Solid State and Electrolytic Ammonia Production

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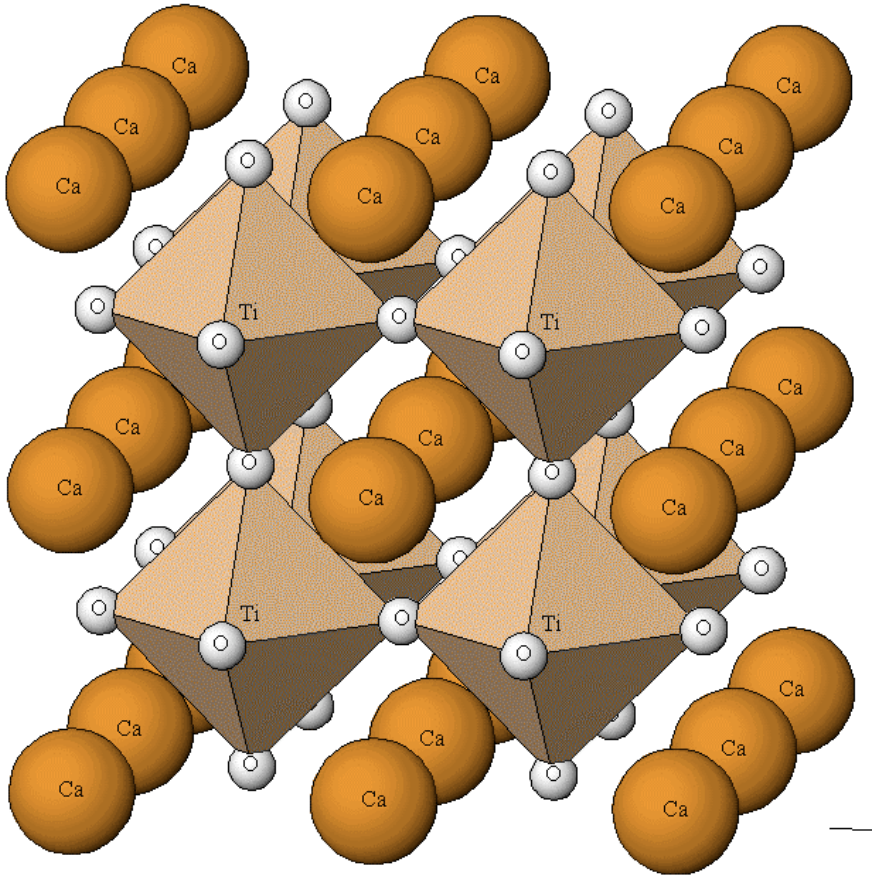
Presentation Outline

- **Protonic ceramics and NH_3 synthesis**
  - Overview of proton conducting ceramics
  - Application of PCCs to ammonia production
  - Benefits and limitations of the technique
- **Molten salts and NH_3 synthesis**
  - Principles of molten salt electrochemistry
  - Catalytic activation and ionization of intermediates
  - Extension to solid-state operation
  - Outlook for the application of the technology

Proton Conduction: Doped Perovskites

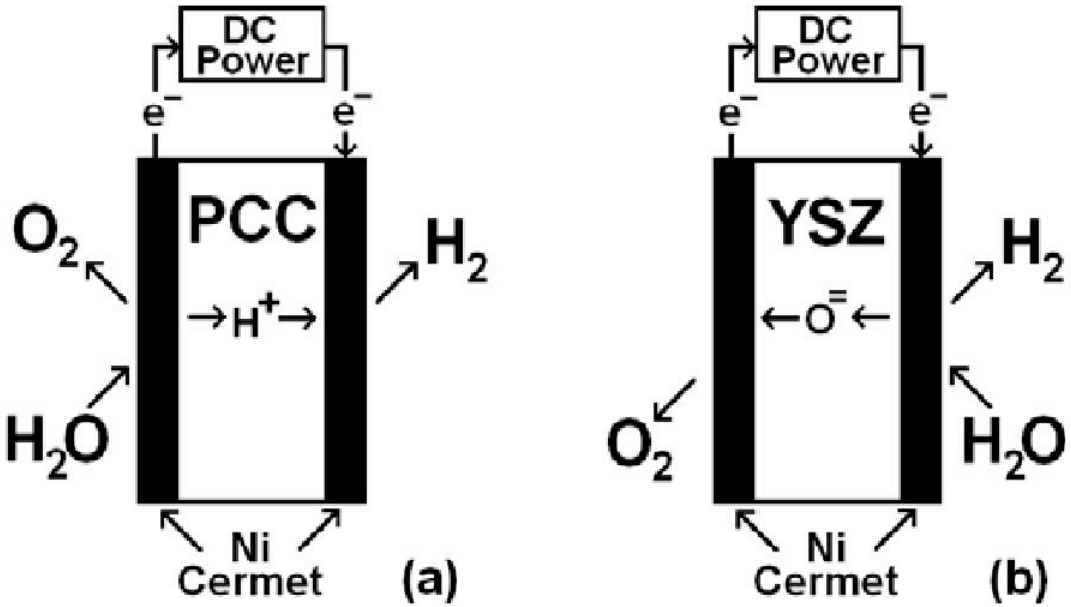
- **General characteristics**
  - ABO_3 (A^{+2}, B^{+4})
  - Must be doped with lower-valence (acceptor) elements
  - Oxygen vacancies replaced by protons after steam treatment
- **Complex perovskites**
  - $A_2(B'B'')O_6$ (A^{+2}, B'^{+3}, B''^{+5})
  - Comparable conductivities to simple perovskites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



AIST, Japan

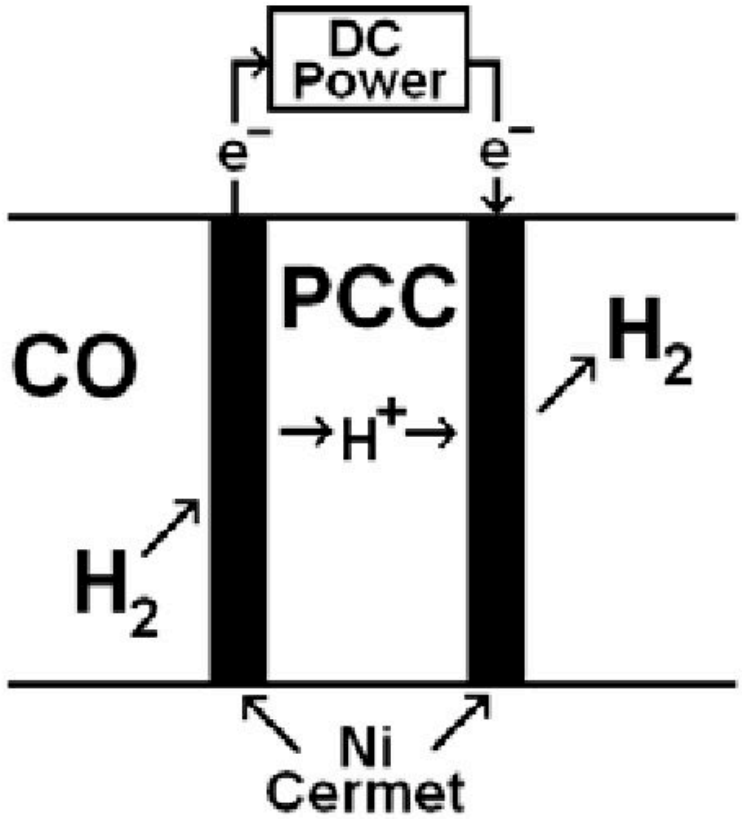
PCC Application: Steam Electrolysis

- **Steam electrolysis**
  - Substitution of electrical energy by thermal energy
  - High thermal efficiencies possible (large scale process)
- **Hydrogen produced is high purity**
- **Dry hydrogen produced using PCC**



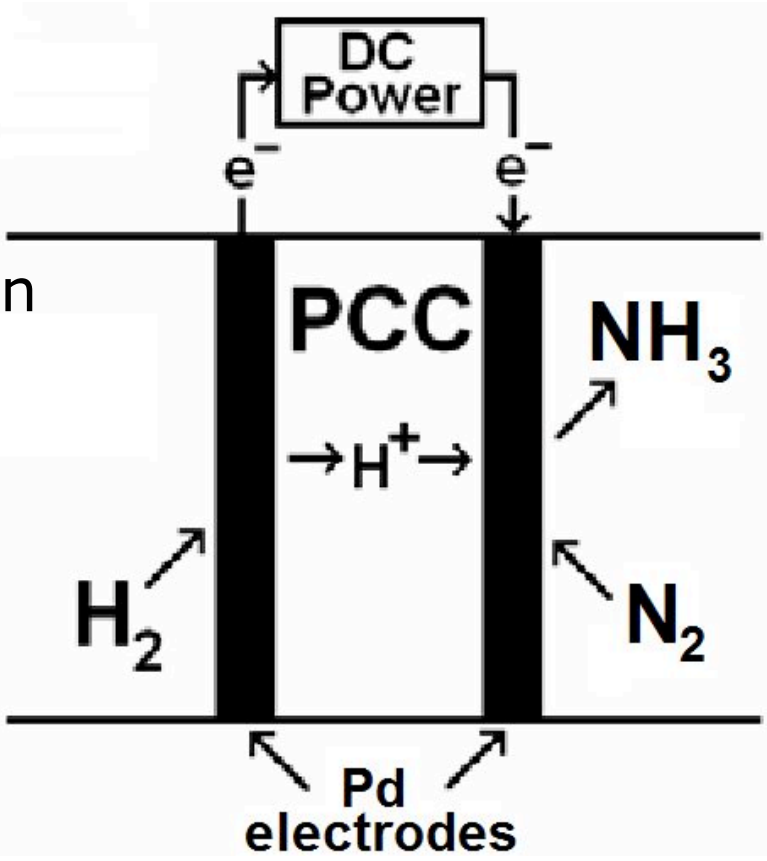
PCC Application: Hydrogen Pumping

- **Very useful for hydrogen purification applications**
  - Separation of hydrogen from syngas
  - High pressures of pure H_2 achievable with reasonable applied voltages
- **Dehydrogenation of hydrocarbons**
  - Production of pure H2 from ethane or propane
  - Side-products of propene, ethylene, or acetylene very valuable



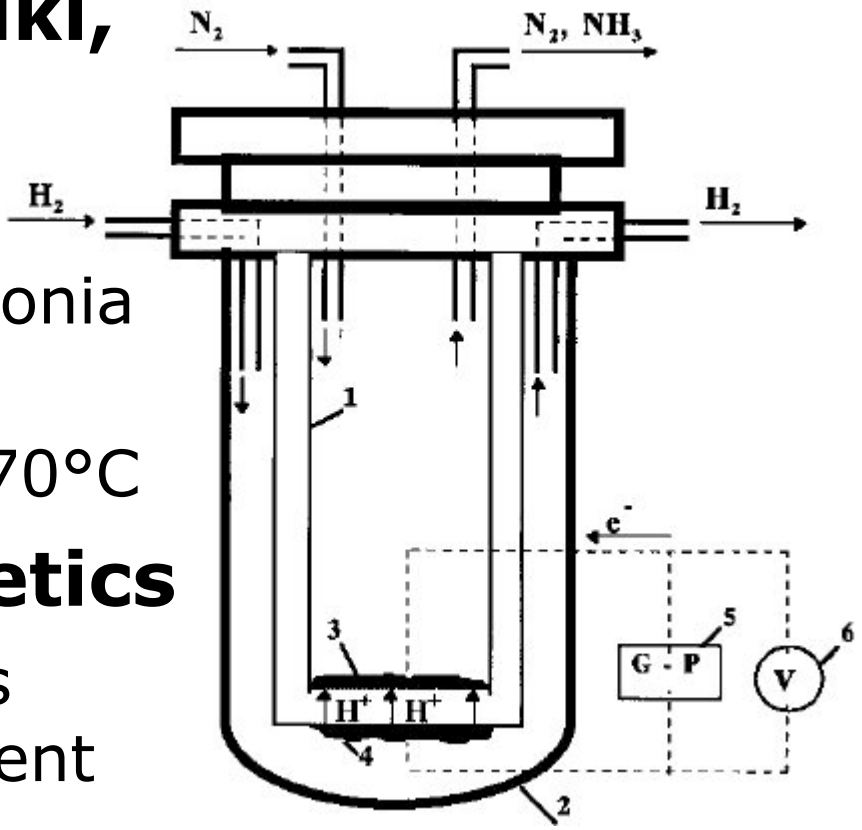
PCC Application: Ammonia formation

- **Utilizes precious metal catalyst (Pd or Pt)**
  - Operating temperature 450-700°C, depending on hydrogen source
  - Elevated temperature increases electrode kinetics
- **Likely better choice for cathode catalyst: Cu or Ni**
- **Other hydrogen sources: steam, syngas, natural gas…**



Work of Marnellos, et al.

- **Work carried out at University of Thessaloniki, Greece**
  - Atmospheric pressure
  - Equilibrium amount of ammonia synthesized
  - 80% current efficiency at 570°C
- **The real difference: kinetics**
  - Different reaction conditions and processes lead to different rate limits
  - This will be key in determining the value of this method



(Marnellos et al, 2000)

Enhanced Reaction Rates

Notes: CCR = Conventional Catalytic Reactor
PCCR = Protonic Ceramic Catalytic Reactor

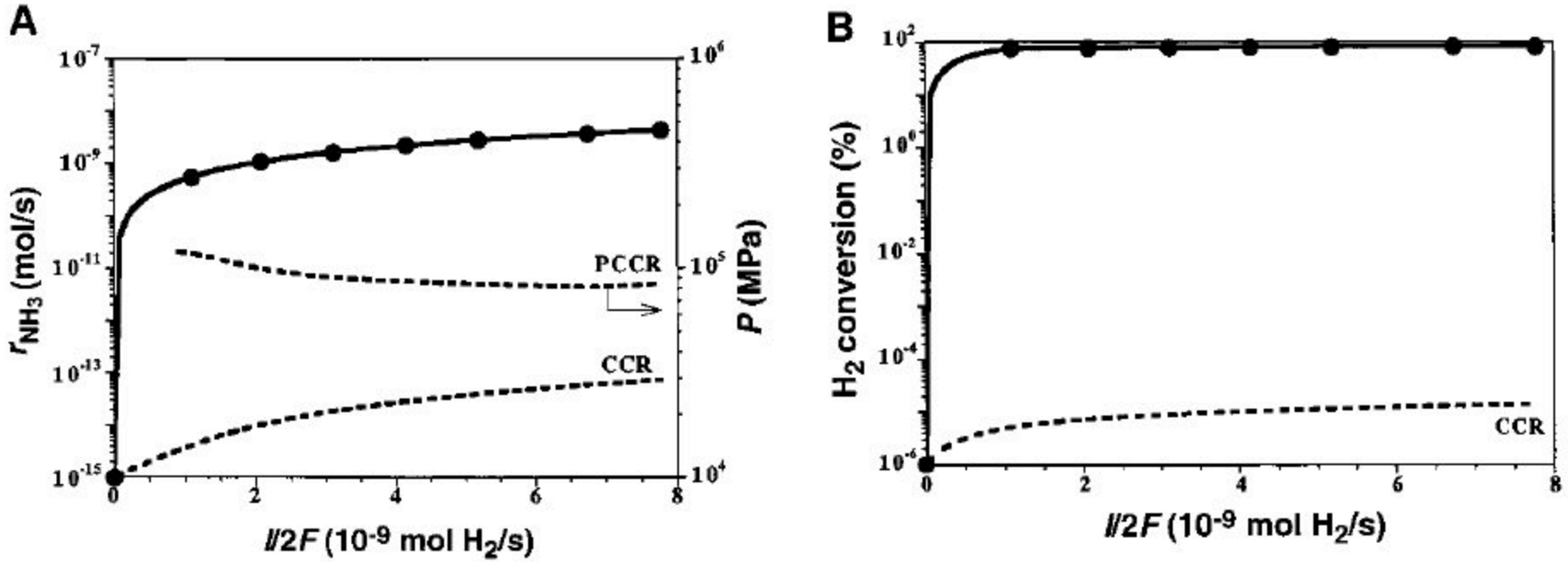


Fig. 2. Dependence of the rate of (**A**) NH_3 formation and of (**B**) the percent conversion of H_2 on the rate of electrochemical hydrogen supply, *I/2F*, under the following conditions: temperature, 570°C, and inlet partial pressure of N_2, 1.8 kPa. In (A), the CCR curve is the calculated NH_3 formation rate in a CCR and the PCCR curve is the calculated total pressure of operation of a CCR. In (B), the CCR curve is the calculated percent conversion of H_2 in a CCR.

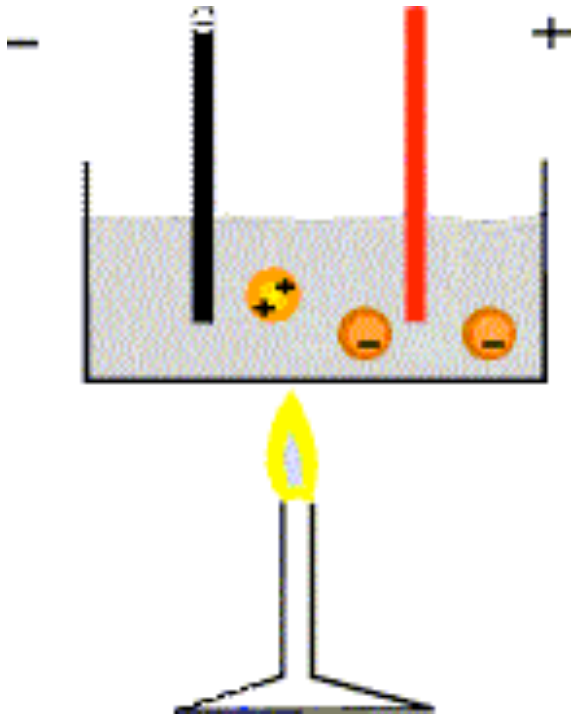
(Marnellos et al)

PCC Ammonia Synthesis

- **Current concerns of large-scale ammonia synthesis**
  - Cost of chemical feedstock (NG)
  - Process efficiency (compression)
  - Energy cost of refrigeration to separate product
  - Cost of next-generation catalysts (Ru, CoMoN)
- **Possible impacts of PCC synthesis**
  - Feedstock unaffected, processing issues may be simplified (steam reforming on anode vs. separate gas processing)
  - Thermodynamics unaffected, but processing costs (compression, recycle) will be
  - Pd is not inexpensive… Cu or Ni?

Molten Salt Electrochemistry

- **Molten salts: properties**
  - High ionic conductivity
  - Usually low vapor pressure
  - Wide operation windows with respect to temperature
  - Eutectic compositions
- **Solubility of ions in salts**
  - Observable dealloying of metals
  - Usually limited to transition metals and salt constituents
  - Ionized species may participate in electric field-driven reactions



(Chem-Pics.co.uk)

Application to Ammonia Synthesis

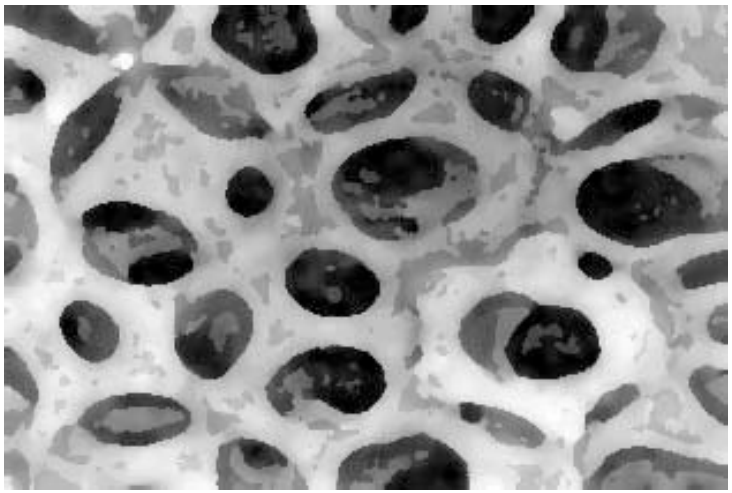
(University of Kyoto)

Details of Salt Synthesis

- **Operating conditions**
  - Atmospheric pressure
  - Temperature: 150 – 600°C
  - Products collected with unused reactants
- **Cell performance/composition**
  - Nitride formation highly efficient
  - Pure LiCl, KCl; or eutectic mix
  - Porous, nickel-based electrodes at T > 400°C
  - Porous, palladium-based electrodes at T < 400°C

Extension to Solid State

- **Immobilization of salt**
  - Molten salt contained within porous ceramic matrix
  - Surface tension prevents flow
  - Ceramic material chosen for chemical and thermal stability

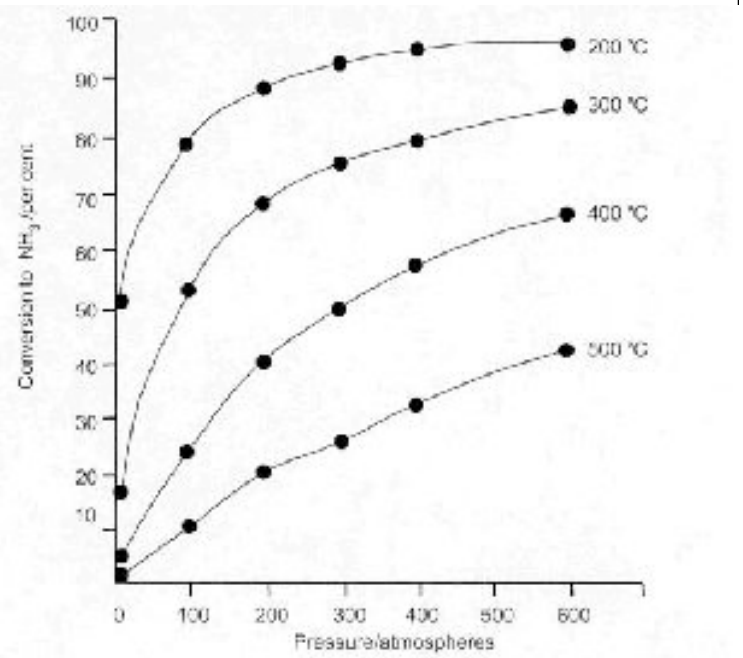


(University of Bath)

- **Electrodes coated on ceramic surface**
  - Sputtering/evaporation
  - Painting/catalyst pastes
  - Co-firing of green ceramic tape
  - Screen printing

Prospects for Molten Salt Ammonia Synthesis

- **Largely the same as PCCs**
  - Kinetic studies not yet published
  - Electrode limitations (mass transfer) just as important
- **Important possibilities**
  - Lower temperature operation: higher equilibrium conversion
  - The big question: will high-value electrical power be used efficiently enough to replace thermal energy and power-intensive compression in Haber-Bosch?



Questions/Discussion

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