Perovskite Adsorbents for Warm-Gas Arsenic and Phosphorus Removal

Erick J. Schutte, David A. Gribble, Jr., Sara L. Rolfe and Douglas S. Jack

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Eltron Research & Development

- Eltron Research & Development Inc.
  - 60 patents (25 licensed)
  - Eltron Water Systems LLC
    - Commercialization of water purification technologies
  - Continental Technologies LLC
    - Design and fabrication of engineered systems and pilot plants

- Eltron Areas of Expertise
  - Energy: Fuels, Fuel Reforming, Membranes
  - Materials & Catalysts
  - Air and Water Purification
  - Electrochemistry
DOE SBIR Project Objectives

- Formulate and synthesize perovskite-based adsorbents containing elements that very strongly bind arsenic and phosphorus, two elements known to irreversibly poison nickel catalysts in SOFCs.

- Demonstrate rapid uptake of arsenic and phosphorus by the adsorbents.

- Demonstrate retention of arsenic and phosphorus by the adsorbents under conditions expected upstream of commercial SOFCs.
Specific Project Goals

- Reduce arsenic and phosphorus in gas streams from ppmv to low ppbv quantities.
- Employ synthetic water-gas-shift mixtures during testing.
- Operate reactor at pressures up to five atmospheres.
- Operate reactor at temperatures between 250-450°C.
Key Results*

*All data acquired during 3-hour test runs, with a 1-hour H₂ reduction phase, at ambient pressure and 300°C using an argon sweep stream containing ~550 ppm arsenic and ~140 ppm phosphorus flowing at 2,000 hr⁻¹.

- Preferred sorbent demonstrated As and P adsorption efficiency of at least 73%.
- Preferred sorbents demonstrated As and P adsorption capacity of at least 4.5%.
- Commercial Cu/ZnO sorbent yielded 47% A.E. and 1% A.C. respectively.
- Preferred sorbents contain no Noble metals and are projected to cost <$5/lb.
Contaminant Background

- Affect ability of Ni in SOFCs to promote electrochemical reactions.
  - Binding on Ni surface reduces active sites for H₂ and CO adsorption and inhibits dissociation of H₂.

- Affect the electrical conductivity in SOFCs
  - As and P form irreversible Ni-As and Ni-P solid phases which leads to a loss of electrical percolation in anode support.

- DOE Polishing Filter Technical Targets
  - Arsenic and Phosphorus - <20 ppbv
  - Sulfur - <60 ppbv (Previous Phase I and II at Eltron using similar adsorbents has proven successful for regenerable sulfur polishing)
Design of Sorbents

- Focus on incorporating metals which form stable arsenides and phosphides into Perovskite (ABO$_3$) based materials.

- Different A-site (large metal cation) and/or B-site (small) atoms in same sorbent leading to disordered variants and mixed phase ceramics.

- High oxygen mobility, and thus the lower stability of oxides, within Perovskite structures increases driving force for formation of M-As and M-P solid phases on adsorbents.
Initial Testing Reactor Designs

- **Breakthrough Reactor**
  - Employ Elemental As and P.
  - Vaporize Elements, Use Inert Sweep.
  - Ni-coated Coupons both Pre- and Post-Sorbent Bed.

- **High Pressure/WGS Reactor**
  - Same Testing Strategy as Breakthrough Reactor
  - Capable of Handling up to 5 Atm Pressure
  - Capable of Employing Simulated WGS Stream.
Initial Testing Reactors
Early Phase I Successes and Issues

- **Successes**
  - Synthesized and Characterized 16 Perovskite and Perovskite-like Adsorbents.
  - Preferred Sorbents Left No Trace of As or P on Post-Reactor Coupon.
  - Preferred Sorbents Out-Performed Commercial Cu/ZnO Sorbent.

- **Primary Issues Which Developed**
  - Contaminant Control – Difficulty in Generating Consistent Concentrations of As and P.
  - Quantifiable Data – Techniques for Quantifying Post-Sorbent Bed As and P Concentrations Needed Refining.
Late Project Reactor Re-Design

- Focus on Steady, Consistent Flow and Quantifiable Contaminant Concentration.
  - Replaced elemental As and P with arsine and phosphine gas (each 10ppm in hydrogen).
  - Equip tanks with mass flow control.
  - Acquired arsine sensor for post-reactor flow sampling.
  - Upgraded safety measures (hydrogen sensors, NaOH bubbler for scrubbing post-reactor gas).
State of Technology and Phase II Focus

- Reactor and Instrumentation Upgraded
  - More Precise Flow Control Using Arsine and Phosphine
  - Novel Detection System Capable of Measuring As and P Below 20ppbv

- Phase II Focus
  - Simulated WGS Stream Addition
  - Sulfur Addition (H₂S)
  - Independent Testing by Leading SOFC Company
  - Pilot Plant Sorbent Scale-Up and Evaluation by Commercial Sorbent Production Company
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