

# Structural Investigation of the Effects of Carbon Coating and Reducing Particle Size on the Electrochemical Performance of $\text{Li}_2\text{FeSiO}_4$ Cathode by using in-situ XAS

Kamil Kucuk<sup>\*1</sup>, Shankar Aryal<sup>1,2</sup>, Elahe Moazzen<sup>3</sup>, Elena V. Timofeeva<sup>3</sup> and C. U. Segre<sup>1</sup>

<sup>1</sup>Department of Physics & CSRRI, Illinois Institute of Technology, Chicago, IL, 60616, USA

<sup>2</sup>Applied Materials Division, Argonne National Laboratory, Lemont IL, 60439, USA

<sup>3</sup>Department of Chemistry, Illinois Institute of Technology, Chicago, IL, 60616, USA

email: [kkucuk@hawk.iit.edu](mailto:kkucuk@hawk.iit.edu)

Lithium iron orthosilicate ( $\text{Li}_2\text{FeSiO}_4$  (LFS)) cathode material with high energy storage capacity and stable cycling performance has recently earned a positive reputation in Li-ion Battery (LIB) applications. **[1]** This material consists of abundant elements which makes it an inexpensive and less toxic cathode candidate, by comparison with Ni-/Co-based expensive and toxic commercial cathodes. **[2]** The main challenge of this material is its low electronic conductivity due to the presence of Si, leading to a poor electrochemical performance with low discharge capacity. **[3]** To address this, we applied three independent approaches: (1) reducing the particle size of LFS samples from micro-scale to nano-scale in order to reduce the diffusion length for intercalating ions; (2) application of a conductive coating to each nanoparticle to facilitate electron transfer; (3) suppressing of metallic iron creation due to the reduction of Fe by carbon during the carbonization process or heat treatment.

A family of LFS materials was synthesized and extensively characterized using in-situ XAS, XRD, and SEM/EDS for structural and morphological analysis, as well as the CV and cycling tests for electrochemical performance diagnosis. Carbon-coating with a minimal amount of metallic iron is determined as an essential condition for achieving higher discharge capacities (more than  $> 166$  mAh/g, which is equivalent to 1 Li-ion). As a benefit of enhancing both electronic conductivity by carbon-coating and Li-ion diffusion kinetics by reducing the particle size to nano-scale, the co-coated and nano-sized NLFS@C was determined to be a competitive cathode with a 1.24  $\text{Li}^+$  ion storage capacity ( $\sim 206$  mAh/g in the first discharge) at 0.1C with a 95.4% cell retention at the end of 35 cycles. The XANES and EXAFS fitting results indicate that the Fe charge never approaches +4 and the number of Fe-O near neighbors remains constant at 4 throughout the charge/discharge cycle, suggesting structural limitations behind this material's low discharge capacity compared to its theoretical value of 332 mAh/g. In summary, the effects of carbon-coating, metallic iron impurities, and reduction of particle size on the NLFS@C cathode were investigated in conjunction with x-ray absorption spectroscopy to correlate morphological and structural characteristics with electrochemical performance.

## **References**

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