

Evaluation of $\text{Li}_2\text{MnSiO}_4$ Cathode

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Overview

Timeline

- Start – October 2008
- Finish – December 2010

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 + FY11: \$650K
- Funding received in FY09: \$300K
- Funding in FY10: \$300K
- Funding in FY11: \$50K

Partners

- Collaboration:
 - Advanced Photon Source (ANL)
- Support: D. Dambournet, A. Abouimrane, K.W. Chapman, P.J. Chupas.
- Project lead: ILias Belharouak

Objectives of this Study

- Understand the capacity fading of $\text{Li}_2\text{MnSiO}_4$ upon cycling.
- Achieve an overall structural and electrochemical evaluations of $\text{Li}_2\text{MnSiO}_4$ material with regard to its possible use in high-energy density Li-ion batteries.

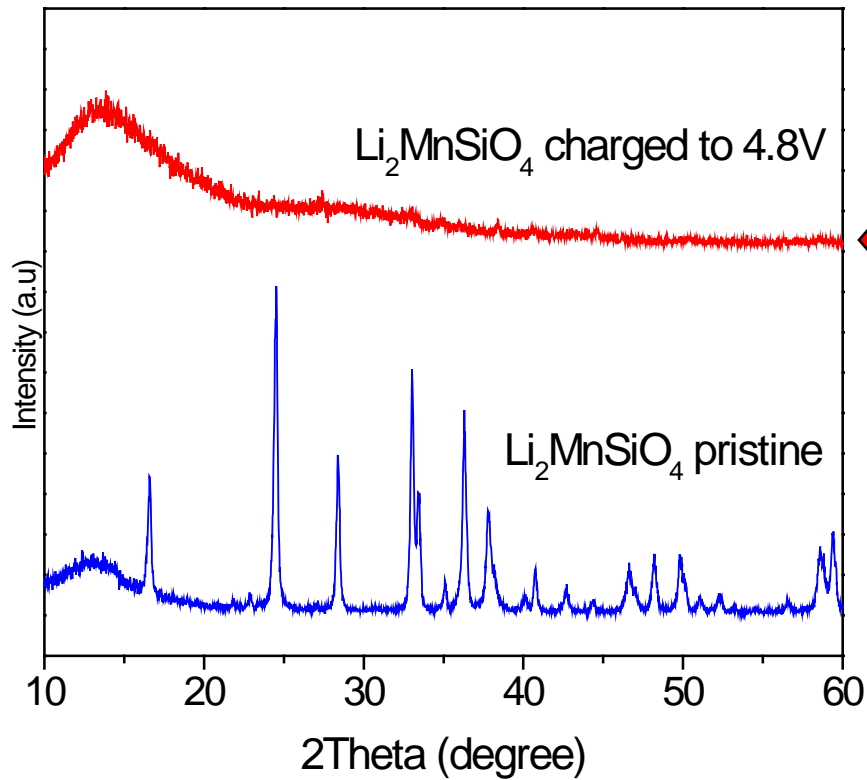
Milestones for FY11

- Perform high-energy x-ray diffraction experiments on charged and discharged $\text{Li}_2\text{MnSiO}_4$ cathode (completed).
- Pair distribution analysis of $\text{Li}_2\text{MnSiO}_4$ electrode upon lithium removal and uptake (completed).
- Understand the discrepancy between the results of conventional and high-energy x-ray experiments carried out on $\text{Li}_2\text{MnSiO}_4$ electrode (completed).

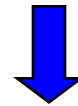
Approach

Possible reasons for the degradation of performance of $\text{Li}_2\text{MnSiO}_4$:

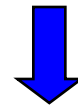
- Jahn-Teller distortion associated with Mn^{3+} and Mn dissolution.
- Loss of crystallinity of $\text{Li}_2\text{MnSiO}_4$ at the end of the first charge.



- Charged $\text{Li}_2\text{MnSiO}_4$ becomes amorphous according to conventional x-ray diffraction measurement with Cu-K α radiation.



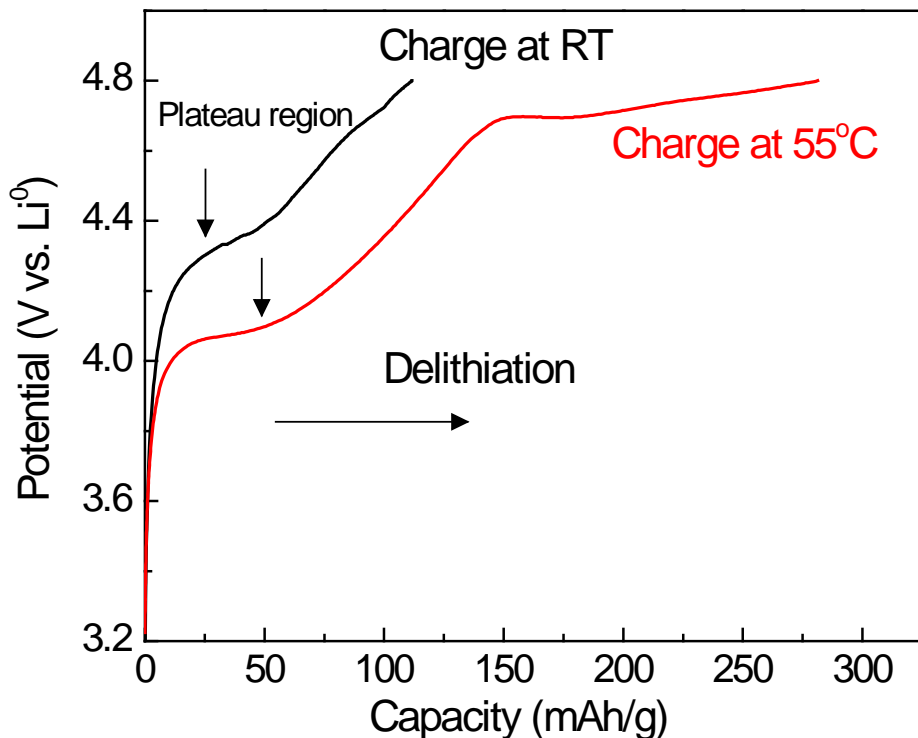
- No long range structural information can be extracted for charged $\text{Li}_2\text{MnSiO}_4$.



- Need to conduct high resolution x-ray on $\text{Li}_2\text{MnSiO}_4$ upon charge

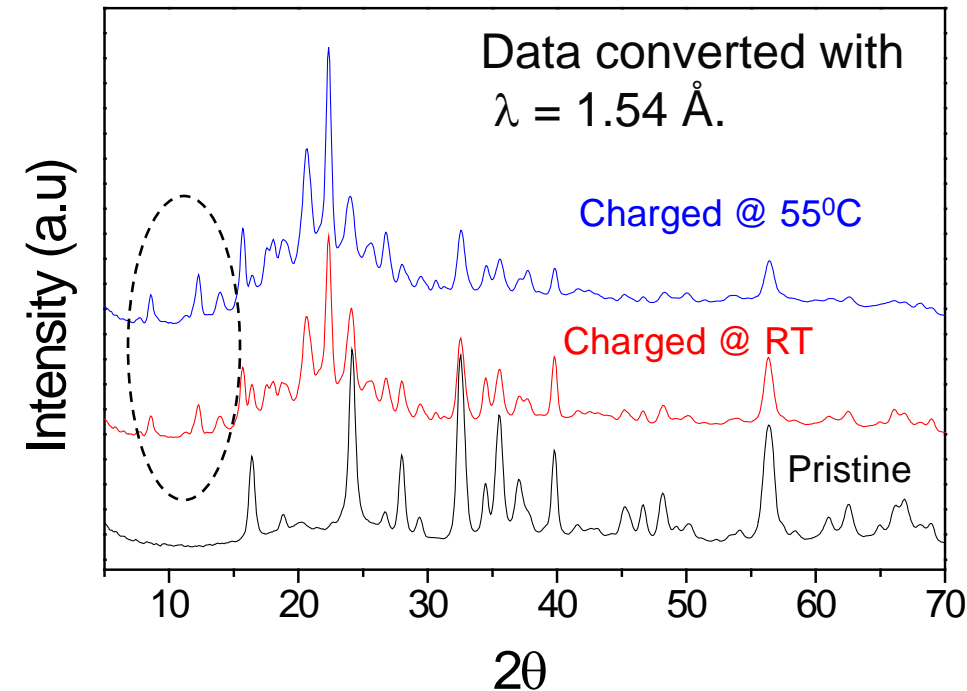
$\text{Li}_2\text{MnSiO}_4$ Electrode Preparation

- $\text{Li}_2\text{MnSiO}_4$ electrodes were charged to 4.8 V at RT and 55 °C.
- Charged electrodes were sealed in capillary kapton prior to measurements.
- High-energy x-ray experiments were carried out at the Advanced Photon Source.



- Both electrodes showed a plateau region at the beginning of the charge process.
- High temperature plateau is much pronounced at lower voltage.
- At 55°C, a second plateau region can be observed above 4.6 V probably due to electrolyte decomposition.

High Energy X-ray Diffraction Results

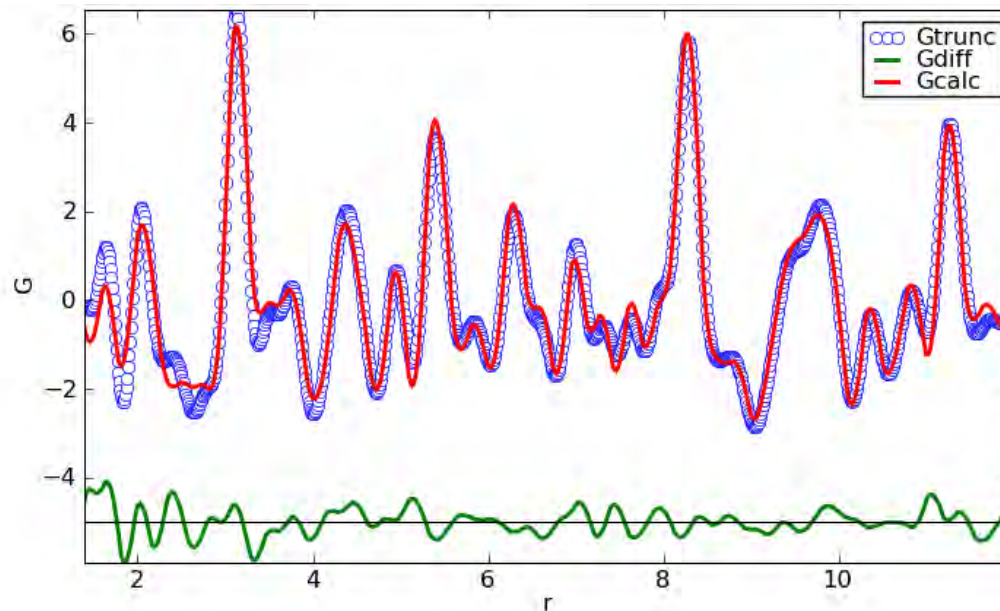


- High-energy x-ray measurements were performed using 0.21028 Å wavelength.
- Results showed that $\text{Li}_2\text{MnSiO}_4$ is still crystalline after delithiation which is in disagreement with the results of conventional x-ray.
- We observed the following:



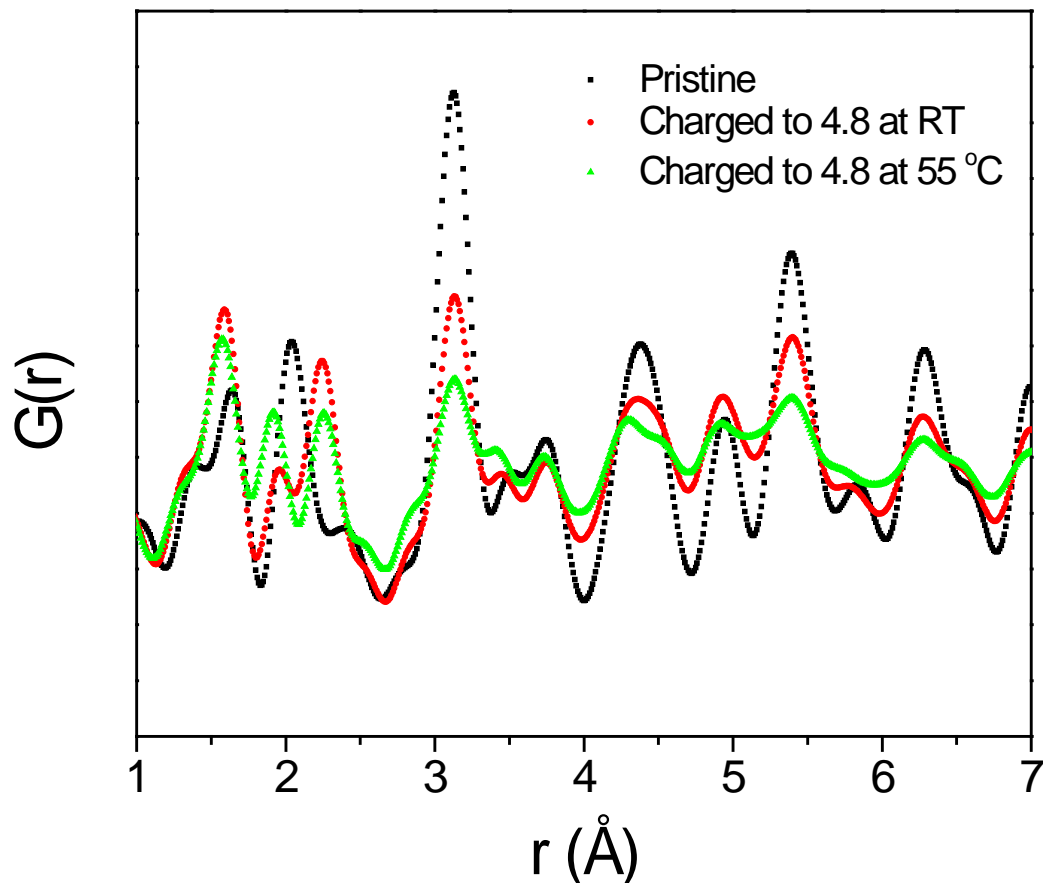
- Decrease of the intensity of the main diffraction lines for the charged $\text{Li}_2\text{MnSiO}_4$ samples.
- Appearance of new diffractions lines for the charged samples.
- Indexation of the new peaks was not possible based on the structural model of $\text{Li}_2\text{MnSiO}_4$ available in the literature.
- Then, we needed to use Pair Distribution Function (PDF) to help us understand the structure of $\text{Li}_2\text{MnSiO}_4$ and the additional x-ray features observed upon charge.

Atomic Pair Distribution Function Analysis of Pristine $\text{Li}_2\text{MnSiO}_4$



- PDF data were obtained by Fourier Transform of the total scattering function $S(Q)$ which contains both Bragg and diffuse intensities.
- PDF refinement revealed the presence of 10% Li_2SiO_3 and 5% MnO in $\text{Li}_2\text{MnSiO}_4$.
- Local range ($<3 \text{ \AA}$) was more difficult to fit due the presence of large amount of carbon and MnO impurity in the electrode.
- Overall, the refinement of $\text{Li}_2\text{MnSiO}_4$ structure is consistent with the structural model of Li_3PO_4 with cationic disorder.

Atomic Pair Distribution Function Analysis of Charged $\text{Li}_2\text{MnSiO}_4$



- There are clear differences between the PDF features of the pristine and charged $\text{Li}_2\text{MnSiO}_4$ samples.
- The new features observed in the PDF patterns of the charged samples could not be interpreted based on $\text{Li}_2\text{MnSiO}_4$ refined structural model.

Summary

- High-energy x-ray results revealed for the first time that $\text{Li}_2\text{MnSiO}_4$ does not become amorphous upon charge.
- Discrepancy between conventional and high energy x-ray results can be explained by the strong absorption coefficient of the manganese. Using conventional x-ray source, most of the intensity is absorbed by the near-surface region of the sample due to the low penetration ability of Cu-K α radiation. It was therefore suggested that the charged $\text{Li}_2\text{MnSiO}_4$ is amorphous. However, high energy x-ray allows to probe the surface and bulk of the sample so that the crystalline character of the charged $\text{Li}_2\text{MnSiO}_4$ could be revealed.
- New x-ray features observed for the charged $\text{Li}_2\text{MnSiO}_4$ suggest that the pristine material undergoes a structural change upon delithiation due the strong Yahn-Teller distortion at the Mn-crystallographic site. This structural change is likely the primary cause for the degradation of the electrochemical performance of $\text{Li}_2\text{MnSiO}_4$.

