

Cryogenic heat capacity measurements and thermodynamic analysis of lithium aluminum layered double hydroxides (LDHs) with intercalated chloride

K. JAYANTHI¹, GRACE NEILSEN^{2,†}, PETER F. ROSEN², CLARK I. ANDERSEN², MATTHEW S. DICKSON², SAMUEL F. EVANS^{3,4}, M. PARANS PARANTHAMAN^{3,4}, BRIAN F. WOODFIELD^{2,*}, AND ALEXANDRA NAVROTSKY¹

¹School of Molecular Sciences and Center for Materials of the Universe, Arizona State University, Tempe, Arizona 85287, U.S.A.

²Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah 84602, U.S.A.

³Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, U.S.A.

⁴The Bredesen Center for Interdisciplinary Research and Graduate Education, The University of Tennessee, Knoxville, Tennessee 37996, U.S.A.

ABSTRACT

Lithium aluminum chloride layered double hydroxide ([Li-Al-Cl] LDH) sorbents selectively recover lithium from geothermal brines, paving the way for increased domestic production of lithium for rechargeable batteries. In this work, cryogenic heat capacity measurements (C_p) were performed from 1.8 to 300 K on several undoped and Fe-doped [Li-Al-Cl] LDH samples with a generalized compositions $\text{Li}_{1-x}\text{Al}_2(\text{OH})_6\text{Cl}_{1-x}$ (undoped) and $\text{Li}_x\text{Fe}_y\text{Al}_{2-y}(\text{OH})_6\text{Cl}_x$ (Fe-doped). Thermodynamic functions were generated from these measurements, and values of $S_{298.15}^\circ$ are reported based on both the C_p measurements and configurational entropy (S_{config}°) arising from positional disorder in the layered structure. These results are combined with previous enthalpy of formation (ΔH_f°) measurements to calculate the Gibbs energy of formation (ΔG_f°) for the samples. In these samples, a higher water content results in a less negative ΔG_f° when doped and undoped samples are considered separately. Limited iron substitution for aluminum results in the most negative ΔG_f° , but a larger dopant amount destabilizes the LDH structure. One of the samples had an anomaly in the heat capacity from 210 to 300 K, which is likely related to the movement of water in the structure due to the large $\text{H}_2\text{O}/\text{Cl}^-$ ratio and the presence of vacancies in the interlayer where H_2O resides. This indicates that the interactions between these species in the interlayer play an important role in stabilizing the LDH structure, and this effect should be further studied using different water/anion ratios.

Keywords: Layered double hydroxides, heat capacity, entropy, Gibbs energy, lithium extraction