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Evaluation of Li_2MnSiO_4 Cathode

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Overview

Timeline

- Start - October 2008
- Finish – September 2014
- 8% 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 FY2009
  - DOE SHARE ($300K)
- FY2010 ($300K)

Partners

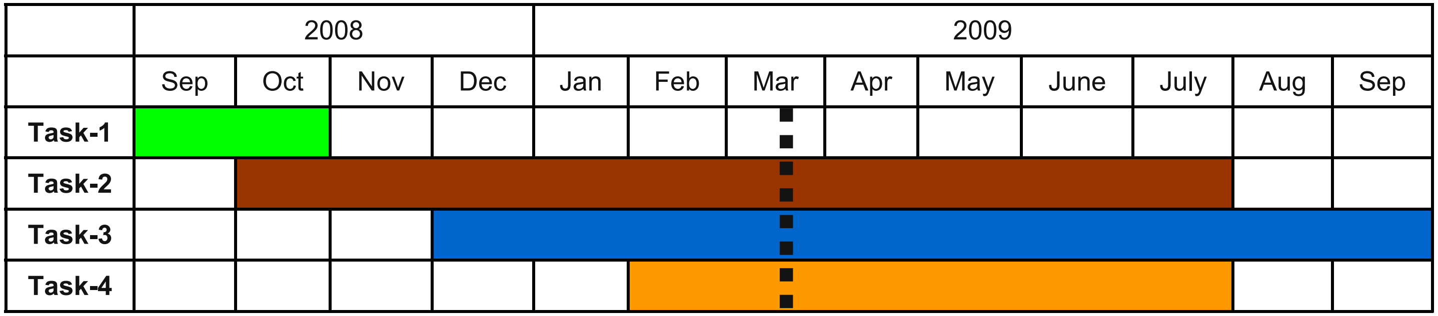
- Project lead: Ilias Belharouak
- Support: A. Abouimrane, K. Amine
- Collaboration:
  - Center of Nanoscale Materials (ANL)
  - Electron Microscopy Center (ANL)

Objective

Evaluation of Li_2MSiO_4 (M= Mn, Fe, Co) silicate cathode for high-energy density lithium batteries

- 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 the structural and electrochemical standpoints with regard to their possible applicability in high-energy density Li-ion batteries.

Milestone for FY2009



- Bibliographical study and materials supply
- Materials preparation and characterization
  - Different preparation methods have been introduced including solid state, Pechini, and sol-gel reactions. The later has been found to be the most effective method to get high purity materials.
  - Physical and structural characterizations have been conducted in order to elucidate the impact of the morphological and atomic arrangement on the electrochemical properties of Li_2MnSiO_4.
  - Several characterization techniques have been used including x-ray diffraction, electron paramagnetic resonance, magnetic measurements, and scanning electron microscopy.
- 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.
  - Positive electrode optimization has been initiated in order to check the impact of the carbon conductive additive on the overall capacity of the material.
- Materials optimization
  - To achieve better electrochemical performances, ways such as carbon coating and ball milling have been adopted to improve the electronic conductivity of Li_2MnSiO_4.

Approach

Structural observation

- Li_2MnSiO_4 can be iso-structural to certain forms of Li_3PO_4: Mn^{2+} ions are present within a $[SiO_4]$ anionic silicate network that replaces $[PO_4]$ anionic phosphate network, and 2-Li ions are available in 3D-dimentional channels.

- Strong covalent Si-O bonds will translate into very stable electrochemical and enhanced safety characteristics.

Electrochemical consideration

- The extraction/insertion of 2-Li ions from/in the host structure is possible because Manganese ions can oxidize and reduce reversibly from 2 to 4 oxidation states, with the generation of 333mAh/g theoretical capacity according to the following scheme: $Li_2Mn^{2+}SiO_4 \leftrightarrow Mn^{4+}SiO_4 + 2Li^+ + 2\bar{e}$

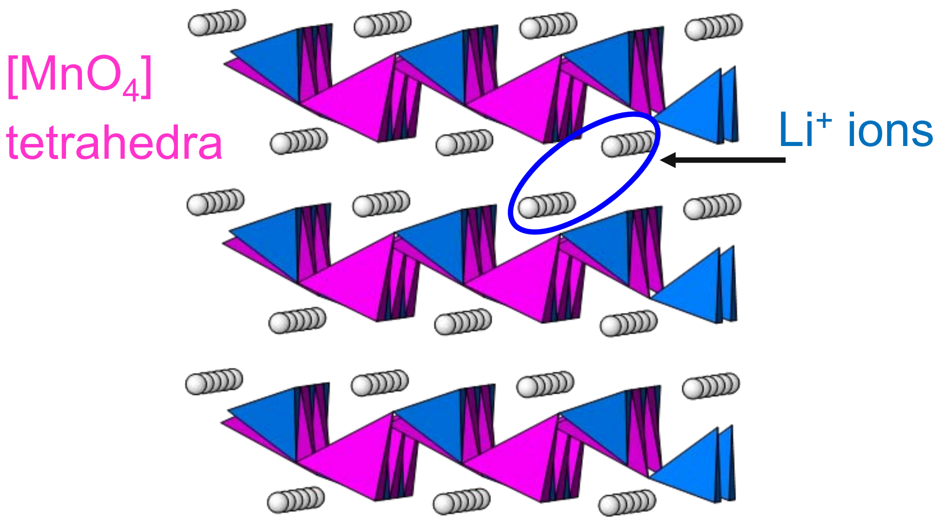
- $Mn^{2+/4+}$ redox couple is preferred because of its higher potential vs. Li^o, so high energy-density can be achieved.

- Low cost of manganese.

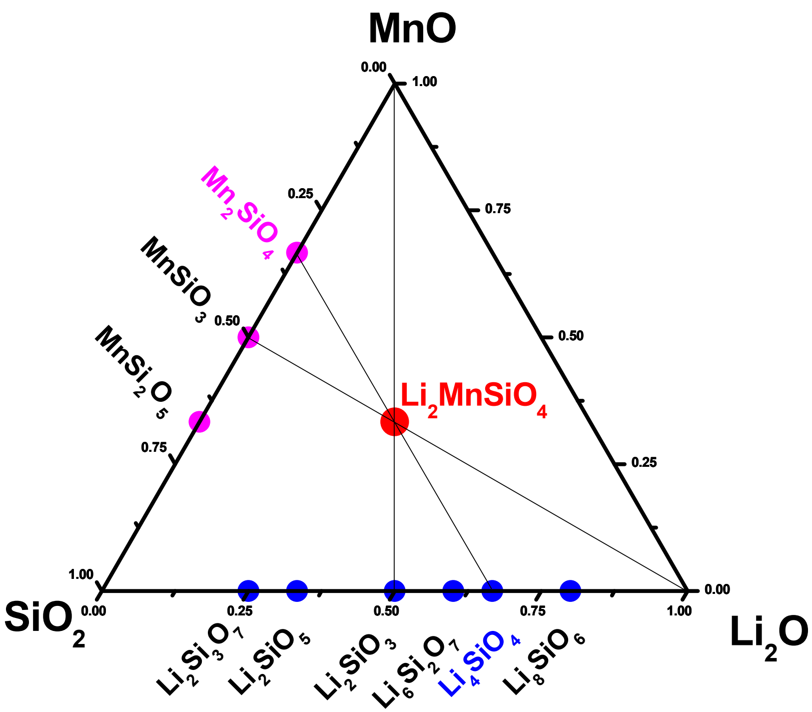
Challenge

- Overcome the intrinsic electronic insulating properties of Li_2MnSiO_4.

(Li_2O-SiO_2-MnO)Phase Diagram and Structure



Structure of Li_2MnSiO_4



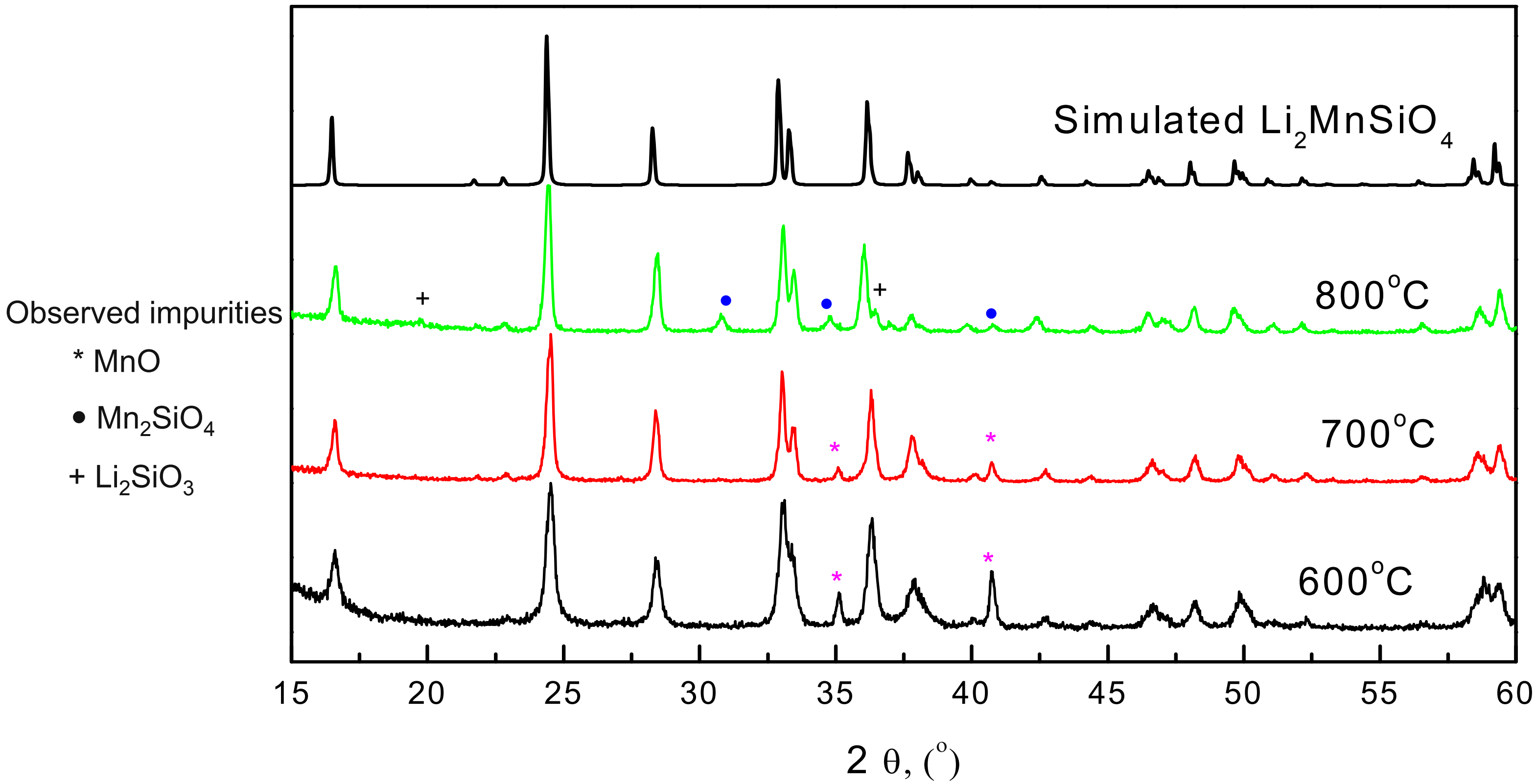
Ternary phase diagram

- The structure of Li_2MnSiO_4 exhibits lithium ions that reside within channels and that are available for extraction and insertion.
- Manganese should be kept as Mn^{2+} ions to avoid the presence of higher oxidation states that will jeopardize the achievement of full capacity.

Li_2MnSiO_4 Preparation

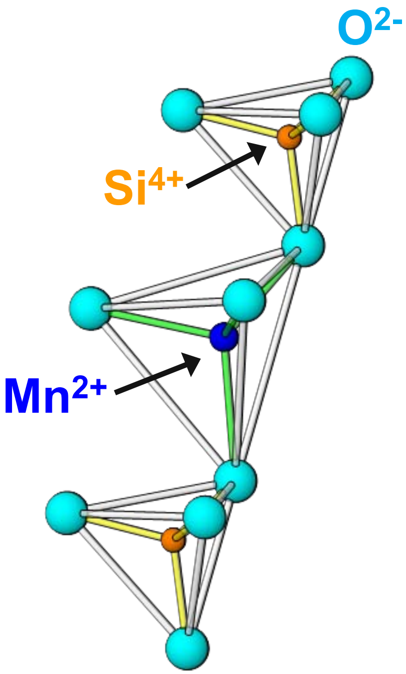
New Sol-Gel Method

Silicon acetate + Lithium acetate + Manganese acetate = transparent gel

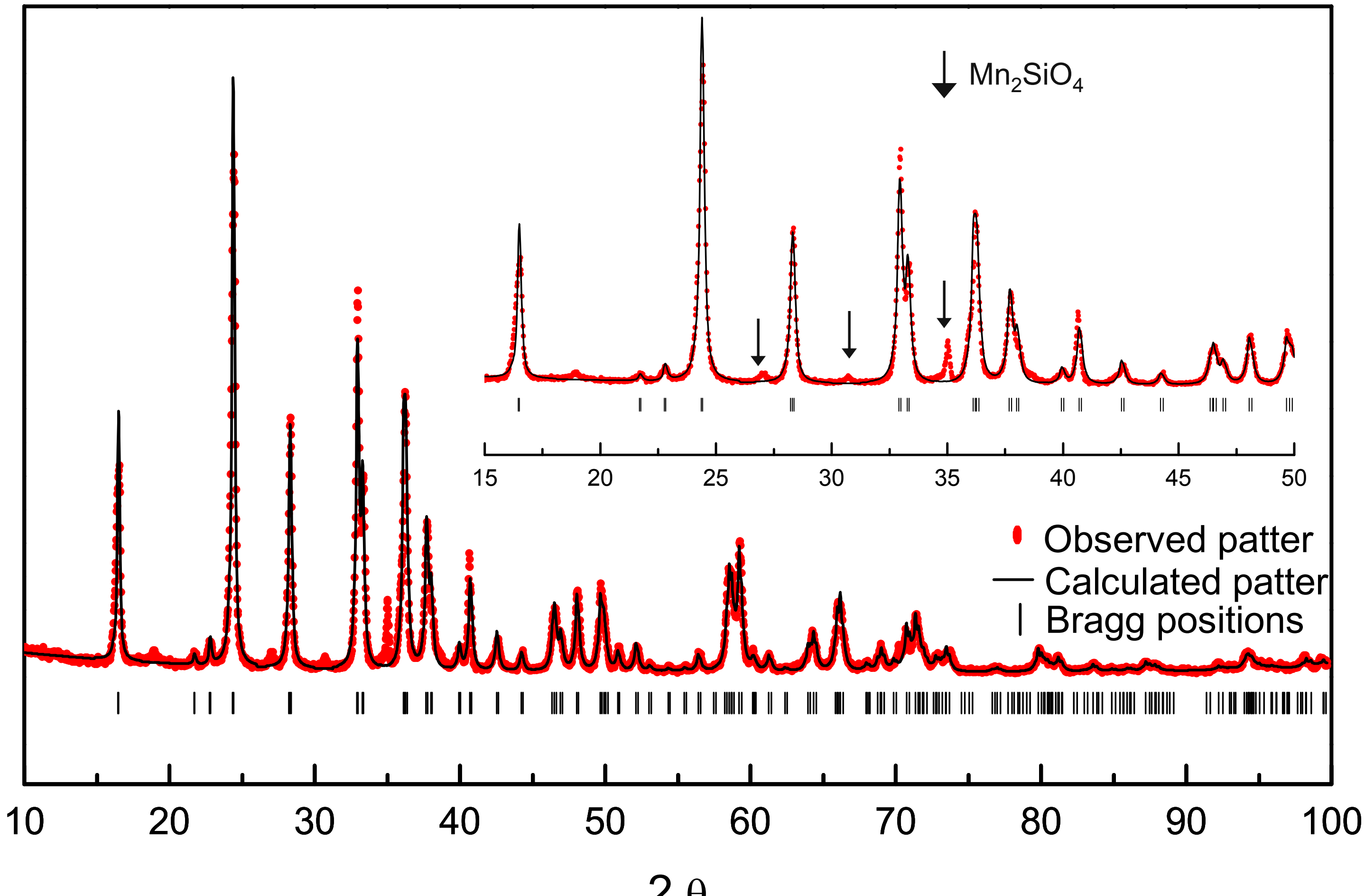


- Sol-gel preparation method has led to obtaining Li_2MnSiO_4 having Li_3PO_4-type structure. The material reported here has the highest purity ever achieved.

Structural Refinement

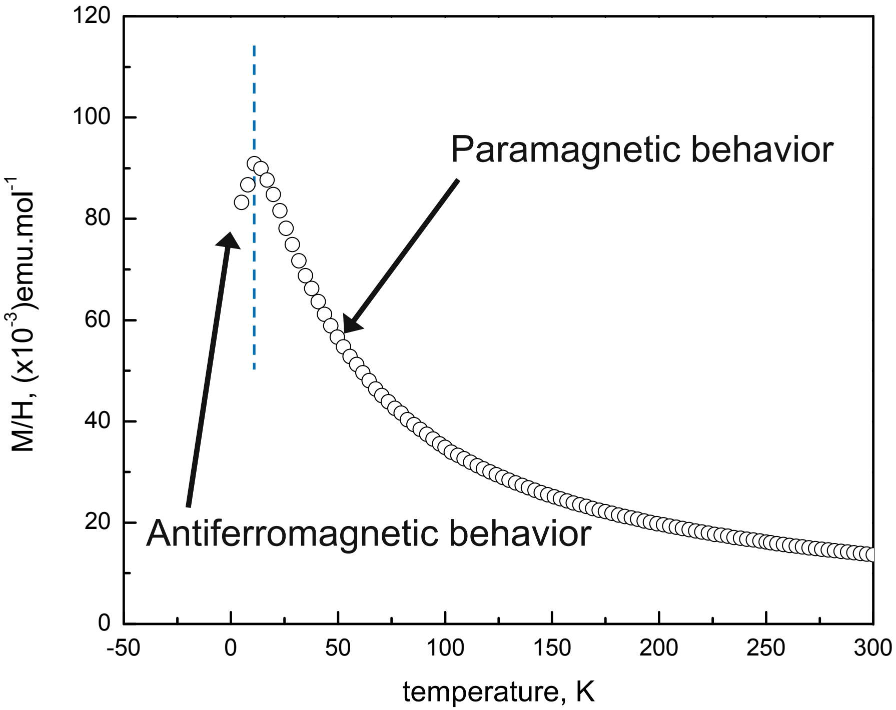


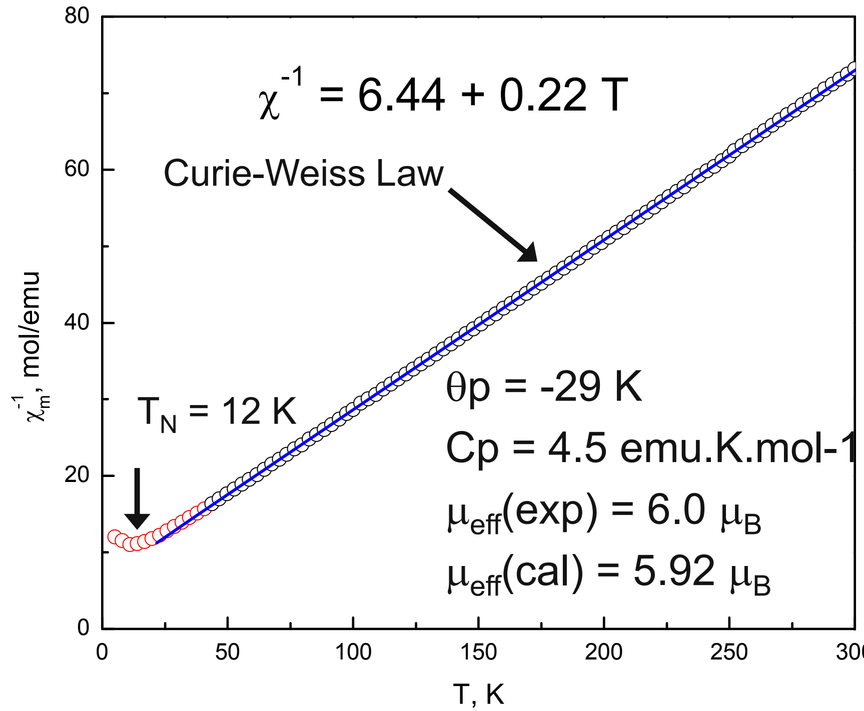
Mn-Si cluster



◆ Rietveld structural refinement analysis has confirmed the structure of Li_2MnSiO_4 that is a derivative of Li_3PO_4-type structure.

Magnetic Measurements (Squid)

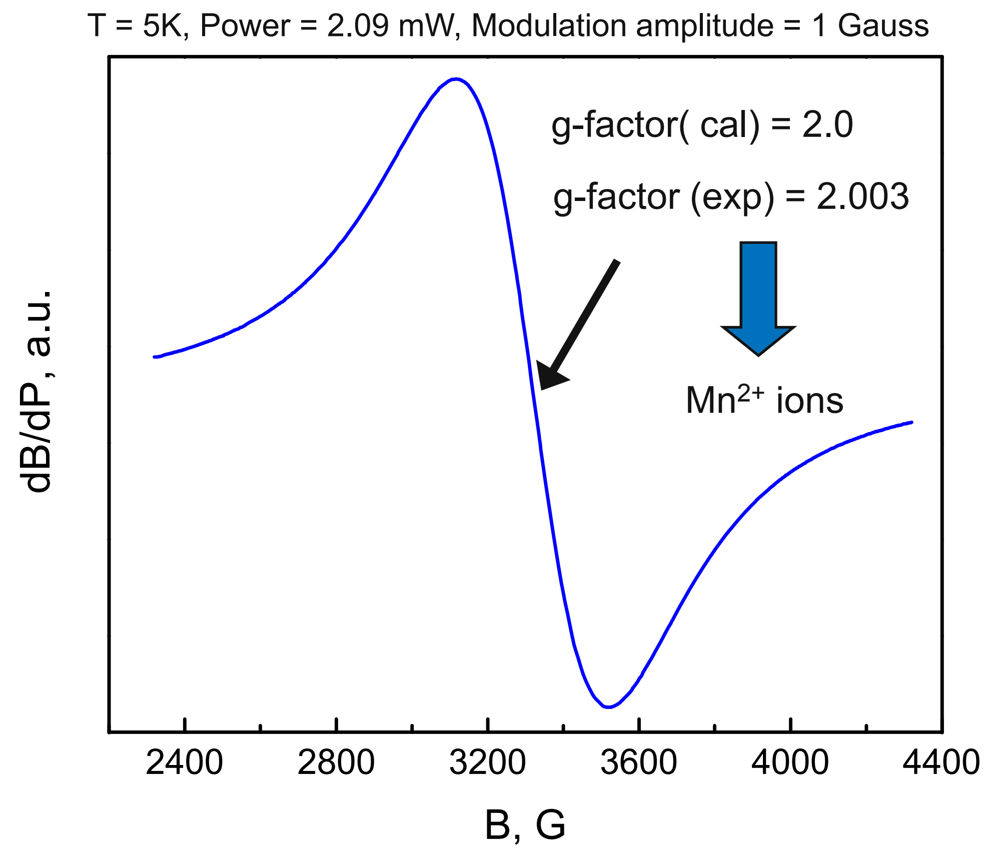




- Antiferromagnetic behavior below 12K
- Paramagnetic behavior above 12K

- The Curie-Weiss law parameters calculated from the paramagnetic part of (χ^{-1} vs. T) confirm that the observed magnetic behavior is that of Mn^{2+} ions.

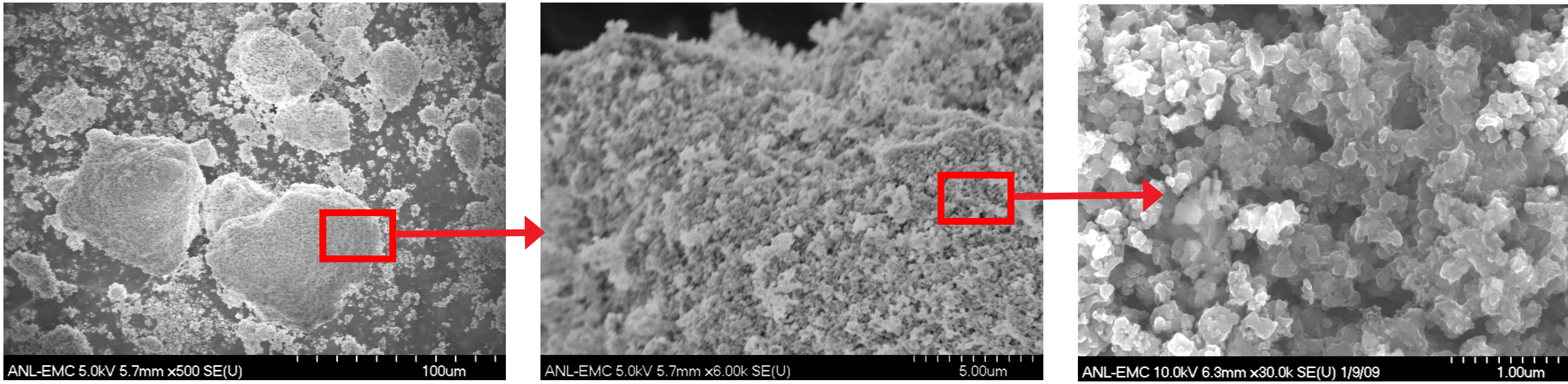
Electron Paramagnetic Resonance Analysis



- The EPR measurement confirms the presence of Mn^{2+} in the structure.
- Broadening of the EPR signal is likely due to a magnetic order that is present at 5K, and confirmed by Squid measurements.

Scanning Electron Microscopy

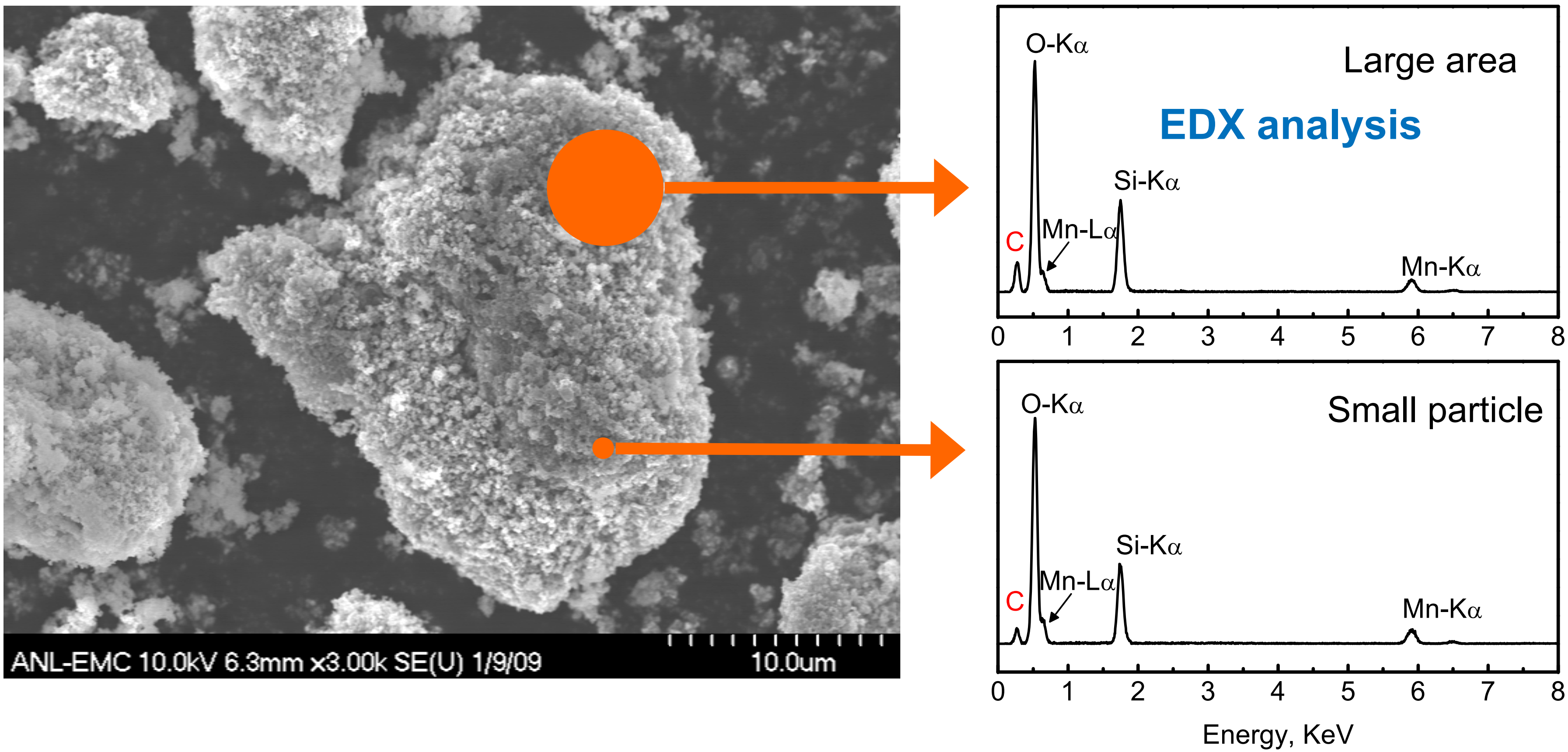
As-prepared Li_2MnSiO_4



- Large aggregates (10 to 100 μm) are observed for the as-prepared Li_2MnSiO_4.
- These large aggregates are made of nanosized particles (100-200 nm).
- The observed morphology may not be suitable to achieve full capacity of the material because of the following:
  - Li_2MnSiO_4,itself, is an insulating material,
  - Despite the presence of carbon conductive additive, only the small particles at the surface of the large agglomerates will be electrochemically active.
- What are the solutions?

Scanning Electron Microscopy (suite)

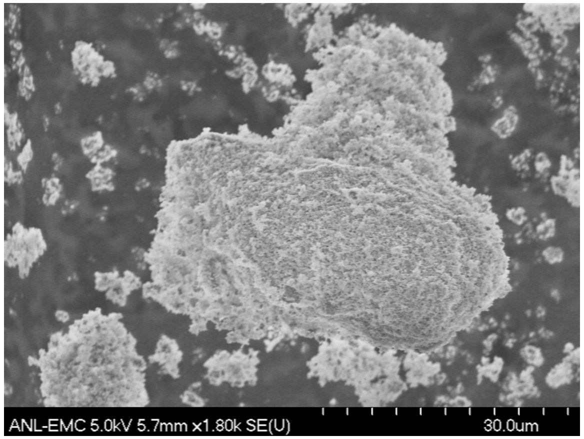
Solution 1: carbon coated Li_2MnSiO_4



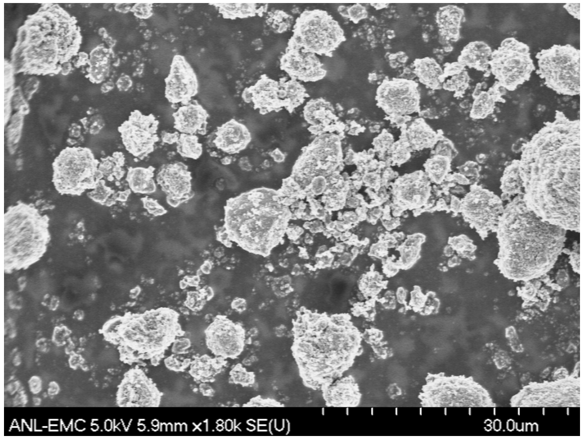
- Li_2MnSiO_4 was homogenously coated with carbon at the particle and bulk levels.
- EDX results confirm the stoichiometry of the material.

Scanning Electron Microscopy (suite)

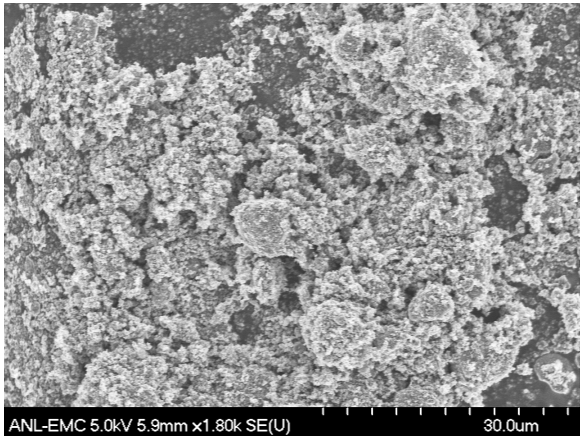
Solution 2: effect of ball-milling Li_2MnSiO_4



Li_2MnSiO_4, As-prepared



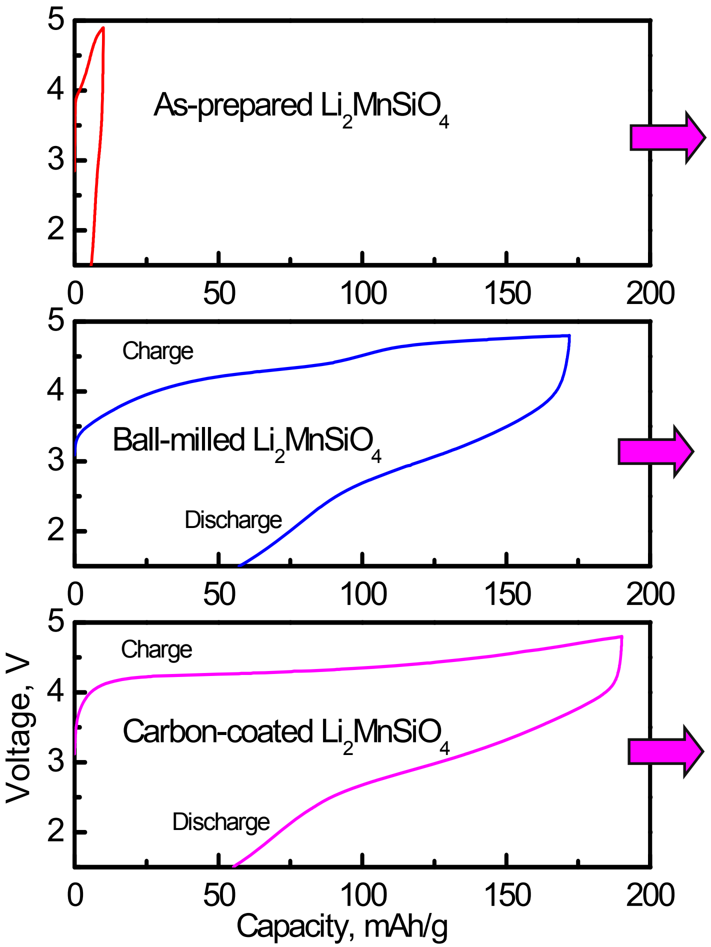
Li_2MnSiO_4, 2h ball milling



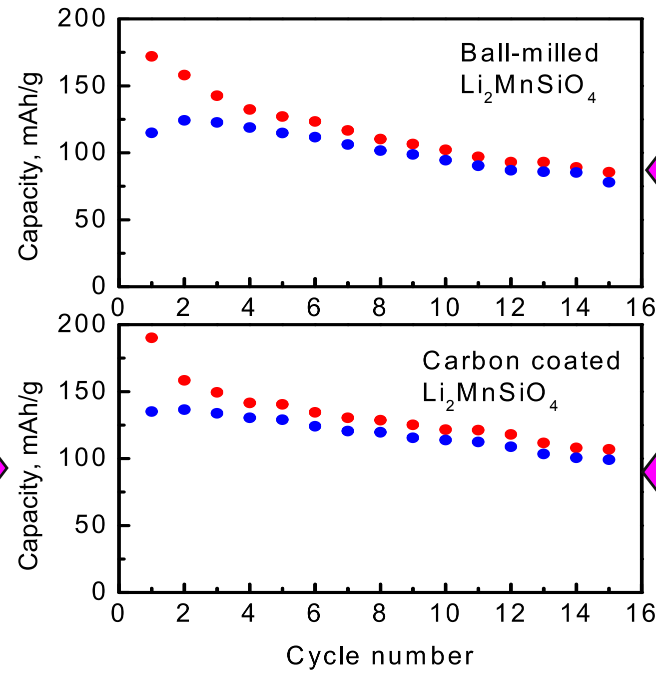
Li_2MnSiO_4, 4h ball milling

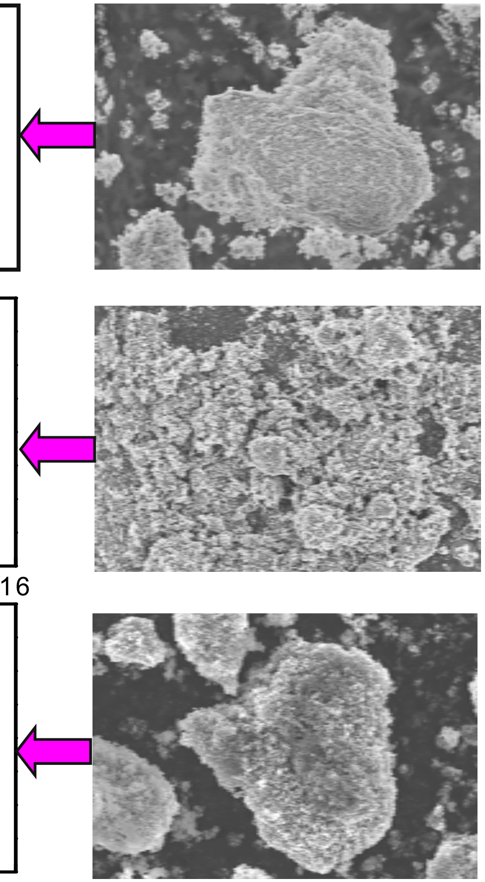
- High-energy ball milling is an effective way to breakdown the large agglomerates of Li_2MnSiO_4 to smaller particles.
- This method has been found to be none destructive because the structure of Li_2MnSiO_4 was preserved after the completion of ball milling.

Electrochemical Characterization



The as-prepared material does not cycle





- Due to its large aggregates and low electronic conductivity, the as-prepared Li_2MnSiO_4 is “almost” electrochemically inactive.
- Significant improvement toward achieving full capacity has been demonstrated by using carbon coating and ball milling of Li_2MnSiO_4.

Future Work

- Develop experimental preparation methods based on a sol-gel process that will inhibit the aggregation of Li_2MnSiO_4 nano-particles into large agglomerates.

- Continue the effort of achieving full capacity of the material using:
  - Carbon coating using carbonaceous additives.
  - High-energy ball milling.
  - Gas phase carbon coating reaction.

- The information learned from the study of Li_2MnSiO_4 will be used to investigate the compositions with iron and cobalt as the electrochemically active ions.

- Achieve an overall evaluation of these materials from the structural and electrochemical with regard to their possible applicability in high-energy density Li-ions batteries.

Summary

- Sol-gel preparation method has led to obtaining Li_2MnSiO_4 having the highest purity ever reported.
- The structure of Li_2MnSiO_4 exhibits lithium ions that reside within channels and that are available for extraction and insertion.
- Rietveld structural refinement analysis has confirmed the structure of Li_2MnSiO_4 that is a derivative of Li_3PO_4-type structure.
- Squid and EPR measurements confirmed that the electronic configuration and magnetic behavior are those of Mn^{2+} ions.
- Li_2MnSiO_4 is constituted by large agglomerates that are made of nanosized particles.
- High-energy ball milling was found to be an effective way to breakdown the large agglomerates without inducing a damage to the atomic scale arrangement of the material.
- Initial carbon coating and ball milling experiments were found to significantly improve the capacity of Li_2MnSiO_4.