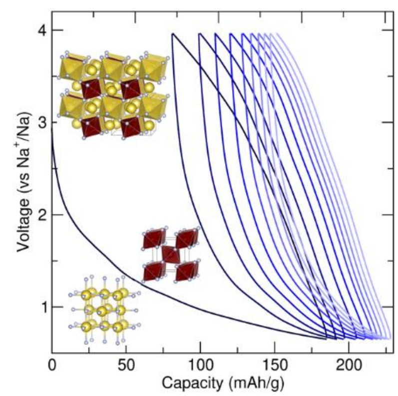
Elucidating reaction processes in conversion-type Na_3FeF_6 for Na-ion batteries

E. E. Foley[a], A. Wong[b], R. C. Vincent[a], A. Manche[a], A. Zaveri[a], G. Ménard[b], and R. J. Clément[a]
[a]Materials Department, University of California, Santa Barbara, 93106
[b]Department of Chemistry and Biochemistry, University of California, Santa Barbara, 93106

Sodium(Na)-ion batteries are the most explored 'beyond-Li' battery systems, yet their energy densities are still largely limited by the positive electrode material. Na_3FeF_6 is a promising earth-abundant cathode and operates through a conversion-type charge-discharge reaction associated with a high theoretical capacity (336 mAh/g).[1] In practice, however, only a third of this capacity is achieved during electrochemical cycling. Poorly-understood electrochemical reaction mechanisms and degradation processes are elucidated here using a suite of long-range and local probes sensitive to amorphous and magnetic phases formed during operation. A previously-unreported reaction mechanism is proposed based on ^{23}Na/^{19}F solid-state nuclear magnetic resonance (NMR), ^{57}Fe Mössbauer spectroscopy, x-ray photoelectron spectroscopy, and magnetometry results, complemented with first principles calculations of NMR and Mössbauer properties. In addition, the reversibility of the conversion process is found to be dependent on the cathode preparation method, as well as the thickness of the electrode film. These findings provide key electrode design criteria for improving performance.



Schematic of electrochemical cycling behavior for Na_3FeF_6.

This work made use of the shared facilities of the UC Santa Barbara MRSEC (DMR 1720256) and Center for Scientific Computing (CNS 1725797, DMR 1720256). E. E. Foley was supported by the NSF Graduate Research Fellowship Program under Grant No. DGE 1650114.

References:

1. R. A. Shakoor, S. Y. Lim, H. Kim, K. W. Nam, J. K. Kang, K. Kang, J. W. Choi, Mechanochemical synthesis and electrochemical behavior of Na_3FeF_6 in sodium and lithium batteries, *Solid State Ionics.* **218** (2012) 35–40. DOI:10.1016/j.ssi.2012.05.002.