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:

\[ MO_x + nH_2O(g) + mO_2(g) + qH_2(g) = MO_{(x+n+2m)}H_{(n+q)}(g) \]

Model SOFC environments

Anode side: \( H_2O(g) + H_2(g) \)
Cathode side: \( H_2O(g) + O_2(g) \)

**Pressure dependence:**

\[ P_{MOH} = K_{eq} P_{H_2O}^n P_{O_2}^m P_{H_2}^q \]

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 SiO$_2$ + H$_2$O(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

- \( \text{Cr}_2\text{O}_3 \) in SOFC
  - Oxide thermally grown on low temperature interconnects
  - Component of \( \text{La}_{1-x}\text{M}_x\text{CrO}_3 \) interconnect
- Many Cr-O-H(g) vapor species

The Cr-O-H system

- **Primary vapor species in H₂O + O₂ environment**

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

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

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

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

  ![Graph showing the relationship between water vapor dependence and oxygen dependence.](image)

  - Water vapor dependence:
    - 0.148 atm O₂ in H₂O/Ar mixtures
    - Slope = 0.96 ± 0.05

  - Oxygen dependence:
    - 0.12 atm H₂O in O₂/Ar mixtures
    - Slope = 0.77 ± 0.06

Temperature Dependence: \( \text{CrO}_2(\text{OH})_2(\text{g}) \) formation

- 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: \( \Delta H^\circ_{r, 861K} = 53.5 \text{ kJ/mol} \), \( \Delta S^\circ_{r, 861K} = -45.6 \text{ J/K mol} \)
The Si-O-H system

- SiO$_2$ 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}

\begin{align*}
\text{log } P(\text{Si-OH}), \text{ bar} &=-7.6 \\
\text{log } P(\text{H}_2\text{O}), \text{ bar} &=-1.2 \\
\text{log } P(\text{Si-OH}), \text{ bar} &=-7.2 \\
\text{log } P(\text{H}_2\text{O}), \text{ bar} &=-0.8 \\
\text{log } P(\text{Si-OH}), \text{ bar} &=-6.8 \\
\text{log } P(\text{H}_2\text{O}), \text{ bar} &=-0.4 \\
\text{log } P(\text{Si-OH}), \text{ bar} &=-5.6 \\
\text{log } P(\text{H}_2\text{O}), \text{ bar} &=-0.2 \\
\text{log } P(\text{Si-OH}), \text{ bar} &=-5.2 \\
\text{log } P(\text{H}_2\text{O}), \text{ bar} &=-0.0 \\
\end{align*}

\text{log } P(\text{Si-OH}), \text{ bar} = \text{log } P(\text{H}_2\text{O}), \text{ bar}

\begin{align*}
T &= 1673 \text{ K} \\
n &= 1.71 \pm 0.02
\end{align*}

\begin{align*}
T &= 1373 \text{ K} \\
n &= 1.99 \pm 0.06
\end{align*}

\begin{align*}
T &= 1173 \text{ K} \\
n &= 1.95 \pm 0.10
\end{align*}

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


The Si-O-H system

\[ \text{SiO}_2 + 2 \text{H}_2\text{O}(g) = \text{Si(OH)}_4(g) \]
\[ \Delta H^0(1200) = 54.6 \pm 2.7 \text{ kJ/mol} \]
\[ \Delta S^0(1200) = -67.5 \pm 2.1 \text{ J/K mol} \]

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

The Al-O-H system

- $\text{Al}_2\text{O}_3$ in SOFC: constituent of sealing glasses, insulators, and/or gas delivery components
- Al-O-H(g) vapor species identified from pressure dependence of $\text{Al}_2\text{O}_3$ 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

Temperature, °C

Log (Partial Pressure), atm

-10
-9
-8
-7
-6
-5

CrO$_2$(OH)$_2$

Si(OH)$_4$

Al(OH)$_3$

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 used in Ni/YSZ anode, Co found in interconnect alloys and CoO in coatings
• Ni-O-H vapor species include $\text{Ni(OH)}_2$, 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

\[\text{CoO} + 0.5 \text{bar } \text{H}_2 + 0.5 \text{bar } \text{H}_2\text{O(g)} \quad \text{SGTE}\]
\[\text{Ni} + 0.5 \text{bar } \text{H}_2 + 0.5 \text{bar } \text{H}_2\text{O(g)} \quad \text{Fact}\]

\[\text{CoO} + \text{H}_2\text{O(g)} = \text{Co(OH)}_2(g)\]
\[\text{Ni} + 2 \text{H}_2\text{O(g)} = \text{Ni(OH)}_2(g) + \text{H}_2(g)\]
Sr-O-H and Ca-O-H systems

- SrO found in LSM cathodes, CaO found in $\text{La}_{1-x}\text{Ca}_x\text{CrO}_{3-\delta}$ 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:**
- $\text{SrO} + 0.5 \text{ bar } \text{O}_2 + 0.5 \text{ bar } \text{H}_2\text{O(g)}$  Fact
- $\text{CaO} + 0.5 \text{ bar } \text{O}_2 + 0.5 \text{ bar } \text{H}_2\text{O(g)}$  Fact

**Graph:**

- $\log_\text{e}(\text{activity})$ vs $T(\text{C})$
- $\text{Sr(OH)}_2(g)$
- $\text{Ca(OH)}_2(g)$

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

- CaO, Cr₂O₃, and La₂O₃ activities, \(a(i)\), in \(La_{1-x}Ca_xCrO_3-\delta\) interconnects can be reduced relative to pure oxides.

- Volatility will be correspondingly reduced
  \[Cr_2O_3 + H_2O(g) + \frac{3}{4} O_2(g) = CrO_2(OH)_2(g)\]

- \(CrO_2(OH)_2(g)\) formation from \(La_{1-x}Ca_xCrO_3-\delta\) (\(x=0\) to 0.1) will be reduced by four orders of magnitude relative to pure \(Cr_2O_3\)

La-O-H system

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

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

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

**Inputs:**

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

\[
Pd + \text{ H}_2\text{O(g)} = \text{Pd(OH)}(g) + \frac{1}{2} \text{ H}_2
\]
Pt-O-H system

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

![Graph showing weight change over time for different gas mixtures and temperatures]
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

0.5 bar O₂, 0.5 bar H₂O

- 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

0.5 bar H₂, 0.5 bar H₂O
Kinetics of volatilization limited by transport through laminar gaseous boundary layer

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

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

- \( J \) = mass loss rate
- \( \rho' \) = boundary layer gas density \( \propto P_{\text{total}} \)
- \( D \) = interdiffusion coefficient \( \propto 1/P_{\text{total}} \)
- \( \rho \) = \( \text{Si(OH)}_4 \) gas density \( \propto P_{\text{SiOH4}} \)
- \( v \) = linear gas velocity
- \( \eta \) = gas viscosity
- \( L \) = characteristic length
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 \( \text{Cr}_2\text{O}_3 \), \( \text{SiO}_2 \), \( \text{Al}_2\text{O}_3 \), Ni, SrO, CaO volatilization in high temperature water vapor are available

• Additional thermodynamic data are needed for gaseous hydroxides formed from \( \text{La}_2\text{O}_3 \), 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), FeO$_2$, FeO, and Fe
- Fe-O-H system studied by transpiration method in H$_2$, H$_2$O

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

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