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New High Power $Li_2MTi_6O_{14}$ Anode Material

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Argonne National Laboratory

May 19th, 2009

Project ID : esp_21_amine

Overview

Timeline

- Start - October 1st, 2008.
- Finish - September 30, 2009.
- 40%

Barriers

- Barriers addressed
  - Safety of the battery.
  - power density of the battery.
  - Cycle & calendar life span of the battery.

Budget

- Total project funding
  - DOE share : 200K

Partners

- Interactions/ collaborations:

  D. Dambournet, I. Belharouak
- Project lead: Khalil Amine

Objectives

- Develop new anode materials that provide very high power capability and outstanding safety.
  - Investigate the applicability of $Li_2MTi_6O_{14}$ (M= Sr, Ba) as anode for high power Li-ion batteries.
  - Explore ways for preparing pure and nanosized $Li_2MTi_6O_{14}$ with full capacity and very high power.
  - Investigate the cycle, calendar life and safety of the cell based on this new anode

Milestones

Month/Year	Milestone or Go/No-Go Decision
May-09	- Develop of a new synthetic method to prepare pure and nano-sized $Li_2MTi_6O_{14}$ anode materials. - Conduct structural and electrochemical characterizations. - Evaluate of this anode with advanced cathode materials.
Sept-09	- Improve the capacity and rate performance through carbon coating and/or high energy ball milling. - Investigate of new phases in the Li_2O-MO-TiO_2 ternary diagram.
Sept-2010	- Explore a process to get a suitable morphology with micron size secondary particles and dense nano-sized primary particles to obtain full capacity of $Li_2MTi_6O_{14}$ and good rate capability.

Approach

- Develop a synthesis route to prepare nano-sized $Li_2MTi_6O_{14}$ anode materials to improve rate capability.
- Investigate the effect of high oxidation state dopant to increase the conductivity and enable the power capability of the material.
- Explore a new synthesis process to get a suitable morphology with micron size secondary particles and dense nano-sized primary particles to obtain full capacity of $Li_2MTi_6O_{14}$ and good rate capability.
- Investigate the effect of coating $Li_2MTi_6O_{14}$ with carbon conductive agent to increase overall material conductivity and improve the rate capability.

Advantage of $Li_2MTi_6O_{14}$ as Anode for Safe and High Power Battery for HEV Applications

- $Li_2MTi_6O_{14}$ material has available space and can accommodate lithium atoms within its 3D-structure.

- $Li_2MTi_6O_{14}$ is a high voltage anode material (1~1.5V):
  - *Doesn't require SEI (good for safety and long life)*
  - *No significant volume and structural change (good for stable cycling).*
  - *High ionic conductors materials (good for rate capability)*

- $Li_2MTi_6O_{14}$ enables very long cycle and calendar life and significantly improves the safety of the battery.

- $Li_2MTi_6O_{14}$ provides lower resistance at the micron scale particle than the established $Li_4Ti_5O_{12}$ used by the industry as anode for HEV's.

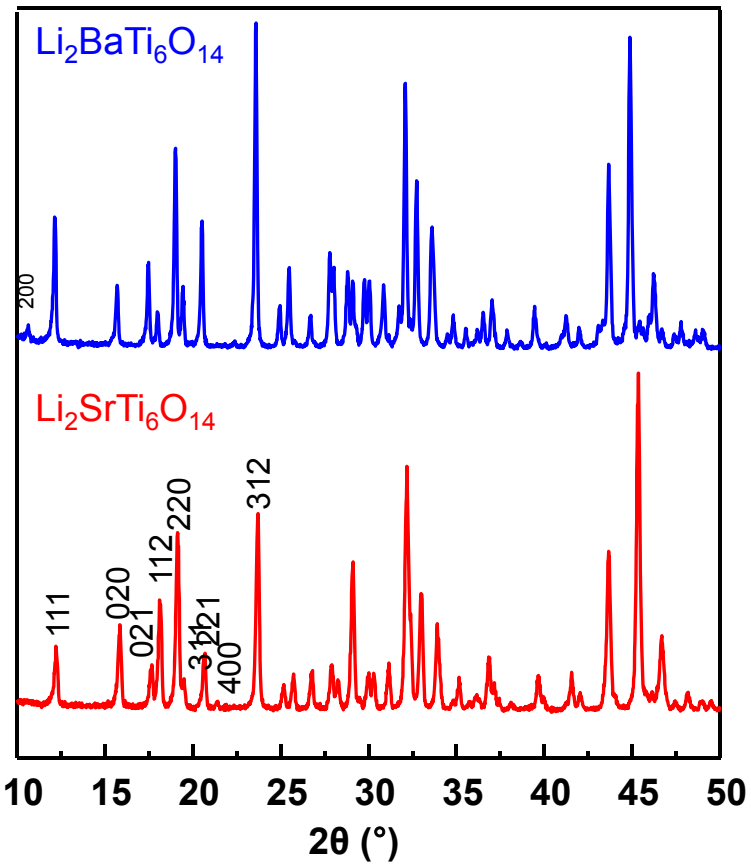
- $Li_2MTi_6O_{14}$ provides higher capacity (180mAh/g) than the established $Li_4Ti_5O_{12}$ (150mAh/g)

Conventional Materials Preparation

- $Li_2MTi_6O_{14}$ (M=Ba, Sr) can be prepared by solid state reaction:

$$Li_2CO_3 + MCO_3 + 6\ TiO_2 \rightarrow MLi_2Ti_6O_{14} + 2\ CO_2\uparrow \quad (T=1000°C)$$

X-ray diffraction patterns

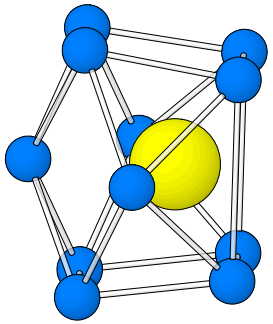


Symmetry: orthorhombic
Space group: Cmca
Unit cell parameters:

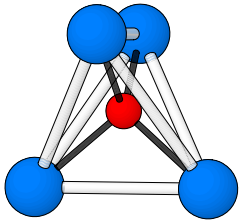
$Li_2BaTi_6O_{14}$	$Li_2SrTi_6O_{14}$
a=16.570 Å	a=16.566 Å
b=11.150 Å	b=11.148 Å
c=11.458 Å	c=11.468 Å

$Li_2BaTi_6O_{14}$ and $Li_2SrTi_6O_{14}$ are isostructural

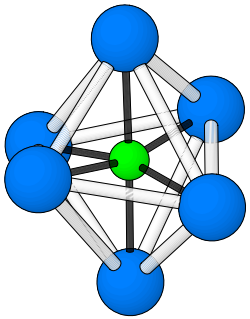
Structural Description of $Li_2MTi_6O_{14}$



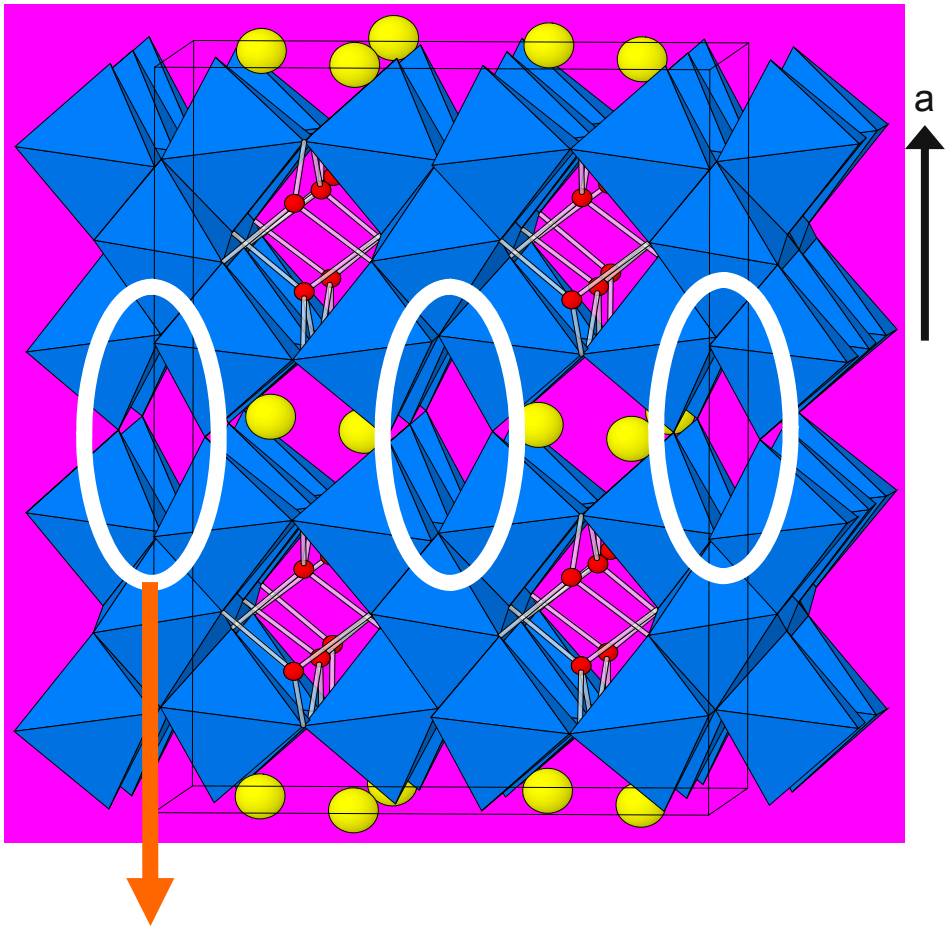
M Site



Lithium Site



Titanium Site

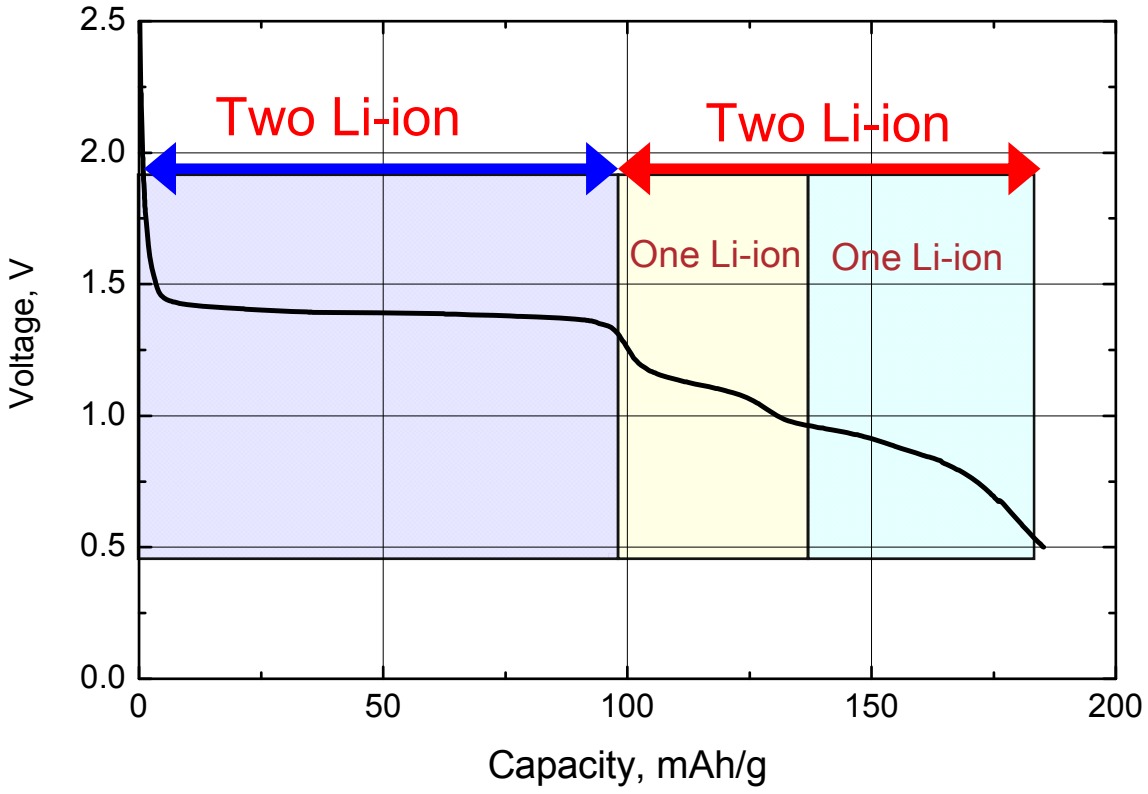


- Open-type structure with empty channels suitable for lithium insertion

Electrochemical Properties

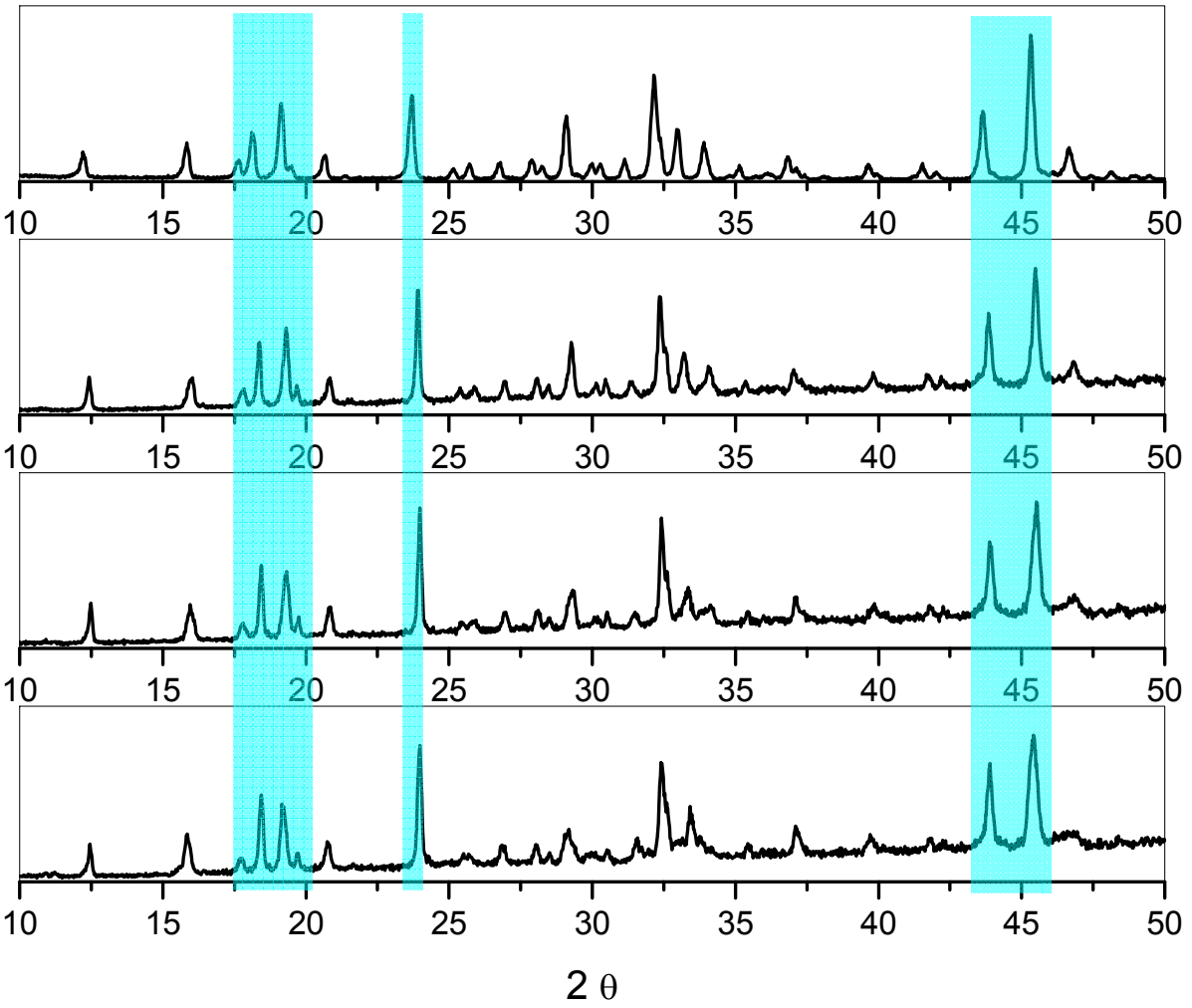
- Theoretically, $Li_2MTi_6O_{14}$ can provide around 250 mAh/g (based on Ti^{4+}/Ti^{3+})
- Experimentally, $Li_2MTi_6O_{14}$ can provide around 180 mAh/g based on:

$$MLi_2Ti_6O_{14} + 4\ Li^+ + 4\ \bar{e} \leftrightarrows Li_6MTi_6O_{14}\ (\sim 180 mAh/g)$$



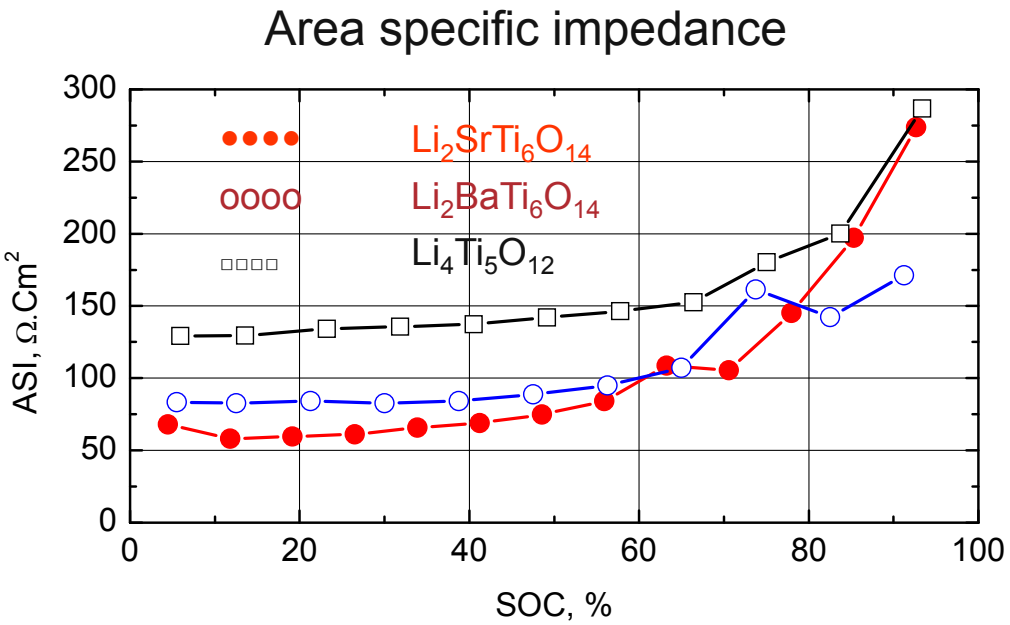
- The material offers a lower operating voltage profile compared to $Li_4Ti_5O_{12}$

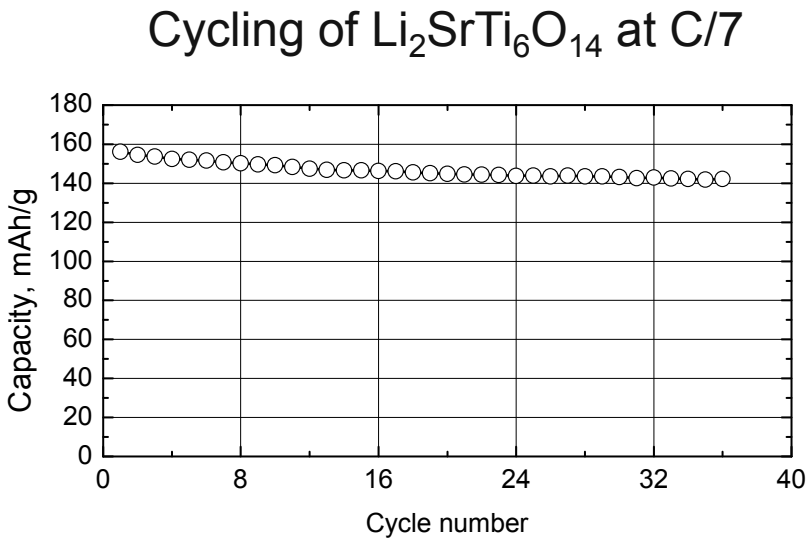
Stability Upon Lithium Insertion



- $Li_2MTi_6O_{14}$ shows outstanding structural stability upon discharge

Stability Upon Lithium Insertion

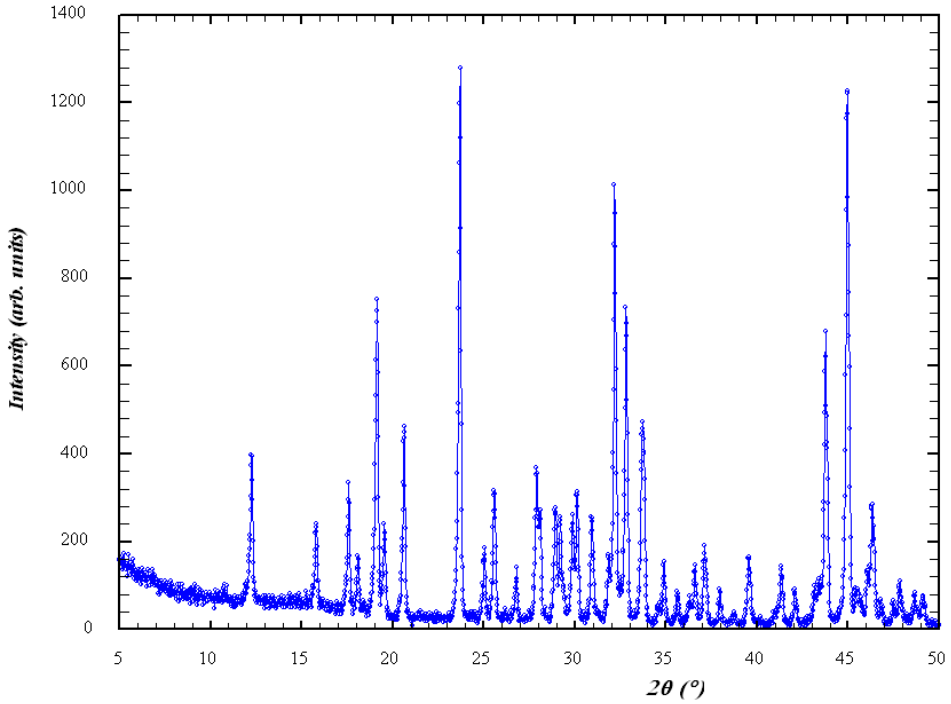




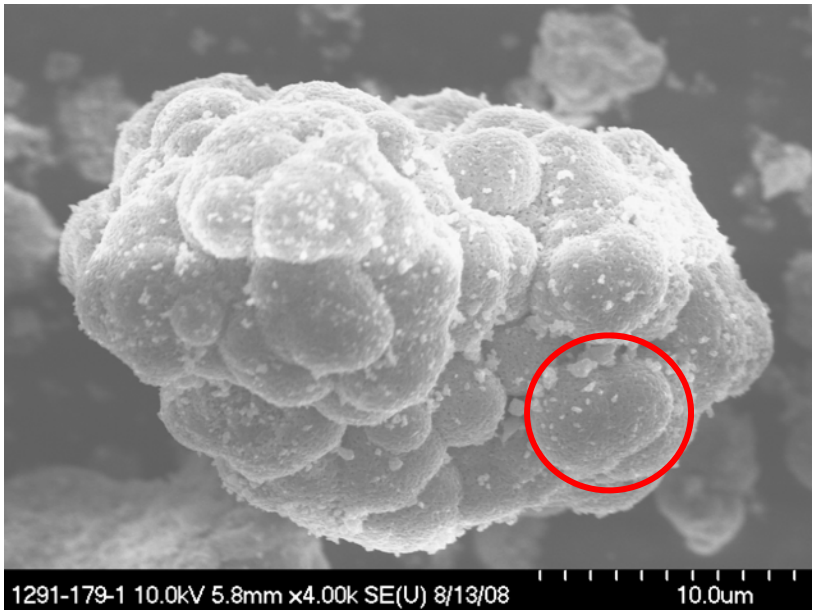
- $Li_2MTi_6O_{14}$ shows lowers area specific impedances compared to $Li_4Ti_5O_{12}$, provides 160 mAh/g, and cycles fairly well.

Sol-Gel Preparation Route for $Li_2MTi_6O_{14}$

- The aim is to prepare nanosized $Li_2MTi_6O_{14}$ to improve the capacity and rate capability

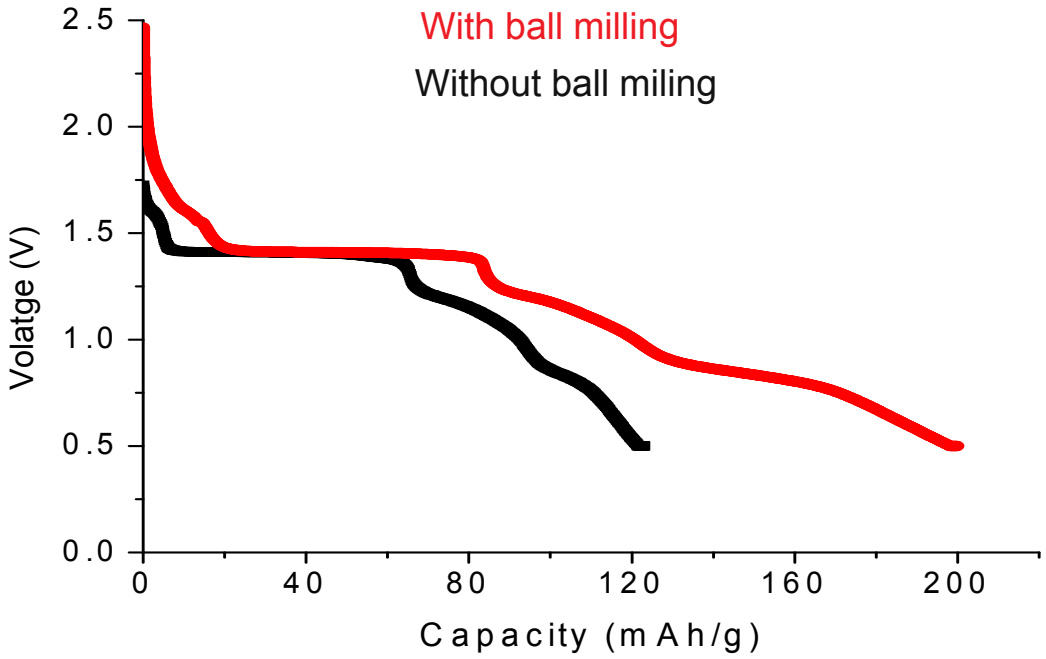


XRD shows pure crystalline phase



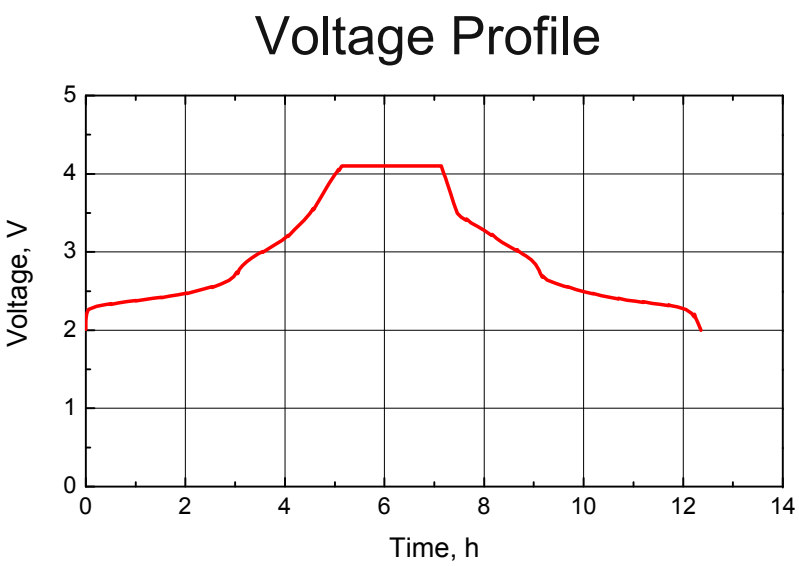
Scanning electron microscopy: large agglomerate, secondary particles ~5μm

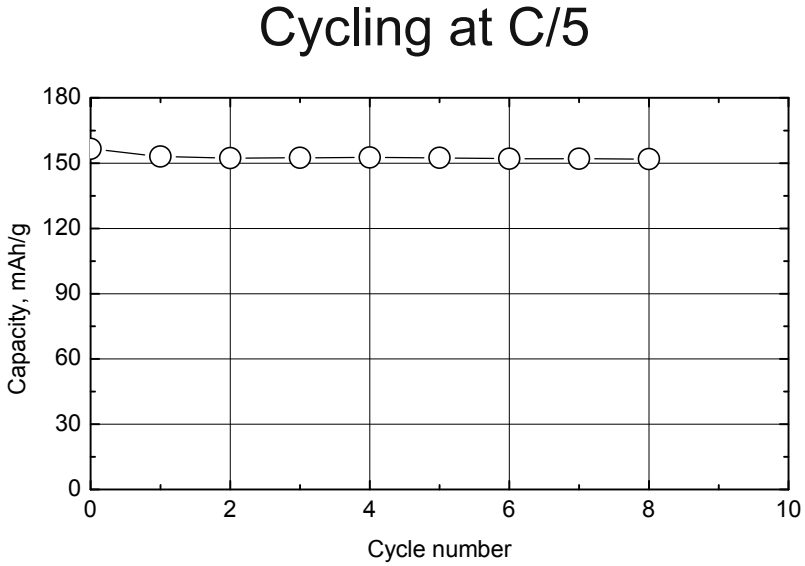
Electrochemical Properties of the Material Prepared by Sol-Gel



- Material prepared by sol-gel synthesis shows low capacity due to large agglomerates.
- Ball milling significantly improves the capacity from 120 to 200 mAh/g.
- Average voltage of the material is 1V, can provide 3.2V system with $LiMn_2O_4$ spinel.

Performance of $Li_{1.1}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{0.9}O_2/Li_2SrTi_6O_{14}$ Battery





Preliminary cycling data of $Li_{1.1}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{0.9}O_2/Li_2SrTi_6O_{14}$ provides an overage voltage of 3V with good preliminary cycling at c/5

Summary

- $Li_2MTi_6O_{14}$ is a promising safe anode that provides a reasonable capacity and a suitable voltage profile for HEVs.
- $Li_2MTi_6O_{14}$ possesses a 3D-dimentional structure where lithium ions can be inserted due to its high ionic conductivity.
- A sol-gel method has been found to provide high purity $Li_2MTi_6O_{14}$ materials using low temperature and duration time.
- $Li_2MTi_6O_{14}$ has lower area specific impedance than $Li_4Ti_5O_{12}$, so high rate capability could be enabled if a nanophased material can be prepared.
- ball-milling $Li_2MTi_6O_{14}$ has shown to improve the capacity of the material.
- $Li_2SrTi_6O_{14}$ provide an average voltage of 1V lower than the 1.5 flat voltage in $Li_4Ti_5O_{12}$ and can lead to high energy density than $Li_4Ti_5O_{12}$

Future works

- Improve the capacity and rate performance through high energy ball milling of the particles.

- Investigate the effect of high oxidation state dopant to increase the conductivity of the material and enable the power capability of the material.

- Explore a new synthesis process to get a suitable morphology with micron size secondary particles and dense nanosized primary particles to obtain full capacity of $Li_2MTi_6O_{14}$ and good rate capability.

- Investigate the effect of coating $Li_2MTi_6O_{14}$ with carbon conductive agent to increase overall material conductivity and improve the rate capability.