Material Challenges in High Temperature Processes for Hydrogen Production

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Hydrogen production using nuclear energy is a clean and promising technology to decrease CO₂-emissions. Potential advantages compared to water electrolysis are:
- high efficiency and reduced electricity requirement,
- inexpensive materials.

Electrolysis and thermo-chemical processes:

\[ \text{H}_2\text{O}(g) \rightarrow \frac{1}{2} \text{O}_2(g) + \text{H}_2(g) \]

Co-electrolysis:

\[ \text{H}_2\text{O}(g) + \text{CO}_2(g) \rightarrow \text{O}_2(g) + \text{H}_2(g) + \text{CO}_2(g) \]
Goal

- Enable durable, efficient, cost-competitive, clean hydrogen production technologies.

Outline

- Nuclear hydrogen production technologies
- High temperature steam electrolysis (HTSE)
- Challenges, and fundamental research in:
  - degradation mechanisms of the present devices
  - interfaces for higher-efficiency in the materials
- Concluding remarks
## Nuclear hydrogen production processes

- Research and development in the Nuclear Hydrogen Initiative (NHI) of DOE-NE on a range of hydrogen production technologies that can be supported by nuclear energy.

<table>
<thead>
<tr>
<th>Temperature range</th>
<th>Low (RT)</th>
<th>Intermediate (500-700°C)</th>
<th>High (&gt;800°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermo-chemical</td>
<td>Copper-Chlorine</td>
<td>Sulfur-Iodine</td>
<td></td>
</tr>
<tr>
<td>Hybrid (Themo-electro-chemical)</td>
<td>Calcium-Bromine</td>
<td>Hybrid-Sulfur</td>
<td></td>
</tr>
<tr>
<td>Electrochemical</td>
<td>Water electrolysis</td>
<td>Steam electrolysis</td>
<td>Steam electrolysis</td>
</tr>
</tbody>
</table>
Sulfur-Iodine (SI) Process

- **Purpose:** Splitting the H$_2$O into H$_2$ and O$_2$ using catalysis at lower temperatures than pyrolysis.
- **SI cycle,** with maximum temperature above 850°C, using the thermal energy from the nuclear reactor

**Sulfur-Iodine Thermochemical Water-Splitting Cycle**

\[
2\text{H}_2\text{O} + \text{I}_2 + \text{SO}_2 \rightarrow 2\text{HI} + \text{H}_2\text{SO}_4
\]

\[
\text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{SO}_2 + \frac{1}{2} \text{O}_2
\]

\[
2\text{HI} \rightarrow \text{I}_2 + \text{H}_2
\]
Hybrid-Sulfur (Hy-S) Cycle

- Purpose: eliminating some of the corrosive chemical steps from the thermochemical SI cycle
- Hy-S, with maximum temperature above 850°C, using the thermal and the electrical energy from the nuclear plant.

Hybrid-Sulfur Water-Splitting Cycle

\[ 2\text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2 \text{ (El.)} \]

\[ \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{SO}_2 + \frac{1}{2} \text{O}_2 \]
High Temperature Steam Electrolysis (HTSE)

- Purpose: To split steam, $H_2O_{(g)}$, electrochemically while spending $>30\%$ less electrical energy than water electrolysis.
- HTSE, with maximum temperature at $830^\circ C$, using the thermal and the electrical energy from the nuclear plant.

\[
H_2O_{(g)} \rightarrow H_2(g) + \frac{1}{2} O_2(g)
\]

-Largest amount of hydrogen production rate, and the longest duration of operation demonstrated within the NHI program.
High temperature steam electrolysis (HTSE)

- HTSE uses a solid oxide electrolysis cell (SOEC).
  - Materials are conducting ceramic oxides.
  - Device is based on the solid oxide fuel cells (SOFC).
- Cells are “stacked” together in series for power management.

Solid oxide electrolysis cell, SOEC

- Dense Electrolyte: \((\text{Y}_2\text{O}_3-\text{ZrO}_2, \text{YSZ})\)
- Porous Anode: \((\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3 \text{composite})\)
- Porous Cathode: \((\text{Ni-YSZ})\)

Electrolysis reaction:

\[
\text{H}_2\text{O} (l) + 4\text{e}^- \rightarrow \text{H}_2 (g) + 2\text{O}^= \]

Oxygen transfer:

- Oxygen ions move through the electrolyte.
- Oxygen gas is produced at the cathode.
- Water is produced at the anode.
Long-term performance of present HTSE

- >1200 NL/hr of H₂ production was demonstrated by Ceramatec & INL with a dual stack module for 2000 hrs.

Dual-stack SOEC module


Degradation of the present SOEC stack performance is the outstanding problem.
# Degradation mechanisms in SOECs

<table>
<thead>
<tr>
<th><strong>High-level Problem</strong></th>
<th><strong>Specific Questions on:</strong></th>
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</thead>
<tbody>
<tr>
<td>Cr-poisoning, in the oxygen electrode (Cr is coming from the interconnect)</td>
<td>• Distribution and reaction species with Cr</td>
</tr>
<tr>
<td></td>
<td>• Getter agents for Cr to avoid its entry to the electrode.</td>
</tr>
<tr>
<td>Electrode – electrolyte interface delamination, in the oxygen electrode</td>
<td>• Interface mechanical/adhesion stability against high flux of oxygen evolution</td>
</tr>
<tr>
<td></td>
<td>• Interface chemical stability (interdiffusion)</td>
</tr>
<tr>
<td></td>
<td>• Secondary blocking phase (zirconate) formation</td>
</tr>
<tr>
<td>Decomposition / interdiffusion of cations at the interfaces, of the oxygen electrode</td>
<td>• Between cobaltite-manganite layers</td>
</tr>
<tr>
<td></td>
<td>• At manganite-zirconia particles</td>
</tr>
<tr>
<td></td>
<td>• Decreasing electrical conductance of cobaltite due to decomposition</td>
</tr>
<tr>
<td>Si-poisoning on the hydrogen/steam electrode (Si is coming from the cell seals)</td>
<td>• Distribution and reaction species with Si</td>
</tr>
<tr>
<td></td>
<td>• Specific position - on Ni or on Ni-zirconia interfaces.</td>
</tr>
<tr>
<td></td>
<td>• Electrochemical nature where Si gets deposited.</td>
</tr>
</tbody>
</table>
Cr-contamination in oxygen electrode

- Cr fluorescence spectra on the oxygen electrode showed presence of Cr in the bond-layer at ~10v%.
  - A large loss of active surface area

- The pre-edge peak shows evidence of Cr$^{6+}$ near the center of the electrode ➔ Multiple Cr-reaction species
  - Cr transport mechanism – solid state diffusion? Volatilization?
Delamination between electrode and electrolyte

- Reasons for deformation at the electrode/electrolyte interface
  - Secondary phase formation with high lattice- and thermal-mismatch
  - Steam-leak leading to reduction and decomposition of the manganite

- Tools to probe the reasons of deformation
  - High-resolution electron microscopy; in diffraction and spectroscopy
  - High-resolution Auger electron spectroscopy
Avoiding degradation in SOECs

- **Goal: ensure the chemical stability**
  - At the electrode/interconnect interface
    - Protective coating on the interconnect to decrease Cr loss.
  - At the electrode/electrolyte interface
    - Composition gradient, with A-site deficiency, to avoid zirconate formation
    - Thin-film protective interlayer, ceria, to avoid interaction of the electrode material with the zirconia electrolyte.

- Fundamental understanding of the degradation mechanisms in SOECs are leading to *evolutionary improvements* in the HTSE performance within the existing framework of materials, device design, and operating temperature (>800°C).
There is the need to reduce the operating temperature for prolonged life-time, and thus reduced cost.

Reduced temperature can allow the use of a wider range of nuclear reactors for supporting the SOECs.

At lower temperatures, major source of energy loss is poor performance of the $O_2$-electrode.

Goal:

- **Revolutionary advances** in electrode materials (structures and compositions) for higher efficiency in $H_2$ production at intermediate temperatures (500-700°C).
Limiting reactions and pathways in oxygen electrode

Overall oxygen reaction (OR): $O_2 \leftrightarrow \frac{1}{2}O_2 + 2e^- + Vo^-$

For $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ at a micro-scale

At high temperature: limited by surface charge transfer – external interface
At low temperatures: limited by bulk transport – internal interfaces
Opportunity for intermediate temperature SOECs

Opportunity for improving the transport properties through the understanding and tailoring of the interfaces:

- structural and chemical nature
Importance of interface structure

- Dense thin-film electrodes
  - Fabricated by pulsed laser deposition.
  - Electrolyte substrate: (100) single-crystal YSZ.

Comparison of epitaxial and non-epitaxial LSM

LSM: Epitaxial (110)  
LSM: No epitaxy, textured

Structure of the surface and the grain boundaries is important.

Characterization of the electrode surface

- **In situ x-ray characterization** of the oxygen electrode materials
- X-ray absorption spectroscopy: oxidation state, atomic environment
  - Grazing incidence-angle scattering geometry for surface sensitivity
- Set-up, *a first*, shown here at the Advanced Photon Source.

→ The change in the chemical state of the A-site cations is occurring at the surface, associated with the improvement of the electrode.

La $L_{III}$ edge XANES for $La_{0.8}Sr_{0.2}MnO_3$ anodic polarization at 700°C.

Interf...s in oxygen electrocatalysis

Electrode (La_{0.8}Sr_{0.2}MnO_3)
Electrolyte Y_2O_3 - ZrO_2

Conductivity Enhancement

- Obtain fundamental level knowledge about the layer/grain size-effect:
  - Chemical, physical, and structural properties of the electrode interfaces
    - Defect chemistry
    - Strain state

Charge transport
Catalytic activity

Ionic conduction in CaF_2/BaF_2 nanoscale heterostructures, Sata et al., *Nature*, 408, 2000
Characterization of interface transport properties

- **Site-specific high-resolution microscopy and spectroscopy** is needed to characterize:
  - Important relationship between the defect chemistry and strain and the conductivity and catalytic activity at the interface and near-interface regions (while under polarization):

**Synthesis and nano-fabrication**

**Structure and defect chemistry**

**Transport and electronic structure**

Becker et al., *PRL*, **89**, 2002
Predictive modeling capability is needed for identifying the promising interface structures in a more efficient way.

- Close coupling with the experiments using model material systems.

Goal: Elucidating and predicting the transport properties

- First principles calculations:
  - formation energies for charged defects in a given interface configuration
  - Strain state of the interface

- Atomistic simulations
  - Charge transfer and transport properties at the interface

Multidisciplinary approach for studying the conducting interfaces

- With capabilities that we have and are developing at MIT, and with external collaborations:

**Phenomena**

- Thermodynamic equilibrium reconstructions near the interfaces
- Structure of the transition states
- Transport of oxygen, cations, and vacancies

**Experiments**

- Site-specificity, crystallography, microchemistry.
- Reaction energetics, chemical bonding, electronic structure; at surfaces and interfaces.
- Reaction pathways, diffusivities; on model, simple, clean microstructures.

**Modeling / Simulations**

- Electronic Structure:
  - Atomistic: Dynamic & static re-configuration.
  - Electronic Structure: Inter-atomic potentials, full electronic structures, formation energies.
- Atomistic: Reaction pathway & mechanism, diffusivity
- Mesoscale, continuum: Electrochemical response

With capabilities that we have and are developing at MIT, and with external collaborations:
Concluding remarks

- Nuclear energy can provide clean non-electric energy carriers.
- Hydrogen production processes at high temperature and corrosive environment have severe materials constraints.
- Degradation of materials for steam electrolysis must be mitigated.
- “Activity” and “degradation” are competing phenomena in determining the operating temperature of the SOECs.
- A fundamental understanding is needed for the important role of interfaces on the activity of the conducting materials for steam electrolysis electrodes, using advanced scientific characterization tools.
- A predictive capability is needed using advanced multiscale modeling and simulations.
Acknowledgements

- Drs. David Carter, Deborah Myers and Jennifer Mawdsley, ANL, for SOEC materials and degradation.
- Drs. Kee-Chul Chang and Hoydoo You, ANL, for in situ x-ray characterization of surfaces.
- Dr. Burc Misirlioglu, MIT, for transport at interfaces.
Internal / buried interface transport properties

- Important relationship between: the **phases and defect chemistry** and the **conductivity and catalytic activity at the interface** and near-interface regions (while under polarization):
  - Site-specific high-resolution microscopy and spectroscopy is needed.

Oxygen Incorporation Enhancement

- **Synthesis and nano-fabrication**
  - Nano-laminate heterolayers
  - Electrode
  - Trench

- **Transport and electronic structure**

- **Structure and defect chemistry**
  - 90° [010] tilt GB
  - 5 nm

Oxygen exchange profile using SIMS

Cr-Co-O particles found on the surface of the oxygen electrode bond coat

- Plan view of bond coat of a cell from the 2000 h stack
- X-ray diffraction revealed a spinel phase (AB$_2$O$_4$)
  - Cr:Co ~ 9:7 by EDS
- Cr-containing spinel also found using SEM and Raman spectroscopy in the 1000 h stack
  - Particles ~ 1 μm
  - Cr:Co ~ 2:3
## Comparison of Four Nuclear Hydrogen Technologies

<table>
<thead>
<tr>
<th>Hydrogen Production Process</th>
<th>Nuclear Reactor Type</th>
<th>Product Flexibility Hydrogen/Electricity?</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-pressure, low-temperature water electrolysis (HPE)</td>
<td>Advanced Light Water Reactor (ALWR)</td>
<td>Yes</td>
</tr>
<tr>
<td>High-temperature steam electrolysis (HTE)</td>
<td>High-Temperature Gas-Cooled Reactor (HTGR)</td>
<td>Yes</td>
</tr>
<tr>
<td>High-temperature sulfur-iodine cycle with extractive HI (SI)</td>
<td>High-Temperature Gas-Cooled Reactor (HTGR)</td>
<td>Pure hydrogen</td>
</tr>
<tr>
<td>Hybrid sulfur thermo-electro chemical (HyS)</td>
<td>High-Temperature Gas-Cooled Reactor (HTGR)</td>
<td>Fixed hydrogen and electricity production</td>
</tr>
</tbody>
</table>

Cost and performance assumptions based on information from Technology Insights (06, 07).

<table>
<thead>
<tr>
<th>Plant</th>
<th>Levelized Cost [$/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPE-ALWR</td>
<td>2.98</td>
</tr>
<tr>
<td>HTE-HTGR</td>
<td>2.93</td>
</tr>
<tr>
<td>SI-HTGR</td>
<td>3.26</td>
</tr>
<tr>
<td>HyS-HTGR</td>
<td>2.97</td>
</tr>
</tbody>
</table>
Plant Evaluations: Summary of Results

- **Price assumptions**
  - Average prices: Electricity 50 $/MWh, Hydrogen 3 $/kg
  - Price volatility: 0.12 (per year), GBM process
  - Hydrogen/electricity correlation: 0.5

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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>HPE-ALWR</td>
<td>No</td>
<td>17</td>
<td>1084</td>
<td>9.99</td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td>Yes</td>
<td>283</td>
<td>1078</td>
<td><strong>10.85</strong></td>
<td>69.2</td>
</tr>
<tr>
<td>HTE-HTGR</td>
<td>No</td>
<td>83</td>
<td>1183</td>
<td>9.80</td>
<td>100.0</td>
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<tr>
<td></td>
<td>Yes</td>
<td><strong>295</strong></td>
<td>1170</td>
<td>10.52</td>
<td>82.4</td>
</tr>
<tr>
<td>SI-HTGR</td>
<td>No</td>
<td>-348</td>
<td>1249</td>
<td>8.89</td>
<td>100.0</td>
</tr>
<tr>
<td>HyS-HTGR</td>
<td>No</td>
<td>19</td>
<td>841</td>
<td>9.72</td>
<td>100.0</td>
</tr>
</tbody>
</table>

- With current cost and performance estimates, the flexible electrochemical technologies (HPE-HTGR and HPE-ALWR) are the most profitable
  - Hydrogen remains the main product for these plants, but they switch to electricity production a substantial amount of time