Understanding thermal stability in doped zirconia aerogels for high temperature applications

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Developing lightweight, high-performance aerospace thermal protection systems (TPS)

TPS Needs:
- Manage heat loads
- Withstand mechanical loads
- Lightweight
- Reusable when possible

Our Aims:
- Reduce thermal conductivity to improve performance.
- Reduce mass/volume to lower costs.
Aerogels are highly insulating and lightweight materials

Highly porous structure of aerogel is responsible for its extremely low thermal conductivity.

Low density = Low solid conductivity

Pore sizes ≤ mean free path of gas = Low gas convection

High SSA: 200 to 1000 m\(^2\)/g
High Porosity: 90 to 99.9%
Low Density: 0.2 to 0.05 g/cm\(^3\)

Low thermal conductivity: 0.009 W/(m•K) in atmosphere and 0.003 W/(m•K) under vacuum

Collapse of pore structure and loss of favorable properties occurs upon thermal exposure

Loss of SSA, porosity
↑ thermal conductivity,
cracking, and shrinkage

Large SSA & porosity contribute to driving force for densification

Develop aerogel to maintain porosity at high temperatures (≥1200°C) for use as insulation in next-gen aerospace applications

Lide, D. R., ed; “Thermal conductivity”, CRC Handbook of Chemistry and Physics (100th ed.).
High yttria concentration improves thermal stability in yttria-stabilized zirconia (YSZ) aerogels

Doping ZrO$_2$ with > 30 mol% YO$_{1.5}$ improved the stability of the pore structure to 1200 °C.

Improved thermal stability in context of thermodynamic ($\gamma$) and kinetic ($D_{Zr}$) factors

- Reduced surface energy will reduce the driving force for elimination of surface area.¹

- Reduced diffusivity with increased yttria content may slow kinetics of densification & crystallite growth²-⁴

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Expanded dopant study (Y, Yb, Gd, Ca, Ce) didn’t lead to improved stability

Best Performers*
1000 °C: 30Y, 30Gd, 30Ce
1200 °C: 30Y, 30Gd

With 10 samples at 4 different conditions, becomes difficult to discern differences in behavior

*Best performance dictated by maximum SSA and pore volume at a given temperature

With available material properties, difficult to establish new property-stability relationships

\[
\text{% Change} = \frac{\text{SSA}_f - \text{SSA}_i}{\text{SSA}_i} \times 100\%
\]

Increased dopant concentration leads to reduced densification.

Increased dopant concentration leads to reduced densification.

How do weighted cation properties relate to SSA and pore volume \((V_{\text{BJH}})\) at 1000 °C?

<table>
<thead>
<tr>
<th>Property</th>
<th>Radius</th>
<th>Charge</th>
<th>Mass</th>
<th>SSA Area (SSA)</th>
<th>Pore Volume (V_{\text{BJH}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius</td>
<td>0.54</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Charge</td>
<td>0.50</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass</td>
<td>0.44</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Radius</td>
<td>0.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Charge</td>
<td>0.47</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass</td>
<td>0.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Wider availability of material property data (such as surface energy, cation diffusivity, etc.) would enable more thorough analysis of property-stability relationships.

In general, scatter predominates for these relationships and for others not depicted here.
Surface modification of aerogels have shown promise in inhibiting coarsening & densification

**Wu et al. Capping Approach**

Capped surface hydroxyl groups with non-condensable group with hexamethyldisilane (HMDS)

Applied to SnO$_2$, TiO$_2$, and ZrO$_2$ aerogels

Capped surface hydroxyl groups with a non-condensable group prevents crystal growth & pore collapse

Capped

Uncapped

**Zu et al. Coating Approach**

Prepared MO$_x$/(MO$_x$-SiO$_2$)/SiO$_2$ core-shell metal oxide aerogels produced via alkoxide chemical liquid deposition

Applied to Al$_2$O$_3$, ZrO$_2$, and TiO$_2$ aerogels

Formation of SiO$_2$ particles on the aerogel surface prevent particle growth and phase transformation


Application of SiO\textsubscript{2} coatings to best YSZ compositions show excellent stability to 1000 °C

According to EDS, the molar ratio for 30YSZ is:

<table>
<thead>
<tr>
<th>Zr</th>
<th>Y</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>0.55</td>
<td>3.01</td>
</tr>
</tbody>
</table>

More Si than Zr and Y!

Application of SiO$_2$ coatings to best YSZ compositions show excellent stability to 1000 °C

From 1000 to 1200 °C, SiO$_2$ coating enables viscous sintering and enhances densification.

Thanks to Nachiket Shah (UIUC MatSE) for TEM of aerogel samples.
Application of SiO$_2$ coatings to best YSZ compositions show excellent stability to 1000 °C

SiO$_2$ coating delays crystallization of YSZ and strongly inhibits crystallite growth.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T (°C)</th>
<th>Crystallite Size (nm)</th>
<th>a (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30YSZ</td>
<td>600</td>
<td>5.8</td>
<td>5.163</td>
</tr>
<tr>
<td>30YSZ-SiO$_2$</td>
<td>600</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>30YSZ</td>
<td>1000</td>
<td>21.7</td>
<td>5.163</td>
</tr>
<tr>
<td>30YSZ-SiO$_2$</td>
<td>1000</td>
<td>3.2</td>
<td>5.162</td>
</tr>
<tr>
<td>30YSZ</td>
<td>1200</td>
<td>55.3</td>
<td>5.163</td>
</tr>
<tr>
<td>30YSZ-SiO$_2$</td>
<td>1200</td>
<td>13.9</td>
<td>5.153</td>
</tr>
</tbody>
</table>

Temperatures > 1200 °C required for crystallization of silica

(1) Why does SiO$_2$ coating improve thermal stability to 1000 °C?

(2) Beyond 1000 °C, how is the SiO$_2$ coating evolving in relation to the YSZ aerogel?
Summary

1. Aerogels are promising candidates for lightweight, highly insulating materials, but the pore structure must be preserved to $T \geq 1200 \, ^\circ C$.
2. Reduced surface energy and cation diffusivity are hypothesized to improve aerogel thermal stability.
3. Increased dopant concentration from 15 to 30 mol% $\frac{M}{(M+Zr)}$ reduces densification of the pore structure (Gd, Y perform best).
4. Post-synthetic modification of YSZ aerogels with $\text{SiO}_2$ coatings significantly improves thermal stability to 1000 °C but promotes viscous sintering beyond this temperature.

Looking Forward

1. Wider availability of material property data (surface energy, cation diffusivity, etc.) may help understand source(s) of variability in aerogel thermal stability.
2. The source of thermal stability and instability in $\text{SiO}_2$-coated YSZ aerogels needs to be identified via evaluation of the chemistry and structure of the aerogel and coating.
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- NASA Glenn Research Center
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