

Synthesis and Lithiation Paths of Dirutile and Rutile LiMnF_4 : Two New Conversion Cathode Materials

Nancy Twu, Xin Li, Charles Moore, Gerbrand Ceder
 Massachusetts Institute of Technology
 77 Massachusetts Avenue, 13-5051
 Cambridge, MA 02139

Driven by the need for new cathode battery materials with high energy density, fluorides have emerged as promising candidates due to their high voltages. In particular, studies on FeF_3 and FeF_2 have shown the potential of fluorides as conversion electrodes to reach very high energy densities^{1,2}. From high throughput computations³, dirutile LiMnF_4 was identified as a promising cathode with a high conversion voltage and a theoretical specific capacity of 584 mAh/g.

In this work, we study the formation of dirutile LiMnF_4 through a new, low-temperature synthesis route and test for electrochemical activity. We also report the discovery of a new rutile polymorph of LiMnF_4 which has Li-Mn disorder on the cation site. Electron diffraction confirmed both dirutile and rutile LiMnF_4 to convert upon lithiation with different reaction paths, which can be explained by computations of similar energetics.

As seen with other fluoride materials, attainable specific capacity is strongly linked with synthesis and processing conditions. With LiMnF_4 , there was a tradeoff in maintaining phase-pure samples and optimizing samples for high specific capacity. Still, even with very simple synthesis and electrode preparation methods, both rutile and dirutile polymorphs of LiMnF_4 show reversible electrochemical behavior. Further optimization of particle morphology may enhance reaction kinetics and improve specific capacity.

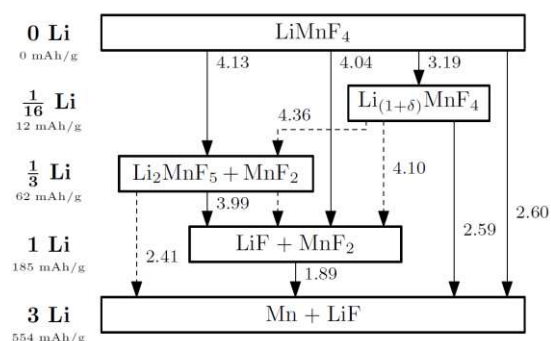


Figure 1. Starting with LiMnF_4 , possible reactions of fluoride compounds with lithium are labeled with their expected onset voltages. The lithium fraction and specific capacity listed at the left are calculated relative to LiMnF_4 .

Acknowledgements

This work is supported by Robert Bosch Corporation and Umicore Specialty Oxides and Chemicals, as well as the National Science Foundation Graduate Research Fellowship under Grant No. 1122374.

References

1. F. Badway et al., J. Electrochem. Soc. (2003)
2. F. Wang et al., JACS (2011)
3. A. Jain et al., Comp. Mat. Sci (2011)
4. K. Wandner et al., Z. anorg. Allg. Chem. (1987)