



# Ammonia: The Key to a Hydrogen Economy



## Ammonia Fuel Cell Systems

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# Presentation Outline

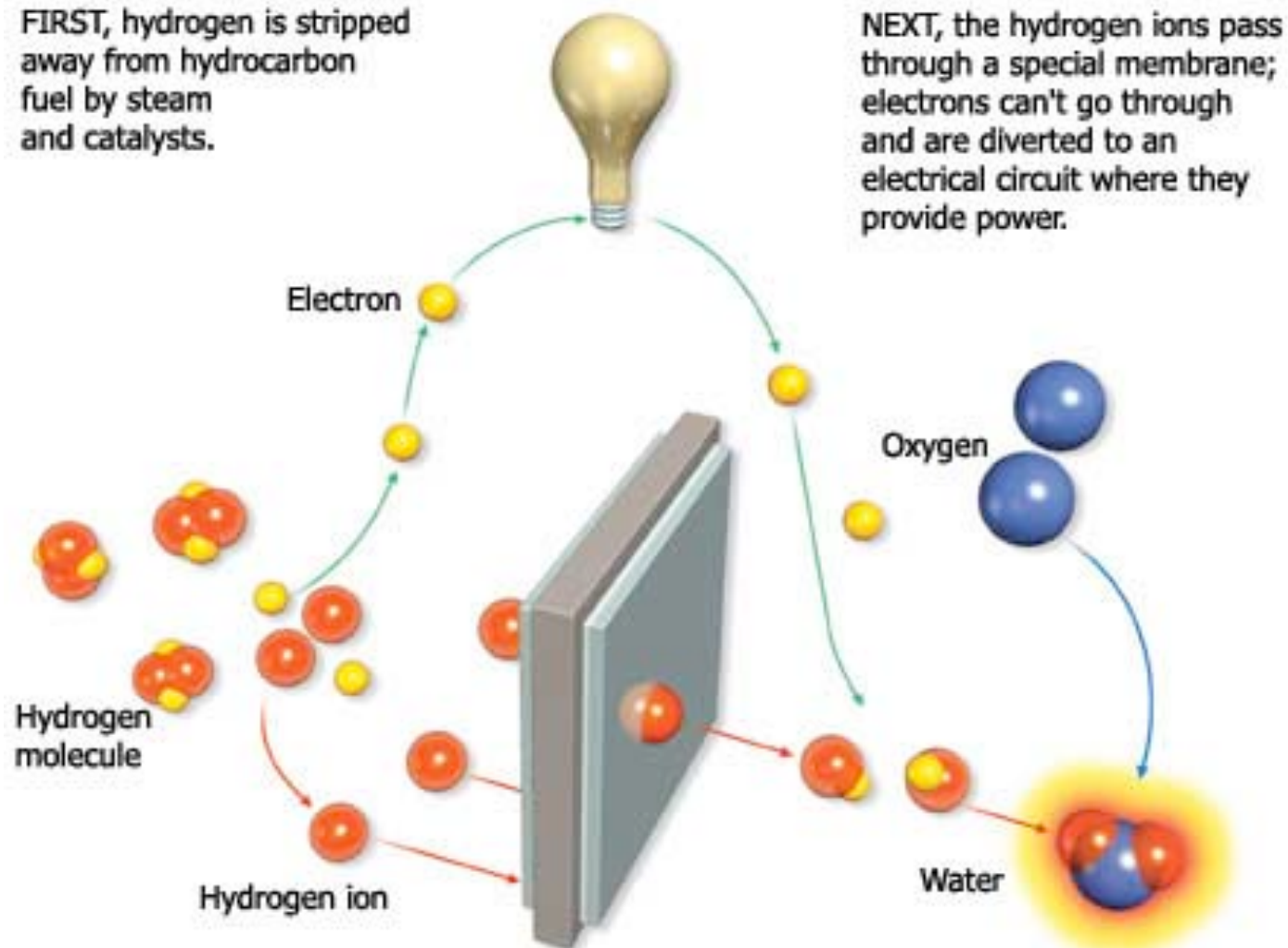


- **Introduction to Fuel Cells**
  - Characteristics
  - Fuel Cell Types
  - Fueling the Fuel Cell
- **Ammonia Fuel Cells**
  - Advantages and Challenges
  - Direct vs. Reformed  $\text{NH}_3$
  - Other Electrochemical Applications
- **High Temperature Fuel Cell Focus**
  - Ammonia and Solid Oxide Fuel Cells
  - Protonic Ceramic Fuel Cells

# The Fuel Cell

FIRST, hydrogen is stripped away from hydrocarbon fuel by steam and catalysts.

NEXT, the hydrogen ions pass through a special membrane; electrons can't go through and are diverted to an electrical circuit where they provide power.



FINALLY, the hydrogen recombines with oxygen from air to make water. The process also releases heat.

*(Lamar University)*

## • Fuel Cell Electrodes

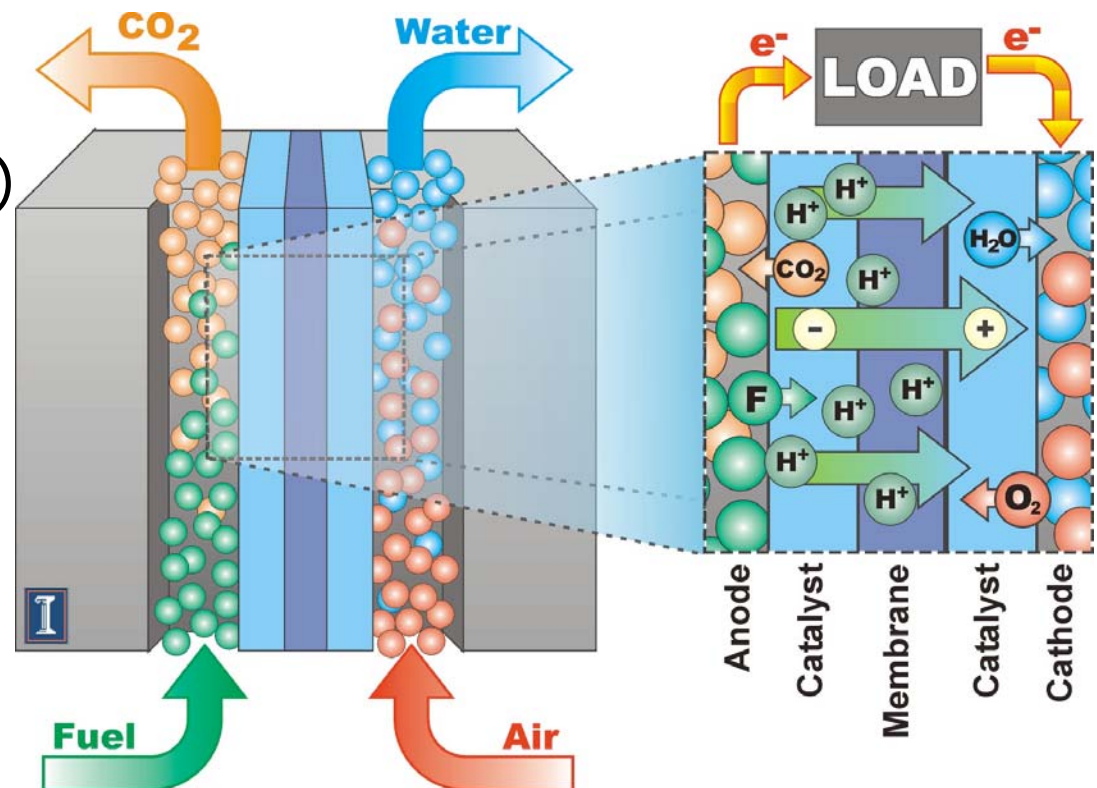
- Anode (oxidation)
- Cathode (reduction)

## • 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<sup>+</sup>]
- **Direct-Methanol Fuel Cells (DMFC)** [80°C, H<sup>+</sup>]
- **Alkaline Fuel Cells (AFC)** [150°C, OH<sup>-</sup>]
- **Phosphoric Acid Fuel Cells (PAFC)** [220°C, H<sup>+</sup>]
- **Protonic Ceramic Fuel Cell (PCFC)** [650°C, H<sup>+</sup>]
- **Molten Carbonate Fuel Cells (MCFC)**  
[700°C, CO<sub>3</sub><sup>2-</sup>]
- **Solid Oxide Fuel Cells (SOFC)** [900°C, O<sup>2-</sup>]



# Operating Temperature: A Key Characteristic



- **Low Temperature Fuel Cell Advantages**

- Quick start-up to operating temperature ( $\sim 100^{\circ}\text{C}$ )
- 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  $\sim 300^{\circ}\text{C}$
- Stainless steel internals may be used below  $\sim 750^{\circ}\text{C}$



# 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



- **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



- Very mild enthalpy of reforming
- $\text{NH}_3$  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

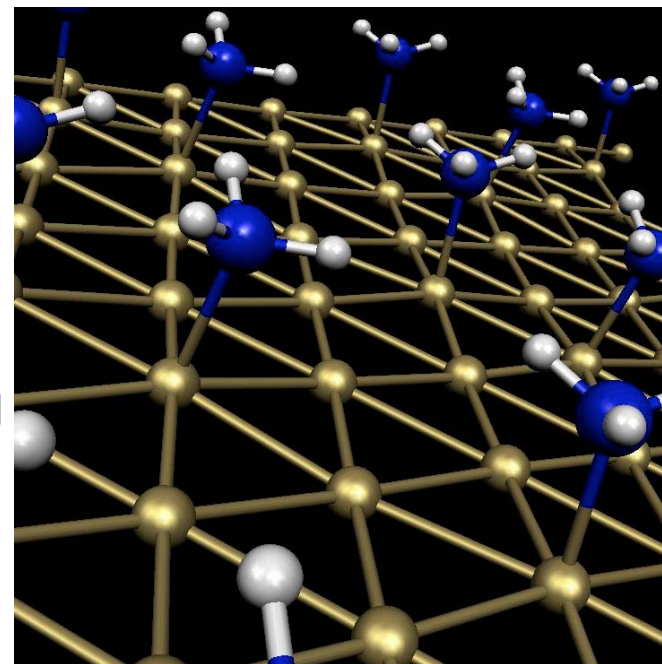
## • Externally reformed ammonia

- Trace  $\text{NH}_3$  incompatible with PEM
- Trace amounts limited by chemical equilibrium
- Reformate usually must be scrubbed



## • Medium/high temperature fuel cells

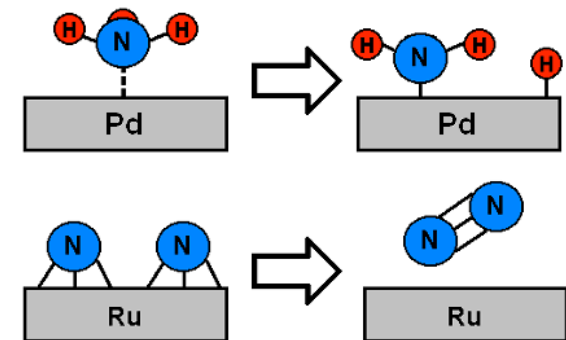
- PAFC: Trace  $\text{NH}_3$  reacts with acid electrolyte
- MCFC:  $\text{NH}_3$  crossover,  $\text{CO}_2$  recycling complication
- SOFC: An excellent fuel choice, but some  $\text{NO}_x$
- PCFC: An excellent fuel choice, no  $\text{NO}_x$



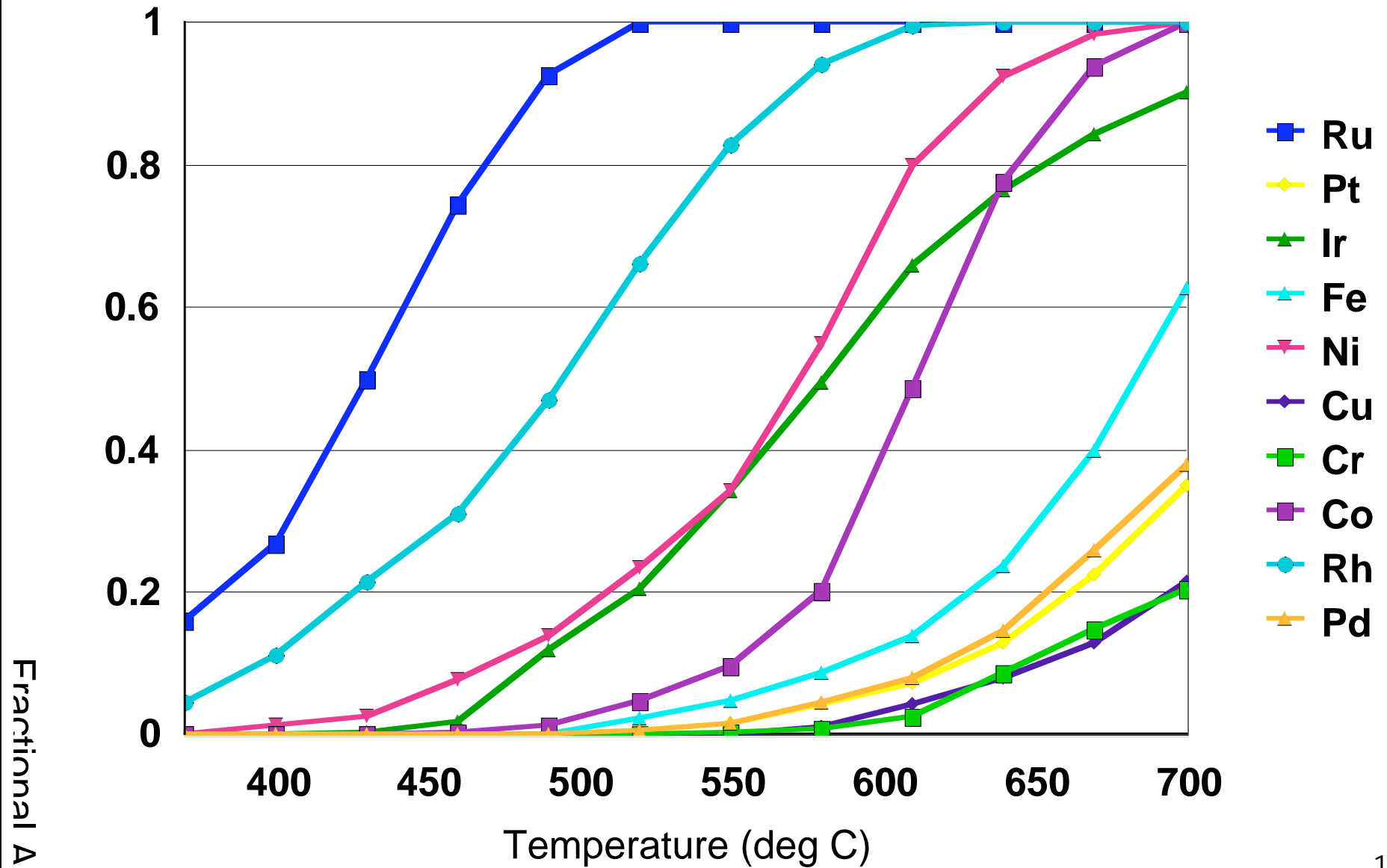
# Ammonia Catalysis

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

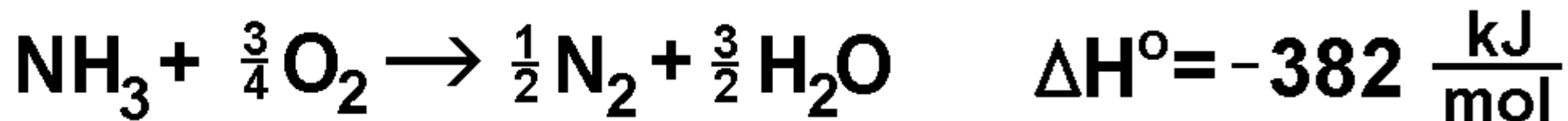
Hydrogen 1.0080 H 1																	Helium 4.003 He 2	
Lithium 6.939 Li 3	Beryllium 9.012 Be 4											Boron 10.811 B 5	Carbon 12.01115 C 6	Nitrogen 14.007 N 7	Oxygen 15.999 O 8	Fluorine 18.998 F 9	Neon 20.183 Ne 10	
Sodium 22.990 Na 11	Magnesium 24.312 Mg 12											Aluminum 26.981 Al 13	Silicon 28.086 Si 14	Phosphorus 30.974 P 15	Sulfur 32.064 S 16	Chlorine 35.453 Cl 17	Argon 39.948 Ar 18	
Potassium 39.102 K 19	Calcium 40.08 Ca 20	Scandium 44.956 Sc 21	Titanium 47.90 Ti 22	<b>Vanadium 50.942 V 23</b>	<b>Chromium 51.996 Cr 24</b>	Manganese 54.938 Mn 25	<b>Iron 55.847 Fe 26</b>	<b>Cobalt 58.933 Co 27</b>	<b>Nickel 58.71 Ni 28</b>	Copper 63.54 Cu 29	Zinc 65.37 Zn 30	Gallium 69.72 Ga 31	Germanium 72.59 Ge 32	Arsenic 74.922 As 33	Selenium 78.96 Se 34	Bromine 79.909 Br 35	Krypton 83.80 Kr 36	
Rubidium 85.47 Rb 37	Sr 87.62 38	Yttrium 88.905 Y 39	Zirconium 91.22 Zr 40	<b>Niobium 92.906 Nb 41</b>	<b>Molybdenum 95.94 Mo 42</b>	<b>Technetium (99) Tc 43</b>	<b>Ruthenium 101.07 Ru 44</b>	<b>Rhodium 102.91 Rh 45</b>	<b>Palladium 106.4 Pd 46</b>	Silver 107.87 Ag 47	Cadmium 112.40 Cd 48	Indium 114.82 In 49	Tin 118.69 Sn 50	Antimony 121.75 Sb 51	Tellurium 127.60 Te 52	Iodine 126.90 I 53	Xenon 131.30 Xe 54	
Cesium 132.90 Cs 55	Barium 137.34 Ba 56	57-71		Hafnium 178.49 Hf 72	Tantalum 180.95 Ta 73	Tungsten 183.85 W 74	Rhenium 186.21 Re 75	Osmium 190.2 Os 76	<b>Iridium 192.2 Ir 77</b>	<b>Platinum 195.09 Pt 78</b>	Gold 196.97 Au 79	Mercury 200.59 Hg 80	Thallium 204.37 Tl 81	Lead 207.19 Pb 82	Bismuth 208.98 Bi 83	Polonium (210) Po 84	Astatine (210) At 85	Radon (222) Rn 86
Francium 223 Fr 87	Radium (226) Ra 88	89-103																



# Ammonia Decomposition



# Ammonia Oxidation

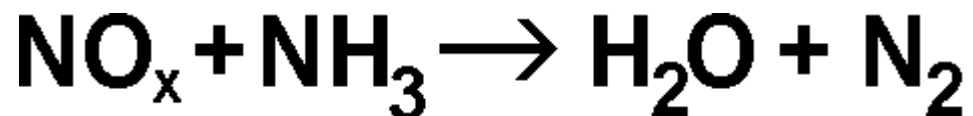


## •Catalytic combustion

- Start-up heat source for fuel cells
- Satisfies "one-fuel" approach

## •Nitrogen oxide control

- Oxidation catalysts (Cu, Fe, Cr)
- Ammonia injection



Univ. of Wisconsin  
Chemistry Dept.



# Fuel Comparison



Fuel	Base MJ/liter	Reformed MJ/liter*
H <sub>2</sub> (5000 psia)	4.0	4.0
H <sub>2</sub> (liq.)	9.9	9.9
NH <sub>3</sub> (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





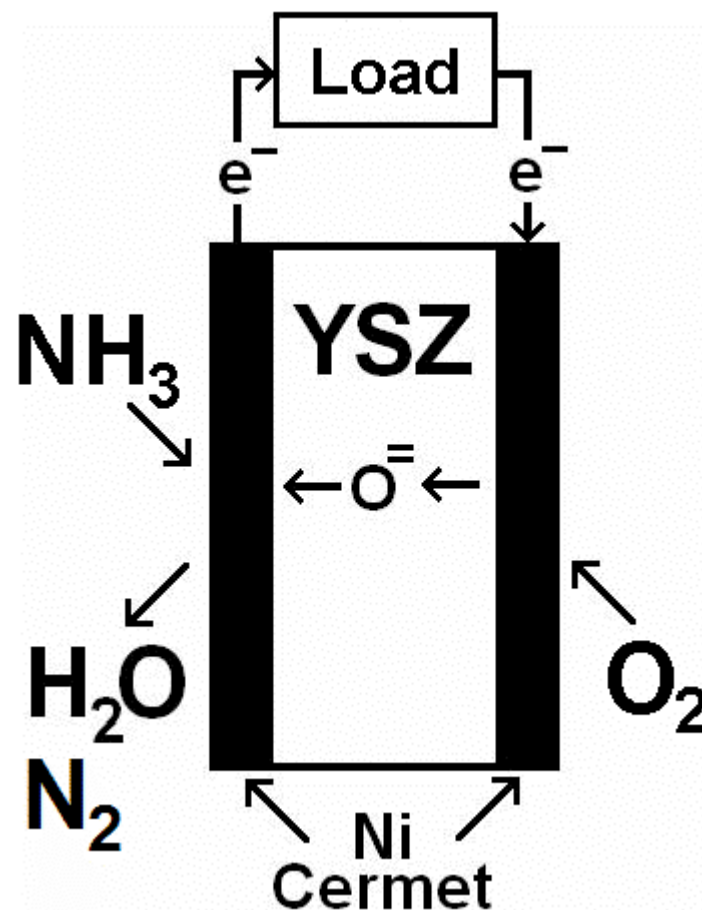
# Direct Fuel Cell Comparison



Fuel Utilized (Electrolyte Type)	Direct Ammonia (PCC)	H <sub>2</sub> 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<sub>x</sub> may appear in exhaust**



- **Standard SOFC**

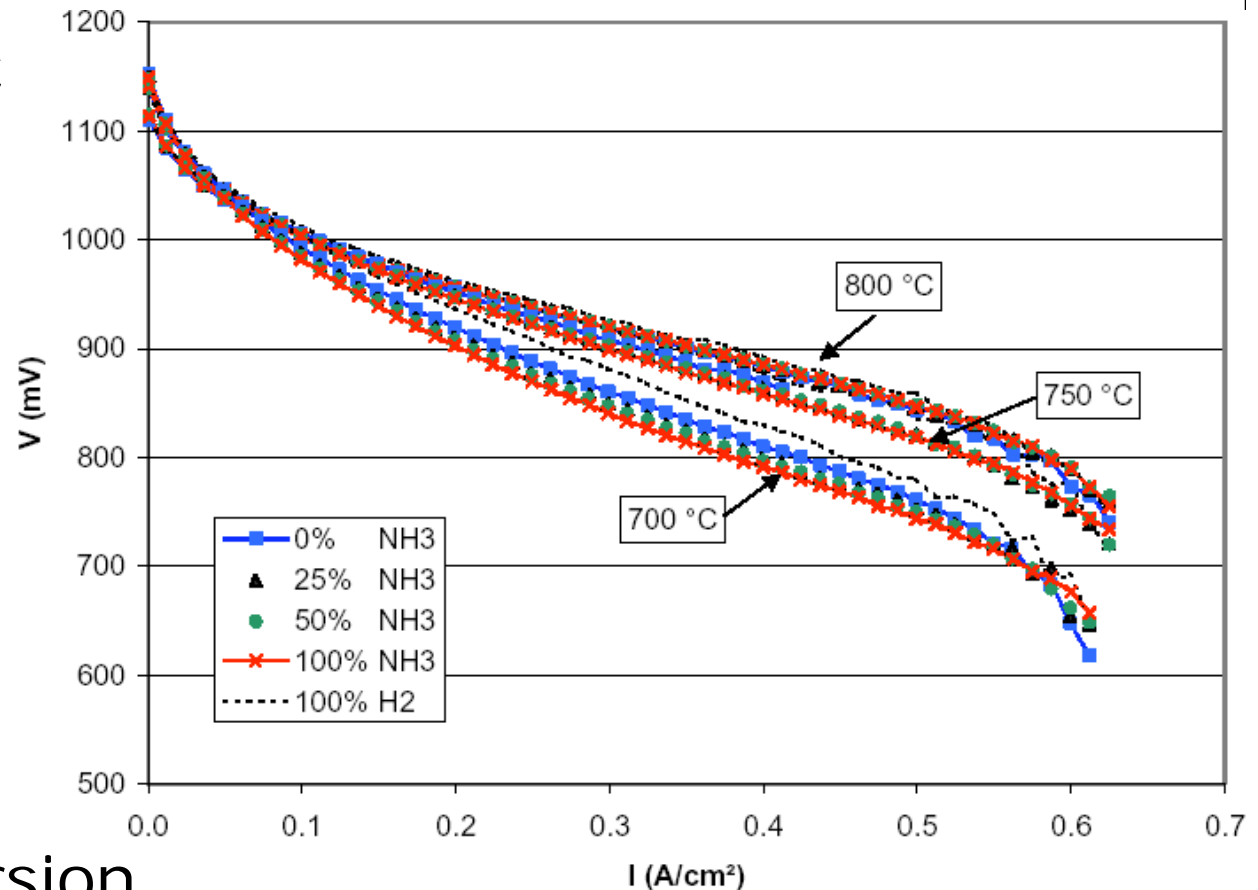
- YSZ electrolyte
- Ni anode
- LSM cathode

- **Carbon-free**

- Dry fuel
- Faster kinetics

- **Conclusions**

- High NH<sub>3</sub> conversion
- NO<sub>x</sub> formed at anode
- Virtually no difference between NH<sub>3</sub> and H<sub>2</sub> feeds



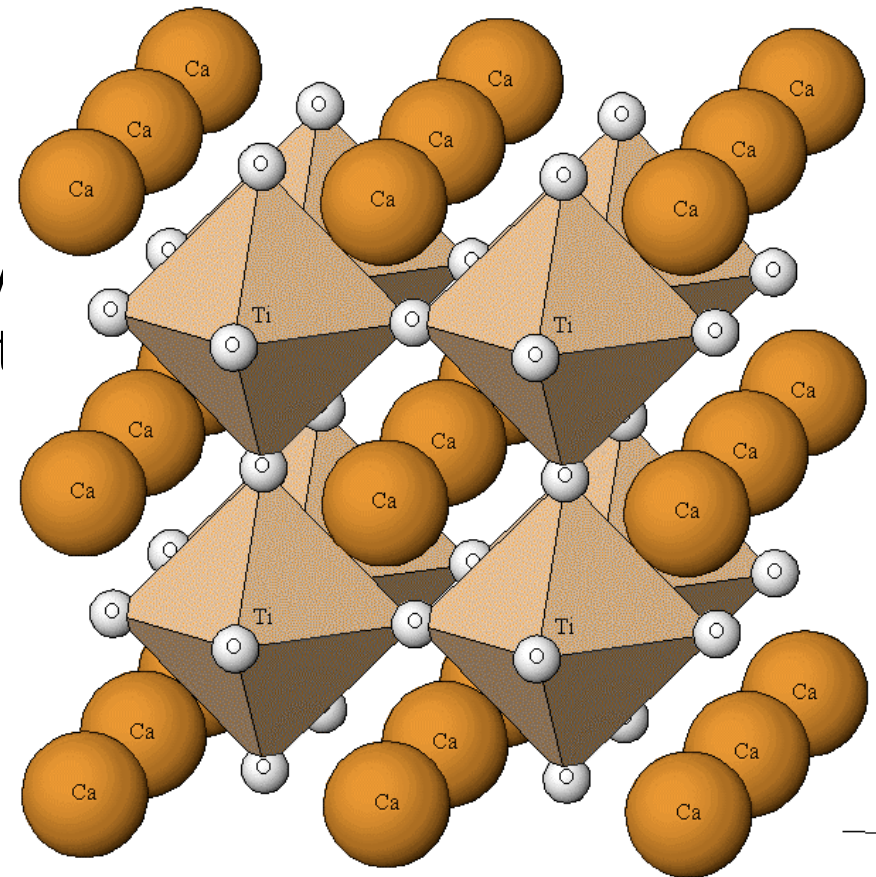
N. Dekker, B. Rietveld ECN (2004)

## • 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

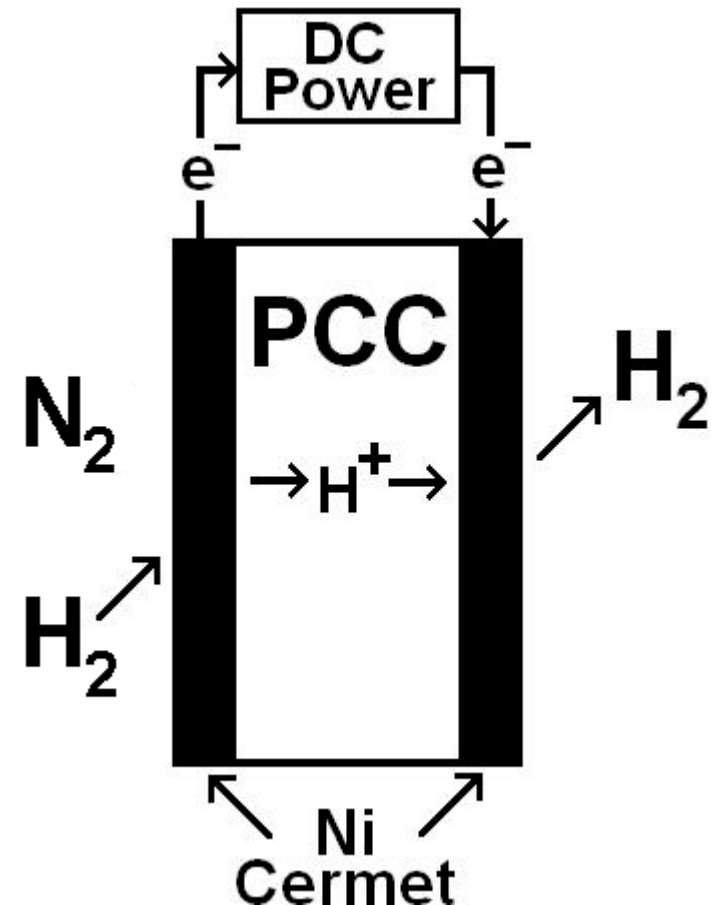
- $A_2(B'B'')O_6$  ( $A^{+2}$ ,  $B'^{+3}$ ,  $B''^{+5}$ )
- Comparable conductivities to simple perovskites
- "Doping" possible by adjustment of  $B'/B''$  ratio



*(AIST, Japan)*

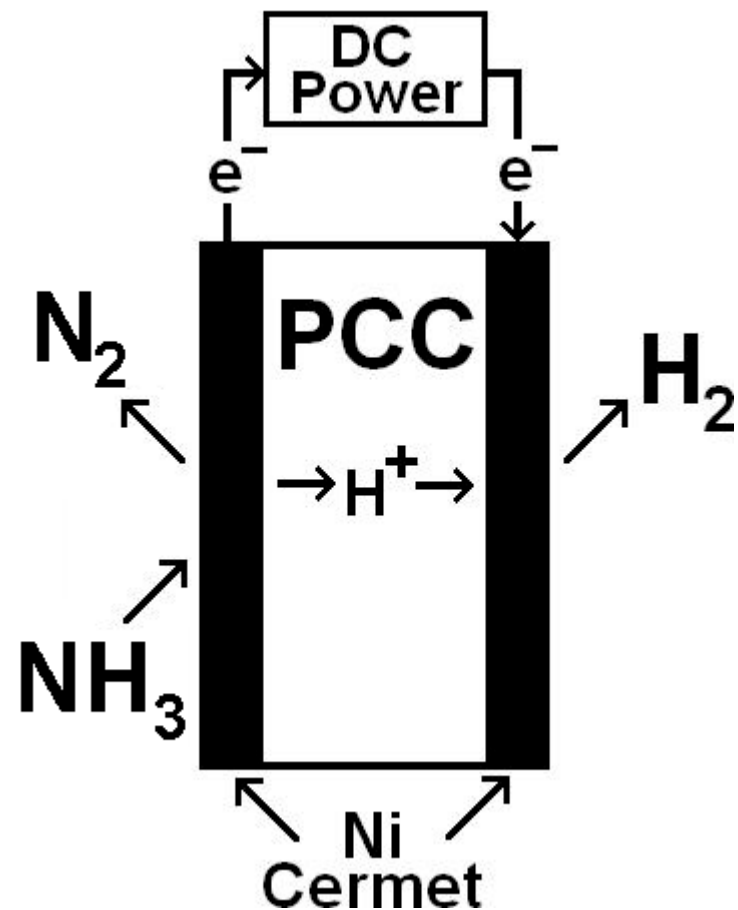
# Pure Hydrogen from Ammonia Reformate

- **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**



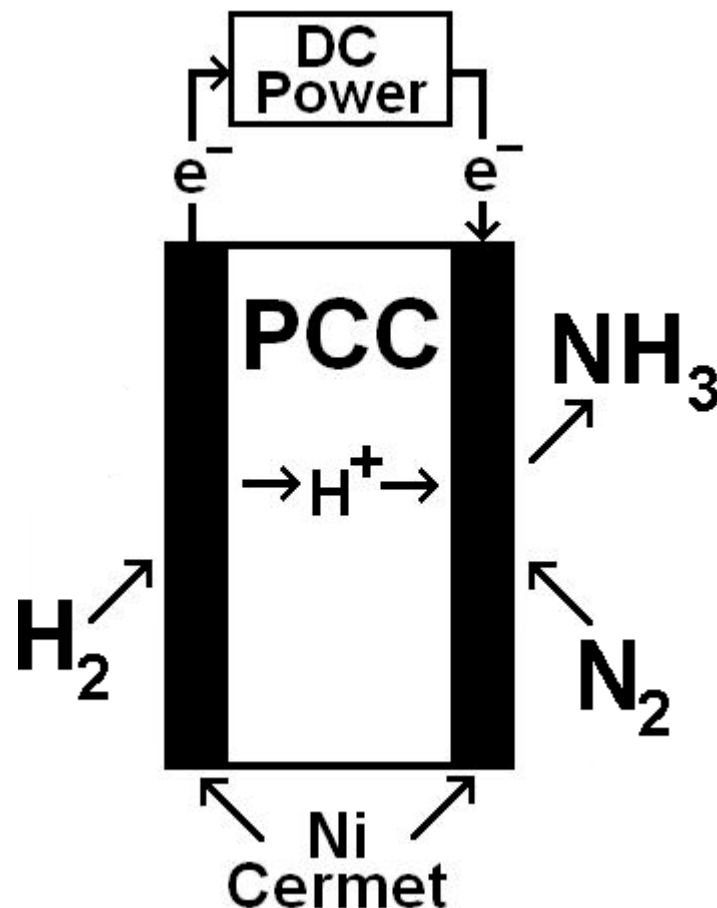
# Protonic Ammonia Electrolyzer

- **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<sub>2</sub> buildup**



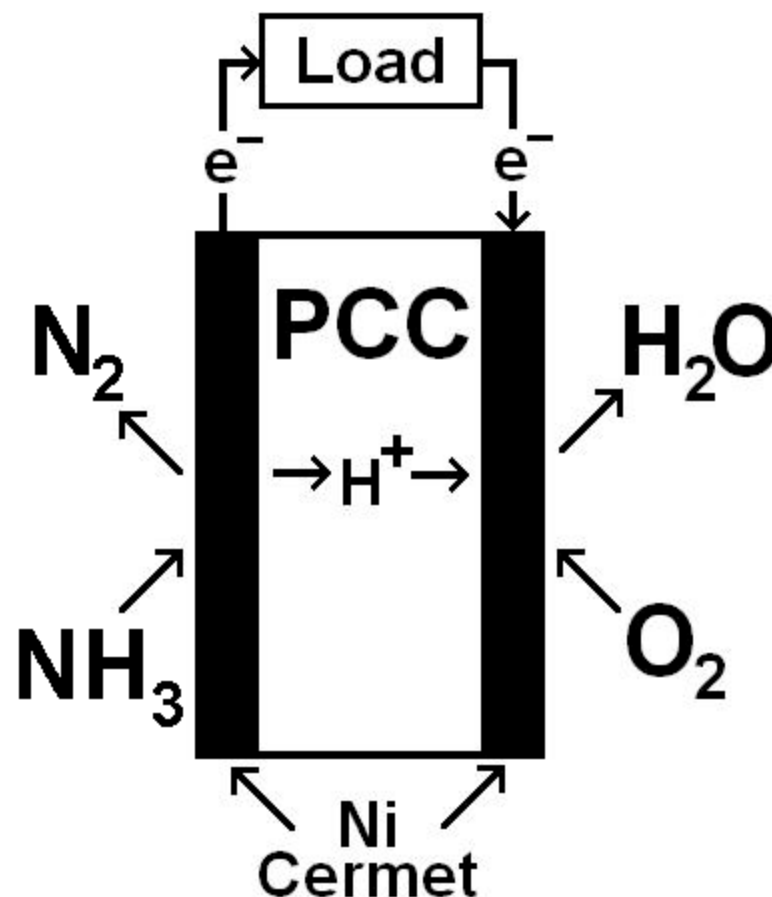


- **An alternative to packed-bed heterogeneous catalysis**
  - Verified experimentally
  - May also use higher alkenes for hydrogen source
- **May be carried out at atmospheric pressure!**
- **Limited by thermodynamic equilibrium, just as in Haber synthesis**



# 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<sub>x</sub>-free exhaust**





# Questions?

