Search for High Energy Density Cathode Materials

Evaluation of Li_2MSiO_4 (M = Mn, Fe, Co) System

ILias Belharouak (PI)

R. Amine, A. Abouimrane, D. Dambournet, K. Amine.

Argonne National Laboratory

DOE Merit Review

9 June, 2010

Project ID # ES018

Overview

Timeline

- Start – October 2008
- Finish – September 2014
- 15% complete

Barriers

- Energy density of available Li-ion battery technologies
  - Weight, volume, and affordability
- Abuse tolerance
  - Energy storage systems that must be intrinsically tolerant of abusive conditions

Budget

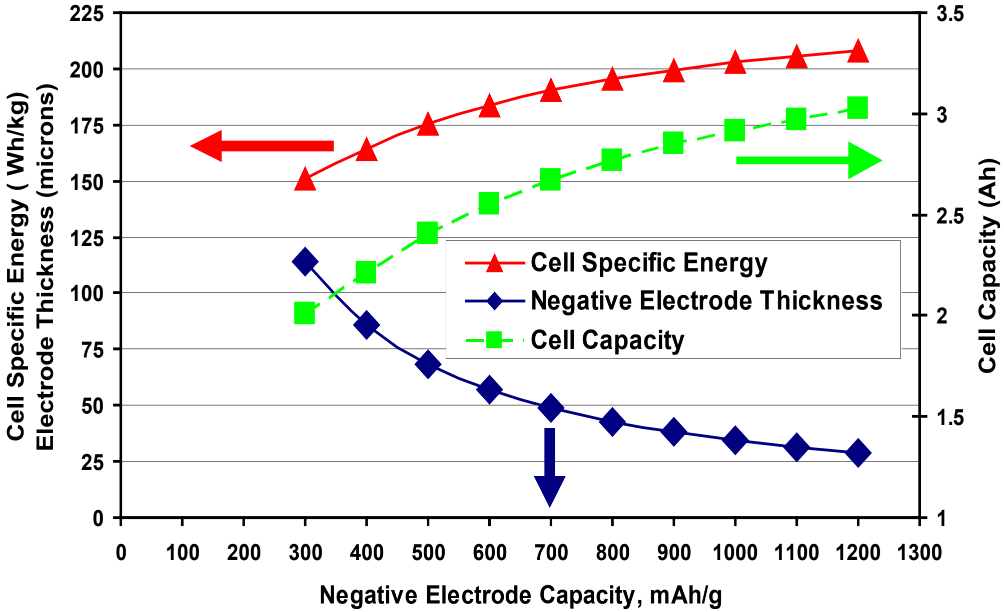
- Total project funding in FY09 + FY10: $600K
- Funding received in FY09: $300K
- Funding in FY10: $300K

Partners

- Collaboration:
  - Center for Nanoscale Materials (ANL)
  - Electron Microscopy Center (ANL)
  - Advanced Photon Source (ANL)
- Support: R. Amine, D. Dambournet, A. Abouimrane, K. Amine.
- Project lead: ILias Belharouak

General Objectives of this Study

Search for High Energy Density Cathode Materials



- When an NCA cathode electrode (100 µm-thick) combined with higher capacity anodes, only about third of energy density increase is expected in 18650 cell.
- There are technological hurdles (electrode design) to what higher-capacity anode can add to the value of energy density in a Li-ion cell based on available cathode materials.
- Search for high-energy density (gravimetric and volumetric) cathode materials is equivalent to the search for <u>high-capacity</u> (per Kg), <u>high-potential</u>, <u>high packing</u> bulk density cathode materials.

Term Objectives of this Study

Evaluation of Li_2MSiO_4 (M = Mn, Fe, Co) System

- Develop new preparation methods to synthesize high purity Li_2MSiO_4 (M = Mn, Fe, Co) materials.
- Understand the structure of these materials at the local and bulk levels.
- Check whether these materials pertain to the concept of 2-lithium ions extraction and insertion cathode materials.
- Develop ways to overcome the barrier of the insulating properties of these materials.
- Achieve an overall evaluation of these materials from structural and electrochemical standpoints with regard to their possible applicability in high-energy density Li-ion batteries.

Milestones for FY09 and FY10

- Materials preparation and characterization
  - Introduction of new preparation methods including solid state, Pechini, and sol-gel reactions to synthesize pure Li_2MnSiO_4 phase. *(Completed)*
  - Initiation of physical and structural characterizations in order to elucidate the impact of the morphological and atomic arrangement on the electrochemical properties of Li_2MnSiO_4. *(Completed)*
  - Understand the capacity fade observed for Li_2MnSiO_4. *(Ongoing)*
  - Investigation of $Li_2(Mn_{1-x}Fe_x)SiO_4$ stabilized phases. *(Ongoing)*
- Electrochemical performances
  - Positive electrodes made of the as-prepared Li_2MnSiO_4 material have been assembled with lithium negative anode and conventional electrolytes to check the capacity of the material. *(Completed)*
- Materials optimization
  - To achieve better electrochemical performances, ways such as carbon coating, carbon nanotube integration, and ball milling have been adopted to improve the electronic conductivity of Li_2MnSiO_4. *(Completed)*
- Check the applicability of Li_2MnSiO_4 in Li-ion cells. *(Completed)*

General Approach

- Search for high-capacity cathode (per Kg) requires:

  - Materials that can vehicle more than one lithium per their unit formulas.

  - Materials whose active cations has a lower valence.

  - Reduction of matter in the materials (simply Li_2O).

- Enabling of high-potential cathodes above 4V but not exceeding 5V.

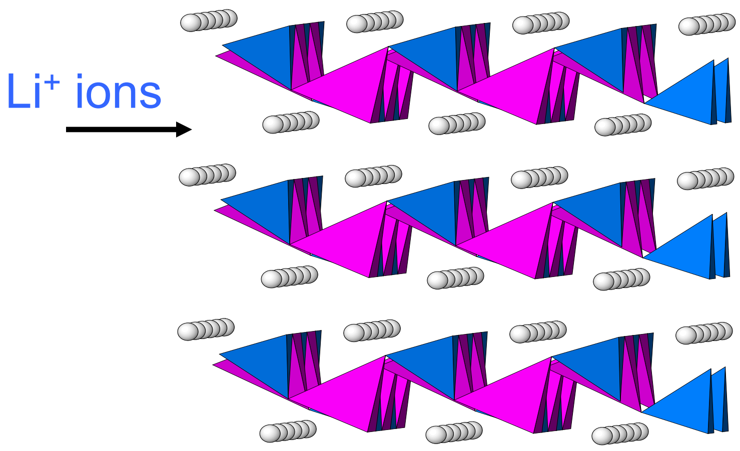
  - Advanced environmentally friendly and economically sound synthetic methods,

  - $LiNi_{0.5}Mn_{1.5}O_4$ (~4.7V,148mAh/g), Li(Mn-or-Co)PO_4 (~4.1V-or-4.8V, 170mAh/g), ANL-composite materials (~4.0V, 250mAh/g).

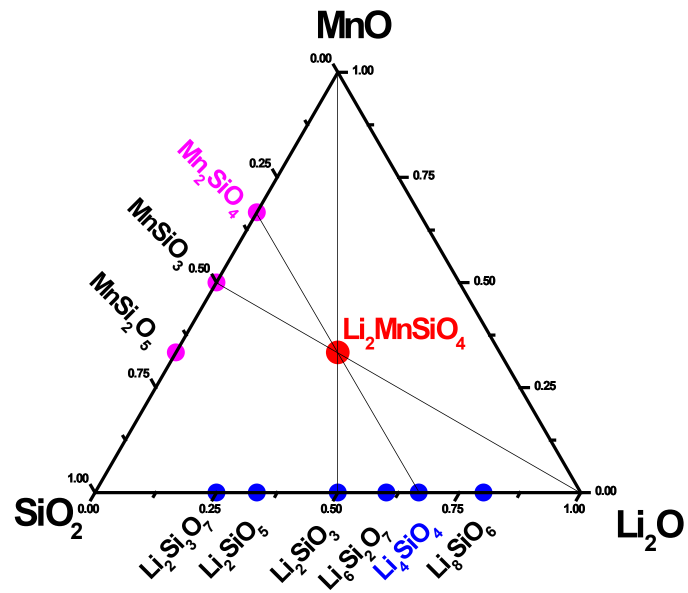
- Optimize packing density of the materials for practical use (morphology and particle size).

Term Approach

Structure Model of Li_3PO_4



Phase Diagram and Structure

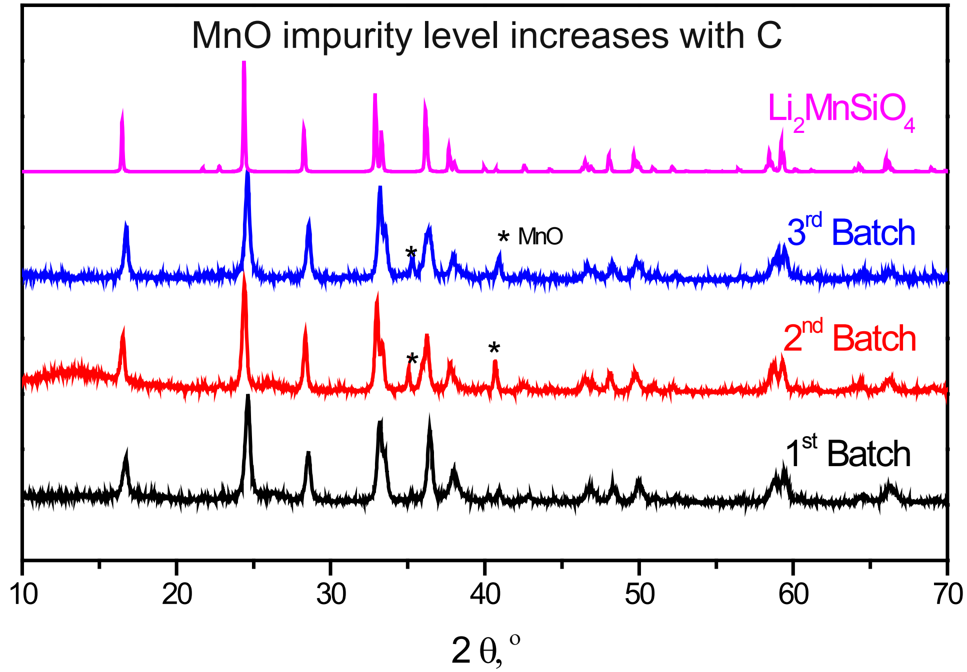


- Li_2MnSiO_4 can be iso-structural to certain forms of Li_3PO_4.
- The extraction/insertion of 2-Li ions can lead to the delivery of 333mAh/g capacity according to the following scheme:

$$Li_2Mn^{2+}SiO_4 \leftrightarrow Mn^{4+}SiO_4 + 2Li^{+} + 2\bar{e}$$

- Strong covalent Si-O bonds can be good for safety.

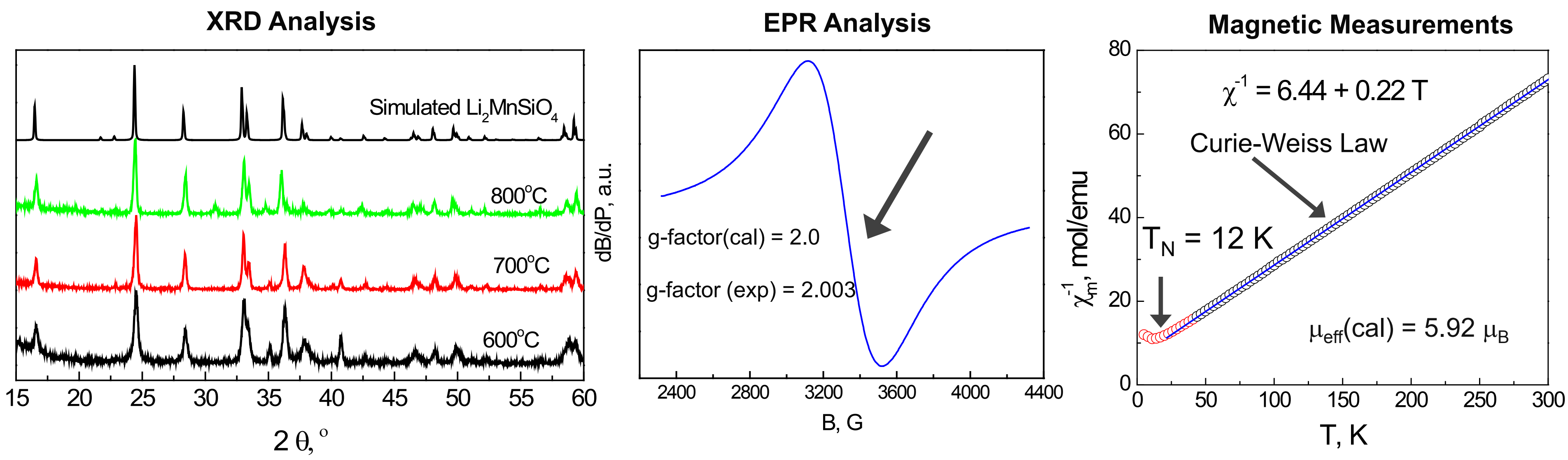
Materials Synthesis



Sol/gel process has been found to yield the purest phases

- Batch 1: gelation occurred in acetic acid medium containing lithium, manganese, and silicon acetates followed by subsequent heat treatments up to 700 ^oC.
- Batch 2: during gelation, high surface area carbon was added to be part a composite material.
- Batch 3: during gelation, cellulose, ethylene glycol, etc. were incorporated to yield a carbon coated material.

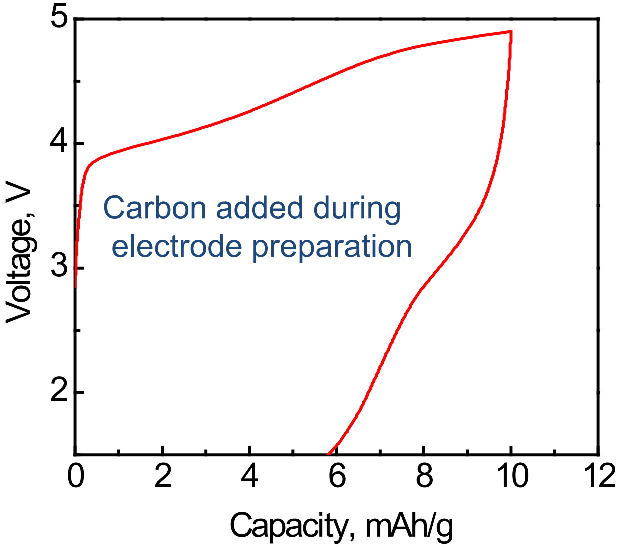
Validation of the Structural Model of Li_2MnSiO_4



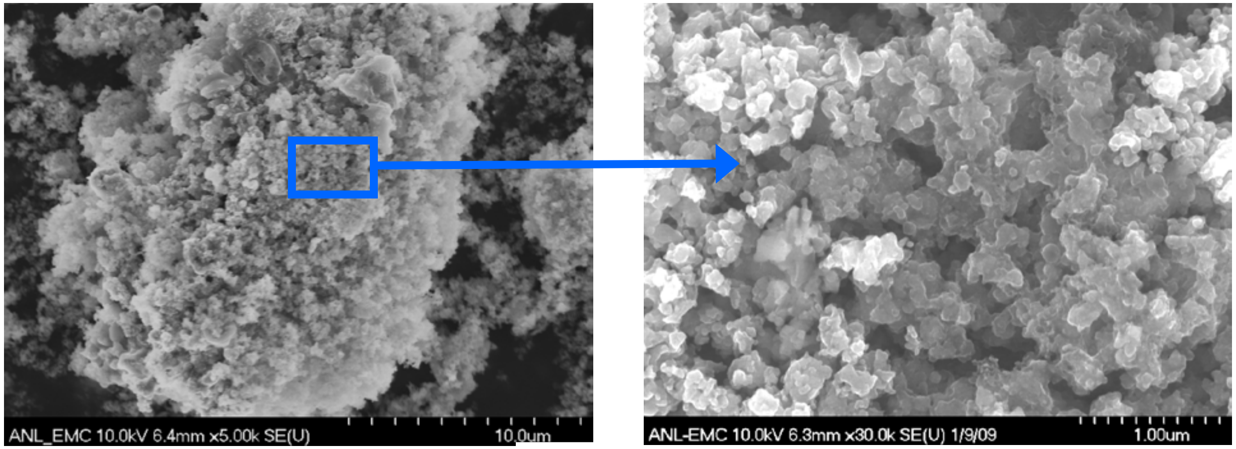
- X-ray diffraction confirmed the structural model of Li_3PO_4 for Li_2MnSiO_4.
- Magnetic measurements confirmed the valence state of manganese that is Mn^{2+}.
- EPR measurements confirmed the occurrence of magnetic interactions at low temperature.

Li_2MnSiO_4 Pristine is Barely Active

Capacity of Li_2MnSiO_4



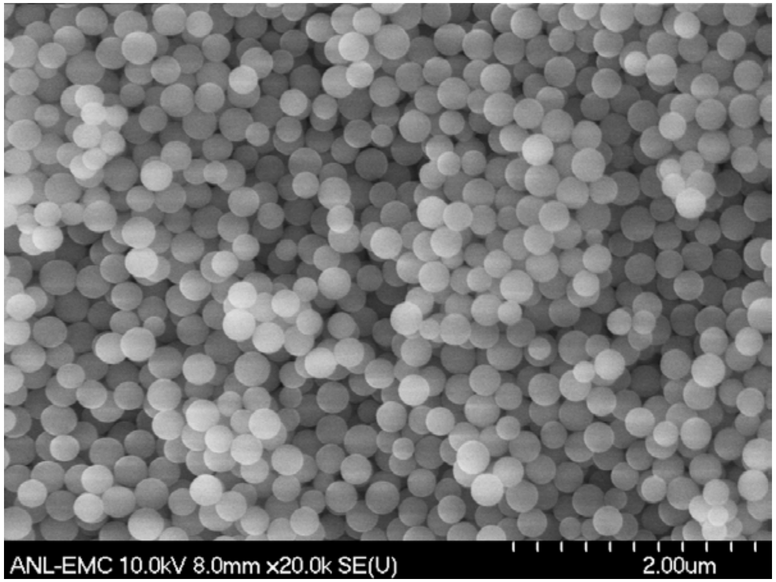
Agglomeration of Li_2MnSiO_4

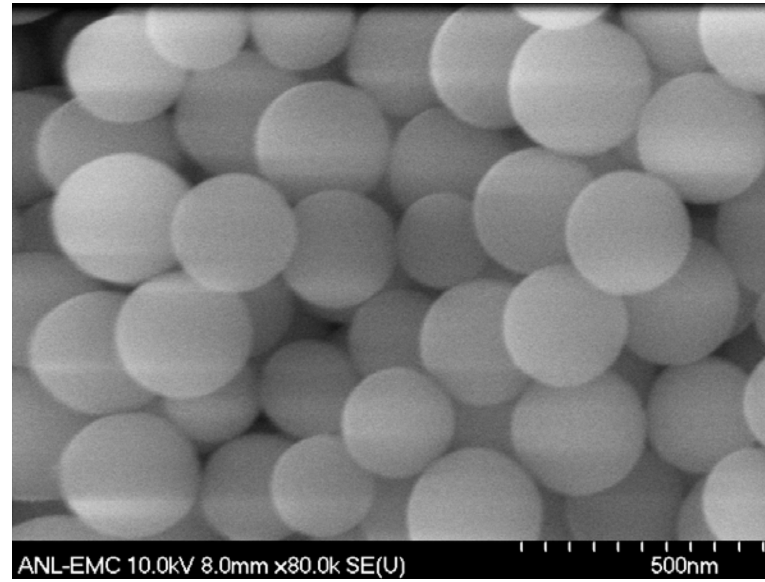


- As-prepared Li_2MnSiO_4 is “almost” electrochemically inactive because of its large aggregates and low electronic conductivity.
- Therefore, particle size reduction and coating have been applied as ways to activate Li_2MnSiO_4.

Particles Size Reduction: Silica Template

200 nm spherical SiO_2

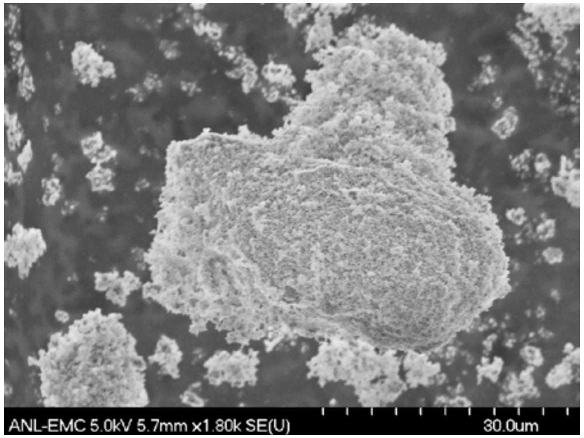




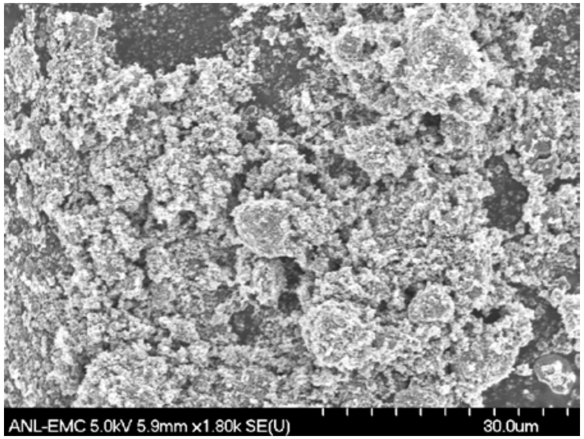
- Develop a simple synthesis method to prepare spherical nano-silica.
- Use the silica template to prepare nano-Li_2MnSiO_4 material.
- On the addition of manganese and lithium sources in solid state reactions, re-agglomeration has been observed.

Particles Size Reduction: Ball Milling

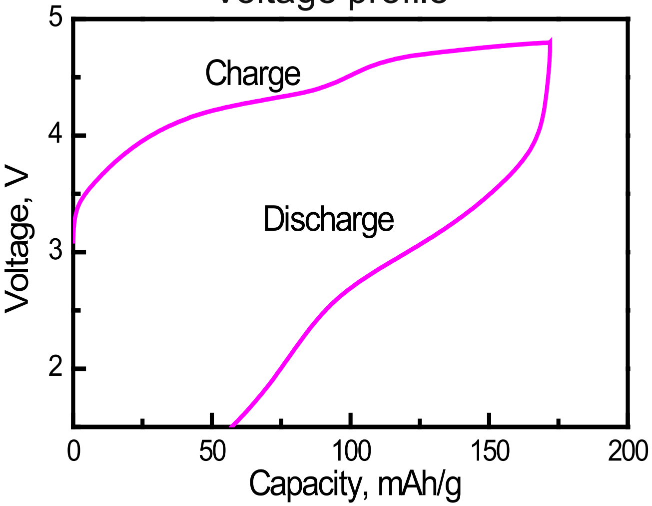
Li_2MnSiO_4, As-prepared



Li_2MnSiO_4, after ball milling



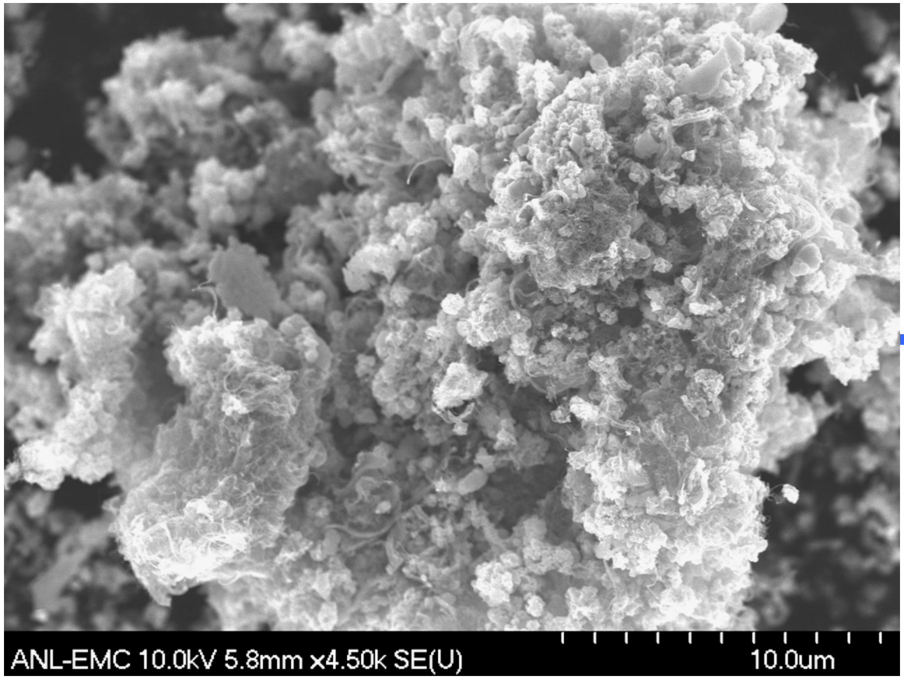
Voltage profile

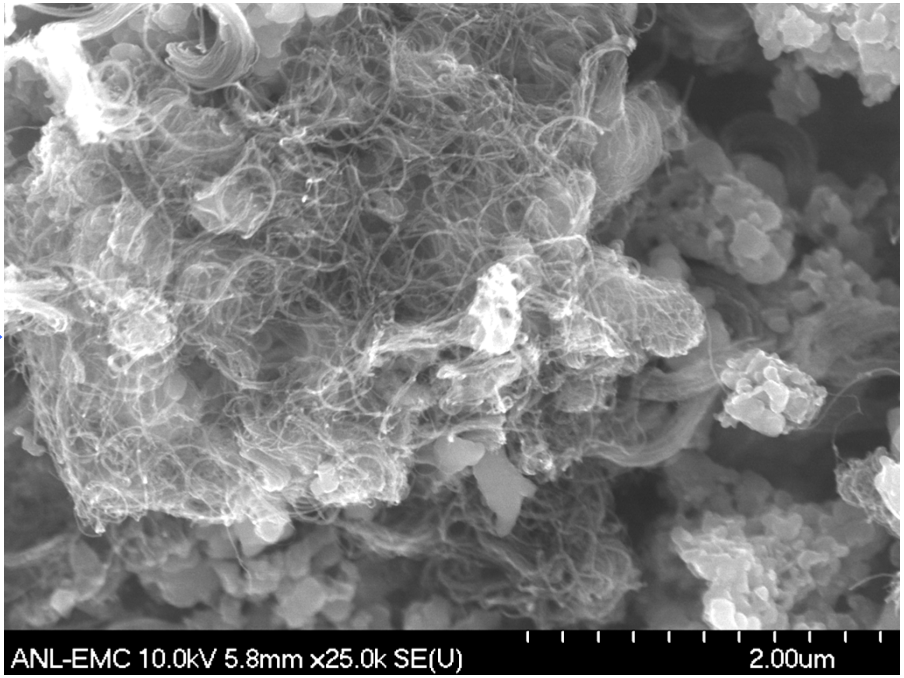


- High-energy ball milling was found to be an effective way to breakdown the large agglomerates of Li_2MnSiO_4 to smaller particles.
- The method has been found to be none destructive because the structure of Li_2MnSiO_4 was preserved after the completion of ball milling.
- Significant improvement of the initial capacity of the material has been observed.

Carbon Integration: Implantation of CNTs

Carbon nanotubes CNTs were injected during the gel maturation process

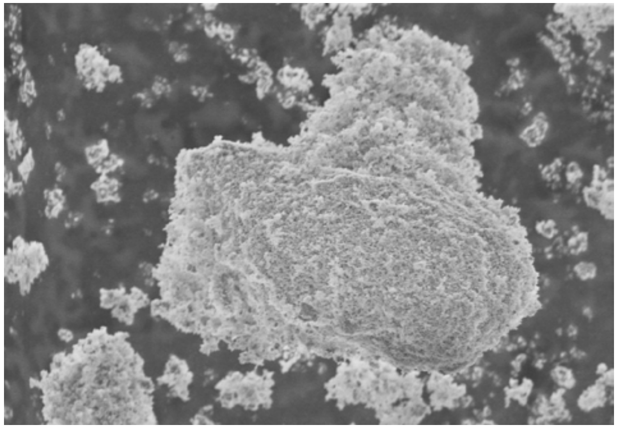




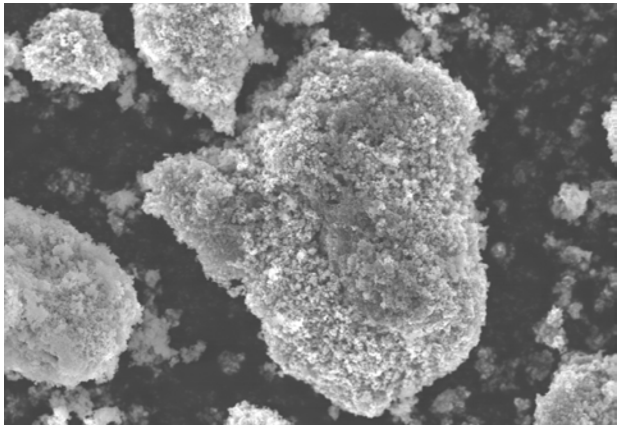
- CNTs were well dispersed within the agglomerates of Li_2MnSiO_4.
- CNTs became parts of the aggregates.
- CNTs formed a conductive network in Li_2MnSiO_4/CNT.

Carbon Integration: Carbon coating

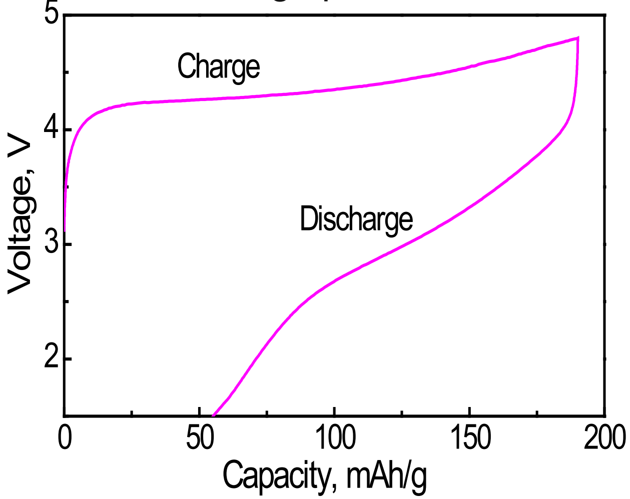
Li_2MnSiO_4, As-prepared



Li_2MnSiO_4, after carbon coating

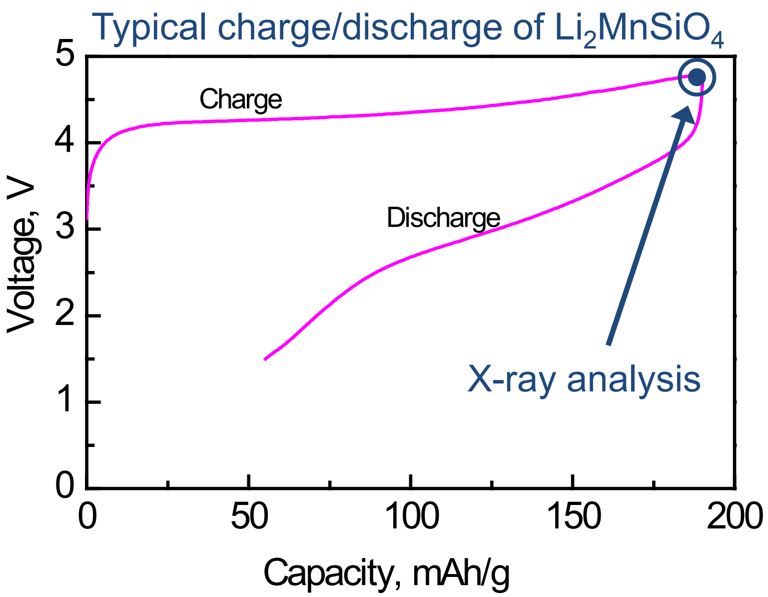


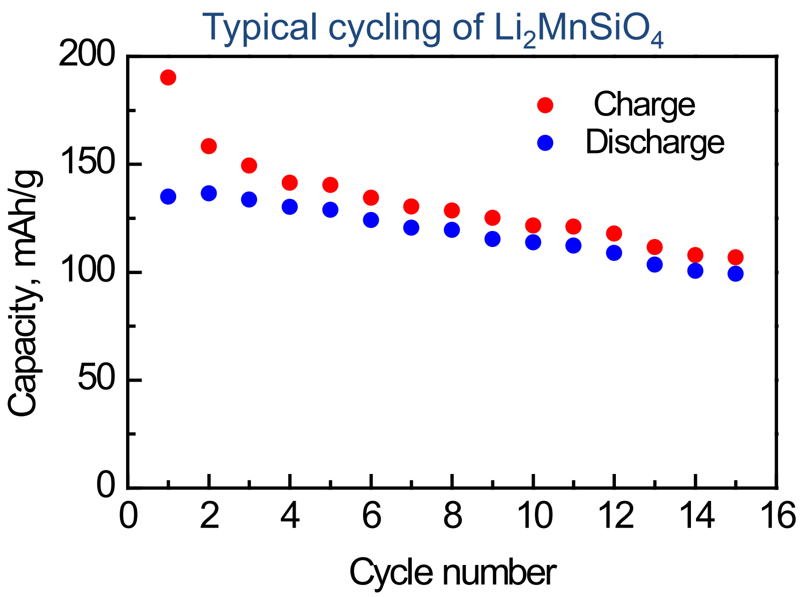
Voltage profile



- Cellulose as a carbon source was added during the preparation of the material.
- Significant improvement of capacity has been observed for carbon-coated Li_2MnSiO_4.

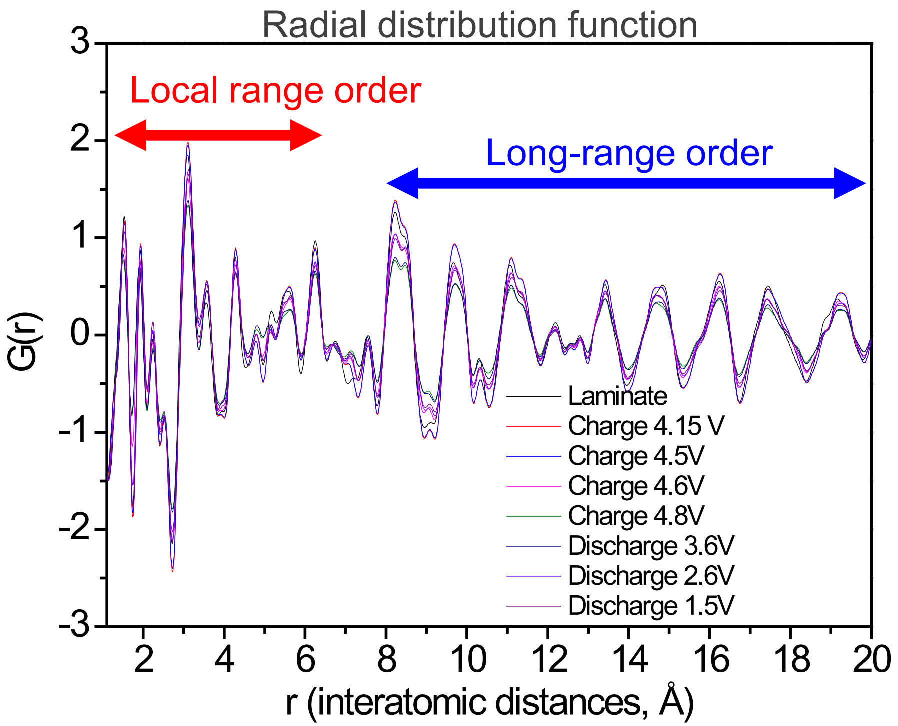
Li_2MnSiO_4 Capacity Fade Issue





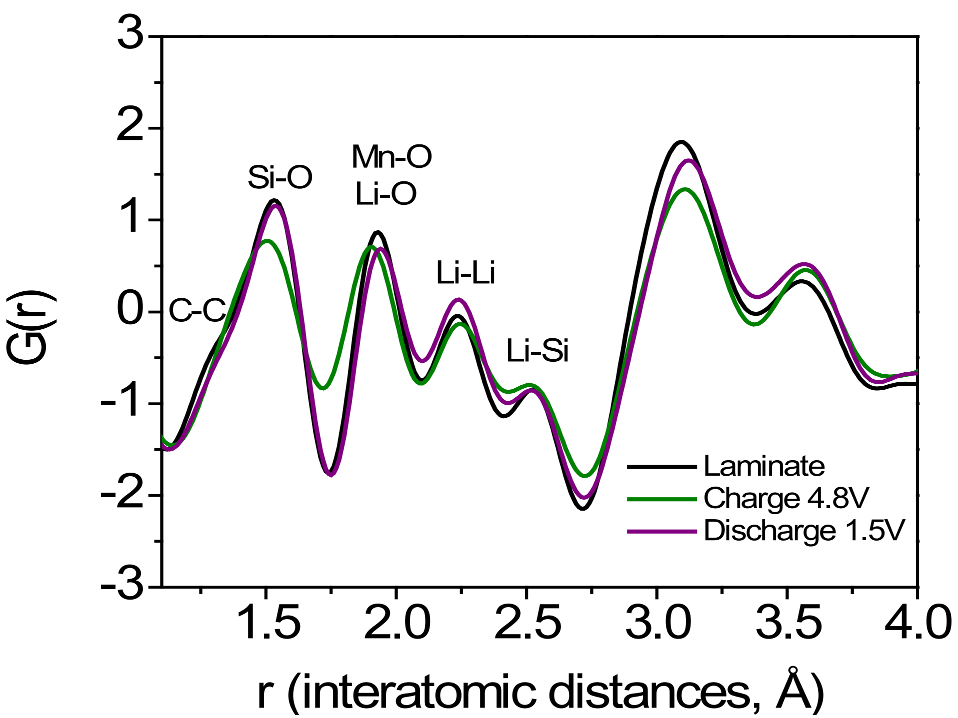
- Evidence of Li_2MnSiO_4 amorphization.
- Amorphoziation is responsible for the quick capacity fade.
- Questions:
  - How can an amorphous phase cycle lithium?
  - Is it possible to impeach the amorphization?
- Answers:
  - PDF analysis: very powerful tool to look at the local structure of amorphous materials.
  - Crystal chemistry and Materials approach.

Pair Distribution Analysis Upon Lithium Removal and Uptake

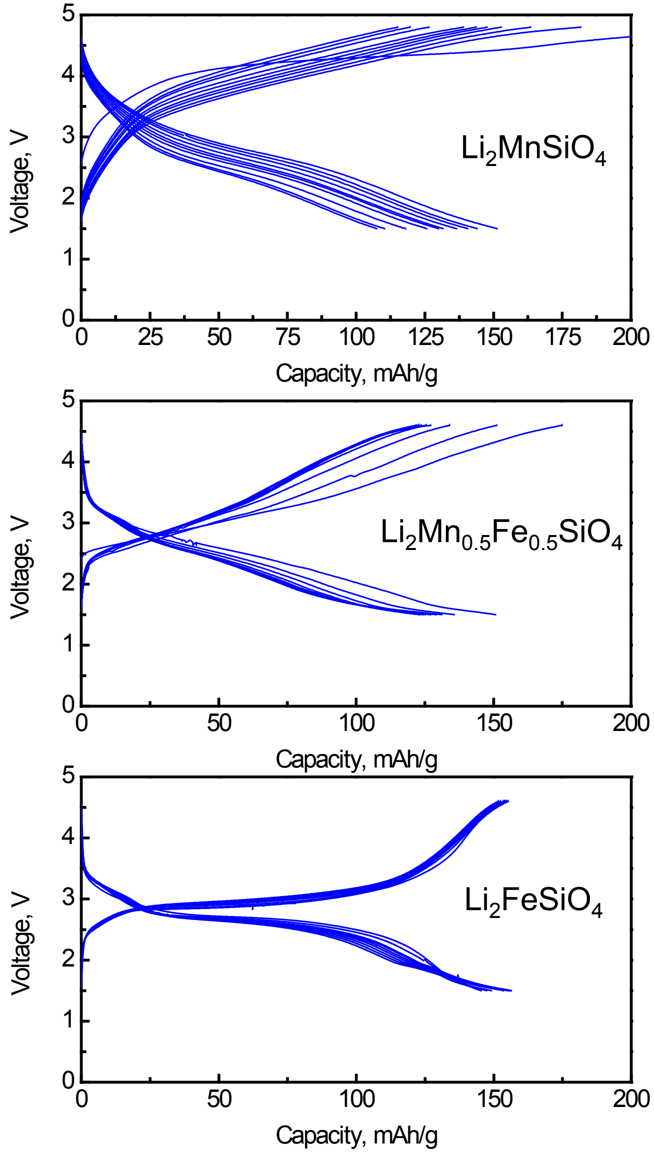


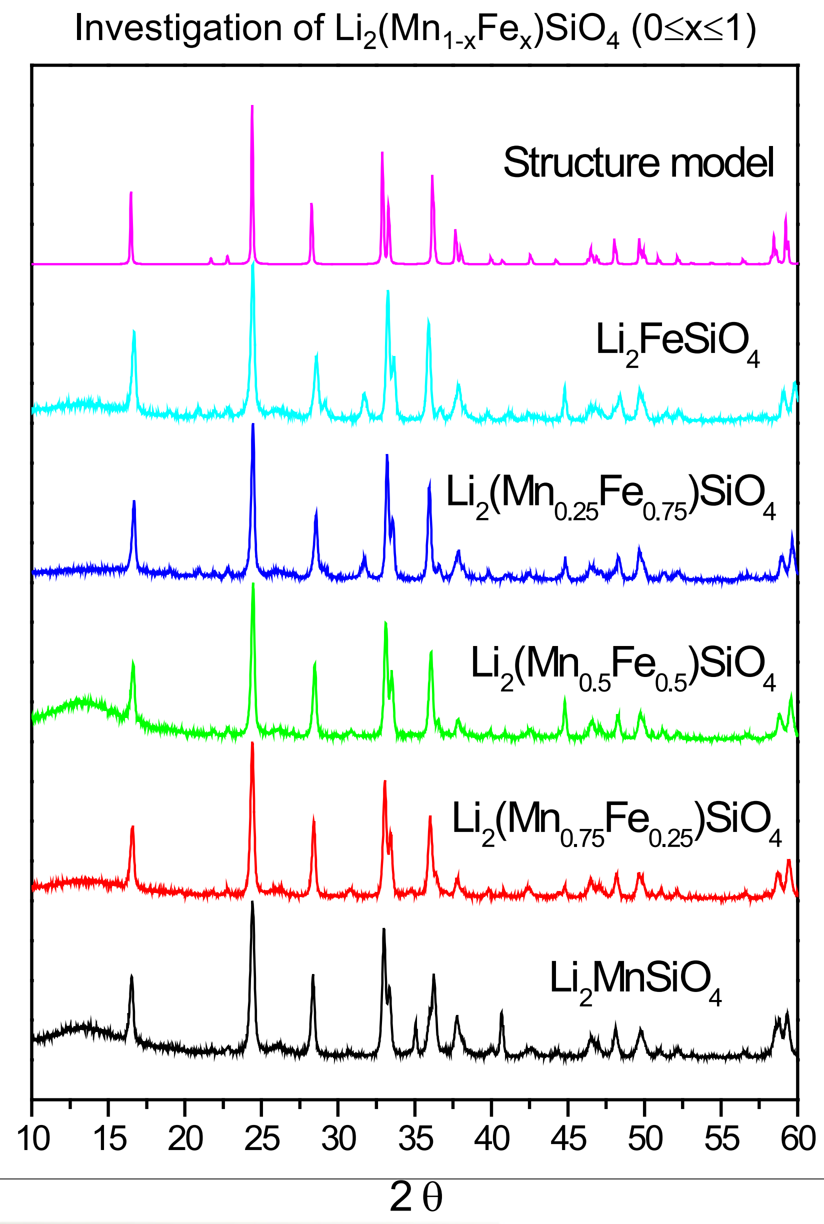
- Radial pair distribution function G(r) gives direct information on interatomic distances.
- G(r) is independent of orientation, it thus provides valuable structural information on glasses and polymers.
- The radial PDF can be calculated directly from x-ray powder diffraction through the use of Fourier Transform.

- The structure of crystalline Li_2MnSiO_4 is kept when the latter is fully charged or discharged.
- Evidence of lithium removal and uptake through the Mn-O shortening and enlargement.
- Full analysis and structural fitting is underway.



Structural Stabilization Through Fe^{2+} Ions Incorporation





Collaborations

- Center for Nano-scale Materials (ANL)

  Magnetic and EPR measurements

- Electron Microscopy Center (ANL)

  Scanning Electron Microscopy SEM of Li_2MnSiO_4 cathode

- Advanced Photon Source (ANL)

  Pair Distribution Function (PDF) analysis of Li_2MnSiO_4 cathode

- Brookhaven National Laboratory (Future)

  X-ray absorption spectroscopy (XANES, EXAFS) and x-ray diffraction

- California Institute of Technology Institute (future)

  Mossbauer spectroscopy on $Li_2Mn_{1-x}Fe_xSiO_4$

Future Work

- Achieve a full understanding on the mechanistic reasons behind the amorphization of Li_2MnSiO_4 upon lithium removal.
- Stabilization of Li_2MnSiO_4 through iron incorporation has shown promise. A full structural and electrochemical investigation of $Li_2Mn_{1-x}Fe_xSiO_4$ is ongoing.
- Achieve an overall evaluation of these materials from the structural and electrochemical with regard to their possible applicability in Li-ions batteries.
- Continue the effort of achieving full capacity of these materials using:
  - Carbon coating and integration using carbonaceous additives and gas phase reaction.
  - Particle size reduction through templating in silica matrix.
  - High-energy ball milling. .
- The information learned from the study of Li_2MnSiO_4 will be used to investigate the compositions with iron as the electrochemically active ion.
- $Li_2Mn_{1-x}Fe_xSiO_4$ Materials will be sent to BNL and Caltech for X-ray absorption spectroscopy and Mossbuaer studies, respectively.
- Explore new multi-electron cathodes.

Summary

- Amorphization is responsible for the capacity fade of Li_2MnSiO_4 upon lithium removal. Pair distribution function analysis confirmed that this is not a structural disintegration of Li_2MnSiO_4. It will be quite challenging to impeach this phenomenon from happening.

- We successfully integrated carbon nanotube as conductive matrix during the synthesis of Li_2MnSiO_4. The materials are on schedule for electrochemical tests. The method can extended to other materials as well.

- Stabilization of Li_2MnSiO_4 through iron incorporation has led to structure stabilization. $Li_2Mn_{1-x}Fe_xSiO_4$ materials have shown promise in terms of capacity retention.