Solid State and Electrolytic Ammonia Production

Jason C. Ganley

Howard University
Department of Chemical Engineering
Washington, DC
Protonic ceramics and NH₃ synthesis
- Overview of proton conducting ceramics
- Application of PCCs to ammonia production
- Benefits and limitations of the technique

Molten salts and NH₃ 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**
  - $\text{ABO}_3$ ($\text{A}^{+2}$, $\text{B}^{+4}$)
  - Must be doped with lower-valence (acceptor) elements
  - Oxygen vacancies replaced by protons after steam treatment

- **Complex perovskites**
  - $\text{A}_2(\text{B}'\text{B}''\text{O}_6$ ($\text{A}^{+2}$, $\text{B}'^{+3}$, $\text{B}''^{+5}$)
  - Comparable conductivities to simple perovskites
  - “Doping” possible by adjustment of $\text{B}'/\text{B}''$ ratio
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 \( \text{H}_2 \) achievable with reasonable applied voltages

- Dehydrogenation of hydrocarbons
  - Production of pure \( \text{H}_2 \) from ethane or propane
  - Side-products of propene, ethylene, or acetylene very valuable

Diagram:
- DC Power
- \( \text{CO} \rightarrow \text{H}^+ \rightarrow \text{H}_2 \)
- \( \text{H}_2 \) from ethane or propane
- Side-products of propene, ethylene, or acetylene
- Ni Cermet
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
• Immobilization of salt
  - Molten salt contained within porous ceramic matrix
  - Surface tension prevents flow
  - Ceramic material chosen for chemical and thermal stability

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

(University of Bath)
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

Jason C. Ganley
Howard University
Department of Chemical Engineering
2300 6th Street, NW
Washington, DC 20059
(202) 806-4796
jganley@howard.edu