



Understanding Macroscopic Li Transport in Li-excess Rocksalts based on Atomistic Insight

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Abstract: Unlike theoretical capacity, practical capacity of intercalation electrode materials depends on having appropriate Li-transport kinetics at multiple length scales. We have recently developed a model to assess the practical capacity of close-packed oxide materials for any cation arrangement, including cation-disordered systems [1]. We demonstrate how atomistic level detail of Li migration needs to be combined with higher length scale percolation theory to understand which materials can have large practical capacity.

Based on first-principles calculations, we identify two different atomic environments through which Li can migrate: 1-TM channels that pass along a transition metal (TM) atom, and 0-TM channels that only involve Li atoms. The activation energy for Li migration through 1-TM channels is highly sensitive to strain, lattice parameters and ordering, whereas 0-TM channels exhibit low diffusion barriers that are mostly independent of their local structure. Hence, structures that possess a percolating network of 0-TM channels can have large capacity as they provide good Li mobility over a large Li concentration range. With this insight we can explain the practical capacity of the four most common rocksalt-type Li-TM oxides: the layered structure provides very good Li mobility through 1-TM channels, but only over a limited Li extraction range. This explains why the practical capacity of stoichiometric layered materials is well below their theoretical capacity. The spinel-like (LT-LiCoO₂) structure supports good Li mobility over the entire range of Li concentrations. The Li mobility in the γ -LiFeO₂ structure is very low, which explains its poor performance as electrode material. Finally, the disordered rocksalt structure provides reasonable Li mobility over a very large Li extraction range, but only if the material contains sufficient Li excess. This understanding leads to new design concepts for high-capacity materials, including fully disordered rocksalts as recently discovered [2].

[1] A. Urban, J. Lee, and G. Ceder, *Adv. Energy Mater.* **4** (2014) 1400478.

[2] J. Lee, A. Urban, X. Li, D. Su, G. Hautier, and G. Ceder, *Science* **343** (2014) 519-522.