Stability of Materials in High Temperature Water Vapor: SOFC Applications

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Solid oxide fuel cell material systems require long term stability in environments containing high-temperature water vapor. Many materials in fuel cell systems react with high-temperature water vapor to form volatile hydroxides which can degrade cell performance. In this paper, experimental methods to characterize these volatility reactions including the transpiration technique, thermogravimetric analysis, and high pressure mass spectrometry are reviewed. Experimentally determined data for chromia, silica, and alumina volatility are presented. In addition, data from the literature for the stability of other materials important in fuel cell systems are reviewed. Finally, methods for predicting material recession due to volatilization reactions are described.
Stability of Materials in High Temperature Water Vapor: SOFC Applications

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Motivation

• Materials in SOFC applications require stability for 10,000 to 100,000 h for desired cell operating performance
• High temperature water vapor is present on both anode and cathode sides of the cell
• Many gaseous metal hydroxide species are thermodynamically stable
• Formation of gaseous metal hydroxides can lead to consumption of thin layers of material and/or transport of metal species to other locations – poisoning cell operation
• Thermodynamic data for gaseous metal hydroxide stability are needed to predict cell degradation
Outline

• Thermodynamics of gaseous metal hydroxide formation

• Experimental techniques for determination of thermodynamic data of gaseous metal hydroxide formation

• NASA GRC experimental determination of thermodynamic stability for Cr$_2$O$_3$, SiO$_2$, and Al$_2$O$_3$ in high temperature water vapor

• Literature review and prediction of thermodynamic stability of Ni, CoO, SrO, CaO, La$_2$O$_3$, MnO, Pd, Pt

• Kinetics of volatilization limited by transport through laminar gaseous boundary layer
Thermodynamics of Gaseous Metal Hydroxide Formation

Generic reaction:
MO$_x$ + nH$_2$O(g) + mO$_2$(g) + qH$_2$(g) = MO$_{(x+n+2m)}$H$_{(2n+q)}$(g)

Model SOFC environments
Anode side: H$_2$O(g) + H$_2$(g)
Cathode side: H$_2$O(g) + O$_2$(g)

Pressure dependence: $P_{MOH} = K_{eq} P_{H2O}^n P_{O2}^m P_{H2}^q$

SiO$_2$ + 2H$_2$O(g) = Si(OH)$_4$(g)
$\frac{1}{2}$ Cr$_2$O$_3$ + H$_2$O(g) + $\frac{3}{4}$ O$_2$(g) = CrO$_2$(OH)$_2$(g)
Ni + 2H$_2$O(g) = Ni(OH)$_2$(g) + H$_2$(g)

Temperature dependence: $K_{eq} = \exp\left(-\frac{\Delta G}{RT}\right) = \exp\left(-\frac{\Delta H - T\Delta S}{RT}\right)$

<table>
<thead>
<tr>
<th>MOH(g)</th>
<th>n</th>
<th>m</th>
<th>q</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(OH)$_4$</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CrO$_2$(OH)$_2$</td>
<td>1</td>
<td>3/4</td>
<td>0</td>
</tr>
<tr>
<td>Ni(OH)$_2$</td>
<td>2</td>
<td>0</td>
<td>-1</td>
</tr>
</tbody>
</table>
Experimental techniques for determination of thermodynamic data of gaseous metal hydroxide formation

- Mass spectrometry
  - Knudsen Effusion Mass Spectrometry (KEMS)
  - High Pressure Free Jet Expansion MS
- Transpiration
- Thermogravimetric Analysis (TGA)
- Flame Spectroscopy
Knudsen Effusion Mass Spectrometry (KEMS)

- Magnetic sector analysis - accurate data
- High vacuum process
- Low water vapor partial pressures (<10^{-5} bar), therefore not representative of SOFC conditions
- Data available in literature:
  - Si-O-H(g)
  - Mn-O-H(g)
  - Pd-O(g)

High Pressure Free Jet Expansion Mass Spectrometry (HPMS)
High Pressure Free Jet Expansion Mass Spectrometry (HPMS)

- Quadrupole analysis – quantitative data difficult
- 1 bar sampling system
- Water vapor partial pressures possible near 1 bar - representative of SOFC conditions
- Data available in literature:
  - Si-O-H(g)
  - Cr-O-H(g)

Free jet sampling mass spectrometric identification of Si(OH)₄(g) from the reaction of SiO₂ + H₂O(g)
The Transpiration Technique
The Transpiration Technique

- Volatile species identified indirectly from pressure dependence
- Accurate pressure and temperature dependence of volatilization reaction is possible
- Water vapor partial pressures 0.1 to 1 bar - representative of SOFC conditions
- Data available in literature:
  - Ni-O-H(g) and Co-O-H(g)
  - Si-O-H(g)
  - Ca-O-H(g)
  - Cr-O-H(g)
Thermogravimetric Analysis (TGA)
Thermogravimetric analysis

- Gas boundary layer characteristics affect volatilization rate
  - Must have well defined gas flow over sample
  - Equilibrium partial pressures of gaseous metal hydroxide calculated from weight loss assuming volatilization is limited by gaseous transport through laminar gas boundary layer
- Volatile species identified indirectly from pressure dependence
- Accurate pressure and temperature dependence of volatilization reaction is possible
- Water vapor partial pressures 0.1 to 1 bar - representative of SOFC conditions
- Data available in literature: Al-O-H(g)
The Cr-O-H system

- **Cr₂O₃ in SOFC**
  - Oxide thermally grown on low temperature interconnects
  - Component of La₁₋ₓMₓCrO₃ interconnect
- **Many Cr-O-H(g) vapor species**

The Cr-O-H system

• Primary vapor species in H₂O + O₂ environment

\[ \frac{1}{2} \text{Cr}_2\text{O}_3(s) + \frac{3}{4} \text{O}_2(g) = \text{CrO}_3(g) \]
\[ \frac{1}{2} \text{Cr}_2\text{O}_3(s) + \text{H}_2\text{O}(g) + \frac{3}{4} \text{O}_2(g) = \text{CrO}_2(\text{OH})_2(g) \]
\[ \frac{1}{2} \text{Cr}_2\text{O}_3(s) + \frac{1}{2} \text{H}_2\text{O}(g) + \frac{1}{2} \text{O}_2(g) = \text{CrO}_2(\text{OH})(g) \]

• Confirmation of volatile species identity from pressure dependent transpiration experiment at 600°C

Recent transpiration studies by Opila et al and Stanisłowski et al have resolved discrepancy in thermochemical data for \( \text{CrO}_2(\text{OH})_2(\text{g}) \) formation.

Data of Opila et al: \( \Delta H^\circ_r, \text{861K} = 53.5 \text{ kJ/mol}, \Delta S^\circ_r, \text{861K} = -45.6 \text{ J/K mol} \)
The Si-O-H system

- **SiO₂** in SOFC: constituent of sealing glasses
- Possible Si-O-H(g) vapor species and experimental method used for identification

\[
\begin{align*}
\text{SiO}_2(s) + 2 \text{H}_2\text{O}(g) &= \text{Si(OH)}_4(g) \\
\text{SiO}_2(s) + \text{H}_2\text{O}(g) &= \text{SiO(OH)}_2(g) \\
\text{SiO}_2(s) + \frac{1}{2} \text{H}_2\text{O}(g) &= \text{SiO(OH)}(g) + \frac{1}{4} \text{O}_2(g)
\end{align*}
\]

Transpiration\textsuperscript{1,2}, HPMS\textsuperscript{3}
KEMS\textsuperscript{4}
KEMS\textsuperscript{4}

Transpiration studies show pressure dependence consistent with Si(OH)_4(g) formation

The Si-O-H system

Temperature dependence for Si(OH)$_4$(g) formation is relatively weak.

$\text{SiO}_2 + 2 \text{H}_2\text{O}(g) = \text{Si(OH)}_4(g)$

$\Delta H^\circ(1200) = 54.6 \pm 2.7 \text{ kJ/mol}$

$\Delta S^\circ(1200) = -67.5 \pm 2.1 \text{ J/ K mol}$

The Al-O-H system

- Al$_2$O$_3$ in SOFC: constituent of sealing glasses, insulators, and/or gas delivery components
- Al-O-H(g) vapor species identified from pressure dependence of Al$_2$O$_3$ volatility in TGA experiments and transpiration experiments with calcium aluminate

\[
\text{Al}_2\text{O}_3 + \frac{3}{2} \text{H}_2\text{O}(g) = \text{Al(OH)}_3(g)
\]
Oxide volatility comparison

![Graph showing oxide volatility comparison](image-url)

- **CrO$_2$(OH)$_2$**
- **Si(OH)$_4$**
- **Al(OH)$_3$**

Log (Partial Pressure), atm vs. Temperature, °C

0.5 atm H$_2$O, 0.5 atm O$_2$
Review of thermodynamic data for materials important in SOFC systems

• Data base and literature review for M-O-H(g) data
• Data evaluation
  – Availability of data for M-O-H(g)
  – Method by which data were obtained
  – Completeness of data
  – Reliability of data
• Calculation of Ni, CoO, SrO, CaO, La$_2$O$_3$, MnO, Pd, Pt stability in model anode/cathode environments using FactSage free energy minimization program
  – Model anode environment: 1 bar 50% H$_2$O(g)/50% H$_2$(g)
  – Model cathode environment: 1 bar 50% H$_2$O(g)/50% O$_2$(g)
• Ranking/summary of volatility trends
Ni-O-H and Co-O-H systems

- Ni used in Ni/YSZ anode, Co found in interconnect alloys and CoO in coatings
- Ni-O-H vapor species include Ni(OH)$_2$, Ni(OH), NiH, Ni$_2$, NiO, and Ni
- Ni-O-H and Co-O-H systems studied by transpiration method in H$_2$, H$_2$O

\[
\text{CoO} + 0.5 \text{ bar } H_2 + 0.5 \text{ bar } H_2O(g) \quad \text{SGTE}
\]
\[
\text{Ni} + 0.5 \text{ bar } H_2 + 0.5 \text{ bar } H_2O(g) \quad \text{Fact}
\]

\[
\begin{align*}
\text{CoO} + H_2O(g) &= \text{Co(OH)}_2(g) \\
\text{Ni} + 2H_2O(g) &= \text{Ni(OH)}_2(g) + H_2(g)
\end{align*}
\]
Sr-O-H and Ca-O-H systems

- SrO found in LSM cathodes, CaO found in La$_{1-x}$Ca$_x$CrO$_{3-\delta}$ interconnects
- Sr-O-H vapor species include $\text{Sr(OH)}_2$, Sr(OH), SrH, Sr$_2$, SrO, Sr, and Sr$_2$O
- Ca-O-H vapor species include $\text{Ca(OH)}_2$, Ca(OH), CaH, Ca$_2$, CaO, and Ca
- Both systems studied by flame spectroscopy, Ca-O-H by transpiration

**Inputs:**
- $\text{SrO} + 0.5 \text{ bar } \text{O}_2 + 0.5 \text{ bar } \text{H}_2\text{O}(g)$  
  
- $\text{CaO} + 0.5 \text{ bar } \text{O}_2 + 0.5 \text{ bar } \text{H}_2\text{O}(g)$  

**Equations:**
- $\text{SrO} + \text{H}_2\text{O}(g) = \text{Sr(OH)}_2(g)$  
- $\text{CaO} + \text{H}_2\text{O}(g) = \text{Ca(OH)}_2(g)$
Activity of components in complex oxides

- CaO, Cr$_2$O$_3$, and La$_2$O$_3$ activities, $a(i)$, in La$_{1-x}$Ca$_x$CrO$_{3-\delta}$ interconnects can be reduced relative to pure oxides.

- Volatility will be correspondingly reduced

$$\text{Cr}_2\text{O}_3 + \text{H}_2\text{O}(g) + \frac{3}{4} \text{O}_2(g) = \text{CrO}_2(\text{OH})_2(g)$$

$$P_{\text{CrO}_2(\text{OH})_2} = K_{eq} a_{\text{Cr}_2\text{O}_3} P_{\text{H}_2\text{O}} P_{\text{O}_2}^{3/4}$$

- CrO$_2$(OH)$_2$(g) formation from La$_{1-x}$Ca$_x$CrO$_{3-\delta}$ (x=0 to 0.1) will be reduced by four orders of magnitude relative to pure Cr$_2$O$_3$

Thermodynamic activities of the components in La$_{1-x}$Ca$_x$CrO$_{3-d}$, x=0-0.21 at 2000K.

La-O-H system

- $\text{La}_2\text{O}_3$ is a component of LSM cathodes and $\text{La}_{1-x}\text{Ca}_x\text{CrO}_{3-\delta}$ interconnects
- La-O-H vapor species include $\text{La(OH)}_3$, $\text{La(OH)}_2$, $\text{La(OH)}$, $\text{La}_2$, $\text{LaO}$, $\text{La}$, $\text{La}_2\text{O}$, $\text{LaO}_2$, and $\text{La}_2\text{O}_2$
- Good review of La-O(g) system
- Origin of data for $\text{La(OH)}_3(g)$ unknown; $\text{La(OH)}_2(g)$ and $\text{La(OH)}(g)$ data estimated

Inputs:
$\text{La}_2\text{O}_3 + 0.5 \text{ bar O}_2 + 0.5 \text{ bar H}_2\text{O}(g)$  Fact

\[ \frac{1}{2} \text{La}_2\text{O}_3 + \frac{3}{2} \text{H}_2\text{O}(g) = \text{La(OH)}_3(g) \]
Mn-O-H system

- MnO is a component of LSM cathodes and oxide spinels formed/coated on metallic interconnects.
- Mn-O-H vapor species include \( \text{Mn(OH)}_2, \text{MnO(OH)}, \text{Mn(OH)}, \text{MnH}, \text{MnO}, \text{Mn}, \) and \( \text{MnO}_2 \).

\[
\begin{align*}
\text{MnO} + \text{H}_2\text{O}(g) &= \text{Mn(OH)}_2(g) \\
\text{MnO} + \text{H}_2\text{O}(g) &= \text{MnO(OH)} + \frac{1}{2} \text{H}_2(g)
\end{align*}
\]

Inputs:
\[
\text{MnO} + 0.5 \text{ bar } \text{H}_2 + 0.5 \text{ bar } \text{H}_2\text{O}(g)
\]

SGTE + Hildenbrand
Pd-O-H system

- Pd used as current collector
- Pd-O-H vapor species include \textbf{PdOH}, Pd, Pd(OH)$_2$, PdO, and PdO$_2$
- No experimental data for hydroxide vapor species, data are estimated
Pt-O-H system

- Pt used as current collector
- Pt-O-H vapor species include PtO$_2$, PtO, and Pt
- No data available for any hydroxide vapor species
- Experimental TGA results indicate that water vapor-Pt interactions are minimal

![Graph showing specific weight change (mg/cm$^2$) over time (h) for different conditions.](image)
Summary of equilibrium gaseous metal hydroxide partial pressures

500°C, 0.5 bar O₂, 0.5 bar H₂O

- Solid bars: good thermodynamic data
- Cross-hatched bars: thermodynamic data unreliable
- Gray cross-hatched bars: some experimental information about stability of gaseous metal hydroxides available, i.e Co(OH)₂(g), PtO₂(g)
Summary of equilibrium gaseous metal hydroxide partial pressures: temperature effects

500°C, 0.5 bar O₂, 0.5 bar H₂O

- Weak temperature dependence for CrO₂(OH)₂(g) and Si(OH)₄(g): minimal durability benefit by reducing temperature
- Stronger temperature dependence for other gaseous metal hydroxides
Summary of equilibrium gaseous metal hydroxide partial pressures: gas environment effects

500°C

- P(MOH) dependent only on P(H₂O) do not change: Si(OH)₄(g)
- P(MOH) dependent on P(O₂) and/or P(H₂) can change dramatically: CrO₂(OH)₂(g) → Cr(OH)₂(g)
- MO – condensed phase reaction with environment can affect P(MOH): Ni/NiO or Co/CoO/Co₃O₄
Kinetics of volatilization limited by transport through laminar gaseous boundary layer

\[ J = 0.664 \left( \frac{\rho' L}{\eta} \right)^{1/2} \left( \frac{\eta}{\rho' D} \right)^{1/3} \frac{D\rho}{L} \]

Applications to SOFC
• Assumes laminar flow
• Assumes flat plate geometry - relevant for planar cell
• Related expression needed for mass transport from tube wall in flowing gas for tubular SOFC components
• More complete model needed to account for gas transport in pores of active surfaces

\[
\begin{align*}
J & = \text{mass loss rate} \\
\rho' & = \text{boundary layer gas density} \propto P_{\text{total}} \\
D & = \text{interdiffusion coefficient} \propto 1/P_{\text{total}} \\
\rho & = \text{Si(OH)\textsubscript{4} gas density} \propto P_{\text{SiOH4}} \\
v & = \text{linear gas velocity} \\
\eta & = \text{gas viscosity} \\
L & = \text{characteristic length}
\end{align*}
\]
Summary and conclusions

- Experimental techniques are available for characterizing volatility of materials under conditions meaningful for SOFC applications
  - Thermodynamic data for prediction of materials durability can be obtained

- Accurate thermodynamic data for Cr$_2$O$_3$, SiO$_2$, Al$_2$O$_3$, Ni, SrO, CaO volatilization in high temperature water vapor are available

- Additional thermodynamic data are needed for gaseous hydroxides formed from La$_2$O$_3$, MnO, Pd, others?

- Component activities in complex oxides/alloys are needed to accurately predict materials durability in SOFC

- Kinetic models that accurately describe vapor transport in SOFC structures and incorporate gaseous metal hydroxide thermodynamics are needed
Acknowledgments

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Fe-O-H system

- Fe found in interconnect alloys and LSF cathodes
- Fe-O-H vapor species include Fe(OH)₂, Fe(OH), FeO₂, FeO, and Fe
- Fe-O-H system studied by transpiration method in H₂, H₂O

\[
\text{Inputs:} \quad \text{Fe} + 0.5 \text{ bar H}_2 + 0.5 \text{ bar H}_2\text{O(g)} \quad \text{Fact}
\]

\[
\text{Fe} + 2 \text{ H}_2\text{O(g)} = \text{Fe(OH)}_2\text{(g)} + \text{H}_2\text(g)
\]