

# Perovskite Adsorbents for Warm-Gas Arsenic and Phosphorus Removal

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

## 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 high-pressure steam at temperatures ranging from 250-400°C.

## 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 between ambient and 5 Bar.
- Operate reactor at temperatures between 250-450°C.

## Key Results

- Preferred sorbents demonstrated As and P adsorption efficiencies as high as 73% versus 47% for a commercial Cu/ZnO material.
- Preferred sorbents demonstrated As and P adsorption capacities as high as 4.5% versus 1.0% for a commercial Cu/ZnO material.
- Preferred sorbents contain no Noble metals and are projected to cost <\$5/lb.

\*All data acquired at ambient pressure and 300°C using an argon sweep stream containing 300-800 ppm As and 30-250 ppm P flowing at 2,000 hr<sup>-1</sup>.

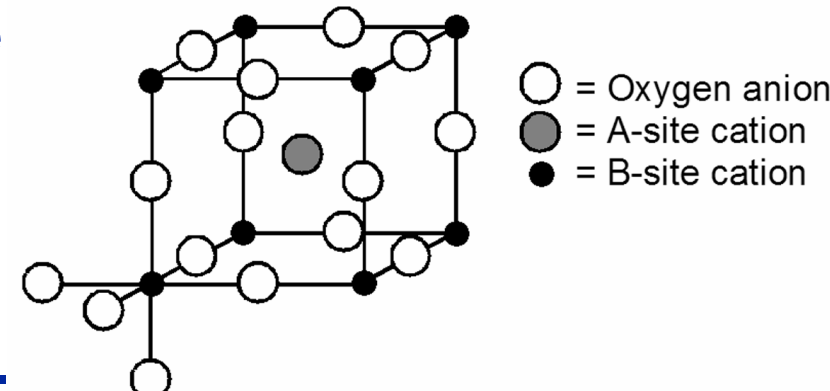
## General Background

### 1. Why Arsenic and Phosphorus?

- Affect ability of Ni in SOFCs to promote electrochemical reactions.
  - Binding on Ni surface reduces active sites for H<sub>2</sub> and CO adsorption and inhibits dissociation of H<sub>2</sub>.
- 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

### 2. What's Eltron's Answer?

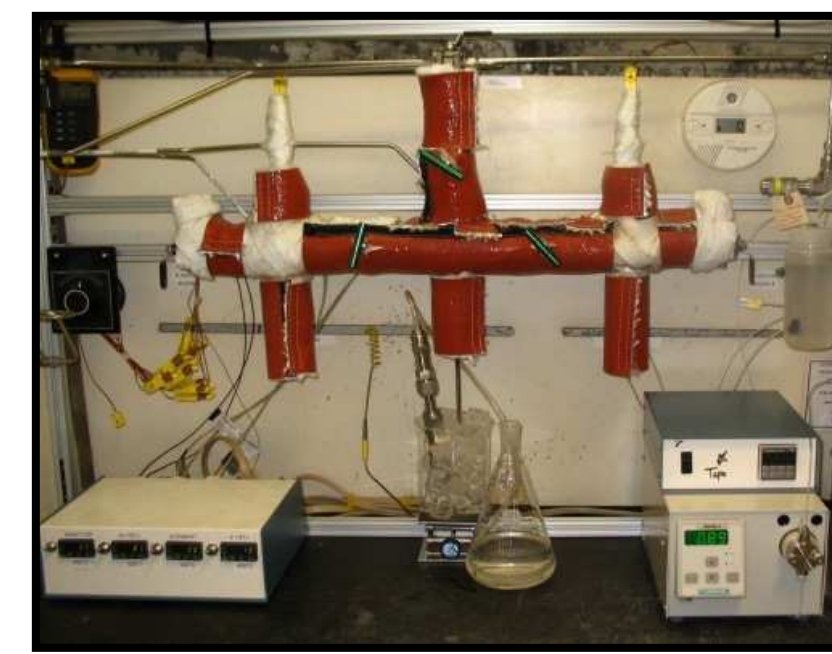
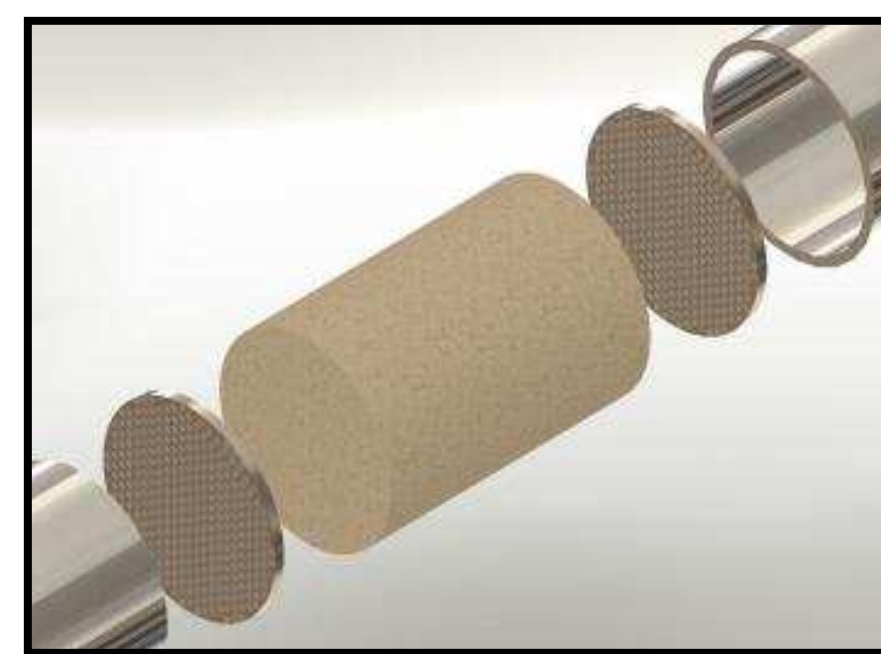
- Focus on incorporating metals which form stable arsenides and phosphides into Perovskite (ABO<sub>3</sub>) based materials.
- Multiple A-site (large metal cation) and/or B-site (small) atoms leading to ordered and disordered variants and some
- High oxygen mobility, and thus the lower stability of oxides, within Perovskite structures increases driving force for formation of M-As and M-P solid phases on adsorbents.



## Reactor Designs and Construction

### ➤ Breakthrough Reactor

- Employ Elemental Arsenic and Phosphorus.
- Vaporize Elements, Use Inert Sweep Gas.
- Ni-coated Coupons both Pre and Post-Sorbent Bed.



### ➤ High Pressure/Synthesis Gas Reactor

- Same Testing Strategy as Breakthrough Reactor
- Capable of Handling 1-5 Atm Pressure
- Capable of Employing Simulated Syn-Gas Stream w/



## Testing Results and Issues

### ➤ Successes

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

### ➤ Primary Issues to Be Resolved

- Contaminant Control – Difficulty in Generating Consistent Concentrations of As and P.
- Quantifiable Data – Refining Techniques for Quantifying Post-Reactor As and P Concentrations Possible.

## Solutions and Future Plans

### ➤ Reactor and Instrumentation Upgrades

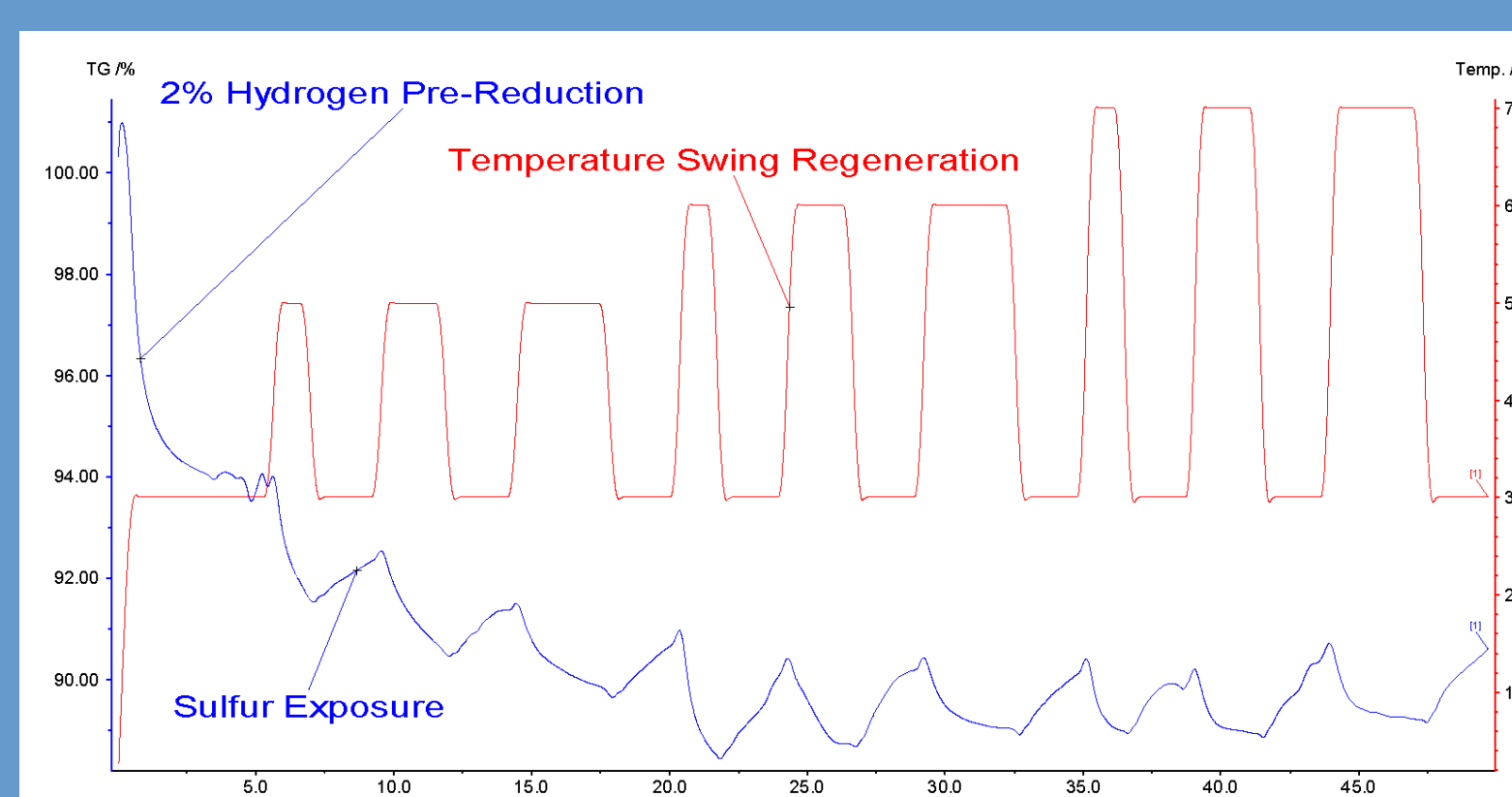
- More Precise Flow Control with Arsine and Phosphine Gas
- Novel Detection System Capable of Measuring As and P Below 20ppbv
- Arsenic Sensor Installed Post-Reactor

### ➤ Phase II Focus

- Simulated Syn-Gas Stream w/Steam Addition
- Sulfur Addition (H<sub>2</sub>S)
- Independent Testing for SOFC Protection by Leading SOFC Company
- Pilot Plant Sorbent Scale-Up and Evaluation by Commercial Sorbent Production Company

## Acknowledgements

Support from the U.S. Department of Energy, Small Business Innovation Research Program DE-SC0000871, Perovskite Adsorbents for Warm-Gas Arsenic and Phosphorus Removal DE-FG02-07ER84666, Perovskite Adsorbents for Warm-Gas Removal of Sulfur



**Eltron Research & Development**  
4600 Nautilus Court South  
Boulder, CO 80301