed.
- **Price** - The price of Pt will likely rise in the short-term in response to increased demand from FCVs. The price is expected to return to its long-term mean when supply catches up with demand.

*http://www.eere.energy.gov/hydrogenandfuelcells/pdfs/tiax_platinum.pdf*

# High-volume Fuel Cell Production is a Concern



**TIAX LLC report to DOE, "Platinum Availability and Economics for PEMFC Commercialization", December 2003**

# Research Perspective

**If long-term demand and price criteria can be met, why are non-PGM electro-catalysts needed?**

- Price stability
- Supply stability

**What are the Barriers?**

- Low catalytic activity for anode and cathode reactions
- Poor stability in the PEM fuel cell environment.

# *Pt Research Topics*

## Possible Collaboration

- Understand Pt’s unique catalytic properties.
- Identify and understand the nature of non-Pt catalytic sites for $O_2$ reduction and $H_2$ oxidation.
- Improve the chemical stability of non-Pt catalytic sites in PEM fuel cell environments.

## Low Cost Materials of Interest

- Macrocyclic organic materials.
- New inorganic catalysts such as tungsten carbide.
- Microbiologic hydrogenase enzymes with Nickel-Iron catalytic sites for hydrogen oxidation.

# *Proposed* Milestones

**By 2006, identify candidate non-Pt catalyst materials**

**By 2010, understand the fundamentals of Iron catalytic sites in macrocyclic organic materials and hydrogenase enzymes**

**By 2010, understand the fundamentals of inorganic non-Pt catalytic sites**

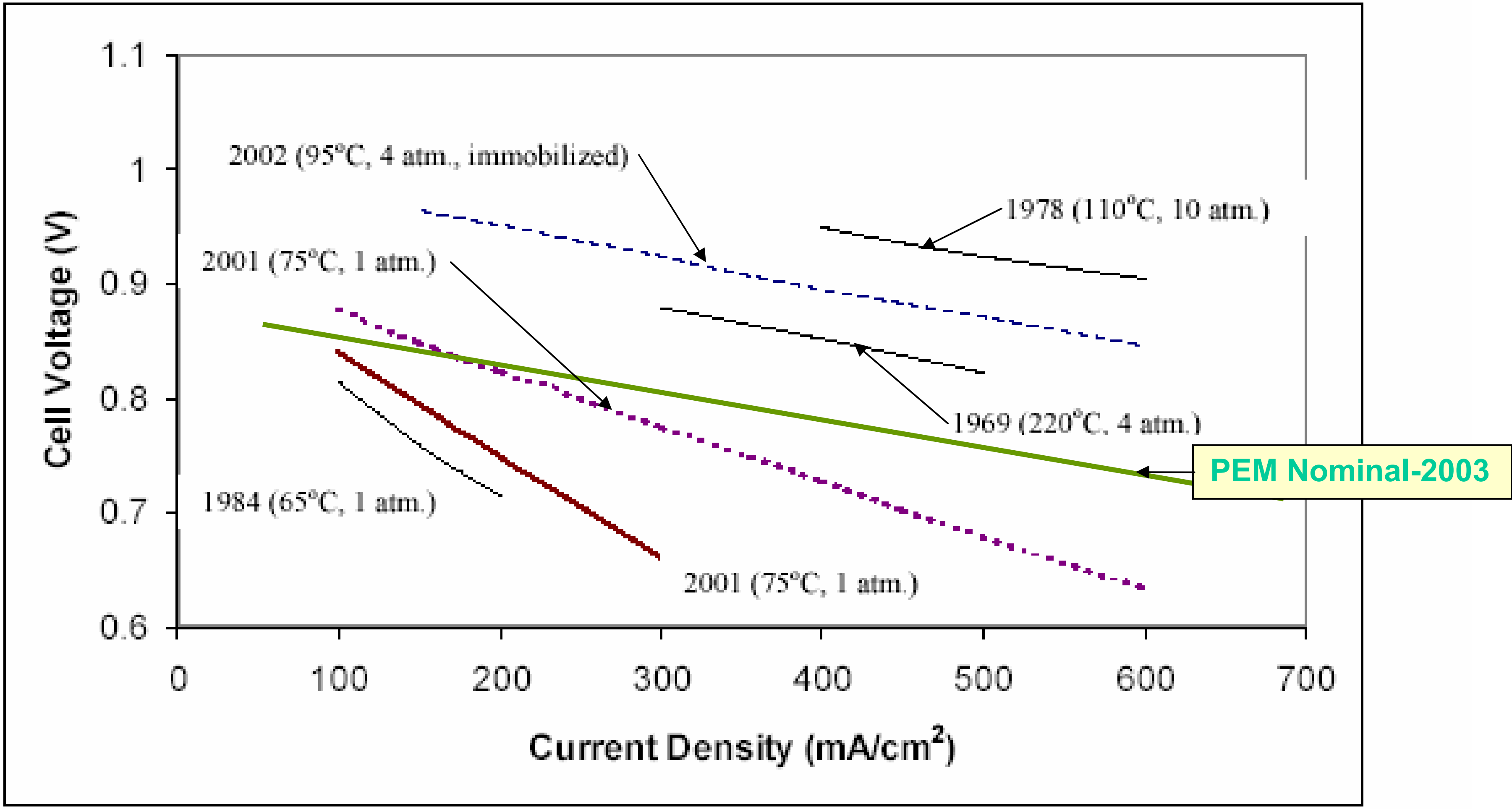
**By 2010, improve the chemical stability of non-Pt catalysts in PEMFC conditions**

# *Alkaline Fuel Cells-Background*

- **AFCs not emphasized in the U.S. because**
  - **Focus was on reformed hydrocarbon fuels**
  - **$CO_2$ in reformed fuel (and air) reacts with potassium hydroxide electrolyte, forming potassium carbonate which precipitates, and degrades performance**
- **AFCs could be reconsidered for following reasons**
  - **FreedomCAR and Fuel Initiative and fuel cell developers throughout the world are emphasizing pure hydrogen**
  - **More efficient $CO_2$/air scrubbers developed**
  - **Research emphasis similar to PEMs may enable AFCs to achieve performance metrics for commercial development**

# *Alkaline Fuel Cells*

Higher current density performance is possible



# *Alkaline Fuel Cells*

## Proposed Approaches

- **Investigate methods to lower electrolyte (cell) resistance to improve AFC stack performance**
- **Continue to investigate non-Pt catalysts to determine what trade-offs can be made that reduce cost and maintain power levels**
- **Identify lower cost materials that can withstand alkaline electrolytes**
- **Optimize recirculated-electrolyte AFCs for their intended application**
- **Continue to investigate hydroxide-ion conducting membranes**

# *Proposed Milestones*

| |
|---|
| **By 2004, hold workshop with manufacturers of recirculated-electrolyte AFCs** |
| **By 2006, complete non-Pt catalyst trade-offs** |
| **By 2006, develop lower cost materials that are resistive to alkaline electrolytes** |
| **By 2010, optimize recirculated-electrolyte AFC designs** |
| **By 2010, lower cell internal resistance and improve/optimize AFC stack performance** |

# Purposes for Testing Fuel Cells

- Fundamental understanding of fuel cell operation
- Durability (effect of fuel composition/ contaminants)
- Validation of performance models
- Compliance with design standards
- Safety
- Development of standardized test methods
  - Independent verification of performance meeting technical targets
  - Provide uniform comparison of fuel cell design/ performance

# *U.S. Fuel Cell Test Facilities*

- **Many organizations have test facilities—largely self-built and proprietary**
- **Examples of non-industry facilities**
  - **Argonne National Laboratory**
  - **Los Alamos National Laboratory**
  - **National Fuel Cell Research Center—UC-Irvine**
  - **Fuel Cell Test and Evaluation Center**
  - **University of Hawaii**

# Research Topics

## Possible Collaboration

- Compilation of reports on testing methodologies-FCTESTNET, JARI, USFCC, etc.
- Benchmarking and validation of results from round robin testing
- Development of global standardized test methods and test facilities

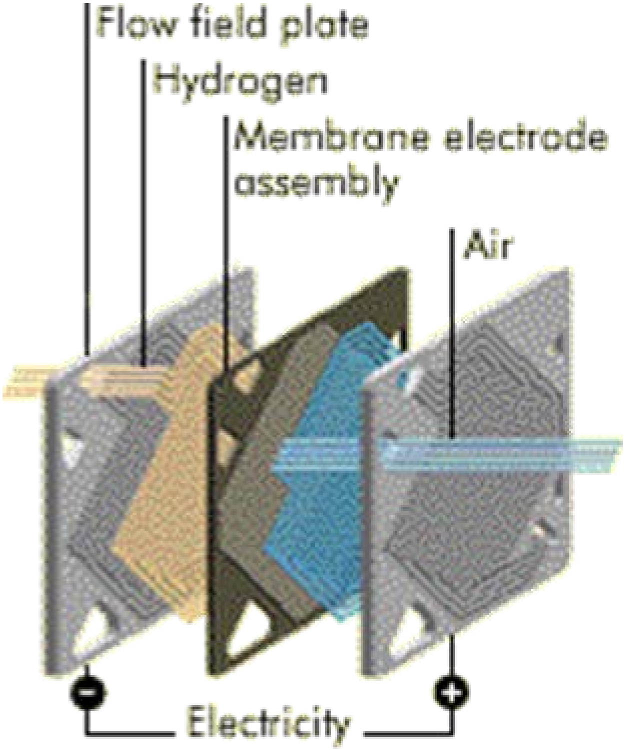
# *Proposed Milestones*

| |
|---|
| **By 2005, compile and compare testing standards and methods** |
| **By 2007, reach agreement on global fuel cell test procedures** |
| **By 2010, complete initial assessment of fuel cell systems against requirements for stationary, portable, and transportation applications** |

# HTM Back up

# *High-Temperature Polymer Electrolyte Membrane Development: Benefits*

- **Reduced sensitivity of Pt anode catalyst to CO poisoning at T >120°C**
  - **Reduced Pt and Ru loading**
  - **PROX eliminated**
- **Easier waste heat rejection for automotive systems**
- **Higher quality heat for stationary CHP applications**
- **Simplified water management**



# *HTMWG Technical Targets for Membranes: Automotive*

| Characteristics | Units | Calendar Year | | |
|---|---|---|---|---|
| | | 2003 Status[a] | 2005 | 2010 |
| Membrane conductivity:<br>at operating temperature<br>at 20° C<br>at -20°C | S/cm | 0.1<br>TBD<br>TBD | 0.1<br>TBD<br>TBD | 0.1<br>TBD<br>TBD |
| Oxygen cross-over[b] | $mA/cm^2$ | 5 | 5 | 2 |
| Hydrogen cross-over[b] | $mA/cm^2$ | 5 | 5 | 2 |
| Cost | $/kW | | 50 | 5 |
| Operating Temperature | °C | 80 | 120 | 120 |
| Durability | Hours | 1000 | >4000 | >5000 |
| Survivability[c] | °C | -20 | -30 | -40 |
| Thermal cyclability in presence of condensed water | | Yes | Yes | Yes |

a) Status is present day 80°C unless otherwise noted
b) Tested in CCM
c) Must be able to bootstrap start at indicated temperature

# HTMWG Technical Targets for Membranes: Stationary

| Characteristics | Units | Calendar Year | | |
|---|---|---|---|---|
| | | 2003 Status[a] | 2005 | 2010 |
| Membrane conductivity, operating temperature | S/cm | 0.1 | 0.1 | 0.1 |
| Oxygen cross-over[b] | $mA/cm^2$ | 5 | 5 | 2 |
| Hydrogen cross-over[b] | $mA/cm^2$ | 5 | 5 | 2 |
| Cost | $/kW | | 50 | 5 |
| Operating Temperature | °C | 160 | 160 | 170 |
| Durability | Hours | 5000 | >15000 | >40000 |
| Survivability | °C | -20 | -30 | -40 |

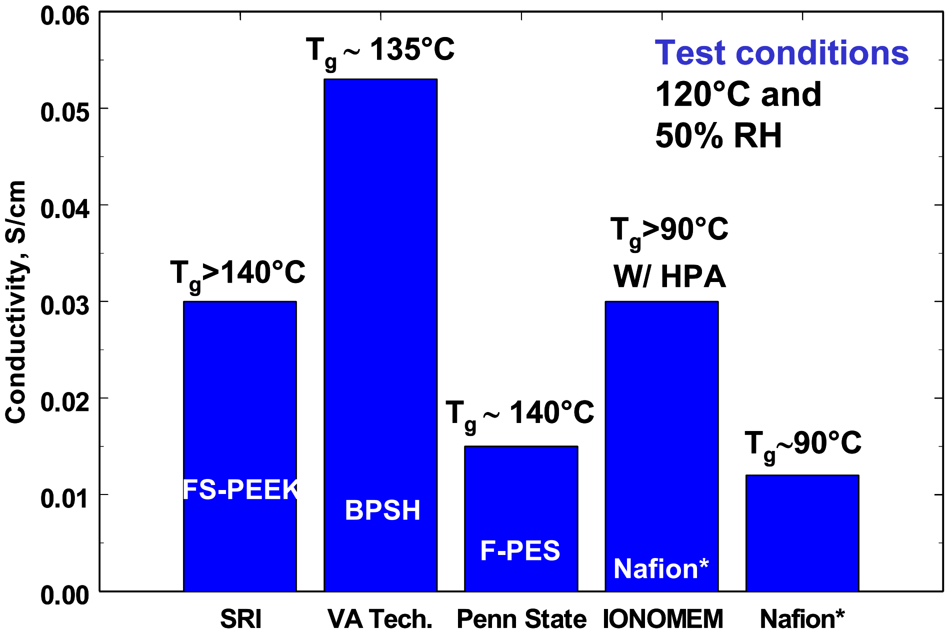
a) Status is present day 80°C unless otherwise noted; targets are for new membrane/CCMs

b) Tested in CCM

# *UTC Fuel Cells HTM Development Program*

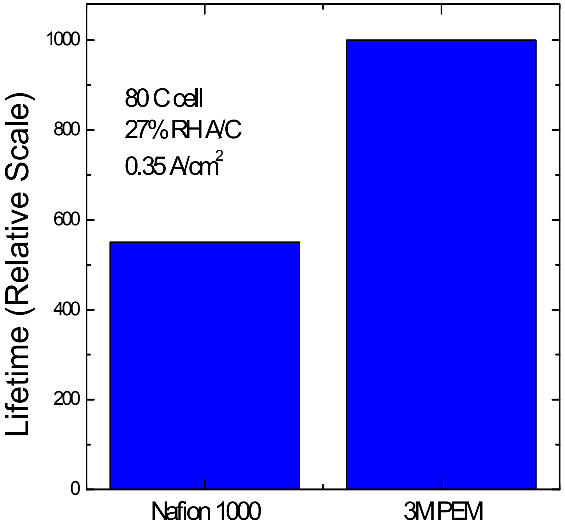
- **Four membrane systems with proton conductivity on the order of 0.01 S/cm at 120° C and 50% RH synthesized.**
  - **BPSH (Virginia Tech)**
  - **Modified S-PEEK (SRI International)**
  - **FPES from (Penn State)**
  - **HPA filled Nafion® (IONOMEM)**

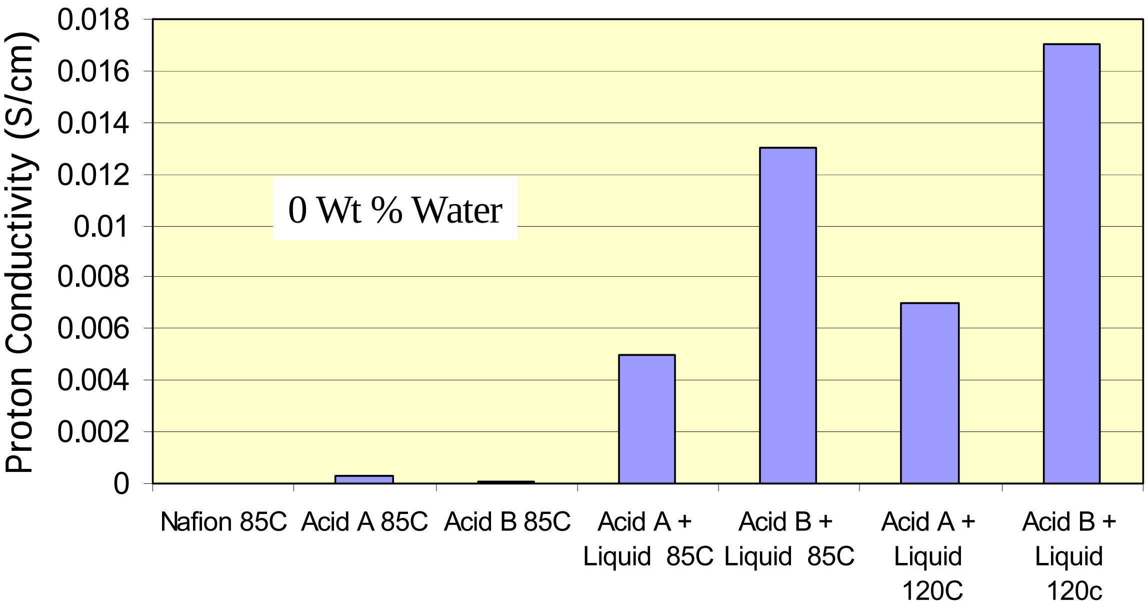
- **Majority of membranes synthesized to date require hydrophilic fillers to conduct at reduced RH.**
- **IONOMEM has established a baseline for HTM performance of 0.6 V at 0.4 A/cm² (120 C, 30% RH).**



# 3M High Temperature Membrane Development Program

- **Demonstrated longer lifetime with 3M's perfluorinated sulfonic acid membrane compared with standard PEM ionomer.**
- **Developed ionic liquid mixtures having 100 to 1000 times greater proton conductivity than anhydrous acids with no added water.**
- **Achieved 40 mS/cm at 120º C**.

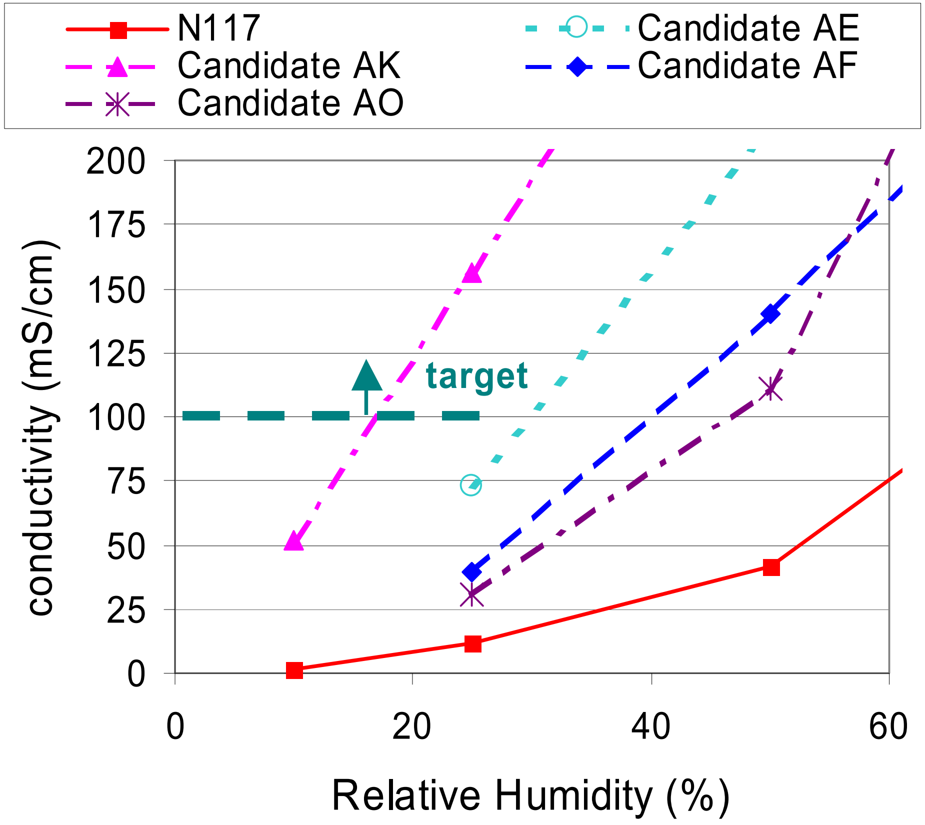




# *DuPont Electrolyte Polymer Development*

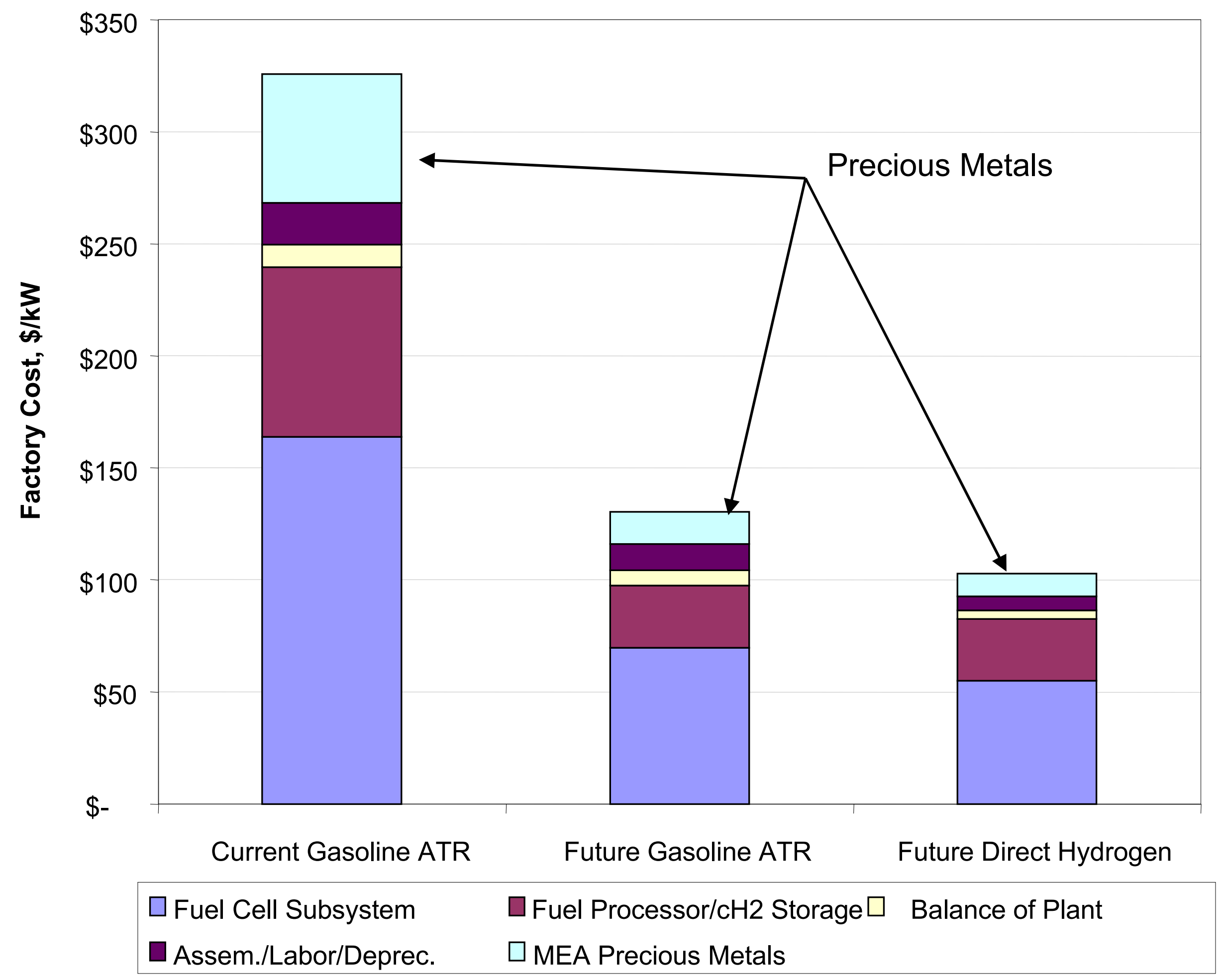
- **13 new electrolyte polymers synthesized in last year.**
- **4 have low-RH conductivity > Nafion® by 150% to 1100%.**
- **One (AK), with functionality designed to increase H-bonding, exceeds low-RH conductivity target.**
- **Issues**
  - **Thermal stability at 120°C & low RH.**
    - **only AE is sufficiently thermally stable**
  - **Mechanical strength and controlled swelling**
    - **only AO is a composite membrane with mechanical strength**

Conductivities measured by 4-point probe at 120°C



# Non-pt electrocatalyst

# *Platinum Accounts for 10-15% of System Cost*



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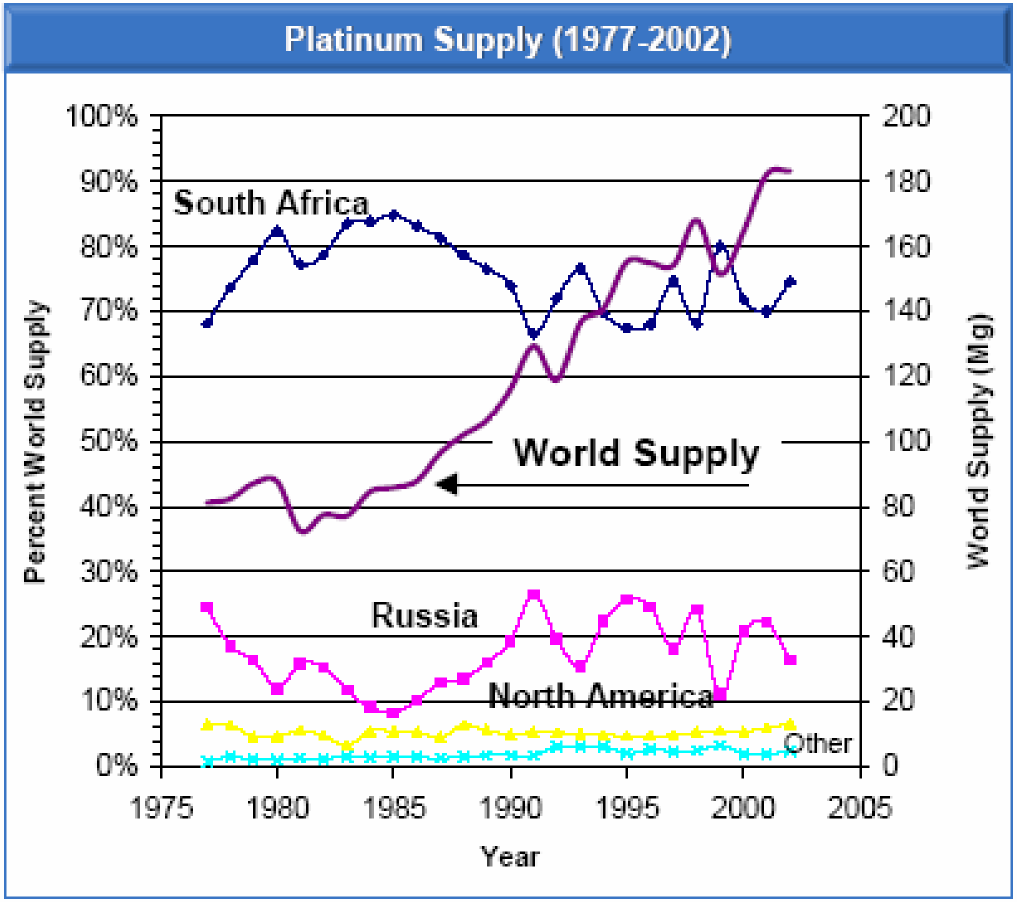
## Requirements for a Non-Pt Electrocatalyst

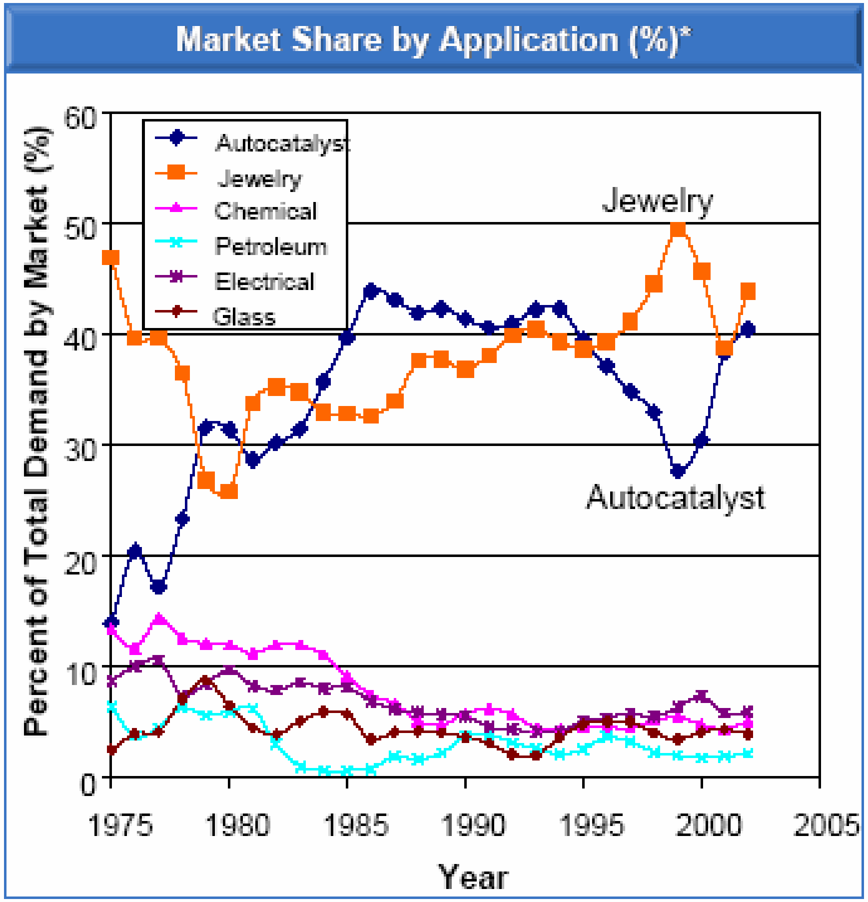
- **5000 hours stability for transportation propulsion and 40,000 for stationary applications**
  - **60–80˚C for current membranes**
  - **120˚C optimum for vehicles, with some activity as low as -40˚C.**
  - **150˚C optimum for stationary applications**
- **Either more active than platinum or much less expensive than platinum.**
- **Selectivity for hydrogen oxidation or oxygen reduction**
- **Cost meeting the DOE MEA target of $5/kW**
- **Inexpensive and environmentally benign precursors and manufacturing processes**
- **Current density of 160 A/cm$^3$ or 160 mA/cm$^2$ for a 10 micron thick catalyst layer at an acceptable potential (e.g., 0.8V vs. RHE)**
- **Turnover of 4 electrons/sec/site on $O_2$ at 0.8 V with a site density of $3 \times 10^{20}$ sites/cm$^3$. Higher turnover frequency compensates for lower site density.**

# Autocatalyst and Jewelry

**South Africa supplies about 80 percent of the world's platinum; the jewelry and autocatalyst markets account for about 80 percent of the demand.**


**Platinum Supply (1977-2002)**

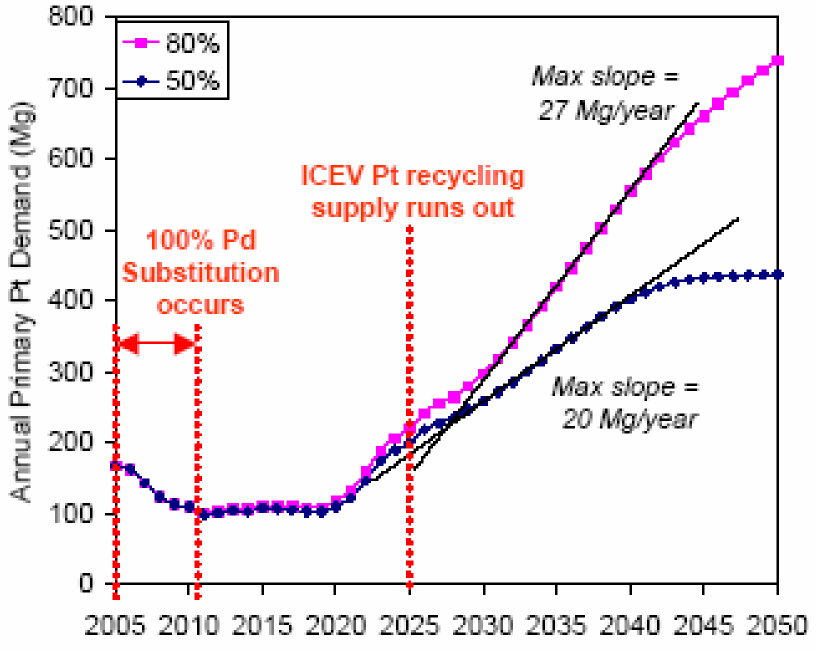
Source: *Johnson Matthey, Platinum 2003.*


**Market Share by Application (%)***

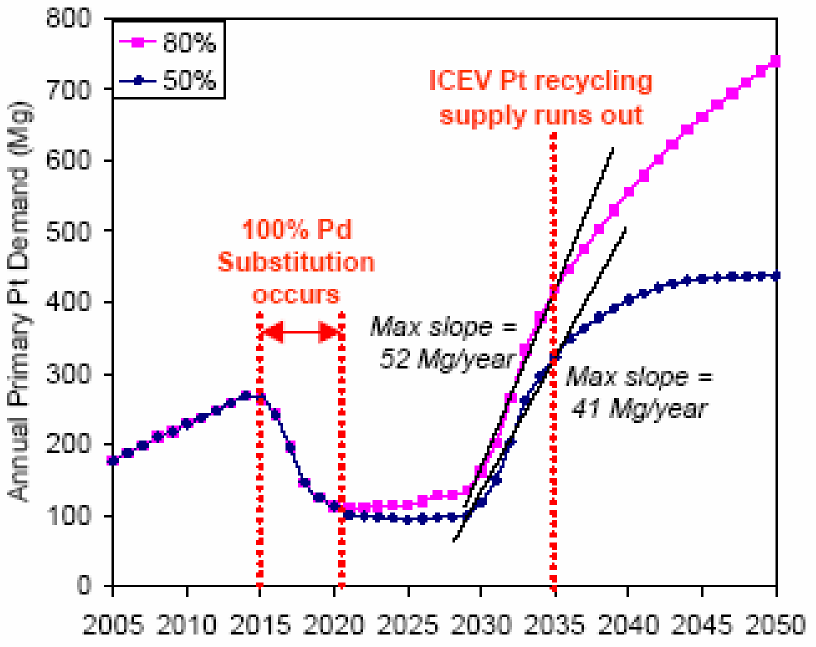
Source: *Johnson Matthey, Platinum 2003.*

# An initial analysis of the substitution of palladium for platinum in ICEV autocatalyst indicates that it may not be a favorable strategy.

## Palladium Substitution - Scenario 1



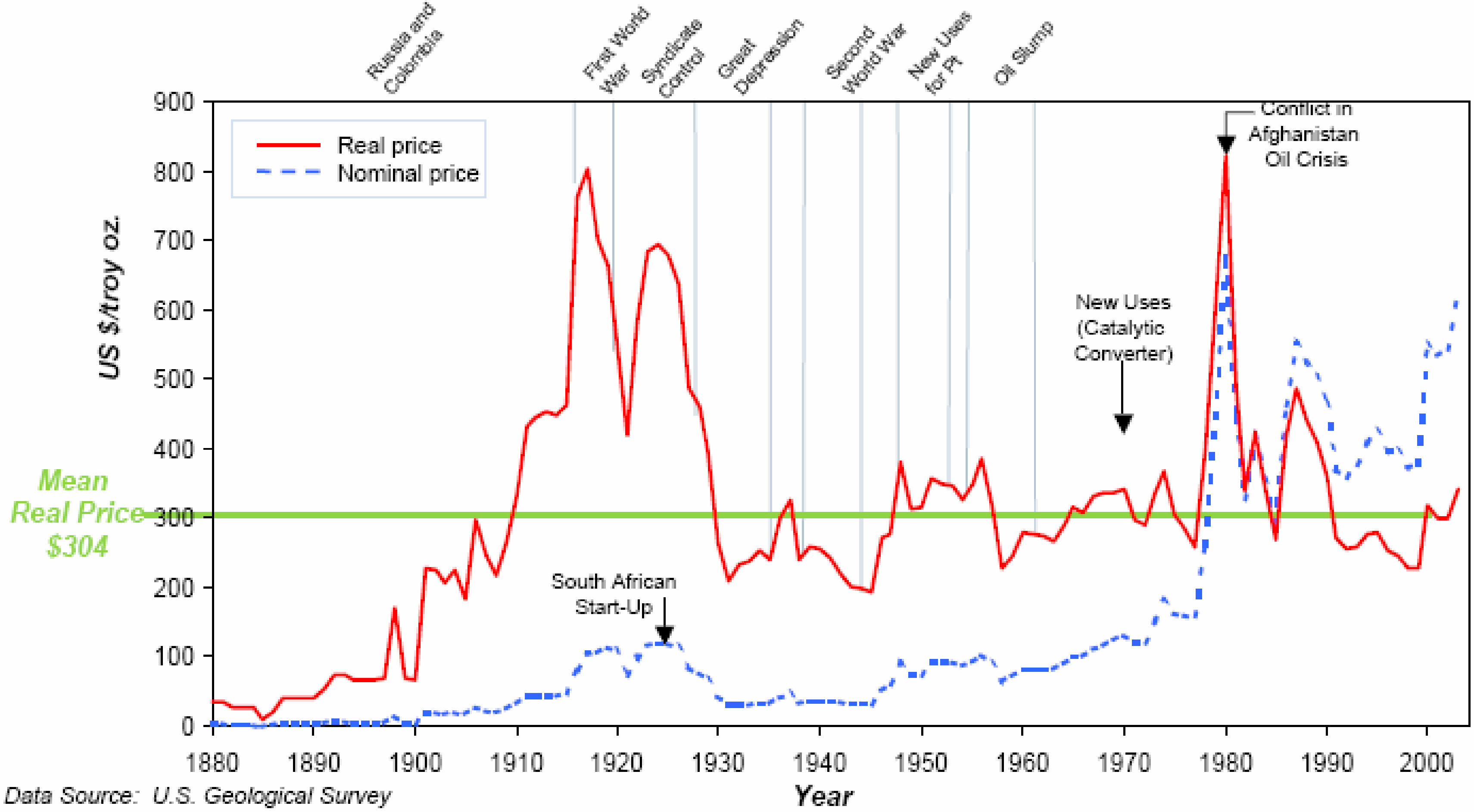
## Palladium Substitution - Scenario 2



**Palladium substitution increased the rate of platinum production due to the loss of the “platinum reservoir” accumulated in catalytic converters prior to the ramp up in FCV production. Both scenarios reduced cumulative demand when compared to the baseline projection.**

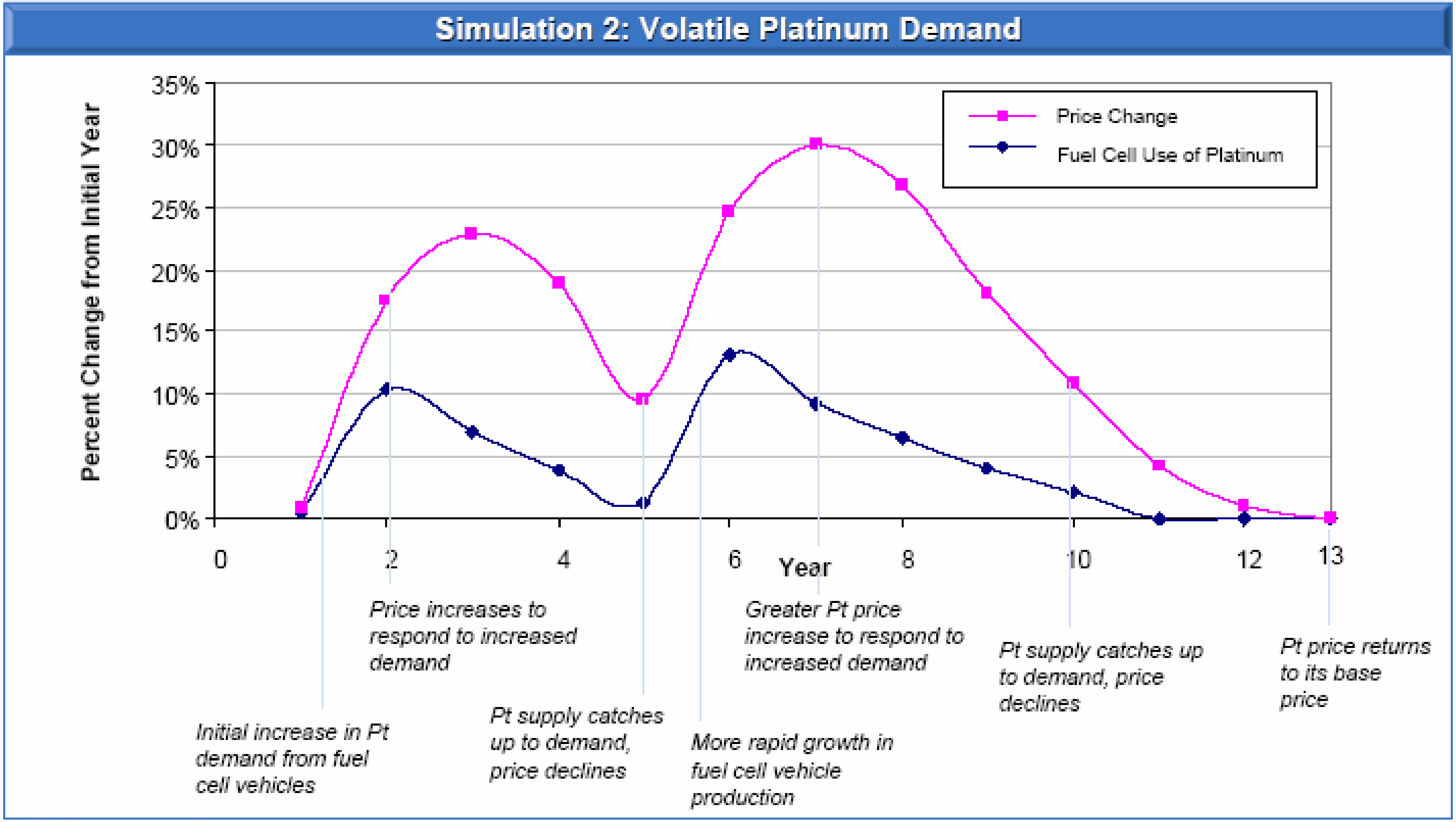
# The price of platinum has been volatile, spiking in response to increased demand, but it has always returned to its long-term mean, indicating a stationary price.

## Nominal versus Real Platinum Prices, 1880–1998



*Data Source: U.S. Geological Survey*
*Source: Vermaak, C.F., "The Platinum-Group Metals," pp. 110*

# The simulation illustrates that increased platinum demand will increase the price in the short-run, but in the long-run the price will return to its base level once supply catches up with demand.



Simulation 2: Volatile Platinum Demand

*Price increases to respond to increased demand*

*Greater Pt price increase to respond to increased demand*

*Pt supply catches up to demand, price declines*

*Pt price returns to its base price*

*Initial increase in Pt demand from fuel cell vehicles*

*Pt supply catches up to demand, price declines*

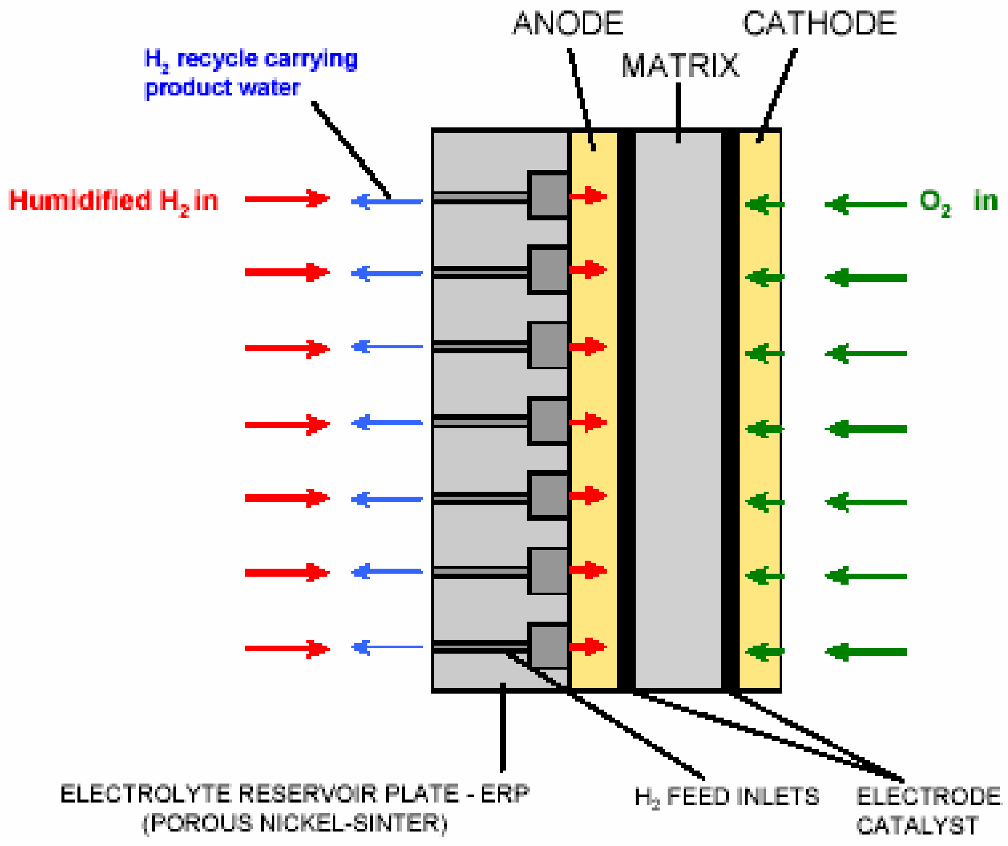
*More rapid growth in fuel cell vehicle production*

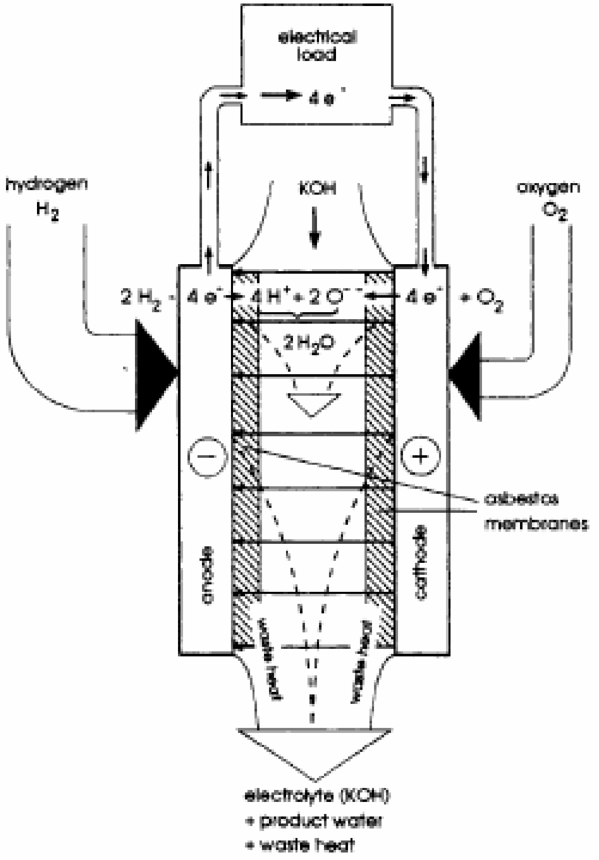
# *Alkaline Fuel Cells*

# *Alkaline Fuel Cells*

**Immobilized-Electrolyte**
**Used by NASA**

**Recirculating-Electrolyte**
**Several organizations have interest**





# Alkaline Fuel Cells-Background

- Recirculated electrolyte systems technology of choice for terrestrial applications
  - Improved thermal management,
  - Improved control over fluid concentration, water-balance/removal, and pH
  - Ambient pressure gas feed
  - Potential low cost

# *Alkaline Fuel Cells*

## Barriers and Needs

- Low recirculated-electrolyte (cell) resistance
- Non-Pt catalysts cannot be run at same current densities as with Pt catalysts
  - Tradeoff is cost saved on other materials compared to the amount spent to make hardware larger to obtain same output power
- Results to date on hydroxide conducting membranes are disappointing
- Alkaline electrolytes, even at low temperatures, are very corrosive and will attack all polymeric and graphite parts
- Peroxide forms at the cathode and is a concern because of its reactivity
- High-purity nickel or other coated metals have demonstrated lifetimes of 5000 to 10,000 hours, which is well short of that required for stationary systems

# *Fuel Cells Test Protocol Backup*

# *Fuel Cell Test Methods in the U.S.*

***Industry largely tests with self-built equipment and proprietary test procedures; standardized testing desired***

- **ASME-PTC 50**
  - **Performance test code for stationary fuel cell power systems—adopted as American National Standard in 2002**
- **SAE**
  - **Recommended practice guides for testing fuel cell systems, fuel reformer subsystems, and fuel cell stack subsystems for automotive application—in balloting process**
- **USFCC**
  - **Single cell test protocol—under development**

# *US FUEL CELL COUNCIL TEST PROTOCOLS*

**Purpose**

- **Facilitate development and qualification of advanced components and materials**
- **Provide a standard approach for conducting tests and format for reporting results**
- **Evaluate impact of various operating parameters on fuel cell performance and stability**

# US FCC TEST PROTOCOLS

**Status**

- **Single cell test methods developed and reproducibility trials in progress**
  - **Building a cell**
  - **Conditioning the cell for test**
  - **Testing the cell**
- **Standardization of test stations initiated**

# US FCC TEST PROTOCOLS

**Plans**

- **Complete development and validation of test methods**
- **Harmonize output with national and international organizations**
- **Develop plans and protocols to determine allowable limits for contaminants in hydrogen fuel streams to fuel cells in transportation applications**

# US FCC TEST PROTOCOLS

## Proposed USFCC Role

- Define design targets for the application
- Perform fundamental cell tests
- Define methods to interpret results
- Define validation tests to confirm results
- Request cooperation in executing the plan
- Publish allowable limits for hydrogen impurities for use by vehicle integrators and coordinating organizations.
  - US DOE and National Laboratories
  - Freedom CAR and Hydrogen Fuel Partnership
  - California Fuel Cell Partnership
  - SAE