

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

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### **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 ( $S_{\text{config}}^\circ$ ) arising from positional disorder in the layered structure. These results are combined with previous enthalpy of formation ( $\Delta H_f^\circ$ ) measurements to calculate the Gibbs energy of formation ( $\Delta G_f^\circ$ ) for the samples. In these samples, a higher water content results in a less negative  $\Delta G_f^\circ$  when doped and undoped samples are considered separately. Limited iron substitution for aluminum results in the most negative  $\Delta G_f^\circ$ , 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  $\text{H}_2\text{O}$  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