Evaluation of Li$_2$MnSiO$_4$ Cathode

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Overview

Timeline
- Start – October 2008
- Finish – December 2010

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

Barriers
- Energy density of available Li-ion battery technologies
- Abuse tolerance

Partners
- Collaboration: Advanced Photon Source (ANL)
- Project lead: ILias Belharouak
Objectives of this Study

- Understand the capacity fading of Li$_2$MnSiO$_4$ upon cycling.
- Achieve an overall structural and electrochemical evaluations of Li$_2$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 Li$_2$MnSiO$_4$ cathode (completed).
- Pair distribution analysis of Li$_2$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 Li$_2$MnSiO$_4$ electrode (completed).
Approach

Possible reasons for the degradation of performance of Li$_2$MnSiO$_4$:
- Jahn-Teller distortion associated with Mn$^{3+}$ and Mn dissolution.
- Loss of crystallinity of Li$_2$MnSiO$_4$ at the end of the first charge.

- Charged Li$_2$MnSiO$_4$ becomes amorphous according to conventional x-ray diffraction measurement with Cu-K$\alpha$ radiation.
- No long range structural information can be extracted for charged Li$_2$MnSiO$_4$.
- Need to conduct high resolution x-ray on Li$_2$MnSiO$_4$ upon charge.
Li$_2$MnSiO$_4$ Electrode Preparation

- Li$_2$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 Li$_2$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 Li$_2$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 Li$_2$MnSiO$_4$ available in the literature.
  - Then, we needed to use Pair Distribution Function (PDF) to help us understand the structure of Li$_2$MnSiO$_4$ and the additional x-ray features observed upon charge.
• 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% \( \text{Li}_2\text{SiO}_3 \) and 5% \( \text{MnO} \) in \( \text{Li}_2\text{MnSiO}_4 \).
• Local range (<3 Å) was more difficult to fit due the presence of large amount of carbon and \( \text{MnO} \) impurity in the electrode.
• Overall, the refinement of \( \text{Li}_2\text{MnSiO}_4 \) structure is consistent with the structural model of \( \text{Li}_3\text{PO}_4 \) with cationic disorder.
Atomic Pair Distribution Function Analysis of Charged Li₂MnSiO₄

- There are clear differences between the PDF features of the pristine and charged Li₂MnSiO₄ samples.

- The new features observed in the PDF patterns of the charged samples could not be interpreted based on Li₂MnSiO₄ refined structural model.
Summary

- High-energy x-ray results revealed for the first time that Li$_2$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-Kα radiation. It was therefore suggested that the charged Li$_2$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 Li$_2$MnSiO$_4$ could be revealed.

- New x-ray features observed for the charged Li$_2$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 Li$_2$MnSiO$_4$. 