

Supplementary Information

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

J. Matthew Kurley,^a Phillip W. Halstenberg,^a Abbey McAlister,^a Stephen Raiman,^b Sheng Dai,^{a,c} and Richard T. Mayes*^a

^aChemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA 37831

^bMaterials Science & Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA 37831

^cDepartment of Chemistry, University of Tennessee, Knoxville, Tn 37996

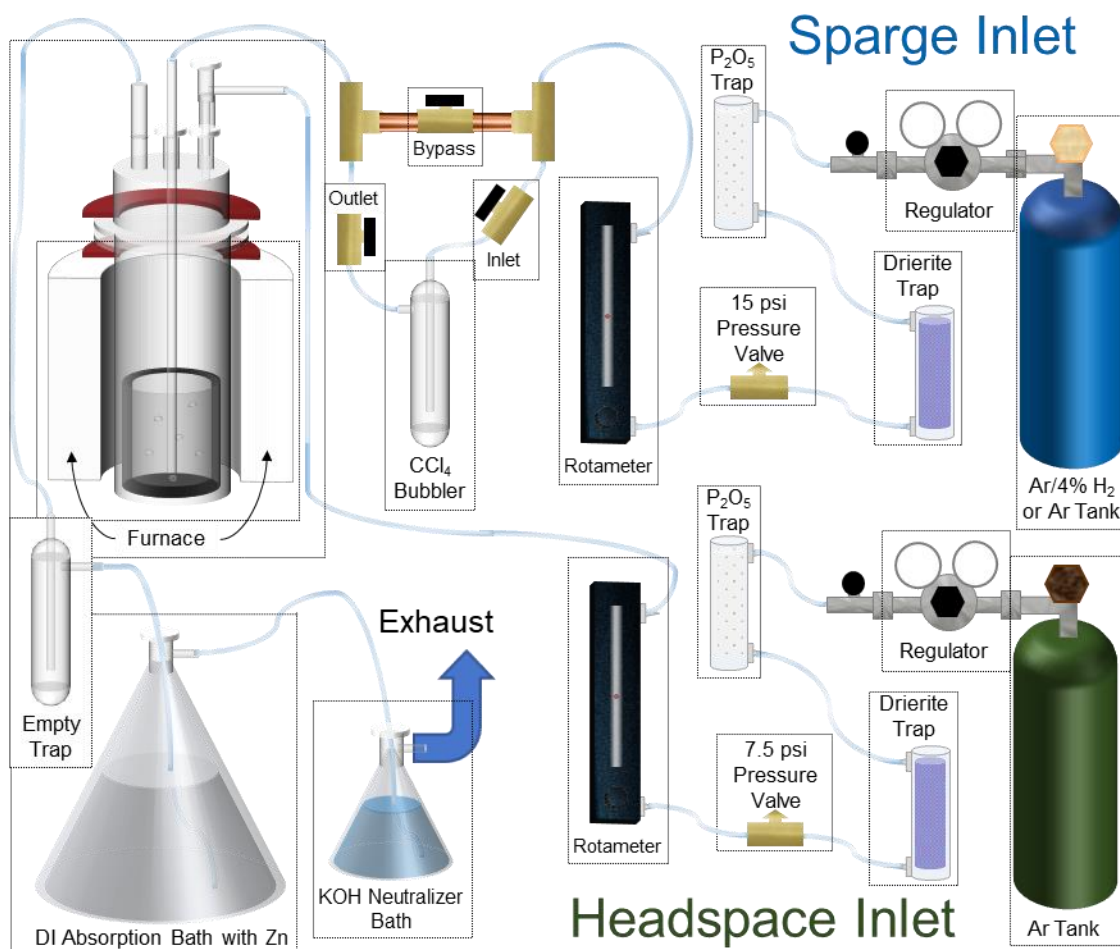
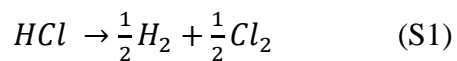


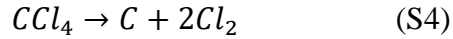
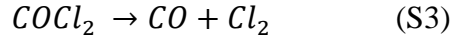
Figure S1. Schematic of the system used to purify the salts. Gas supplies for the space above the salt (headspace, green) and through the salt (spurge, blue) are dried before entering the reactor.

Thermodynamic Equations

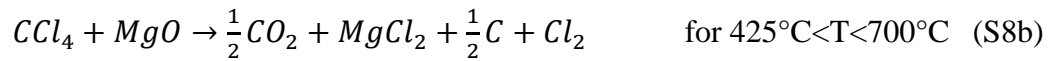
HCl, CO+Cl₂, COCl₂, and CCl₄ were evaluated for the thermodynamic favorability of decomposition as well as reacting with MgO, O₂, and H₂O. The amounts of the impurity and purifying agents were kept constant for all cases to evaluate the efficacy of each reagent.

Decomposition Equations

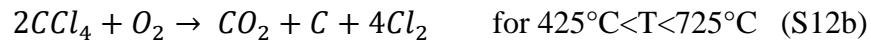




MgO Equations

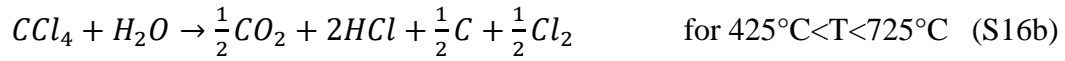


O₂ Equations



H₂O Equations





The decomposition of CO was less favorable than recombination of CO and Cl₂, so combining to form COCl₂ was evaluated (Equation S2). Equations S2 and S3 are the reverse of one another since COCl₂ decomposes to CO+Cl₂. Decomposition of CCl₄ becomes more favorable with higher temperatures from entropy generated by forming 2 moles of chlorine gas. However, the increased favorability of CCl₄ over the other purifying reagents arises because of the ability to remove O by forming CO, a reaction CO+Cl₂ and COCl₂ cannot undergo.

The reactions of CCl₄ with MgO (S8a-c), O₂ (S12a-c), and H₂O (S16a-c) are compared below (Figure S2). Carbon tetrachloride required multiple equations for MgO (S8a-c), O₂ (S12a-c), and H₂O (S16a-c) because the reaction changes. The first transition occurs at ~425°C when CCl₄ spontaneously decomposes (Equation S4). The second transition occurs at ~700°C when O removal via CO (Equations S8c, S12c, and S16c) becomes favored over CO₂ (Equations S8a&b, S12a&b, and S16a&b). The transitions are demarcated with squares on the CCl₄ curve (green) in Figures 2b-d. The curves representing CCl₄ reacting with MgO, O₂, and H₂O takes the lowest ΔG for all three equations (Figure S2).

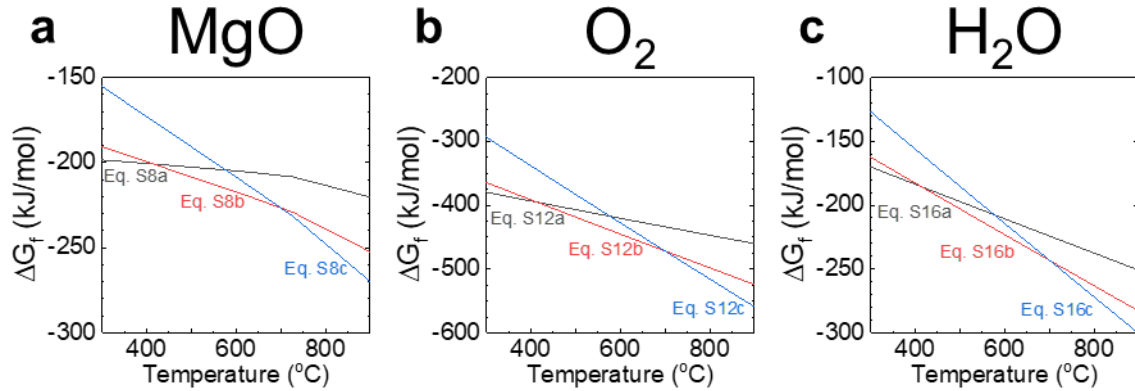


Figure S2. Plots of ΔG_f versus temperature for the reaction between CCl₄ and MgO (a), O₂ (b), or H₂O (c). The curves depicted represent the formation of CO₂ without (grey) and with (red) decomposition of CCl₄ as well as the formation of CO by decomposing CCl₄ (blue).

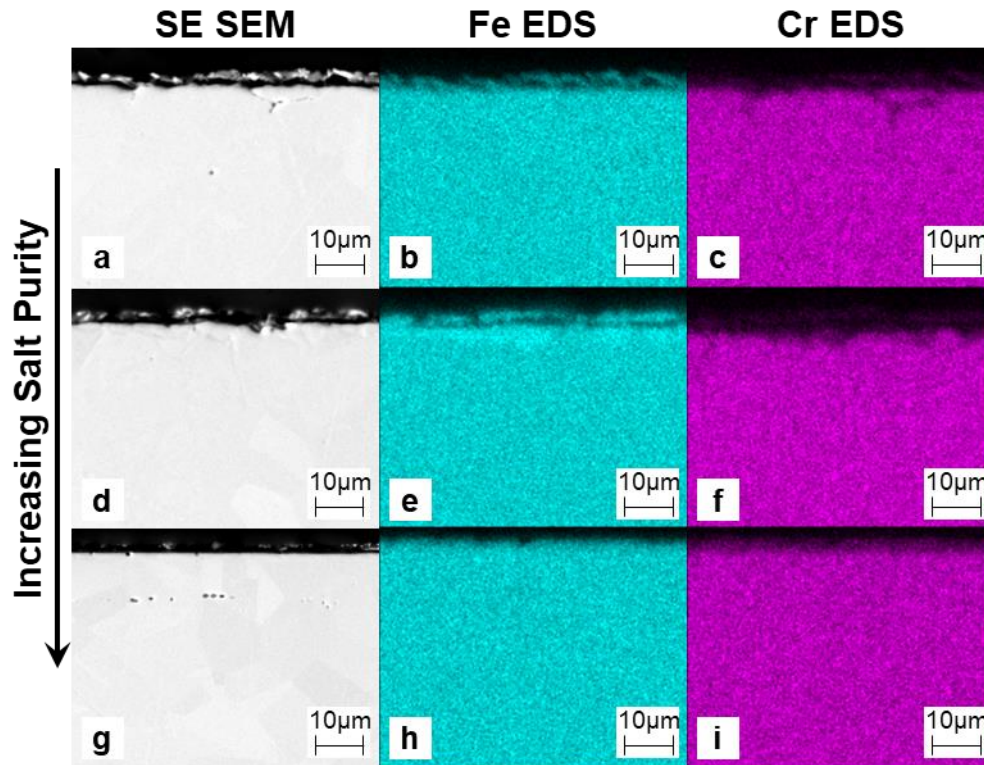


Figure S3. (a-c) Scanning electron micrograph (a), Fe (b) EDS map, and Cr (c) EDS map of cross-sectioned SS316L corrosion coupons exposed to low purity salt. (d-f) Scanning electron micrograph (d), Fe (e) EDS map, and Cr (f) EDS map of cross-sectioned SS316L corrosion coupons exposed to moderate purity 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.

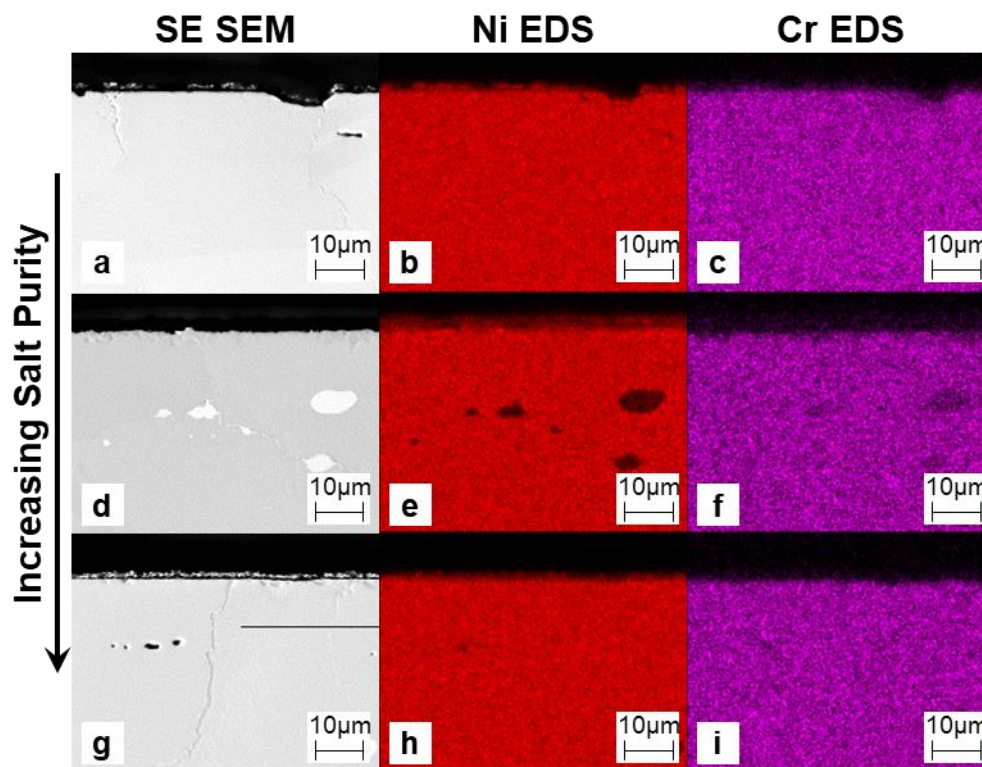


Figure S4. (a-c) Scanning electron micrograph (a), Ni (b) EDS map, and Cr (c) EDS map of cross-sectioned ALLOY-N corrosion coupons exposed to low purity salt. (d-f) Scanning electron micrograph (d), Ni (e) EDS map, and Cr (f) EDS map of cross-sectioned ALLOY-N corrosion coupons exposed to moderate purity 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.

Stainless Steel 316L

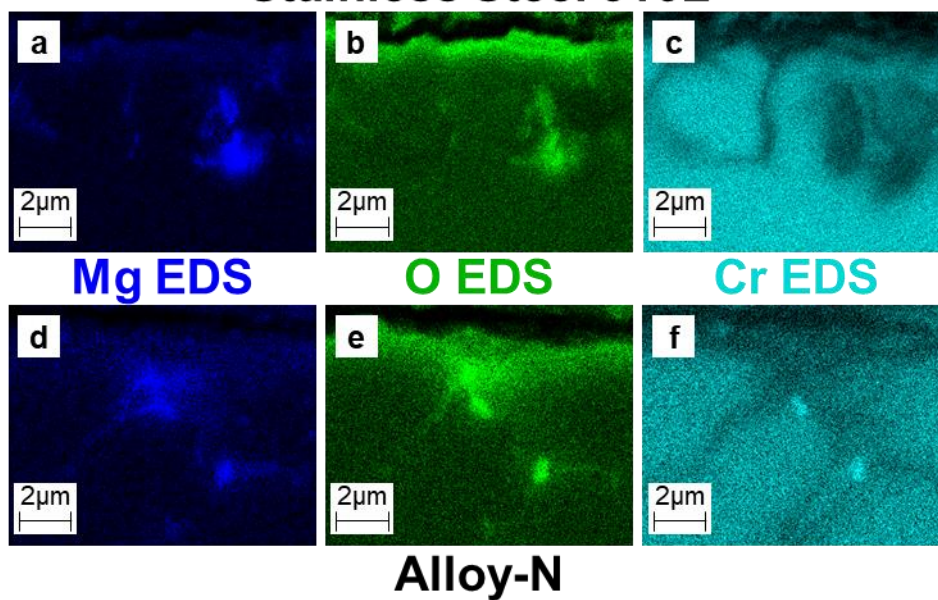


Figure S5. (a-c) Mg (a), O (b), and Cr (c) EDS map of cross-sectioned SS316L corrosion coupons exposed to low purity salt. (d-f) Mg (d), O (e), and Cr (f) EDS map of cross-sectioned Alloy-N corrosion coupons exposed to low purity salt. The samples were sealed in quartz ampules under vacuum and held at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