

Stabilization of ion-exchange materials for lithium recovery from brines

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Summary

Sedimentary brines, such as those in the Western Canadian Sedimentary Basin (WCSB) have emerged as promising alternative sources of lithium. While the brine resource in place is vast, the resource grade is low relative to conventional sources such as hard rock and salar deposits, often in the tens to hundreds of parts-per-million lithium. Thus, commercializing lithium production from basinal brines in the WCSB requires a highly selective, scalable, robust and low-cost recovery technology. In this talk, we will discuss efforts to stabilize one of the most promising direct lithium extraction (DLE) materials, spinel lithium manganese oxide (LMO) nanoparticles. Among the challenges that will be addressed are detrimental interactions between LMOs and dissolved organic compounds and hydrogen sulphide found in many brines, and ensuring that the LMO nanoparticles are bound by or embedded into suitable materials so that they can be used effectively at scale.

Development of Direct Lithium Extraction (DLE) sorbents

A primary challenge in commercializing lithium in sedimentary brines, such as those in the WCSB, is the development of robust and cost-effective direct lithium extraction (DLE) technologies (Rassenfoss, 2023). Among the most promising solid-phase DLE technologies are lithium-selective ion exchange sorbents of the spinel type, primarily of the manganese (Mn) and titanium (Ti) types (Safari et al., 2020). While Mn-based DLE sorbents have higher potential lithium loadings and faster lithium uptake kinetics than Ti-based sorbents, Mn(IV) in the structure of these materials is subject to reduction by dissolved organic compounds and/or hydrogen sulphide found in many brines (Figure 1; Seip et al., 2021).

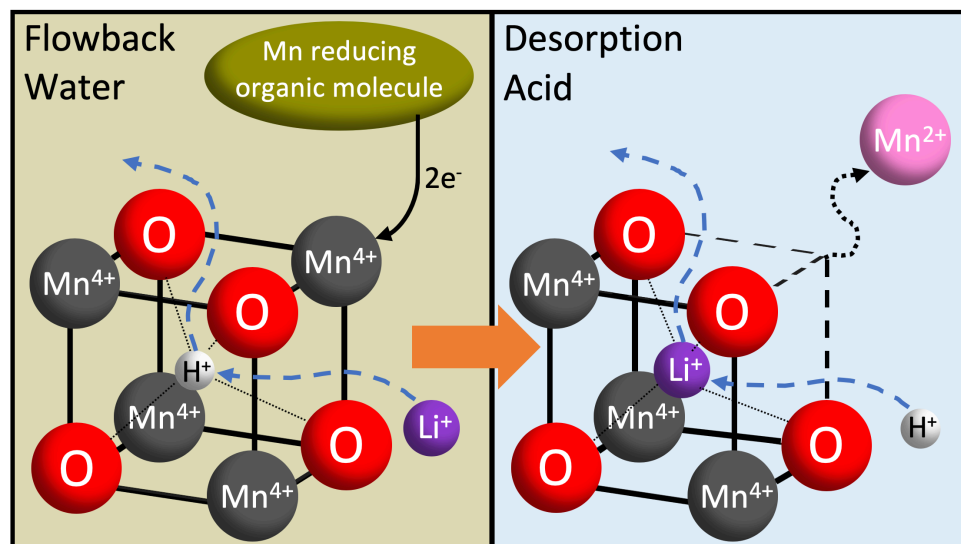


Figure 1: Reductive dissolution of Mn(IV) in manganese lithium spinel oxide DLE sorbents, induced by dissolved organic compounds or hydrogen sulphide found in sedimentary brines. Figure adapted from Seip et al. (2021).

In this research program, we address Mn loss from the sorbent in two ways: by coating the sorbent nanoparticles with zirconium oxide to prevent contact between reductants in the brine and the DLE materials (Figure 2a), and by doping the Mn spinel oxide nanoparticles with divalent cations, such as Mg^{2+} to stabilize their structure and thereby lessen Mn reduction and loss (Figure 2b).

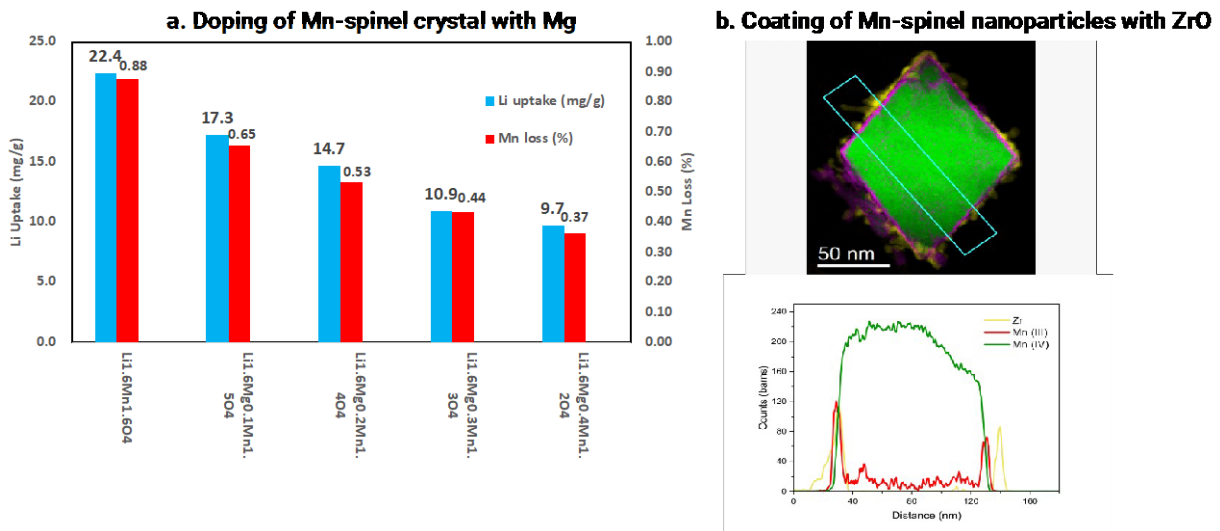


Figure 2: (a) results of doping of $Li_{1.6}Mn_{1.6}O_4$ with increasing Mg^{2+} , showing decreased Mn loss and concomitant lower Li uptake; (b) high resolution transmission electron microscopy (HRTEM) – electron energy loss spectroscopy (EELS) imaging of a ZrO_2 coated Mn spinel oxide DLE sorbent, showing decreased Mn(IV) reduction.

Our results show that both coating with ZrO_2 and doping of the crystal structure with Mg^{2+} are promising approaches. Compared to the undoped $Li_{1.6}Mn_{1.6}O_4$ base sorbent, doping of the Mn spinel oxide, to a maximum of $Li_{1.6}Mg_{0.4}Mn_{1.2}O_4$ results in a nearly 58% drop in Mn loss; however, the stabilization of the sorbent structure also leads to a 57% drop in the maximum lithium uptake. Coating with ZrO_2 leads to little change in the maximum lithium uptake, but a 50% reduction in Mn loss. Future efforts will aim to optimize the sorbent coating process, test other potential dopants, and investigate the embedding of sorbent nanoparticles into polymeric matrices in an effort to minimize sorbent degradation during the DLE process.

Acknowledgements

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References

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