Environment-friendly And Cheap Li_2FeSiO_4/C Cathode For Lithium-ion Battery

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Project Description

Lithium iron orthosilicate (Li_2FeSiO_4, (LFS)) is a promising cathode with high theoretical capacity ($331\ mAh/g$) due to two Li per formula **[1]**. The main challenge of this material is its low electronic conductivity leading to the poor reversibility of charge and discharge reactions resulting in rapid capacity fading. To address this, we performed four independent strategies:

1. Reducing particle size of LFS samples from micro-scale to nano-scale in order to reduce diffusion path for intercalating ions.

2. Determining optimum annealing temperature (T_A).

3. Carbon coating to each nanoparticle to facilitate electron transfer.

4. Doping material with trivalent cation (Al^{+3}) in Fe-site to increase concentration of charge carriers;

Particle Size and Morphology

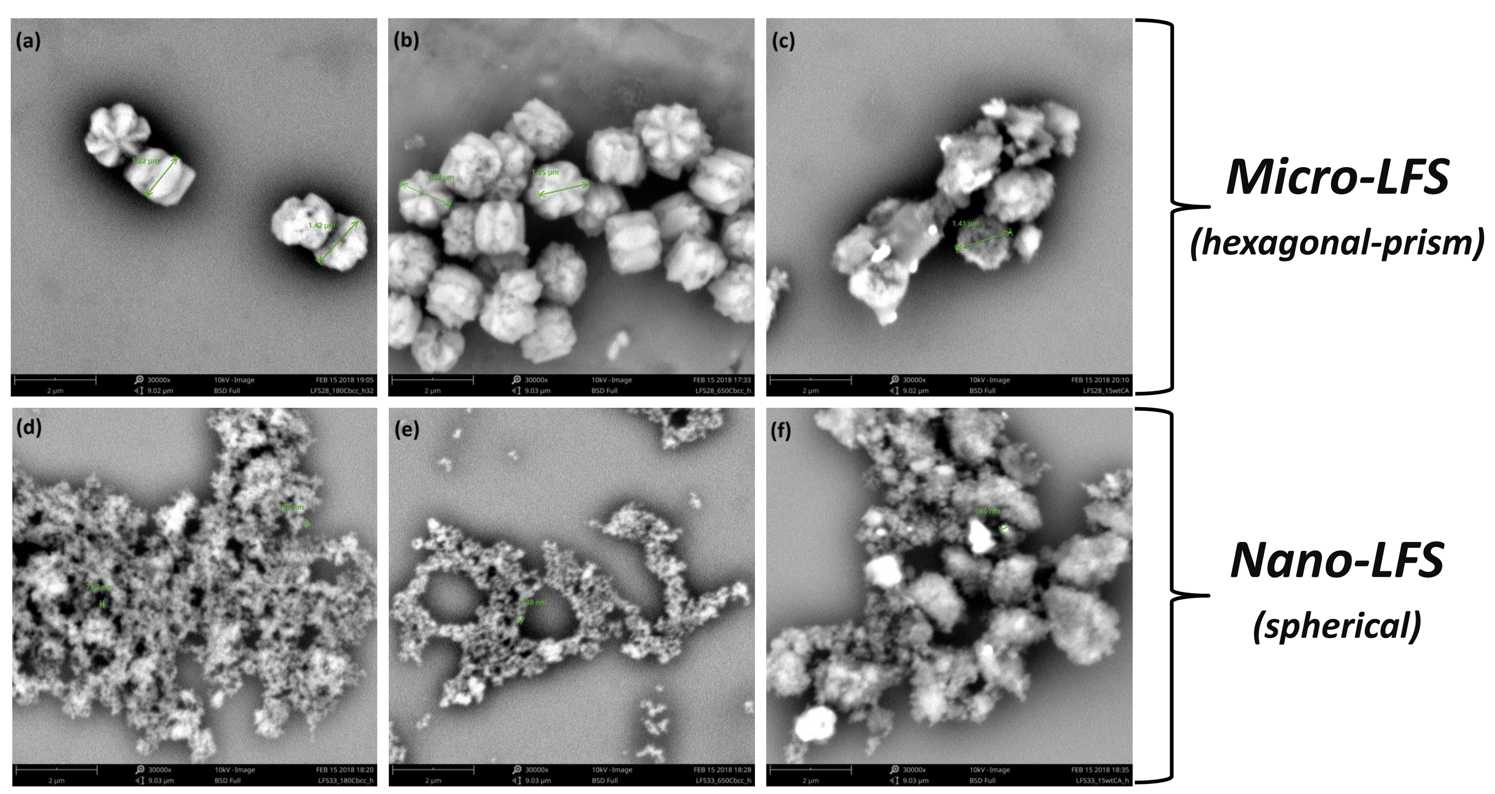


Figure: (a) Micro-size LFS sample as synthesized at 180℃, **(b)** micro-size LFS sample after calcined at 650℃, **(c)** micro-size LFS sample after coated with citric acid and calcined at 650℃, **(d)** nano-size LFS sample as synthesized at 180℃, **(e)** nano-size LFS sample after calcined at 650℃, **(f)** nano-size LFS sample after coated with citric acid and calcined at 650℃.

Crystalline Phase Analysis and XRD Fit

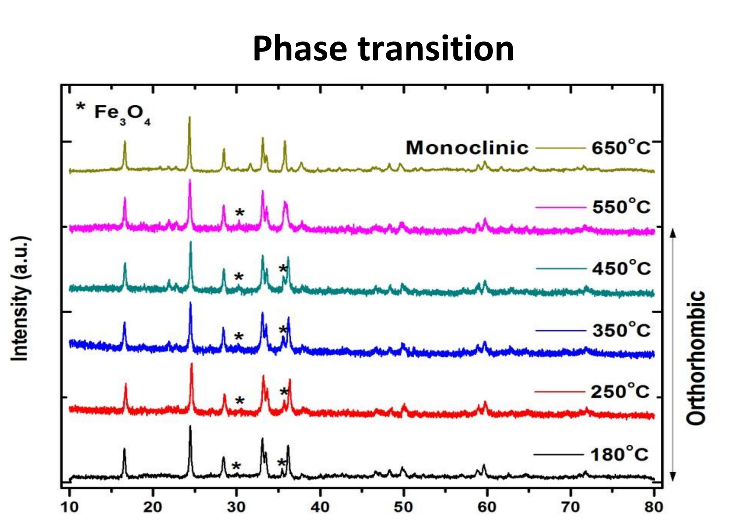


Figure: Phase transition from orthorhombic to monoclinic upon (T_A)

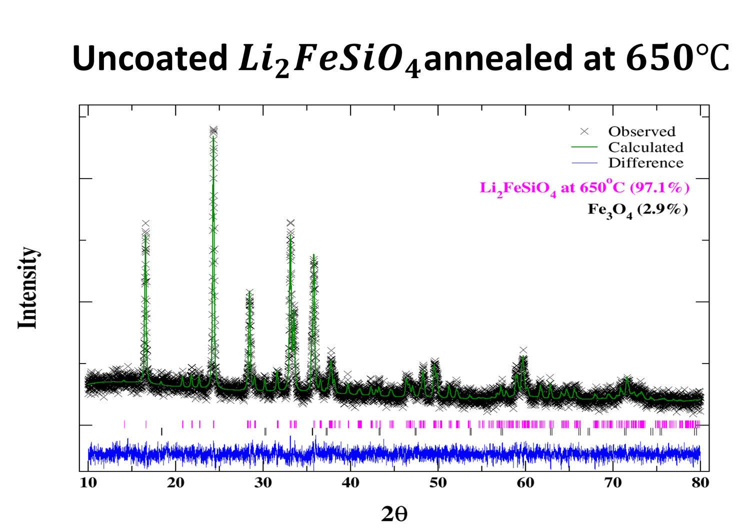


Figure: XRD refinement of uncoated and undoped LFS sample calcined at 650℃.

Orthorhombic phase at 180℃:

$\boldsymbol{a} = 6.27(A^o), \boldsymbol{b} = 10.69(A^o), \boldsymbol{c} = 4.97(A^o)$
$\boldsymbol{\alpha} = 90°, \boldsymbol{\beta} = 90°, \boldsymbol{\gamma} = 90°$

$\boldsymbol{Reduced\ \chi^2} = 1.234,\ \boldsymbol{wR_p} = 0.016,$
$\boldsymbol{R_p} = 0.013, \quad \boldsymbol{P(nm)} = 67.8nm$

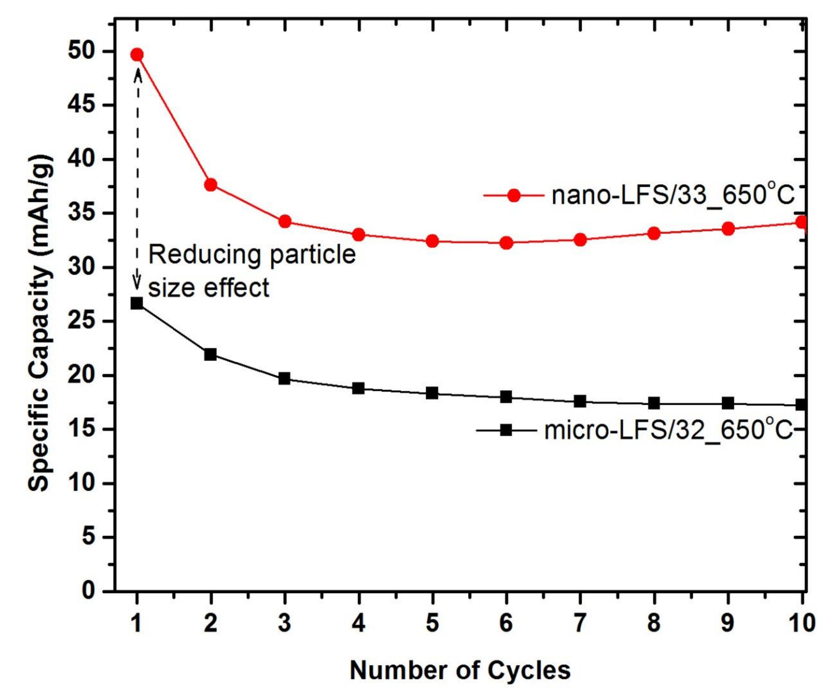
Monoclinic phase at 650℃ with 2.9% Fe_3O_4:

$\boldsymbol{a} = 8.24(A^o), \boldsymbol{b} = 5.01(A^o), \boldsymbol{c} = 8.22(A^o)$
$\boldsymbol{\alpha} = 90°, \boldsymbol{\beta} = 99.2°, \boldsymbol{\gamma} = 90°$

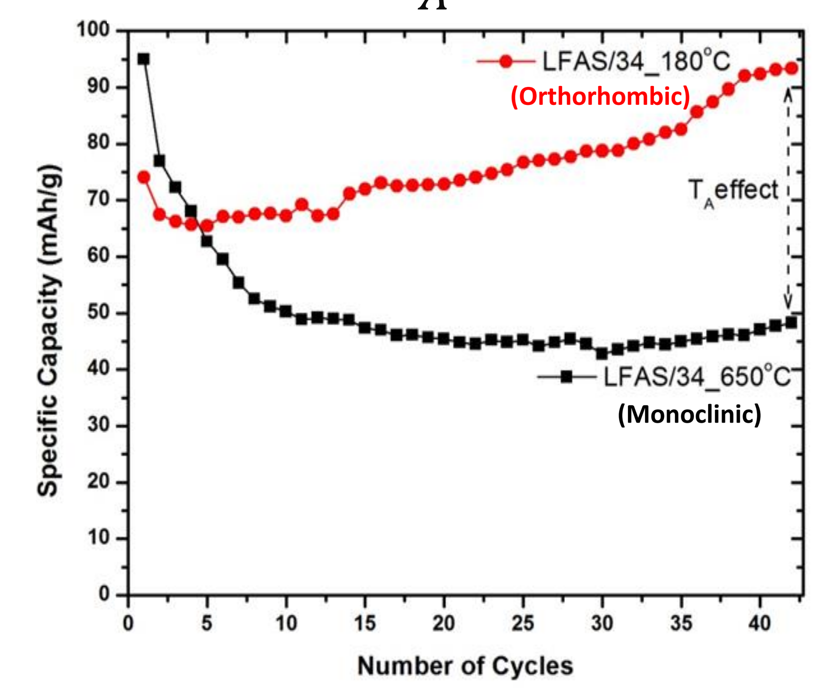
$\boldsymbol{Reduced\ \chi^2} = 1.143,\ \boldsymbol{wR_p} = 0.0156,$
$\boldsymbol{R_p} = 0.0125, \quad \boldsymbol{P(nm)} = 75.8$nm

Electrochemical Performance Results

1. Reducing Particle Size Effect



2. T_A Effect:



3. Carbon-coating Effect

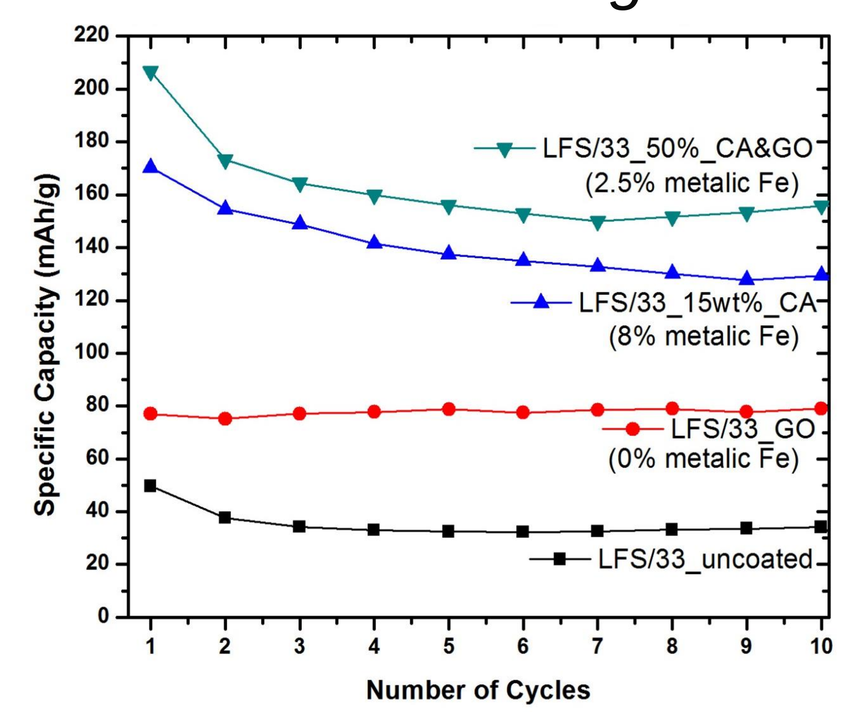
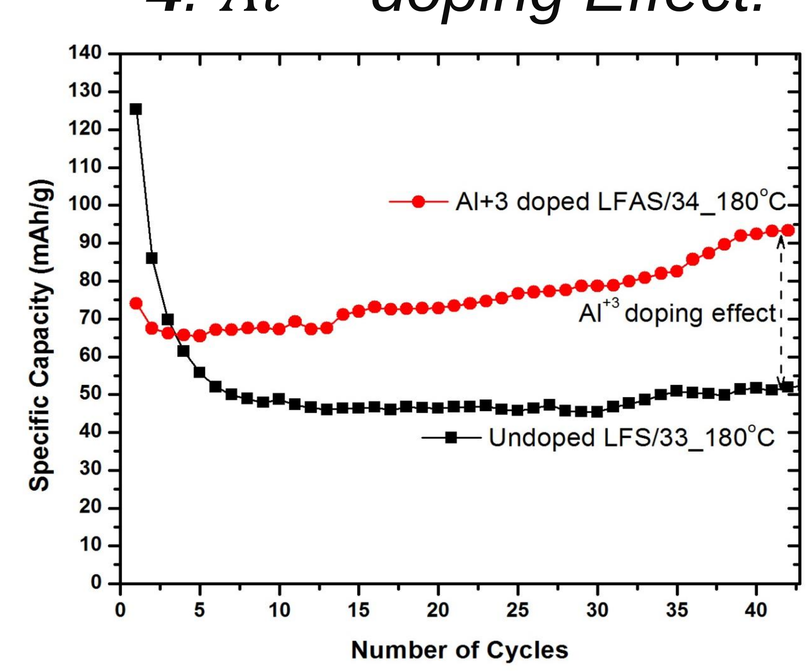
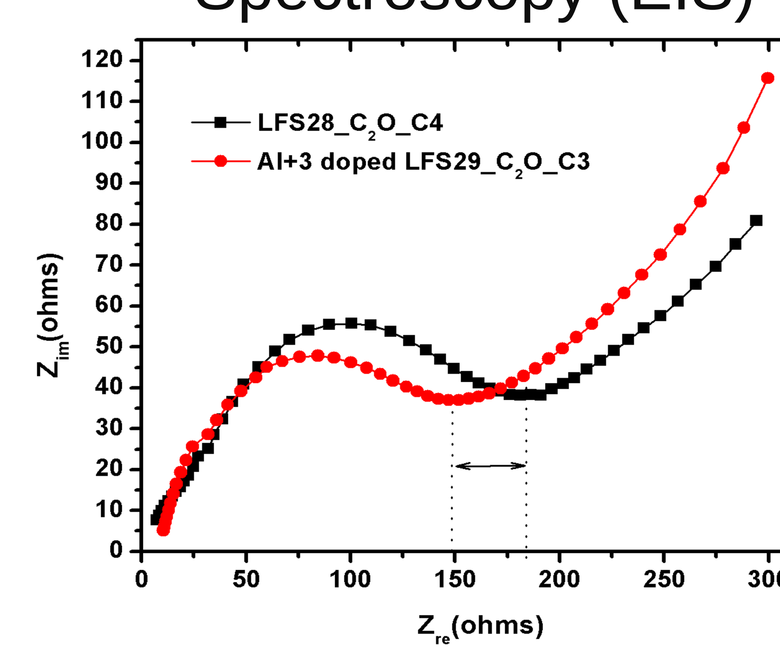


Figure: The effect of carbon coating on undoped LFS sample synthesized in nano-size and coated with Graphene-oxide(GO), Citric Acid (CA) and 50%CA&50%GO.

4. Al^{+3}-doping Effect:



Electrochemical Impedance Spectroscopy (EIS)



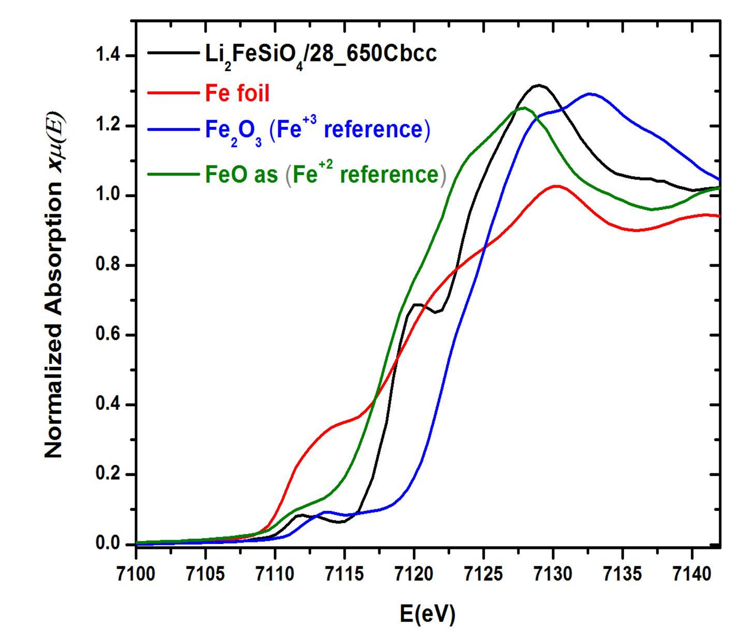
Doped LFAS showed about two times higher performance than undoped LFS. EIS patterns showed that 5% Al^{+3} doped LFS samples in micro-size display higher electronic conductivity and kinetics than undoped LFS samples with respect to charge transfer. This result can be shown as a proof of that doped LFS samples have better electrochemical performance than undoped LFS samples.

XAS analysis

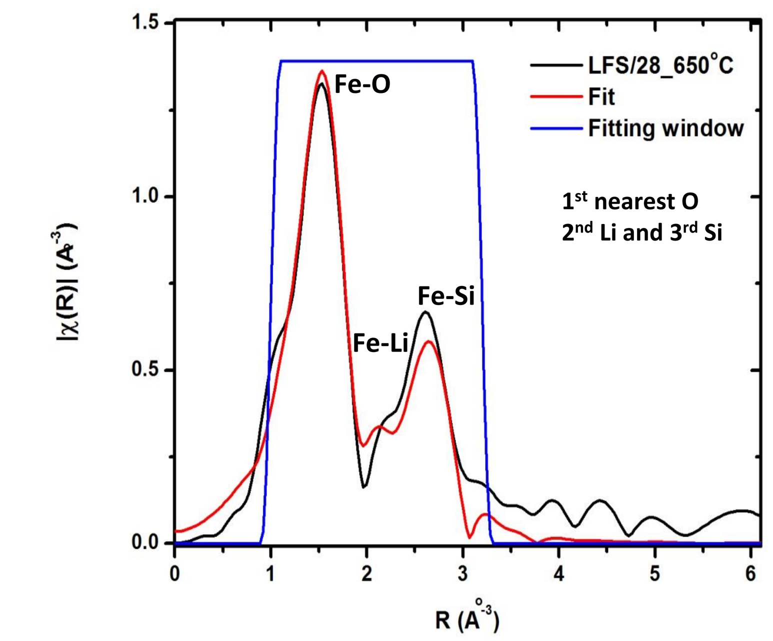
XAS data of micro-size LFS samples was taken at Sector 10 BM line at ANL's Advanced Photon Source. All Fe K-edge data were taken in fluorescence mode with a Lytle detector.

- The oxidation of Fe was estimated by XANES;
- Local environment of Fe in LFS nano-materials was determined by EXAFS.

XANES Analysis

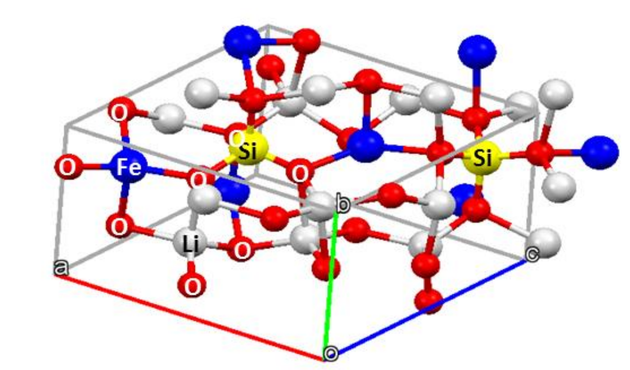


EXAFS Modeling



Fit results:

$Path$	N	$R(A^o)$	$\sigma^2(A^{o^2})$
$Fe-O$	$3.20 \pm (0.473)$	$1.987 \pm (0.0129)$	$0.005 \pm (0.002)$



Conclusions

In this project, the main objective was to improve the electrical conductivity of LFS and ultimately to enhance better electrochemical performance. To do that, all strategies were successfully carried out. As a result, nano-size and Al^{+3} doped LFS samples(uncoated) showed about two times higher specific capacity than undoped and micro-size LFS samples(uncoated). Carbon coating was determined as an inevitable approach to reach its higher performance. Orthorhombic LFS samples annealed at lower temperatures ($< 650℃$) indicated better performance than monoclinic LFS samples calcined at 650℃. XANES analysis showed that the oxidation state of Fe in all LFS samples is same. EXAFS modeling says the nearest neighbor of Fe is Oxygen, 2nd seems Li and 3rd is Si

Acknowledgements

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References

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