Ab Initio Prediction of Structure, Kinetics and Electrochemical Properties of Li-Intercalation Electrodes

G. Ceder, A. Van der Ven, D. Morgan.

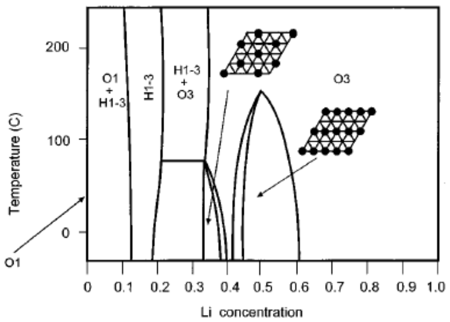
Department of Material Science and Engineering,
Massachusetts Institute of Technology, Cambridge,
Massachusetts 02139, USA.

Many of the important properties of Li intercalation electrodes are quite amenable to calculation by means of modern first principles methods. Intercalation voltage [1], phase stability[2, 3], Li diffusion[4], and electronic behavior[5] of the cathode oxides can be extracted from quantum mechanics, making it possible to rapidly pre-screen new electrode compounds for these basic properties.

Density Functional Theory (DFT) is the most widely used framework in which to perform computational quantum mechanics. Both the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA) are applicable to lithium-transition metal oxides, though the GGA often gives a better representation of strongly magnetic systems, such as the Mn-oxides[6]. While both methods give useful results for intercalation oxides, the strong effects of electron correlation, which are approximated in LDA and GGA, can cause error in regions with low electron density. I will demonstrate how some of this error can show up in low density compounds such as phosphates, or in the Van der Waals region of layered transition metal oxides.

Density Functional Theory calculations directly result in energies of compounds and their electronic structure. As a reasonably good approximation, the average voltage of an intercalation reaction can obtained from the zero Kelvin energy of the lithiation reaction. As a result, DFT can be used to predict with reasonable accuracy the electrode voltage for any compound, whether it has been synthesized previously or not. In general, the results of such voltage calculations are 0.25 to 0.75 V below experimentally measured values, though voltages in phosphate compounds may be underestimated even more.

Properties, such as diffusion, or phase stability, can not be directly extracted from quantum mechanical calculations and require the construction of property models which use the zero temperature energy calculations as input. In the case of phase stability, a highly accurate approach can be formulated with lattice-like models which account for the contribution of configurational entropy to the free energy. The figure below shows the phase diagram of Li_xCoO_2 as calculated from first principles.



Once the details of the Li configuration as function of composition and temperature are known, diffusion can be studied with kinetic lattice models.
While diffusion of lithium is rapid in these materials and largely determined by steric and screened electrostatic effects, diffusivity of the transition metal depends on subtle electronic effects. We show that the lack of stability of many Mn containing compounds can be explained by a temporary charge disproportionation which gives Mn^{3+} a very high mobility

Putting these tools together we show how one can rationalize the behavior of different lithium-transition-metal oxides and make suggestions for improved materials.

References

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Acknowledgments

This work was supported by the Assistant Secretary for Energy. Efficiency and Renewable Energy, Office of FreedomCAR and Vehicle Technologies of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, Subcontract No. 6517748 with the Lawrence Berkeley National Laboratory.