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Development of lithium manganese oxides for direct lithium extraction from brine

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Global demand for lithium continues to increase as lithium-ion batteries are a central component of electric transportation and grid-scale energy storage, yet forecasts indicate that conventional hard-rock deposits and salar brines will be unable to meet demand within the coming decade. In response, alternative low-grade lithium resources, such as sedimentary brines, are now attracting increasing attention in the United States and Canada. Despite the vast resources in place, the low lithium concentrations and complex chemistries of sedimentary brines require lithium separation technologies that are highly selective and durable in order to be economically viable. Ion-exchange based direct lithium extraction (DLE) materials, particularly lithium manganese oxides (LMOs), are a promising approach due to their rapid lithiation kinetics and strong lithium selectivity; however, their performance is strongly influenced by brine chemistry. Previously, we found that dissolved organic compounds and aqueous sulfide species promote reductive dissolution of structural Mn(IV), along with inherent Jahn-Teller distortion within the spinel lattice during lithiation and protonation that induces local structural instability leading to Mn disproportionation (1). To mitigate these degradation pathways, we systematically evaluated a suite of stabilization strategies, including the doping of the lattice with cations, surface coatings, and the design of engineered composite materials. Laboratory tests using brines from the Western Canadian Sedimentary Basin show that coating LMO with a nano-scale layer of zirconium dioxide shields the LMO surfaces from reactive organic species (2), while divalent cation doping enhances structural stability by suppressing Jahn-Teller distortion, with both approaches individually reducing Mn dissolution by 50%. Furthermore, incorporating LMO particles into polyvinylidene fluoride (PVDF) composites or polyethersulfone (PES) beads immobilizes the sorbent and limits exposure to harmful organic compounds due to the hydrophobic and oleophilic character of the polymer matrices. As a result, these composite-stabilized LMOs can sustain over 250 lithium-recovery cycles, compared with only 5-10 cycles for unmodified materials. Overall, our findings indicate that chemically and structurally stabilized LMOs provide a durable, scalable, and economically viable pathway for sustainable lithium recovery from brines with diverse chemistries.

(1) Seip, A. *et al.* (2021) Chemical Engineering Journal 426: 130713.

(2) Shivakumar *et al.* (2025) Chemical Communications 61(59): 11013-11016.