We model mass transport at the atomic level using density function theory calculations, comparing activation energies to experimentally obtained values to determine if mass transport is rate limiting and also used to screen candidate reactions for those that have low kinetic barriers.

Calculated activation energies can be compared to experimentally obtained values to determine if mass transport is rate limiting and also used to screen candidate reactions for those that have low kinetic barriers.

Chemical potential gradients drive mass transport

\[ \mu_{n+} - \mu_{n-} = \phi \Delta F_{\text{m}} \]

\[ \mu_{n+} - \mu_{n-} = \frac{1}{2} \Delta F_{\text{m}} \]

\[ \mu_{n+} - \mu_{n-} = \frac{3}{2} \Delta F_{\text{m}} \]

Formation Energies and Concentrations

\[ \Delta F_{\text{m}} = \Delta F \text{(supercell)} \]

\[ \Delta F \text{(supercell)} = \sum \phi \Delta \mu \]

\[ C = N^{eq} \cdot N^{eq} \cdot N^{eq} \]

\[ N^{eq} \]: number of equivalent configurations

\[ N^{eq} \]: number of sites

Chemical Potential Gradients in Sodium Alanate

Tetrahydride/hexahydride interface

\[ \mu_{n+}^{1/2} + \mu_{n-}^{1/2} + 3\mu_{H}^{1/2} = F(NaAlH_{4}) \]

\[ 2\mu_{n+}^{3/4} + 6\mu_{n-}^{3/4} = F(Na_{2}AlH_{6}) \]

Tetrahydride/aluminum interface

\[ \mu_{n+}^{1/2} + \mu_{n-}^{1/2} + 4\mu_{H}^{1/2} = F(Na_{2}AlH_{6}) \]

\[ \mu_{n+}^{3/4} = F(Al) \]

\[ 2\mu_{n+}^{3/4} = F(H_{2}) \]

Hexahydride/aluminum interface

\[ \mu_{n+}^{3/4} + 6\mu_{n-}^{3/4} + 9\mu_{H}^{3/4} = F(NaAlH_{4}) \]

\[ \mu_{n+}^{3/4} = F(Al) \]

\[ 2\mu_{n+}^{3/4} = F(H_{2}) \]

Mass Transport: \( 3NaAlH_{4} \rightarrow Na_{2}AlH_{6} + 2Al + 3H_{2} \)

The largest fluxes of metal containing defects in NaAlH_{4} are negatively charged Na vacancies, neutral AlH_{3} vacancies, and positive AlH_{4} vacancies.

In Na_{2}AlH_{6}, negatively charged Na vacancies have the largest flux and this is larger than any in NaAlH_{4}.

The chemical potential gradients drive mass transport.

Chemical potential gradients drive mass transport

\[ \mu_{n+} - \mu_{n-} = \phi \Delta F_{\text{m}} \]

\[ \mu_{n+} - \mu_{n-} = \frac{1}{2} \Delta F_{\text{m}} \]

\[ \mu_{n+} - \mu_{n-} = \frac{3}{2} \Delta F_{\text{m}} \]

Formation Energies and Concentrations

\[ \Delta F_{\text{m}} = \Delta F \text{(supercell)} \]

\[ \Delta F \text{(supercell)} = \sum \phi \Delta \mu \]

\[ C = N^{eq} \cdot N^{eq} \cdot N^{eq} \]

\[ N^{eq} \]: number of equivalent configurations

\[ N^{eq} \]: number of sites

Chemical Potential Gradients in Sodium Alanate

Tetrahydride/hexahydride interface

\[ \mu_{n+}^{1/2} + \mu_{n-}^{1/2} + 3\mu_{H}^{1/2} = F(NaAlH_{4}) \]

\[ 2\mu_{n+}^{3/4} + 6\mu_{n-}^{3/4} = F(Na_{2}AlH_{6}) \]

Tetrahydride/aluminum interface

\[ \mu_{n+}^{1/2} + \mu_{n-}^{1/2} + 4\mu_{H}^{1/2} = F(Na_{2}AlH_{6}) \]

\[ \mu_{n+}^{3/4} = F(Al) \]

\[ 2\mu_{n+}^{3/4} = F(H_{2}) \]

Hexahydride/aluminum interface

\[ \mu_{n+}^{3/4} + 6\mu_{n-}^{3/4} + 9\mu_{H}^{3/4} = F(NaAlH_{4}) \]

\[ \mu_{n+}^{3/4} = F(Al) \]

\[ 2\mu_{n+}^{3/4} = F(H_{2}) \]

Mass Transport: \( 3NaAlH_{4} \rightarrow Na_{2}AlH_{6} + 2Al + 3H_{2} \)

The largest fluxes of metal containing defects in NaAlH_{4} are negatively charged Na vacancies, neutral AlH_{3} vacancies, and positive AlH_{4} vacancies.

In Na_{2}AlH_{6}, negatively charged Na vacancies have the largest flux and this is larger than any in NaAlH_{4}.

The chemical potential gradients drive mass transport.

Chemical potential gradients drive mass transport

\[ \mu_{n+} - \mu_{n-} = \phi \Delta F_{\text{m}} \]

\[ \mu_{n+} - \mu_{n-} = \frac{1}{2} \Delta F_{\text{m}} \]

\[ \mu_{n+} - \mu_{n-} = \frac{3}{2} \Delta F_{\text{m}} \]

Formation Energies and Concentrations

\[ \Delta F_{\text{m}} = \Delta F \text{(supercell)} \]

\[ \Delta F \text{(supercell)} = \sum \phi \Delta \mu \]

\[ C = N^{eq} \cdot N^{eq} \cdot N^{eq} \]

\[ N^{eq} \]: number of equivalent configurations

\[ N^{eq} \]: number of sites

Chemical Potential Gradients in Sodium Alanate

Tetrahydride/hexahydride interface

\[ \mu_{n+}^{1/2} + \mu_{n-}^{1/2} + 3\mu_{H}^{1/2} = F(NaAlH_{4}) \]

\[ 2\mu_{n+}^{3/4} + 6\mu_{n-}^{3/4} = F(Na_{2}AlH_{6}) \]

Tetrahydride/aluminum interface

\[ \mu_{n+}^{1/2} + \mu_{n-}^{1/2} + 4\mu_{H}^{1/2} = F(Na_{2}AlH_{6}) \]

\[ \mu_{n+}^{3/4} = F(Al) \]

\[ 2\mu_{n+}^{3/4} = F(H_{2}) \]

Hexahydride/aluminum interface

\[ \mu_{n+}^{3/4} + 6\mu_{n-}^{3/4} + 9\mu_{H}^{3/4} = F(NaAlH_{4}) \]

\[ \mu_{n+}^{3/4} = F(Al) \]

\[ 2\mu_{n+}^{3/4} = F(H_{2}) \]