Supplementary Information

Enabling Chloride Salts for Thermal Energy Storage: Implications of Salt Purity

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Figure S1. Schematic of the system used to purify the salts. Gas supplies for the space above the salt (headspace, green) and through the salt (sparge, blue) are dried before entering the reactor.

**Thermodynamic Equations**

HCl, CO+Cl₂, COCl₂, and CCl₄ were evaluated for the thermodynamic favorability of decomposition as well as reacting with MgO, O₂, and H₂O. The amounts of the impurity and purifying agents were kept constant for all cases to evaluate the efficacy of each reagent.

**Decomposition Equations**

\[
HCl \rightarrow \frac{1}{2}H_2 + \frac{1}{2}Cl_2 \quad (S1)
\]

\[
CO + Cl_2 \rightarrow COCl_2 \quad (S2)
\]
\[ COCl_2 \rightarrow CO + Cl_2 \quad (S3) \]
\[ CCl_4 \rightarrow C + 2Cl_2 \quad (S4) \]

**MgO Equations**

\[ 2HCl + MgO \rightarrow H_2O + MgCl_2 \quad (S5) \]
\[ CO + Cl_2 + MgO \rightarrow CO_2 + MgCl_2 \quad (S6) \]
\[ COCl_2 + MgO \rightarrow CO_2 + MgCl_2 \quad (S7) \]
\[ \frac{1}{2} CCl_4 + MgO \rightarrow \frac{1}{2} CO_2 + MgCl_2 \quad \text{for } T<425^\circ C \quad (S8a) \]
\[ CCl_4 + MgO \rightarrow \frac{1}{2} CO_2 + MgCl_2 + \frac{1}{2} C + Cl_2 \quad \text{for } 425^\circ C<T<700^\circ C \quad (S8b) \]
\[ CCl_4 + MgO \rightarrow CO + MgCl_2 + Cl_2 \quad \text{for } T>700^\circ C \quad (S8c) \]

**O_2 Equations**

\[ 4HCl + O_2 \rightarrow 2H_2O + 2Cl_2 \quad (S9) \]
\[ 2CO + O_2 \rightarrow 2CO_2 \quad (S10) \]
\[ 2COCl_2 + O_2 \rightarrow 2CO_2 + 2Cl_2 \quad (S11) \]
\[ CCl_4 + O_2 \rightarrow CO_2 + 2Cl_2 \quad \text{for } T<425^\circ C \quad (S12a) \]
\[ 2CCl_4 + O_2 \rightarrow CO_2 + C + 4Cl_2 \quad \text{for } 425^\circ C<T<725^\circ C \quad (S12b) \]
\[ 2CCl_4 + O_2 \rightarrow 2CO + 4Cl_2 \quad \text{for } T>725^\circ C \quad (S12c) \]

**H_2O Equations**

\[ HCl + H_2O \rightarrow \text{no reaction} \quad (S13) \]
\[
CO + Cl_2 + H_2O \rightarrow 2HCl + CO_2 \quad (S14)
\]

\[
COCl_2 + H_2O \rightarrow 2HCl + CO_2 \quad (S15)
\]

\[\frac{1}{2}CCl_4 + H_2O \rightarrow \frac{1}{2}CO_2 + 2HCl \quad \text{for } T<425^\circ C \quad (S16a)\]

\[CCl_4 + H_2O \rightarrow \frac{1}{2}CO_2 + 2HCl + \frac{1}{2}C + \frac{1}{2}Cl_2 \quad \text{for } 425^\circ C<T<725^\circ C \quad (S16b)\]

\[CCl_4 + H_2O \rightarrow CO + 2HCl + Cl_2 \quad \text{for } T>725^\circ C \quad (S16c)\]

The decomposition of CO was less favorable than recombination of CO and Cl\(_2\), so combining to form COCl\(_2\) was evaluated (Equation S2). Equations S2 and S3 are the reverse of one another since COCl\(_2\) decomposes to CO+Cl\(_2\). Decomposition of CCl\(_4\) becomes more favorable with higher temperatures from entropy generated by forming 2 moles of chlorine gas. However, the increased favorability of CCl\(_4\) over the other purifying reagents arises because of the ability to remove O by forming CO, a reaction CO+Cl\(_2\) and COCl\(_2\) cannot undergo.

The reactions of CCl\(_4\) with MgO (S8a-c), O\(_2\) (S12a-c), and H\(_2\)O (S16a-c) are compared below (Figure S2). Carbon tetrachloride required multiple equations for MgO (S8a-c), O\(_2\) (S12a-c), and H\(_2\)O (S16a-c) because the reaction changes. The first transition occurs at ~425°C when CCl\(_4\) spontaneously decomposes (Equation S4). The second transition occurs at ~700°C when O removal via CO (Equations S8c, S12c, and S16c) becomes favored over CO\(_2\) (Equations S8a&b, S12a&b, and S16a&b). The transitions are demarcated with squares on the CCl\(_4\) curve (green) in Figures 2b-d. The curves representing CCl\(_4\) reacting with MgO, O\(_2\), and H\(_2\)O takes the lowest \(\Delta G\) for all three equations (Figure S2).
**Figure S2.** Plots of $\Delta G_f$ versus temperature for the reaction between CCl$_4$ and MgO (a), O$_2$ (b), or H$_2$O (c). The curves depicted represent the formation of CO$_2$ without (grey) and with (red) decomposition of CCl$_4$ as well as the formation of CO by decomposing CCl$_4$ (blue).

**Figure S3.** (a-c) Scanning electron micrograph (a), Fe (b) EDS map, and Cr (c) EDS map of cross-sectioned SS316L corrosion coupons exposed to low purity salt. (d-f) Scanning electron micrograph (d), Fe (e) EDS map, and Cr (f) EDS map of cross-sectioned SS316L corrosion coupons exposed to moderate purity salt. (g-i) Scanning electron micrograph (g), Fe (h) EDS map, and Cr (i) EDS map of cross-sectioned SS316L corrosion coupons exposed to low purity salt. All samples were sealed in quartz ampules under vacuum and held at 700°C for 100 hours.
Figure S4. (a-c) Scanning electron micrograph (a), Ni (b) EDS map, and Cr (c) EDS map of cross-sectioned ALLOY-N corrosion coupons exposed to low purity salt. (d-f) Scanning electron micrograph (d), Ni (e) EDS map, and Cr (f) EDS map of cross-sectioned ALLOY-N corrosion coupons exposed to moderate purity salt. (g-i) Scanning electron micrograph (g), Ni (h) EDS map, and Cr (i) EDS map of cross-sectioned ALLOY-N corrosion coupons exposed to low purity salt. All samples were sealed in quartz ampules under vacuum and held at 700°C for 100 hours.

Figure S5. (a-c) Mg (a), O (b), and Cr (c) EDS map of cross-sectioned SS316L corrosion coupons exposed to low purity salt. (d-f) Mg (d), O (e), and Cr (f) EDS map of cross-sectioned Alloy-N corrosion coupons exposed to low purity salt. The samples were sealed in quartz ampules under vacuum and held at 700°C for 100 hours.