ReaxFF Molecular Dynamics study to doped thermochemical heat storage materials

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Thermochemical energy storage

Salt hydrates

\[ \text{salt. } n\text{H}_2\text{O(s)} + m\text{H}_2\text{O} \leftrightarrow \text{salt. } (n + m)\text{H}_2\text{O(s)} + \text{heat} \]
Thermochemical energy storage

Magnesium chloride

\[ MgCl_2 \cdot nH_2O(s) + mH_2O \leftrightarrow MgCl_2 \cdot (n + m)H_2O(s) + \text{heat} \]

- **Advantages**
  - High energy density (~1GJ/m\(^3\))
  - No heat losses
  - Price

- **Challenges**
  - Stability
  - Cyclebility
  - Deliquescence
  - Kinetics
  - Safety (HCl)
Thermochemical energy storage

Proposed solution: doped/double salts
Higher stability (experimental\textsuperscript{[2]} and first principle studies\textsuperscript{[3]})

- Combine salts (MgCl\textsubscript{2}.nH\textsubscript{2}O and CaCl\textsubscript{2}.nH\textsubscript{2}O)
- Study properties
  - Water transport
  - Equilibrium states
  - Thermal conductivity
  - Hydration rates
  - Nucleation
  - Level of doping
  - Anisotropic effects
  - etc.

\textsuperscript{[2]} H.U. Rammelberg “An optimization of salt hydrates for thermochemical heat storage” (2013)
\textsuperscript{[3]} A.D. Pathak, I. Tranca, et al. “First-Principles Study of Chemical Mixtures of CaCl\textsubscript{2} and MgCl\textsubscript{2} Hydrates for Optimized Seasonal Heat Storage” (2017)
Reactive forcefield Molecular Dynamics (ReaxFF MD)

Molecular Dynamics (MD) is a computer simulation method for studying the individual movement of atoms and molecules, by assuming them as particles with interatomic potentials (force fields). Compute trajectories of particles by numerically solve Newton’s equation of motion. ReaxFF allows bond breaking and formation during the simulation.

Diffusion of water through MgCl$_2$.4H$_2$O

- 300K
- 500K

Methodology
Simulation scale

Some examples of results

- Thermal conductivity
- Diffusion of water through the salt
Thermal conductivity: Steady-State Non-Equilibrium MD

1D Fourier’s law

\[ q_z = -k \frac{dT}{dz} \]

Correct for the final size effect
Thermal conductivity of pure salt

MgCl$_2$·6H$_2$O 3x3x8

<table>
<thead>
<tr>
<th>Hydrate</th>
<th>Conductivity [W/mK]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgCl$_2$</td>
<td>0.3 ± 0.04</td>
</tr>
<tr>
<td>MgCl$_2$·H$_2$O</td>
<td>0.4 ± 0.06</td>
</tr>
<tr>
<td>MgCl$_2$·2H$_2$O</td>
<td>0.6 ± 0.08</td>
</tr>
<tr>
<td>MgCl$_2$·4H$_2$O</td>
<td>1.7 ± 0.2</td>
</tr>
<tr>
<td>MgCl$_2$·6H$_2$O</td>
<td>4 ± 0.6</td>
</tr>
</tbody>
</table>

Increase of $k$ with increase of hydrate

ReaxFF MD: MgCl$_2$·nH$_2$O → $k = 0.3 - 4 \ W/mK$

Literature: MgCl$_2$·6H$_2$O → $k = 0.7 \ W/mK$[6]

ReaxFF MD: CaCl$_2$·2H$_2$O → $k = 0.5 \ W/mK$

Literature: CaCl$_2$ → $k = 0.1 \ W/mK$[7]
CaCl$_2$·6H$_2$O → $k = 1.1 \ W/mK$[6]

Diffusivity of $\text{H}_2\text{O}$ through $\text{MgCl}_2\cdot n\text{H}_2\text{O}$

Methodology - Diffusivity
Diffusion of water through the salt crystal

Methodology - Diffusivity
Future goals

Properties of doped salts
• Level of doping
• Nucleation
• Vapor transport
• Thermal conductivity
• Hydration rates
• Stability of the crystals
• Etc.

Scale-up to Grand Canonical Monte Carlo (GCMC)[9]
• Equilibrium of vapor and solid

Consider salts in porous materials

Thank you for your attention