Ammonia Fuel Cell Systems

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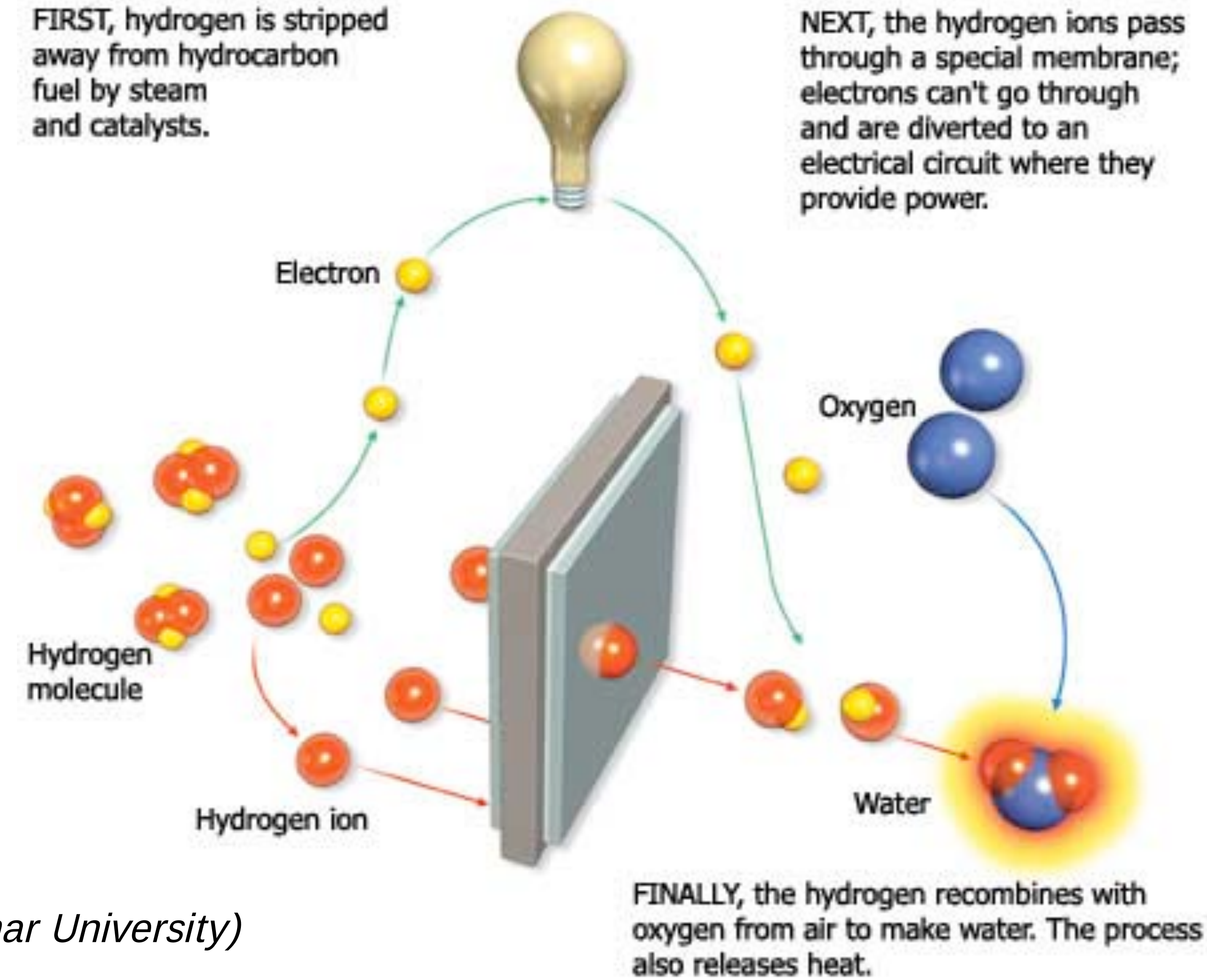
Presentation Outline

- **Introduction to Fuel Cells**
  - Characteristics
  - Fuel Cell Types
  - Fueling the Fuel Cell
- **Ammonia Fuel Cells**
  - Advantages and Challenges
  - Direct vs. Reformed NH_3
  - Other Electrochemical Applications
- **High Temperature Fuel Cell Focus**
  - Ammonia and Solid Oxide Fuel Cells
  - Protonic Ceramic Fuel Cells

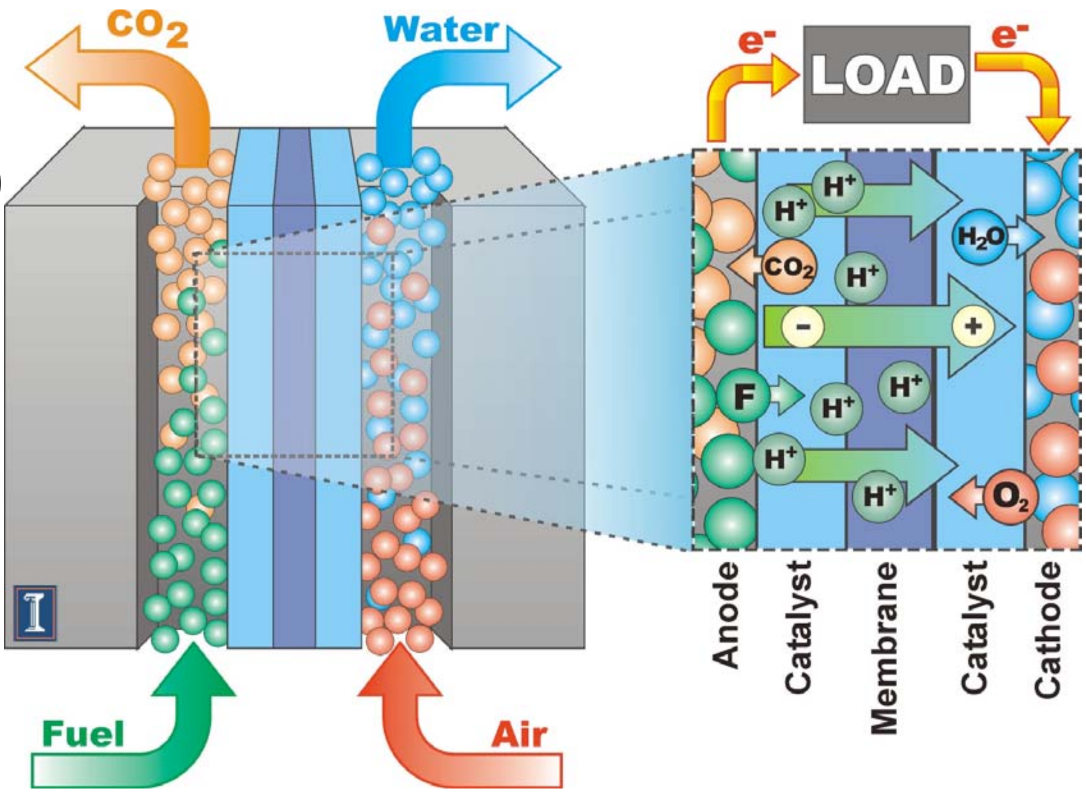
The Fuel Cell



(Lamar University)

Fuel Cell Anatomy

- **Fuel Cell Electrodes**
  - Anode (oxidation)
  - Cathode (reduction)
- **Electrocatalyst**
  - Porous, electrically conductive
  - Cost depends on cell temperature
- **Ionic Membrane**
  - Not electrically conductive
  - Protonic or anionic



Fuel cell operating with air / hydrocarbon feed

Types of Fuel Cells

- Polymer Electrolyte Membrane Fuel Cells (PEMFC) [80°C, H^+]
- Direct-Methanol Fuel Cells (DMFC) [80°C, H^+]
- Alkaline Fuel Cells (AFC) [150°C, OH^-]
- Phosphoric Acid Fuel Cells (PAFC) [220°C, H^+]
- Protonic Ceramic Fuel Cell (PCFC) [650°C, H^+]
- Molten Carbonate Fuel Cells (MCFC) [700°C, CO_3^{2-}]
- Solid Oxide Fuel Cells (SOFC) [900°C, O^{2-}]

Operating Temperature: A Key Characteristic

- **Low Temperature Fuel Cell Advantages**
  - Quick start-up to operating temperature (~100°C)
  - Wide range of cell construction materials
- **High Temperature Fuel Cell Advantages**
  - Fuel flexibility via internal fuel reforming
  - Inexpensive, base metal electrocatalysts
  - Easier heat recovery for increased efficiency
- **Intermediate Temperature Fuel Cells: The Best of Both Worlds?**
  - Precious metal catalysts not needed above ~300°C
  - Stainless steel internals may be used below ~750°C

Hydrogen Fuel Cells

- **Advantages of Hydrogen Fuel**
  - Fast electrocatalytic reaction
  - Protons [H^+] or hydronium ions [H_3O^+] conduct rapidly across acidic membranes
  - Very high energy to weight ratio
  - Carbon-free: eliminates local CO_2 pollution
- **Disadvantages**
  - Compressed H_2: poor energy to volume ratio
  - Liquefied H_2: cryogenic; very energy intensive to create and maintain
  - Safety for handling and storage a very big concern

On-board vs. Internal Reforming

- **Improved System Efficiency**
  - Higher fuel energy density
  - Easier fuel distribution
- **Fuel Reformers**
  - Thermally isolated or integrated
  - May be bulky, problematic
- **Direct Fuel Cells**
  - Internal reforming of fuel
  - Mostly high temperature FCs
  - Reaction intermediates may require consideration

50 kW natural gas reformer
Harvest Energy Technology

Ammonia as a Fuel Cell Fuel

600
12/28 CH4

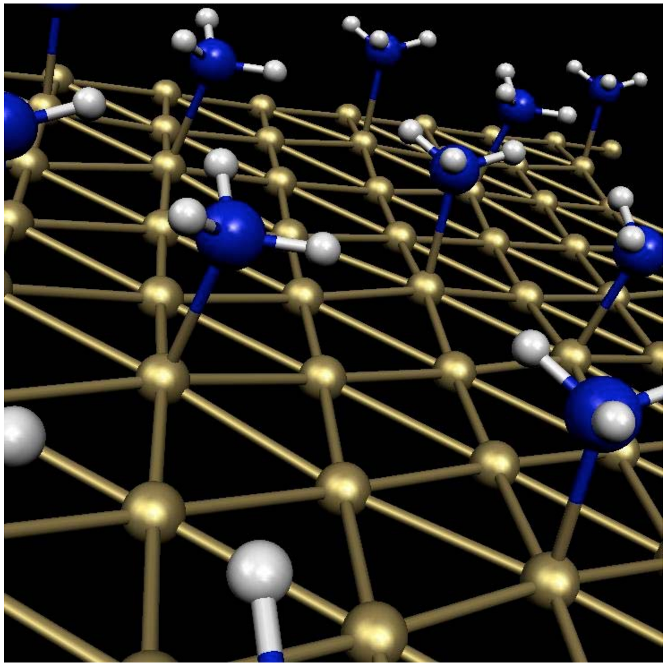
$$2\,NH_3 \rightarrow 3\,H_2 + N_2 \qquad \Delta H^\circ = 46\ kJ/mol$$

- Very mild enthalpy of reforming
- NH_3 is a liquid at room temperature and 10 atm
  - Power density is comparable to other liquid fuels
  - Vaporizes when throttled (no flash line required)
- Essentially non-flammable, non-explosive
- 180 kWh of electricity from 15 gallons ammonia (38 kg) with 50% efficient fuel cell system
- Well-established transport and storage infrastructure already in place

Fuel Cell Suitability of Anhydrous Ammonia

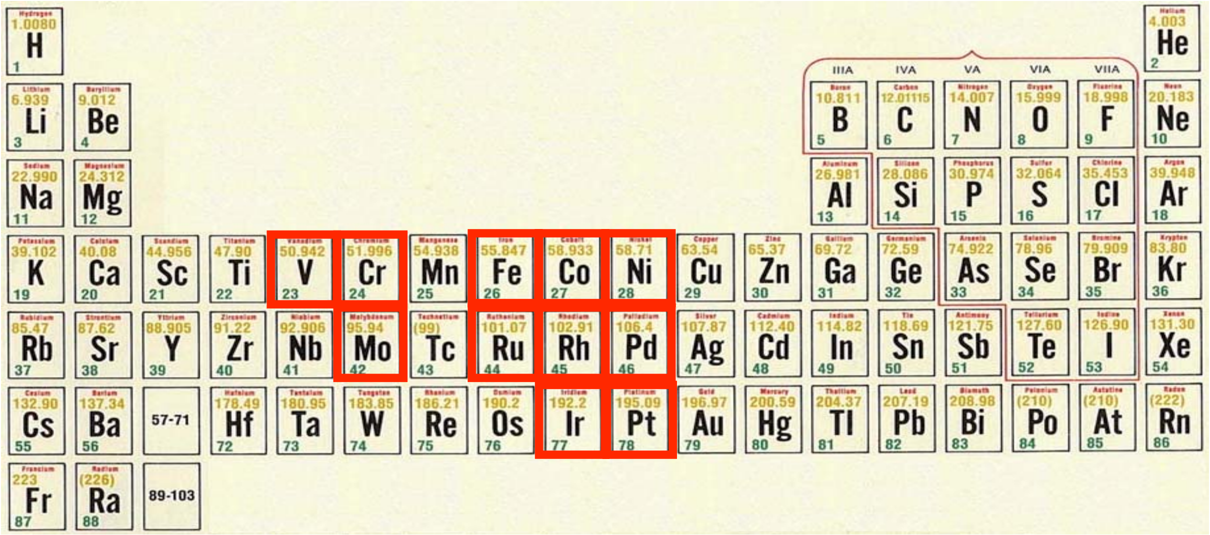
- **Externally reformed ammonia**
  - Trace NH_3 incompatible with PEM
  - Trace amounts limited by chemical equilibrium
  - Reformate usually must be scrubbed

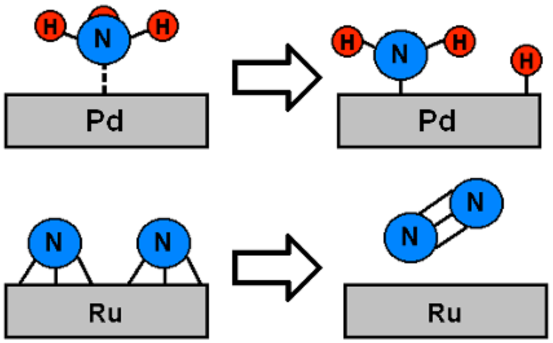
- **Meduium / high temperature fuel cells**
  - PAFC: Trace NH_3 reacts with acid electrolyte
  - MCFC: NH_3 crossover, CO_2 recycling complication
  - SOFC: An excellent fuel choice, but some NO_x
  - PCFC: An excellent fuel choice, no NO_x



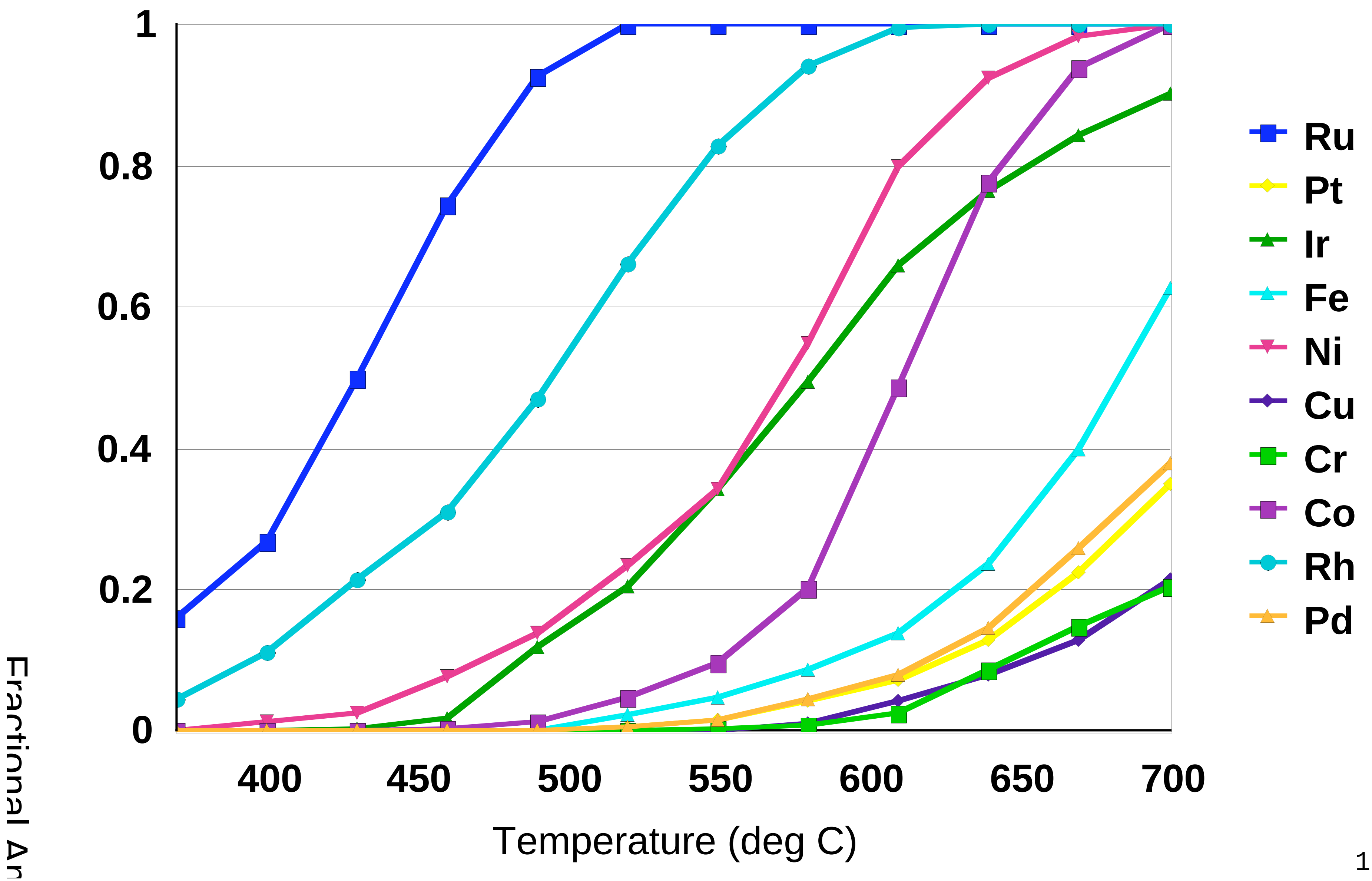
Ammonia Catalysis

- Dual combinations of transition metals used for industrial ammonia processes
  - Ammonia synthesis
  - Ammonia decomposition
  - Ammonia oxidation
- Interesting combinations: Ru/Pd, Fe/Ni





Ammonia Decomposition



Ammonia Oxidation

$$NH_3 + \tfrac{3}{4}O_2 \rightarrow \tfrac{1}{2}N_2 + \tfrac{3}{2}H_2O \qquad \Delta H^o = -382\ \frac{kJ}{mol}$$

- **Catalytic combustion**
  - Start-up heat source for fuel cells
  - Satisfies “one-fuel” approach
- **Nitrogen oxide control**
  - Oxidation catalysts (Cu, Fe, Cr)
  - Ammonia injection

$$NO_x + NH_3 \rightarrow H_2O + N_2$$

Univ. of Wisconsin
Chemistry Dept.

Fuel Comparison

Fuel	Base MJ/liter	Reformed MJ/liter*
H_2 (5000 psia)	4.0	4.0
H_2 (liq.)	9.9	9.9
NH_3 (liq.)	15.3	13.6
Methanol	17.9	10.2
Ethanol	23.4	9.1
Propane (liq.)	29.4	8.6
Gasoline	36.2	9.2
JP-8	40.5	9.7

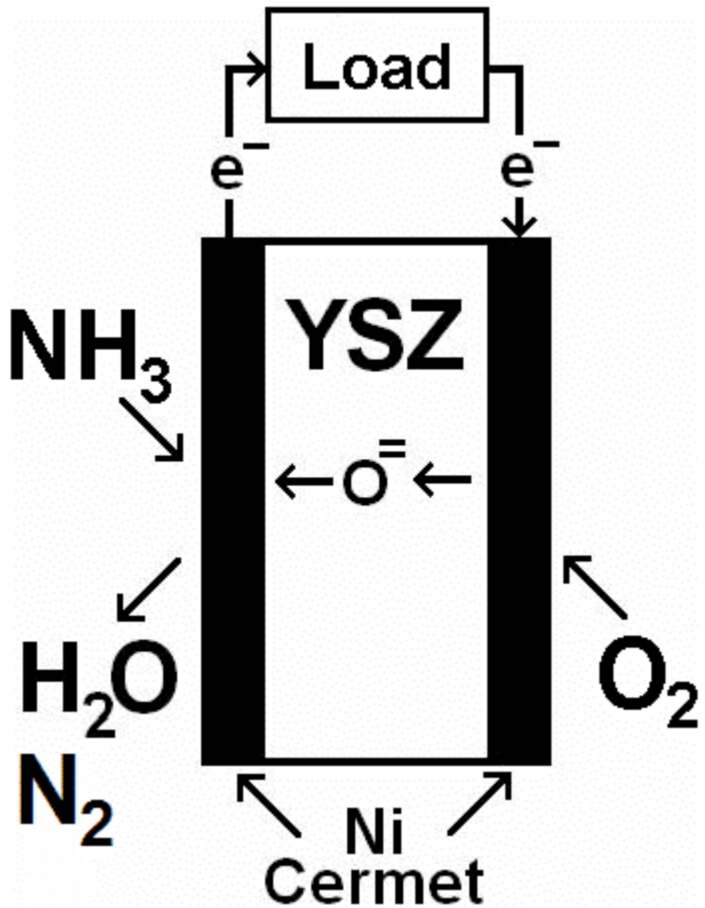
* **Includes heat and water volume required for steam reforming**

Direct Fuel Cell Comparison

Fuel Utilized (Electrolyte Type)	Direct Ammonia (PCC)	H_2 Gas (PEM)	Hydrocarbon (SOFC)
Operating Temperature (°C)	500 - 750	20 - 100	800 - 1000
Materials Construction Cost	Moderate to low (stainless steel)	Low (aluminum)	High (metal oxides/ceramics)
Electrocatalyst Cost (Type)	Low (Ni, Co, La, Mn)	High (Pt, Pd, Ru)	Low (Ni, Co, La, Mn)
Water Product Discharge	At cathode, into air stream	At cathode, into air stream	At anode, dilutes fuel

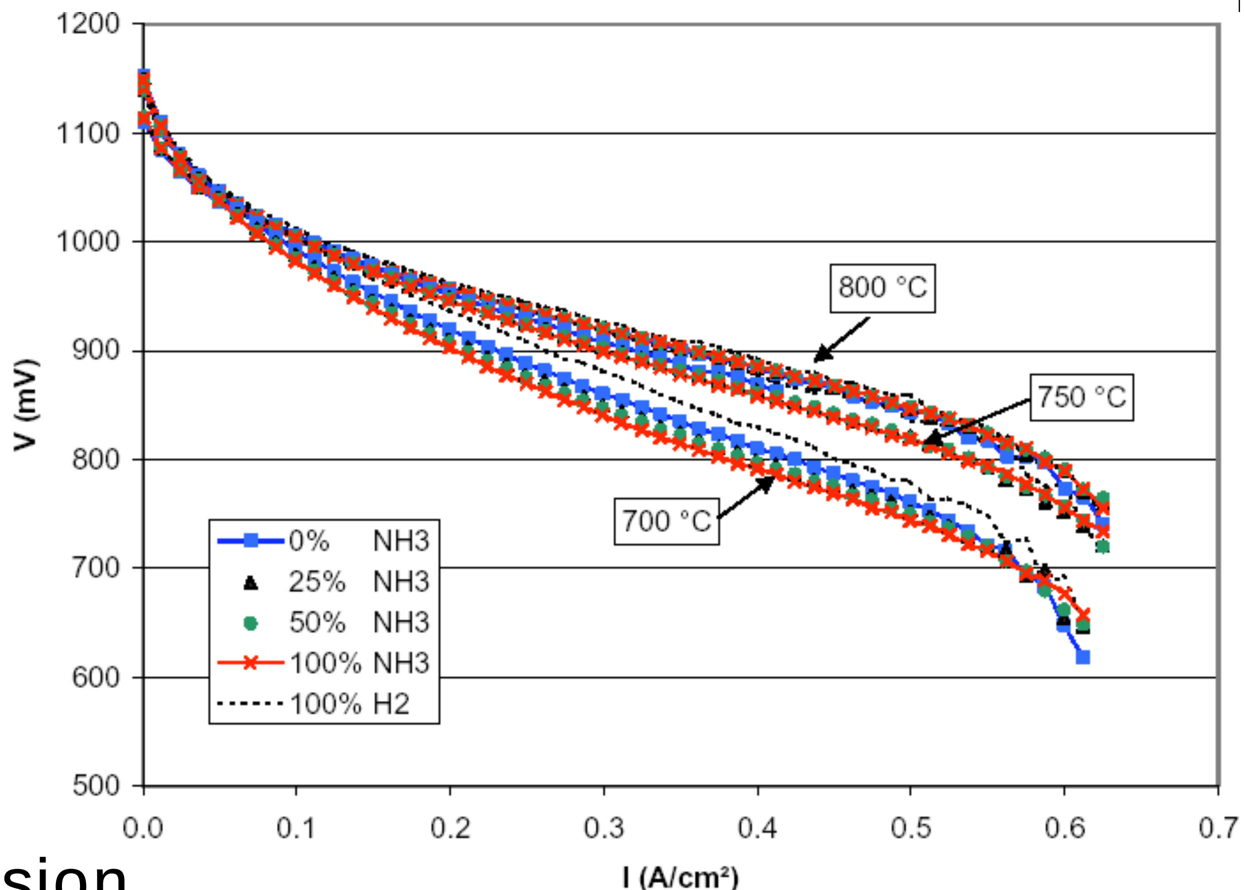
Ammonia Solid Oxide Fuel Cell

- **Utilizes inexpensive base metal catalyst (Ni or Co)**
  - Operating temperature 800-1000°C, depending on electrolyte
  - Elevated temperature allows direct ammonia utilization
- **Complete ammonia conversion not possible**
- **Fuel diluted by steam, product nitrogen**
- **NO_x may appear in exhaust**



NH_3 / SOFC Performance

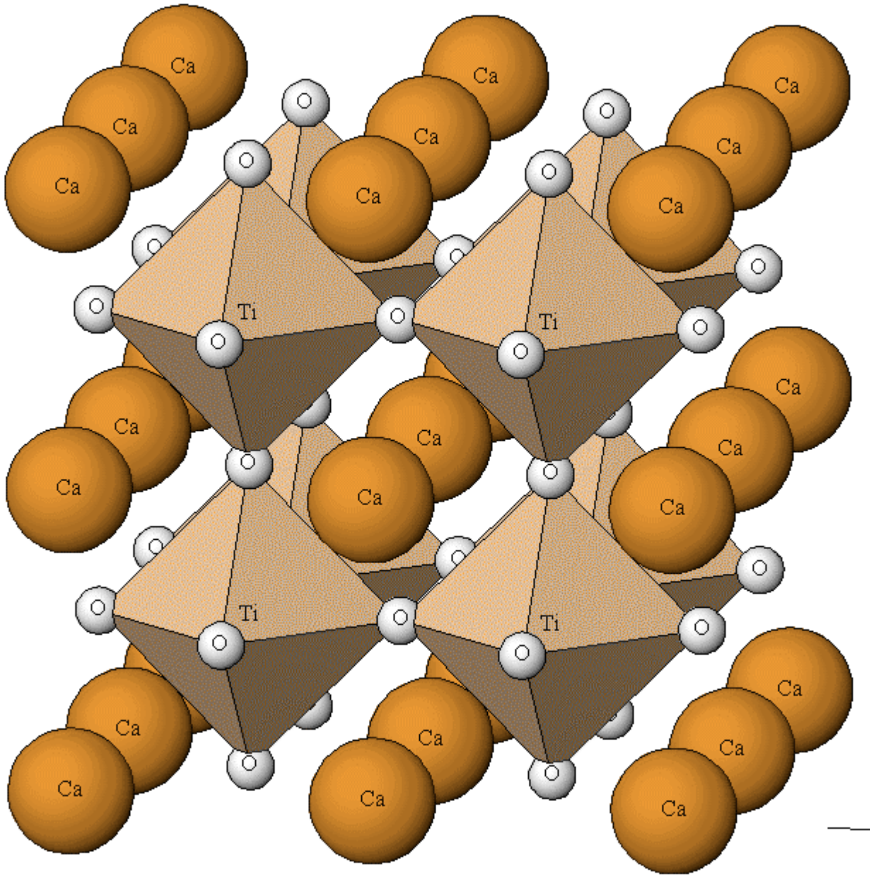
- **Standard SOFC**
  - YSZ electrolyte
  - Ni anode
  - LSM cathode
- **Carbon-free**
  - Dry fuel
  - Faster kinetics
- **Conclusions**
  - High NH_3 conversion
  - NOx formed at anode
  - Virtually no difference between NH_3 and H_2 feeds



N. Dekker, B. Rietveld ECN (2004)

Proton Conducting Perovskites

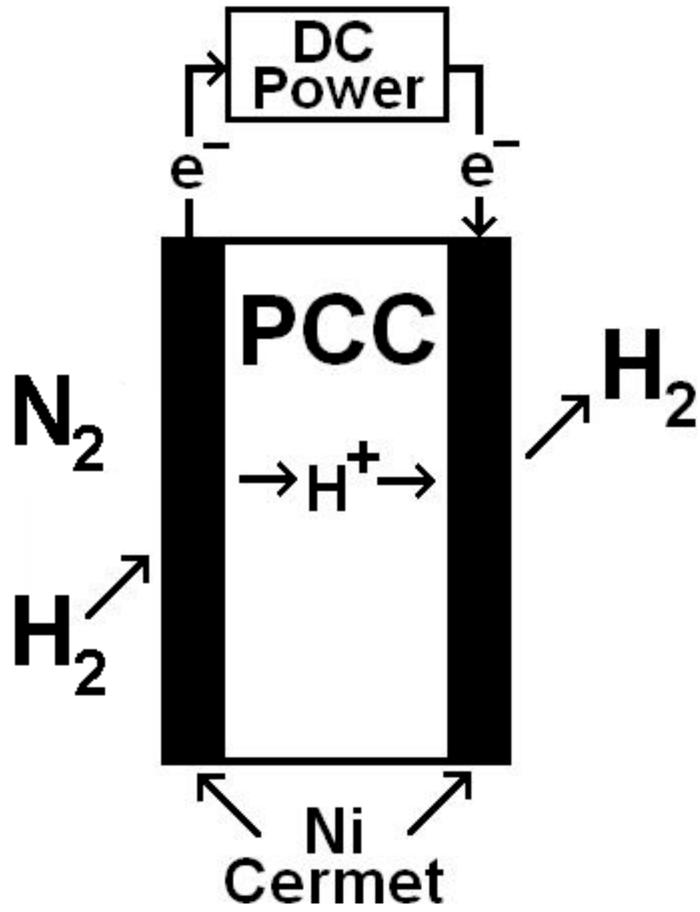
- **General characteristics**
  - ABO_3 (A^{+2}, B^{+4})
  - Must be doped with lower-valence (acceptor) elements
  - Oxygen vacancies replaced by protons after steam treatment
- **Complex perovskites**
  - $A_2(B'B'')O_6$ (A^{+2}, B'^{+3}, B''^{+5})
  - Comparable conductivities to simple perovskites
  - "Doping" possible by adjustment of B'/B" ratio



(AIST, Japan)

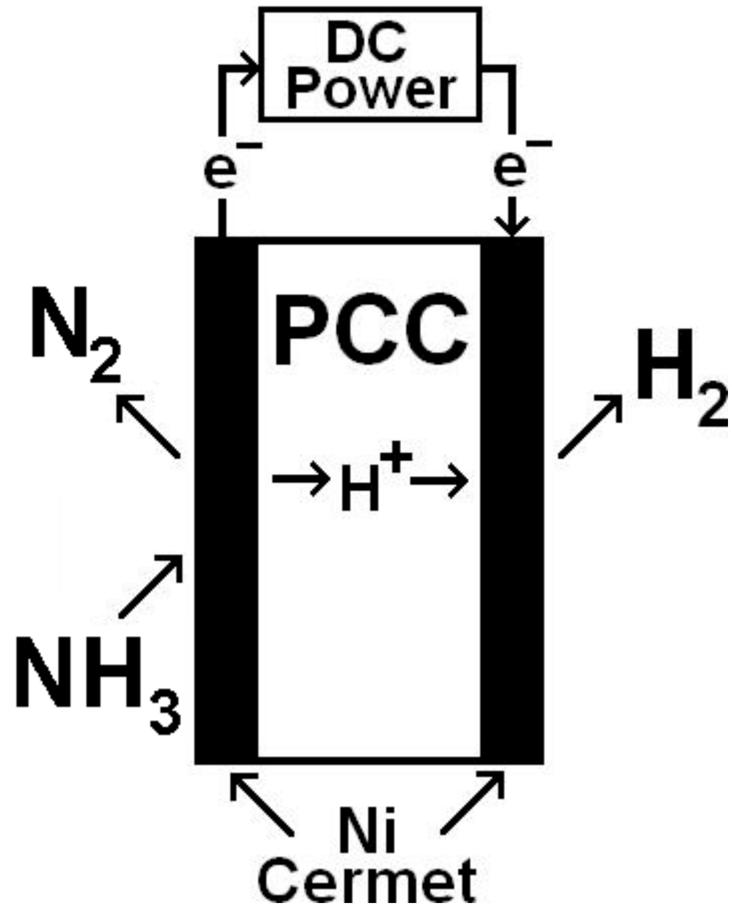
Pure Hydrogen from Ammonia Reformate

- **Protonic ceramic applied as a hydrogen pump**
  - Separation of hydrogen from stream impurities
  - Pressurization of hydrogen stream
- **Removal of CO from syngas**
- **Dehydrogenation reactions to produce propylene, ethylene, acetylene**



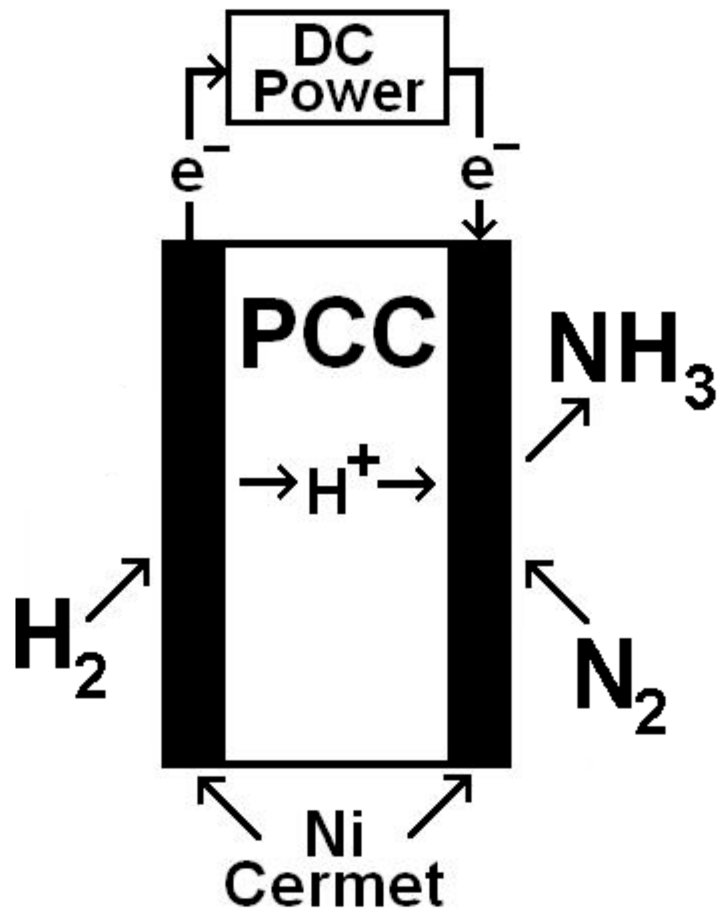
Protonic Ammonia Electrolyzer

- **Substitution of thermal energy with electric power**
  - "Cracked" hydrogen stream is nitrogen-free
  - Mild decomposition energy requires little electric power
- **Complete ammonia conversion possible!**
- **If operated with recycle, will require purging to avoid N_2 buildup**



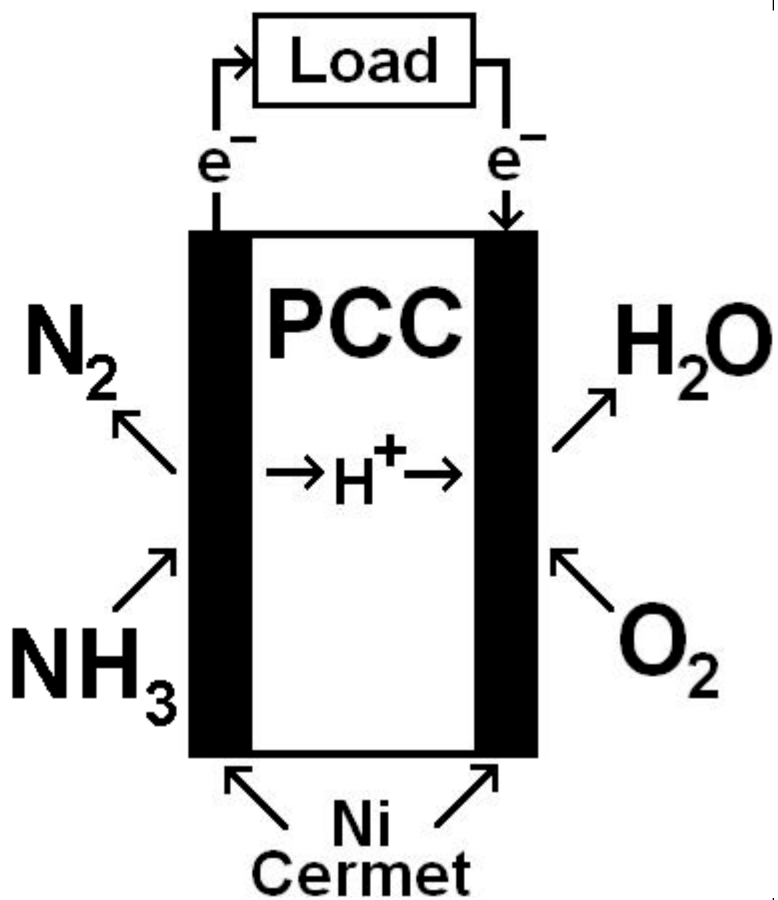
Protonic Ammonia Synthesis

- **An alternative to packed-bed heterogeneous catalysis**
  - Verified experimentally
  - May also use higher alkenes for hydrogen source
- **May be carried out at atmospheric pressure!**
- **Limited by thermodynamic equilibrium, just as in Haber synthesis**



The Protonic Ammonia Fuel Cell

- **Utilizes inexpensive base metal catalyst (Ni or Co)**
  - Operating temperature 450-700°C, depending on catalyst
  - Elevated temperature increases electrode kinetics
- **Complete ammonia conversion IS possible!**
- **Fuel not diluted by steam**
- **NO_x-free exhaust**



Questions?