Co-generation of Carbon-Free Hydrogen and Electricity from Coal in a Steam-Carbon Fuel Cell with Carbon Capture

David U. Johnson\textsuperscript{a}, Brandon Loong\textsuperscript{b}, S. Michael Stewart\textsuperscript{a}
Turgut M. Gür\textsuperscript{c}, Reginald E. Mitchell\textsuperscript{a},

\textsuperscript{a}Department of Mechanical Engineering, Stanford University
\textsuperscript{b}Department of Chemical Engineering, Stanford University
\textsuperscript{c}Department of Materials Science and Engineering, Stanford University

Presented at the
2015 GCEP Symposium
October 13-14, 2015
Project Overall Objective

Our research addresses three aspects of energy production and storage using coal:

1. efficient coal conversion in a specialized fuel cell
2. electrochemical hydrogen production from coal for energy storage
3. CO$_2$ mitigation and capture without separation

This technology could result in a significant reduction in global CO$_2$ emissions over the long term with continued use of coal, our cheapest and most abundant fuel.
Presentation Outline

• Motivation
  - Coal use
  - Hydrogen production
• Background
  - Air/Carbon & Steam/Carbon SOFCs
  - Coupled A/C-S/C SOFC
• Research focus
  - Overcoming sulfur poisoning
    - Sulfur sorbents
    - Sulfur tolerant anodes
  - Comprehensive modeling
• Concluding remarks
Motivation: Coal Use

Coal is the cheapest and most abundant fuel on earth.

At 2004 production levels, proven U.S. coal reserves could last about 250 years.

Worldwide, coal-fired power plants account for 30% of the carbon dioxide dumped into the atmosphere each year.

Environmentally benign use of coal as an energy resource requires CO$_2$ capture and sequestration.
Motivation: Hydrogen Production

- Hydrogen is the most abundant element in the universe
- Hydrogen is an efficient energy carrier
- Environmentally clean fuel when combusted or oxidized
- Suitable for large scale energy storage
  - Offers sustainability of solar, wind, and other renewables
  - “Peak shaving” to store cheap electricity
- Suitable for distributed generation
  - Stand-alone, or part of “Smart Grid”
  - Clean transportation fuel (for FC vehicles)
- Carbon-neutral when generated from biomass

The problem: \( H_2 \) is not naturally available
We have demonstrated our air-carbon SOFC that produces electricity and can use a variety of carbons as the resource. YSZ is used as the membrane. Oxide ions are transported via a vacancy mechanism across the crystal lattice of the YSZ ceramic membrane towards the anode where they react with the carbonaceous fuel to form CO₂.

We next demonstrated our steam-carbon SOFC that permits the production of both electricity and H₂ when the cell is heated. Steam and carbon are physically separated by the YSZ membrane permitting carbon-free H₂ production.

We are now coupling the steam-carbon/air-carbon electrochemical cell that permits simultaneous production of hydrogen and electricity.

This coupled cell is capable of spontaneously generating both hydrogen and electricity.
Sulfur in coal and biomass
Coal and biomass materials contain sulfur, resulting in 500 to 10,000 ppm of gaseous $\text{H}_2\text{S}$ and COS when gasified, depending on the conditions.

Sulfur poisoning
Sulfur poisons the common electrode materials. Substantial loss in the performance of nickel-based anodes for CO oxidation is observed, with losses in power density as high as 60%.

Nickel-based catalysts are unsuited for applications where sulfur is present.

A Two-Pronged Approach
Our efforts in resolving sulfur problems take two paths:

- Efforts directed at identifying sorbents that reduce the concentrations of $\text{H}_2\text{S}$ and COS in the gas phase
- Efforts directed at identifying electrode materials that can tolerate low levels of sulfur
Sulfur Sorbent Studies

Identification of Sorbents

Among the goals of this project is to identify sorbents capable of reducing the sulfur content of the syngas produced from coal and biomass to less than 5 ppmv.

The Gibbs free energy change for sulfur removal under a variety of sulfur partial pressures was calculated for various metals and metal oxides and used to assess the potential for sulfur capture.

In general alkaline metals are better sulfur sorbents than alkali metals.

As such, we have selected CaO, SrO and BaO to investigate for their ability to reduce H₂S and COS concentrations.

Elements that are sulfur sorbents regardless of phase or oxidation state (dark green). Elements that are sulfur sorbents depending on phase or oxidation state (light green). Elements that are not sulfur sorbents (red), and those whose performance as a sulfur sorbent is not known (grey).
Metal Oxide Sorbents

**CaO, BaO and SrO**
Equilibrium calculations indicate the potential for CaO, BaO and SrO sorbents removing H$_2$S and COS from syngas.

**Sorbents dispersed in the fuel**
Metal oxide sorbents require an excess of sorbent relative to the sulfur in the fuel, due to the low utilization of the sorbent, a consequence of mass transport limitations through the particle bulk.

It may also be possible to improve sorbent utilization by dispersing the sorbent across the fuel source, thereby using the fuel as a support.

---

Mole-% H$_2$S and COS in the gas phase after Wyodak coal syngas is passed over CaO (black), SrO (red), and BaO (blue). The syngas contained 0.0556% H$_2$S and 0.00337% COS, by volume, at 1173 K.
Norit® Char

Norit® char, a synthetic filamentary carbon is used as a model sulfur-containing carbon source because it is a commercially available, high-surface area biomass char, eliminating the time consuming process of producing large quantities of biomass chars for sorbent studies.

Using wetness impregnation, we have successfully dispersed CaO, SrO and BaO into the bulk of the Norit® char.
Dispersed Sorbent Studies

Fuel Cell Performance
Fuel cells were operated at 900 °C when charged with Norit® blended with CaO, BaO and SrO. Cells were characterized using linear sweep voltammetry and electrochemical impedance spectroscopy (EIS).

Voltammetry
For linear sweep voltammetry, the voltage of the cell was varied from 1 V to 0.45 V at a rate of 10 mV/s and the current was recorded.

Higher voltage attained with better sorbents, probably due to better sulfur scrubbing capacity of BaO over SrO and CaO.

Red: Norit®, no sorbent
Blue: CaO/Norit®
Green: SrO/Norit®
Black: BaO/Norit®
Dispersed Sorbent Studies

Fuel Cell Lifetime
Fuel cell performance (OCV) and lifetime are both improved with addition of the sorbents, but there is still significant degradation. Better lifetime is exhibited with SrO over CaO.

Electrochemical Impedance Spectroscopy
EIS measurements were taken at 0, 3, 6, and 12 hours.
Dispersed Sorbent Studies

X-Ray Diffraction Measurements
The MEA of the as received fuel cell consists of both an yttrium-stabilized zirconia (YSZ) phase (red) and a NiO phase (green).

The anode catalyst layer of the membrane electrode assembly after conditioning in H₂: additional Ni, NiS, and ZrO₁.₆S₀.₄ phases.

Although CaO, BaO and SrO impart anode protection due to their ability to remove sulfur, anode degradation is still significant. This supports our efforts to develop perovskites.
Perovskites (ABO$_3$ type compounds)

Compared to nickel anodes, many perovskites have shown superior resistance towards both carbon coking and sulfur poisoning problems that are prevalent during electrochemical oxidation of hydrocarbon fuels.

Doped Perovskites

Bulk conductivity measurements of doped perovskites that have been investigated for use as sulfur tolerant SOFC anodes are shown in the table.

<table>
<thead>
<tr>
<th>Perovskite</th>
<th>Bulk Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.75}$Sr$</em>{0.25}$Cr$<em>{0.5}$Mn$</em>{0.5}$O$_3$</td>
<td>1.5</td>
</tr>
<tr>
<td>Gd$<em>2$Ti$</em>{1.4}$Mo$_{0.6}$O$_7$</td>
<td>1.4</td>
</tr>
<tr>
<td>Sr$<em>2$MgMoO$</em>{6.5}$</td>
<td>5</td>
</tr>
<tr>
<td>La$<em>{0.3}$Sr$</em>{0.7}$TiO$_3$</td>
<td>500</td>
</tr>
<tr>
<td>La$<em>{0.7}$Sr$</em>{0.3}$VO$_3$</td>
<td>150</td>
</tr>
<tr>
<td>LaVO$_3$</td>
<td>6</td>
</tr>
</tbody>
</table>

The high conductivity of La$_{0.3}$Sr$_{0.7}$TiO$_3$ and its ability to oxidize CO makes it an ideal candidate as a sulfur tolerant anode material.
XRD of Synthesized Perovskites

Synthesized Materials
A number of materials have been synthesized to date:

XRD Spectra
XRD data from synthesis of several perovskites that we have synthesized using a solid-state procedure: the parent SrTiO$_3$ (ST) and the doped variations using La and Ba.

The materials show a single cubic perovskite lattice.

<table>
<thead>
<tr>
<th>Lattice parameters</th>
<th>Reference</th>
<th>a (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST</td>
<td>3.905</td>
<td>3.905</td>
</tr>
<tr>
<td>LST</td>
<td>3.915</td>
<td>3.914</td>
</tr>
<tr>
<td>LBST</td>
<td>3.910</td>
<td>3.935</td>
</tr>
<tr>
<td>BST</td>
<td>3.950</td>
<td>3.945</td>
</tr>
</tbody>
</table>

Rietveld refinement yielded the lattice parameter, a, which are in good agreement with literature values.
XPS of Synthesized Perovskites

XPS Spectra

XPS data show no impurity peaks, indicating a clean synthesis. The surface carbon content is low in both samples indicative of high temperature reaction conditions that remove most of the carbonates found in the starting precursors.

Measured compositions closely match expected formula values
H$_2$-Air LST Fuel Cell

Electrochemical Characterizations

We have established a qualifying procedure for electrochemically verifying correct sealing of the fuel cells.
Modeling Carbon Fuel Cells

Button and Tubular Fuel Cell Geometries

Finite-element models of a planar, button-type carbon-air fuel cell and an axi-symmetric, tubular carbon-air fuel were developed to determine the relationship between overall cell efficiency, hydrogen production rate, and electricity production.

The models include:

- **Electrochemistry**
- **Mass Transport**
  - Convection and diffusion
  - Darcy’s law (porous media)
- **Carbon bed chemistry of dry gasification** (Boudouard reaction)
- **Heat Transfer**
  - Gas phase convection/conduction
  - Wall-to-wall radiation
  - Fuel bed convection, conduction, and radiation
Cell Voltage

The operating voltage is an input to the model. Current density is calculated, iteratively.

\[ V_{\text{cell}} = V_{\text{OCV}} - \eta_{\text{ohmic}} - \eta_{\text{anode}} - \eta_{\text{cathode}} \]

Nernst Equation  
Ohm’s Law  
Butler-Volmer Equation  
EIS measurements

\[ E_{\text{act,a}} = 161 \pm 5 \text{ kJ/mol} \]
\[ E_{\text{act,c}} = 190 \pm 2 \text{ kJ/mol} \]
Representative CFC Model Results

Model Input: \( V_{\text{cell}} = 0.7 \, \text{V}, \quad h = 5 \, \text{cm}, \quad \text{tube spacing} = 5 \, \text{cm} \)
Predicted Carbon Fuel Cell Performance

Model Predictions

- Independent variables: carbon bed height, freeboard height, tube spacing, extent of anode recirculation and the cell voltage.
- Calculated output: power density and cell efficiency

\[
\begin{align*}
P &= \frac{V_{\text{cell}}}{A} \int j \, dA \\
\eta_{\text{cell}} &= \frac{PA}{\dot{m}_{\text{char}}HHV_{\text{char}}}
\end{align*}
\]

Power density as a function of bed height and tube spacing at a fixed cell voltage of 0.7 V

Cell efficiency as a function of bed height and tube spacing at a fixed cell voltage of 0.7 V
Modeling: Modifications for Hydrogen

Coal contains hydrogen
A representation of bituminous coal structure

Dry gasification
Hydrogen is a major gasification product
Dry gasification of Wyodak Coal at 900 °C

<table>
<thead>
<tr>
<th>Species</th>
<th>mole percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>40.56</td>
</tr>
<tr>
<td>CO₂</td>
<td>25.34</td>
</tr>
<tr>
<td>H₂</td>
<td>18.84</td>
</tr>
<tr>
<td>H₂O</td>
<td>15.04</td>
</tr>
<tr>
<td>H₂S</td>
<td>0.0556</td>
</tr>
<tr>
<td>SO₂</td>
<td>6.59E-07</td>
</tr>
<tr>
<td>HCl</td>
<td>1.24E-03</td>
</tr>
<tr>
<td>Cl₂</td>
<td>6.94E-17</td>
</tr>
<tr>
<td>O₂</td>
<td>3.22E-15</td>
</tr>
<tr>
<td>N₂</td>
<td>0.148</td>
</tr>
<tr>
<td>NH₃</td>
<td>6.93E-05</td>
</tr>
<tr>
<td>COS</td>
<td>3.37E-03</td>
</tr>
<tr>
<td>CH₄</td>
<td>1.26E-03</td>
</tr>
</tbody>
</table>

Our carbon fuel cell model needed to be modified to account for hydrogen in the coal and biomass.
H₂ Electrochemistry

 Voltammetry

 T Dependence

 P H₂ Dependence

 H₂ Oxidation Mechanism¹

 R1: \( \text{H}_2(g) + 2(\text{Ni}) \leftrightarrow 2\text{H(Ni)} \)

 R2: \( \text{H(Ni)} + \text{O}^2-(\text{YSZ}) \leftrightarrow (\text{Ni}) + \text{OH}^-_{\text{YSZ}} + \text{e}^-(\text{Ni}) \)

 R3: \( \text{H(Ni)} + \text{OH}^-_{\text{YSZ}} \leftrightarrow (\text{Ni}) + \text{H}_2\text{O}_{\text{YSZ}} + \text{e}^-(\text{Ni}) \)

 R4: \( \text{H}_2\text{O}_{\text{YSZ}} \leftrightarrow \text{H}_2\text{O}_g + (\text{Ni}) \)

 R5: \( \text{O}^*(\text{YSZ}) + (\text{YSZ}) \leftrightarrow \text{O}^{2-}(\text{YSZ}) + V_{O^{\bullet\bullet}}(\text{YSZ}) \)

 EIS

 T Dependence

 P H₂ Dependence

Syngas Electrochemistry

T Dependence  Concentration Dependence  Predicting Syngas OCV

Voltage Dependence

Theoretical justification for this empirical finding is needed.
Concluding Remarks

**Coupled Fuel Cell**
Air/carbon and steam/carbon fuel cells can be coupled so as to produce both $H_2$ and electricity, simultaneously.

**Sulfur Sorbents**
CaO, SrO and BaO can reduce $H_2S$ and COS concentrations in syngas to below 10 ppm permitting improved fuel cell performance but cell lifetime is not appreciably extended.

**Sulfur Tolerant Anodes**
Lanthanum, barium and strontium doped titanates have been synthesized that have the potential to be sulfur tolerant anodes with excellent CO oxidation capabilities.

**Fuel Cell Modeling**
Hydrogen in the coal (or biomass) must be taken into accounted for accurate predictions of fuel cell performance. Both CO and $H_2$ are oxidized electrochemically at the anodic surfaces of the SOFC.
Concluding Remarks

Thank you for your attention.

Questions?