Novel Fuel Cells for Coal Based Systems

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Thomas Tao, presenter, CellTech Power
3 Generations of LTA-SOFC Development


Gen 1: “Bubbling Anode”
First Coal

Gen 2: “Internal separator”

Gen 3.0: “Reverse Anode”

Gen 3.1: Direct JP-8

Gen 3.2 &: Stack

Direct coal & biomass

DSO

CERDEC

DOE, EPRI

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Fuel Cells for Real Fuels
LTA-SOFC: Characteristics

Voltage Threshold 0.78V @1,000°C, Hydrogen, Gen 3.1 LTA-SOFC
Direct Coal Power Using Liquid Tin Anode

SOFC

Sn(l) + 2 O²⁻ = SnO₂ + 4 e⁻
SnO₂ + C(s) = 2 CO₂(g) + Sn
All Forms of Coal Will Make Soot - damage to Ni anode SOFC
Liquid Tin Anode Fuel Cell Direct Coal – 3 Alternative Configurations

**Electrochemical Looping**
Based on Coal-Tin Reactor
DE-NT0004111, DE-ER85006

1. Oxygen ions extracted from air by cathode and cross the electrolyte
2. Ions react with tin, releasing electrons and forming tin oxide
3. Tin oxide is independently reduced back to tin by reaction with fuel
4. Fuel directly contacts tin

**Insitu Gasifier**
Based on Portable Power Cell
DE-ER95350S10

1. Oxygen ions extracted from air by cathode and cross the electrolyte
2. Ions react with tin, releasing electrons and forming tin oxide
3. Tin oxide is independently reduced back to tin by reaction with fuel
4. Tin-fuel interaction can occur inside tin or across a porous ceramic membrane
5. Coal or other solid fuel is gasified insitu by the cell reaction products

**External Gasifier**
Based on Portable Power Cell

1. Oxygen ions extracted from air by cathode and cross the electrolyte
2. Ions react with tin, releasing electrons and forming tin oxide
3. Tin oxide is independently reduced back to tin by reaction with fuel
4. Tin-fuel interaction occurs across a porous ceramic membrane

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LTA- SOFC Electrochemical Looping - Tin Bath Concept for MW coal plant

- Separates fuel cleaning and reaction gases from Power Production module.
- Direct Coal-biomass feed into anode
- Tubular configuration without ceramic porous separator
- Carbon dioxide sequestration

LTA Cell Array

Cleaning

Tin

Tin Oxide

Power

Ash

SO₂

CO₂
LTA-SOFC Coal Tin Bath Power Plant Concept

High-Level PFD of LTASOFC with CCS

Most thoroughly analyzed concept to-date
- 63% System efficiency with CO2 capture and compression
- System CAPEX: $1400 – 2400/kW (similar to IGCF)
- Near 100% CO2 capture

- Tin provides separation of ash/impurities
- Requires development of Tin Coal Reactor similar to liquid metal gasifiers
- High tin recirculation rate required to meet O2 transport requirements.
- Tin anode requires electric current break
LTA-SOFC Coal Tin Bath System Cost Estimate

Preliminary System Cost Structure (2007 $)

- LTASOFC
- IGFC

Cost breakdown:
- Fuel Cell
- TCR or Gasifier
- Steam Cycle
- ASU
- Gas Clean-Up
- Other

Cost in $/kW:
- LTASOFC
- IGFC
LTA-SOFC In-situ Gasification Concept

- Tubular same as current Gen 3 cells
- Tin anode contained by porous ceramic separator and electrolyte

Direct Fuel Conversion through internal gasification

Coal → Gasification Section → Ash

Cathode Air

Gen 3.X LTA-SOFC Gas Phase

Separator
Liq Tin (500 micron)
Electrolyte Cathode

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LTA-SOFC In-situ Gasification Concept

- Uses cells with porous separator like existing CellTech Gen 3
  - No direct contact between tin anode and solid fuel.
  - Gasification is driven by CO₂ and H₂O produced by cells (no Oxy plant required).
  - Isolated anodes allow cell voltage build up.
  - Ash, tar and carbon clogging of separator could be an issue.
  - Volatile metal oxides in coal impact on cells unknown.
  - Could test concept with Gen 3.1 cells and lab gasifier.
  - Cathode air flow may increase to remove cell heat load.
LTA-SOFC Gen 3 for direct coal
Gasification cell using porous separator

\[
\text{SnO}_2 + 2\text{CO} = \text{Sn} + 2\text{CO}_2 \\
\text{SnO}_2 + 2\text{H}_2 = \text{Sn} + 2\text{H}_2\text{O}
\]

\[
2\text{O}^- + \text{Sn} = \text{SnO}_2 + 4\text{e}^- 
\]

\[
\text{H}_2\text{O}, \text{CO}_2 
\]

\[
\text{SnO}_2, \text{SnO}_2 
\]

\[
\text{H}_2\text{CO} 
\]

\[
\text{O}_2 + 4\text{e}^- = 2\text{O}^- 
\]

CellTech Power
Fuel Cells for Real Fuels
LTA-SOFC External Gasification Concept

- Tubular same as current Gen 3 cells
- Tin anode contained by porous ceramic separator and electrolyte
- Direct Fuel Conversion through internal gasification

Uses cells with porous separator like existing CellTech Gen 3
- Compatible with existing gasifiers
- Reduced gas clean-up (Sulfur, CO)
- Lowest efficiency

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Fuel Cells for Real Fuels
Issues related to coal impurity

- Impact on liquid tin anode
- Impact on electrolyte
- Impact on other cell components
Fuel Impurity Impact on Liquid Tin Anode

- Molten tin fluid state: Structure or surface cannot be damaged by contamination
- Gravimetric separation of ash from molten tin
- Addition of tin during plant operation is feasible and loss of tin not an issue: tin compounds of sulfur and halogens, volatile tin monoxide, volatile residual tin in ash

Evaluating fuel impurity impact on tin is a lesser issue
Coal Impurity Impact on Electrolyte

- Yttria stabilized zirconia and phase destruction
- Modeling for zirconia phase stability
- Predictor for harmful elements and their list
Impurity Impact on Electrolyte

Yttria stabilized zirconia and phase destruction

- Yttria stabilized zirconia
  - Tetragonal - low yttria, partially stabilized
  - Cubic - high yttria, fully stabilized

- Phase destruction
  Yttrium was displaced by higher CE elements and migrated to grain boundary

- Exposed to Mo oxides, YSZ cracked
- SEM/EDAX
  Indicating yttria migrating to grain boundary
SnO$_2$ reduction by coal - setup

Experimental concept for the chemical reactor that operates at 1000°C to separate the pre-charged mixture of coal and tin dioxide into tin and slag with a vented gas.

Coal contaminants with potential to harm ZrO$_2$ based electrolyte: Arsenic, Chromium, Molybdenum, Manganese, Uranium, Niobium, Selenium, Vanadium, Tantalum, Tellurium and Tungsten
Impurities found in Sn from SnO\textsubscript{2} reduction by coal (US Wyoming)

Ranking of soluble elements in molten tin based on their Gibbs free energy (Nernst Potential)

Only those elements in coal with Nernst Potential less than 0.9 V were found in tin (sample S5)

<table>
<thead>
<tr>
<th>Element</th>
<th>S5 Concentration (ppm wt)</th>
<th>Oxide, valance at highest or stable</th>
<th>Nernst Potential @1,000°C</th>
<th>Coulombic Energy CE</th>
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<tbody>
<tr>
<td>Ag</td>
<td>1.1</td>
<td>1</td>
<td>-0.24</td>
<td>0.16</td>
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<tr>
<td>Se</td>
<td>&lt; 0.01</td>
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<td>-0.2</td>
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<td>Rh</td>
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<td>0.06</td>
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<td>0.34</td>
<td>1.96</td>
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<td>Cu</td>
<td>29</td>
<td>1</td>
<td>0.39</td>
<td>0.23</td>
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<tr>
<td>Bi</td>
<td>13</td>
<td>3</td>
<td>0.4</td>
<td>0.52</td>
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<tr>
<td>Pb</td>
<td>150</td>
<td>2</td>
<td>0.49</td>
<td>0.3</td>
</tr>
<tr>
<td>Te</td>
<td>&lt; 0.1</td>
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<td>0.56</td>
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<tr>
<td>Ni</td>
<td>2.9</td>
<td>2</td>
<td>0.65</td>
<td>0.52</td>
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<tr>
<td>Sb</td>
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<td>0.66</td>
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<td>Cd</td>
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<tr>
<td>Co</td>
<td>0.28</td>
<td>2</td>
<td>0.75</td>
<td>0.55</td>
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<tr>
<td>S</td>
<td>23</td>
<td>4</td>
<td>0.75</td>
<td>1.95</td>
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<tr>
<td>Sn Matrix</td>
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<td>4</td>
<td>0.82</td>
<td>1.04</td>
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<tr>
<td>Fe</td>
<td>51</td>
<td>3</td>
<td>0.85</td>
<td>0.98</td>
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<tr>
<td>Ge</td>
<td>&lt; 0.01</td>
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<td>0.87</td>
<td>1.36</td>
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<td>In</td>
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<td>0.89</td>
<td>0.67</td>
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<td>W</td>
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<td>1.8</td>
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<tr>
<td>Mo</td>
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<tr>
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<td>1.01</td>
<td>0.13</td>
</tr>
<tr>
<td>Cr</td>
<td>&lt; 0.005</td>
<td>4</td>
<td>1.07</td>
<td>1.31</td>
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<tr>
<td>V</td>
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<td>5</td>
<td>1.07</td>
<td>1.67</td>
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<tr>
<td>Mn</td>
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<td>3</td>
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<td>0.93</td>
</tr>
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<td>0.87</td>
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<td>1.27</td>
<td>0.18</td>
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<td>5</td>
<td>1.4</td>
<td>1.41</td>
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<tr>
<td>Ta</td>
<td>&lt; 5</td>
<td>5</td>
<td>1.55</td>
<td>1.41</td>
</tr>
<tr>
<td>U</td>
<td>&lt; 0.005</td>
<td>6</td>
<td>1.55</td>
<td>1.48</td>
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<tr>
<td>Si</td>
<td>&lt; 0.01</td>
<td>4</td>
<td>1.77</td>
<td>1.8</td>
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<tr>
<td>Ti</td>
<td>&lt; 0.005</td>
<td>4</td>
<td>1.85</td>
<td>1.18</td>
</tr>
<tr>
<td>Al</td>
<td>&lt; 0.05</td>
<td>3</td>
<td>2.2</td>
<td>1</td>
</tr>
<tr>
<td>Zr</td>
<td>&lt; 0.005</td>
<td>4</td>
<td>2.22</td>
<td>1</td>
</tr>
<tr>
<td>Li</td>
<td>&lt; 0.005</td>
<td>1</td>
<td>2.23</td>
<td>0.24</td>
</tr>
<tr>
<td>Mg</td>
<td>&lt; 0.01</td>
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<td>2.39</td>
<td>0.47</td>
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<tr>
<td>Sr</td>
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<tr>
<td>Be</td>
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<td>2.51</td>
<td>0.8</td>
</tr>
<tr>
<td>Ca</td>
<td>&lt; 0.01</td>
<td>2</td>
<td>2.6</td>
<td>0.36</td>
</tr>
<tr>
<td>Sc</td>
<td>&lt; 0.005</td>
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<td>2.65</td>
<td>0.72</td>
</tr>
<tr>
<td>Y</td>
<td>&lt; 0.001</td>
<td>3</td>
<td>2.66</td>
<td>0.6</td>
</tr>
<tr>
<td>Tl</td>
<td>0.04</td>
<td>3</td>
<td>&lt;0.9</td>
<td>0.61</td>
</tr>
</tbody>
</table>
Potential Coal Contaminant Solubility in Tin at condition of tin-coal reactor

<table>
<thead>
<tr>
<th>Spiked Element</th>
<th>Initial amount (ppm wt)</th>
<th>ICP-OES Results (ppm wt)</th>
<th>Pure Sn GDMS results (ppm wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>4000</td>
<td>1098</td>
<td>2.7</td>
</tr>
<tr>
<td>V</td>
<td>4000</td>
<td>10</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>Mo</td>
<td>4000</td>
<td>9</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>Nb</td>
<td>4000</td>
<td>115</td>
<td>&lt; 0.005</td>
</tr>
<tr>
<td>As</td>
<td>4000</td>
<td>2535</td>
<td>1</td>
</tr>
<tr>
<td>Mn</td>
<td>4000</td>
<td>2405</td>
<td>0.2</td>
</tr>
<tr>
<td>W</td>
<td>4000</td>
<td>60</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>Ta</td>
<td>4000</td>
<td>8</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>Se</td>
<td>4000</td>
<td>44.7</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>Cl</td>
<td>4000</td>
<td></td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>S</td>
<td>4000</td>
<td>8</td>
<td>0.07</td>
</tr>
<tr>
<td>P</td>
<td>4000</td>
<td>203</td>
<td>0.08</td>
</tr>
<tr>
<td>Si</td>
<td>4000</td>
<td>5</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>Br</td>
<td>4000</td>
<td></td>
<td>&lt; 0.05</td>
</tr>
<tr>
<td>I</td>
<td>4000</td>
<td></td>
<td>&lt; 0.05</td>
</tr>
</tbody>
</table>

Solubility Experiment: tin spiked, 1,000°C, 1% H2O in H2, 5 hours, cooled

ICP-OES analysis results: including both dissolved and entrained

Results imply the maximum possible solubility of impurity in tin at coal-tin reactor condition
Electrochemical testing - setup

Setup:
Gen 3.1 cell
Hydrogen as fuel

Tin spiked with potential coal contaminants such as V, As, Ta, Ti, Mo, Nb, P, Cl, Si, Na and Cr, etc.
Potential Coal Contaminant Impact on LTA-SOFC

LTA-SOFC Performance with Contaminant Spiked into Tin
Constant Current = 4.8 amp @ 3% H₂O in H₂

<table>
<thead>
<tr>
<th>Element</th>
<th>ppm</th>
<th>Time (hrs)</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta</td>
<td>8</td>
<td>100</td>
<td>2.1</td>
</tr>
<tr>
<td>V</td>
<td>10</td>
<td>66</td>
<td>9.6</td>
</tr>
<tr>
<td>Nb</td>
<td>115</td>
<td>100</td>
<td>34.4</td>
</tr>
<tr>
<td>Cr</td>
<td>1098</td>
<td>24</td>
<td>12.9</td>
</tr>
</tbody>
</table>

Percent Voltage Drop at end of Test

Testing conditions:
Gen 3.1 LTA-SOFC cells
Tin individually spiked to the maximum possible concentration
Constant current 4.8 amp @ 3% H₂O in H₂
LTA-SOFC Gen 3.1 cell collectively spiked with V, As, Nb, Mo and Cr to 1,500ppm

Post Mortem analysis:

Electrolyte damage found

Oxide crystals of Cr, V found on YSZ surface
Summary

Demonstration of Feasibility of Liquid Tin Anode SOFC as Direct Coal Conversion Fuel Cell

- Three liquid tin anode configuration concepts for direct coal conversion
- Fuel impurities cause degradation / damage to electrochemical component
- Tin’s potential as a media for removing or reducing fuel contaminants including from coal, biomass and diesel
- Ongoing projects in progress to address individual contaminant and coal ash
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NSF IIP-1013755, Dr. Anthony Walters
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DOD DARPA-DSO/ARMY Contract W911NF-07-C-0032, Dr. Valerie Browning
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DOD ARL/CERDEC Contract W911NF-08-1-0115, Dr. Rob Mantz
DOD ONR contract N00014-08-1-0962, Dr. Michele Anderson
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DOD ARL, contract W911NF-09-C-0165, Dr. Rob Mantz

CellTech Team:
Thomas Tao, Jeff Bentley, Mark Koslowske, Linda Bateman,
Mike Slaney, Zena Uzep, Jonathan Brodie