Developing High Capacity, Long Life, and High Power Anodes

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DOE merit review

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Overview

Timeline

- Start - October 1st, 2009.
- Finish – September 2014
- 40% complete

Barriers

- Safety of the battery.
- Power density of the battery.
- Cycle & calendar life span of the battery.

Budget

- Total project funding: 2* 600K
  - FY10: 2*300K
  - FY09: 2*300K

Partners

- D. Dambournet, I. Belharouak, A. Abouimrane, (CSE/ANL).
- P. Chupas, K. Chapman, Advanced Photon Source, (IPS/ANL).
- X. Q Yang, Brookhaven National Lab.
- FMC, Northwestern University

Objectives (Merger of two projects)

- Develop new advanced anode materials with long life and improved Safety.
  - First project: focus on a advanced high-power anodes for HEV applications.
  - Second project: focus on a advanced high-energy and long life anodes for PHEV applications.

- Main tasks are:
  - Develop a low cost synthesis methods.
  - Full structural and electrochemical characterizations of the prepared anode materials.
  - Demonstrate the applicability of these anodes in half and full cells.

Approaches

First project: high-power and long life anodes.

- $Li_2MTi_6O_{14}$ (M=Ba, Sr, 2Na) materials were selected based on the following criteria:
- High-potential anodes (~1.4V) can provide long life & better safety because they don't require an SEI layer.
- Anodes possess lower potentials than $Li_4Ti_5O_{12}$ (LTO), expect high voltage cells when combined with cathodes. (low number of cell in a battery pack compared to LTO, low cost)
- Anodes have higher theoretical capacity compared to $Li_4Ti_5O_{12}$.
- Materials are good ionic conductors thus can enable high-power capability in cells.
- Anodes can be coupled with high-power 4V and 5V spinel materials.

Second project: high capacity and long life anodes.

- Two advanced anode systems are being studied:
- Titanium oxides:
  - High theoretical capacity (335 mAh/g) based on Ti^{4+}/Ti^{3+}.
  - Facile materials preparation and low cost processing.
  - No SEI layer need so much better safety is expected compared to graphite.

- New silicon-based composites system with high packing density, low irreversible loss and long cycle life.

Milestones FY May 09 – May 10: High-Power and Long Life Anodes

- Development of a new synthesis method to prepare high purity $MLi_2Ti_6O_{14}$ (M= 2Na, Ba, Sr) compounds. (*Completed)*

- Comparative studies between $Ba/SrLi_2Ti_6O_{14}$ and $Na_2Li_2Ti_6O_{14}$ based on structure, morphology and electrochemical properties. (*Completed)*

- Selection of a candidate for further electrochemical characterization: full cells study and HPPC tests. *(On going)*

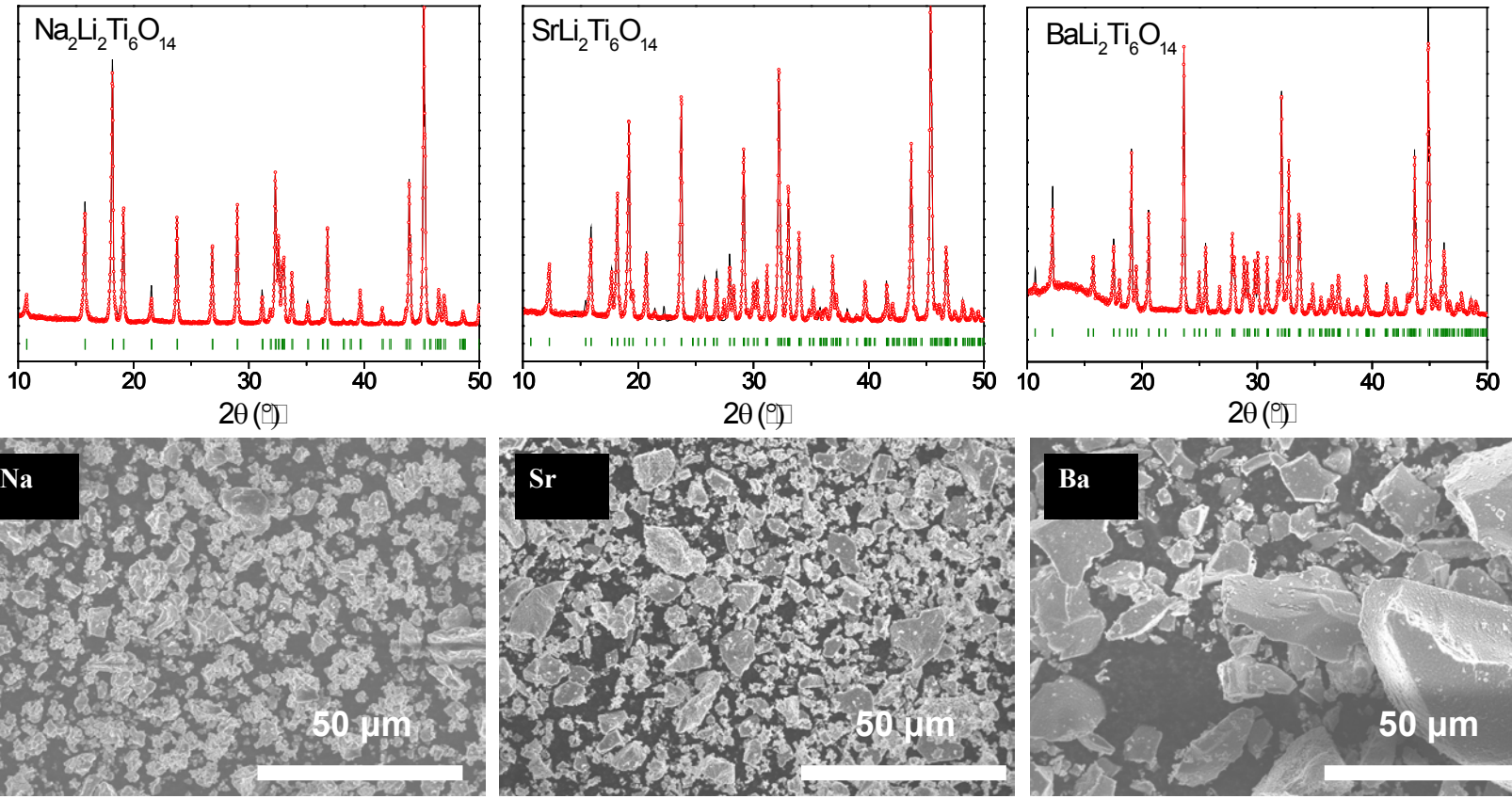
- Improvement of the pulse power performance of these materials to meet the HEV requirements through cell design and material design improvement . *(On going)*

- Investigation of safety and stability in electrolyte. *(On going)*

First Project
Development of a high power and long life anodes

Synthesis of $MLi_2Ti_6O_{14}$ Materials

- Development of a sol-gel process to prepare $MLi_2Ti_6O_{14}$ materials.



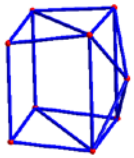
- Sol gel method was found to be adequate to prepare pure and well crystallized $Na_2Li_2Ti_6O_{14}$, $SrLi_2Ti_6O_{14}$ and $BaLi_2Ti_6O_{14}$ compounds.
- Solids consist of 500 nm primary particles that agglomerate in larger particles. $Ba_2Li_2Ti_6O_{14}$ showed larger agglomerates which had a negative impact on power & capacity of the material.

Structural Characterization

- Rationales behind the selection of $MLi_2Ti_6O_{14}$ type structure

[TiO_6] framework

11-fold coordinated position



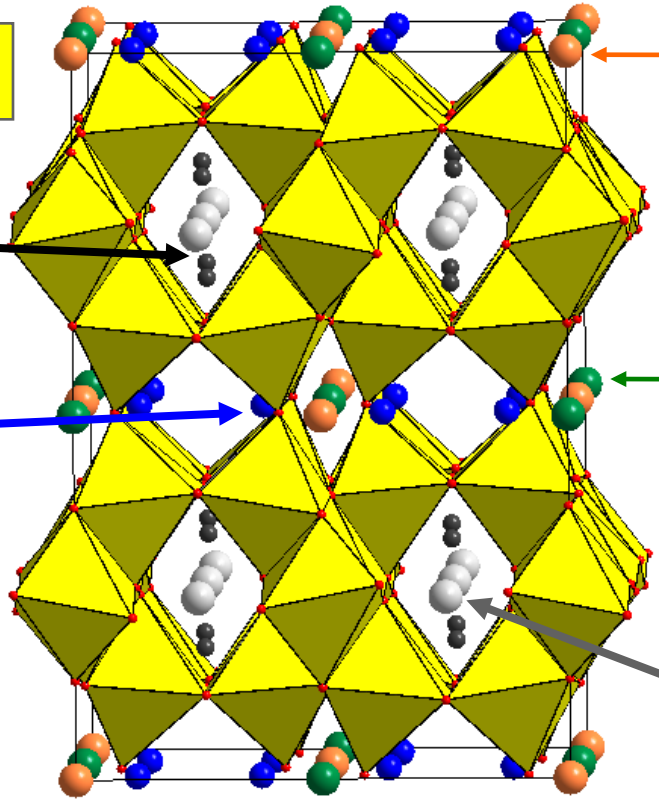
[LiO_4]

2*8f Wyckoff positions

"M"=Na: fully occupied

"M"=Sr, Ba: half occupied

One 8f position available for hosting Li^+ in Sr, Ba based compounds



4a (0, 0, 0)

4b (½, 0, 0)

8c (¼, ¼, 0)

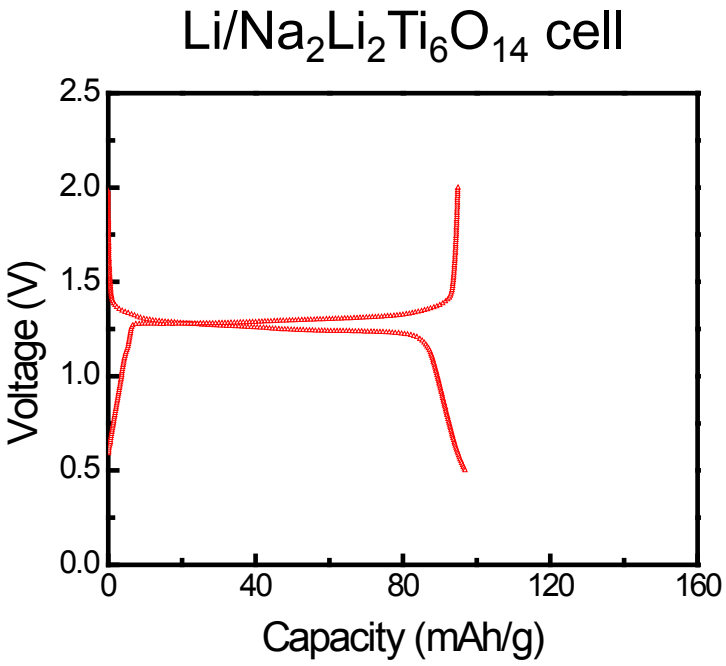
Vacant sites

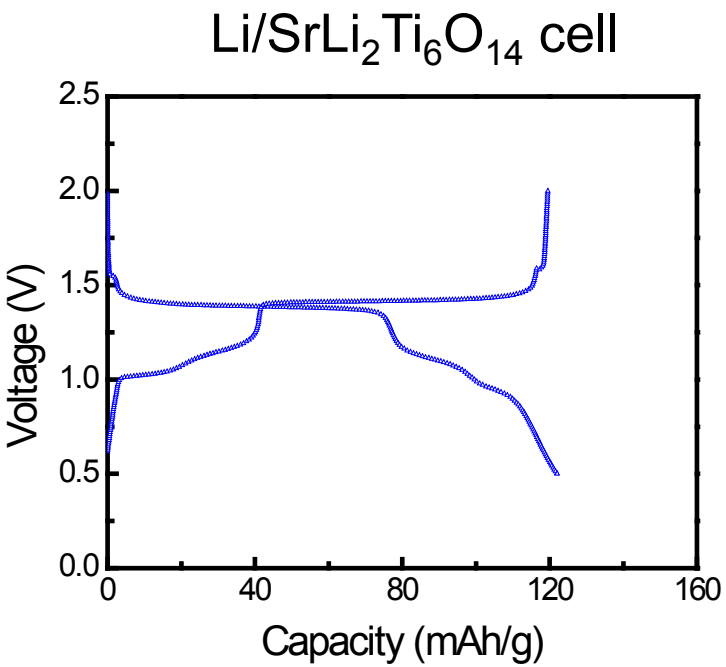
Suitable for Li ions

Insertion of $2Li^+$ ions per unit formula

- $MLi_2Ti_6O_{14}$ materials possess a 3D type structural framework with crystallographic vacant sites that can host lithium ions.
- $Ba/SrLi_2Ti_6O_{14}$ display additional vacant sites compared to $Na_2Li_2Ti_6O_{14}$.

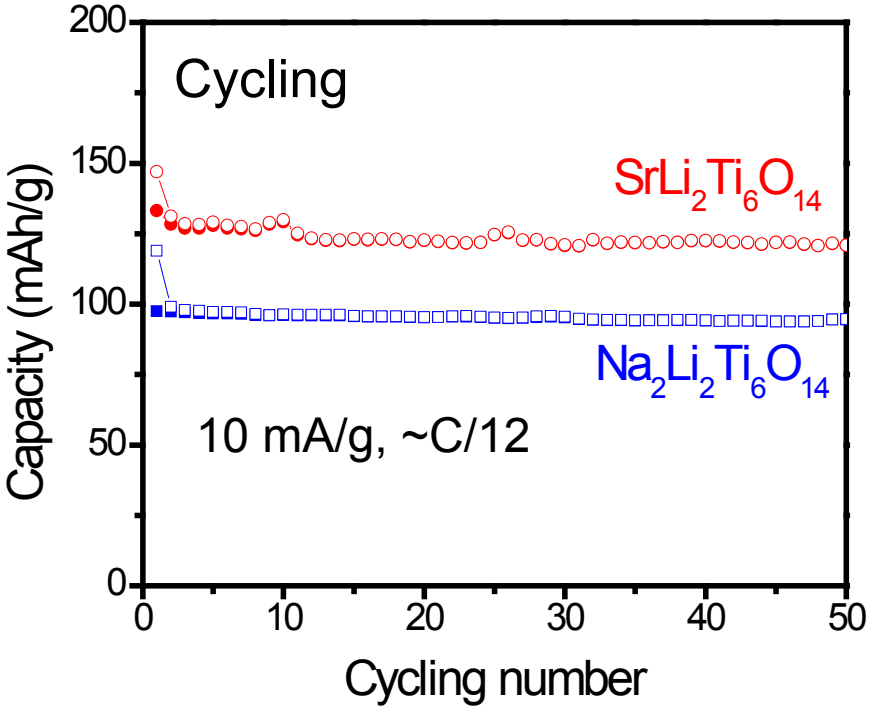
Voltage Profile of Lithium Cells

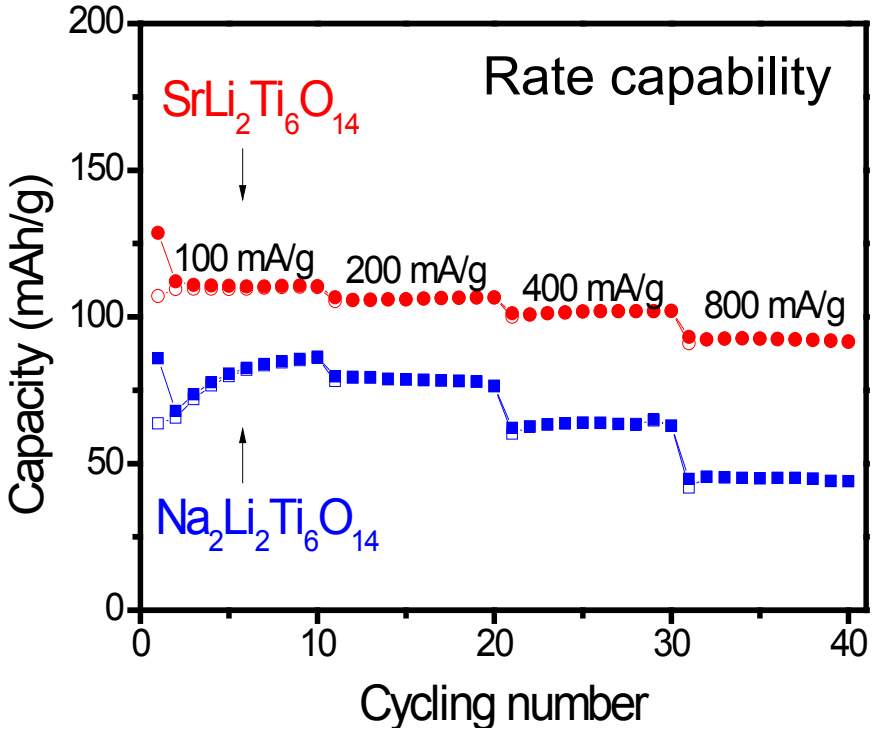




- Both $Na_2Li_2Ti_6O_{14}$ and $SrLi_2Ti_6O_{14}$ display an average voltage lower than $Li_4Ti_5O_{12}$, i.e. 1.25V (Na) and 1.4V (Sr).
- $SrLi_2Ti_6O_{14}$ showed higher capacity than $Na_2Li_2Ti_6O_{14}$.

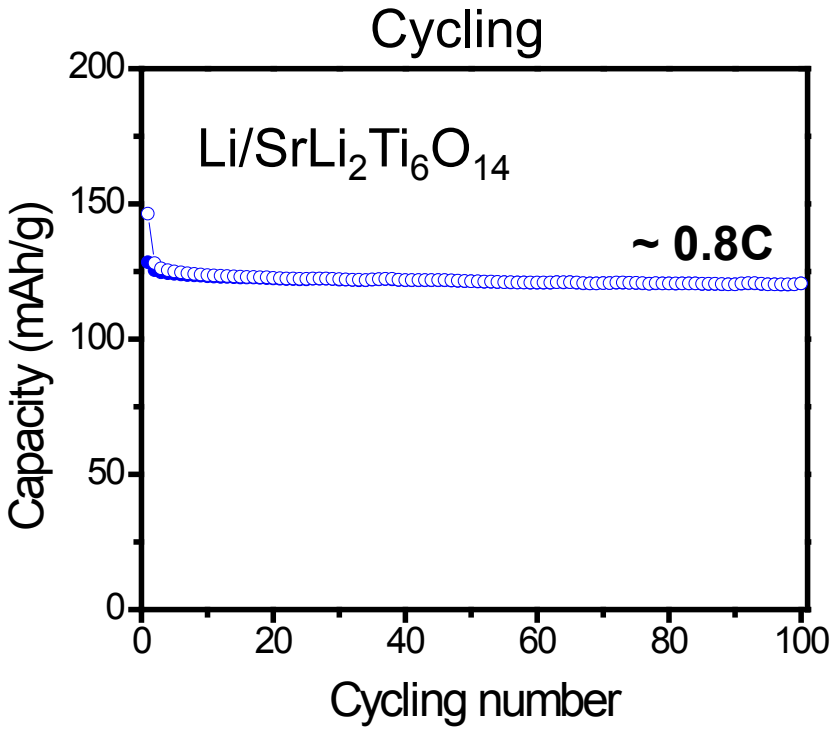
Cycling and Rate Capability

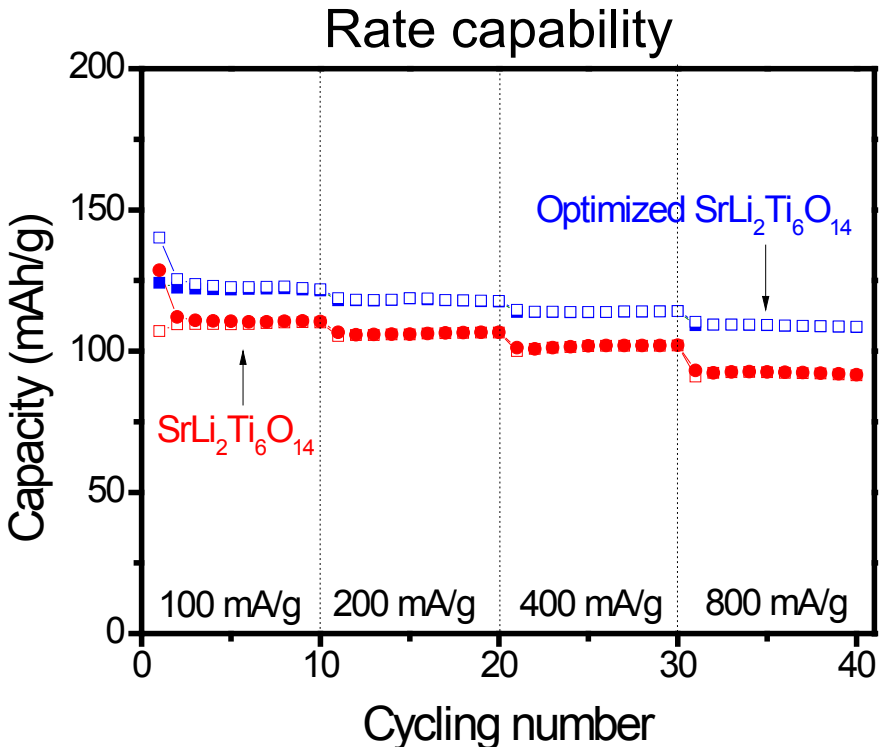




- Good cycling with high coulombic efficiency.
- Reversible insertion of $3Li^+$ in $SrLi_2Ti_6O_{14}$ and $2Li^+$ in $Na_2Li_2Ti_6O_{14}$
- $SrLi_2Ti_6O_{14}$ anode showed superior rate capability, i.e. 92-mAh/g capacity under a 5C rate.

Optimization of $SrLi_2Ti_6O_{14}$ Anode

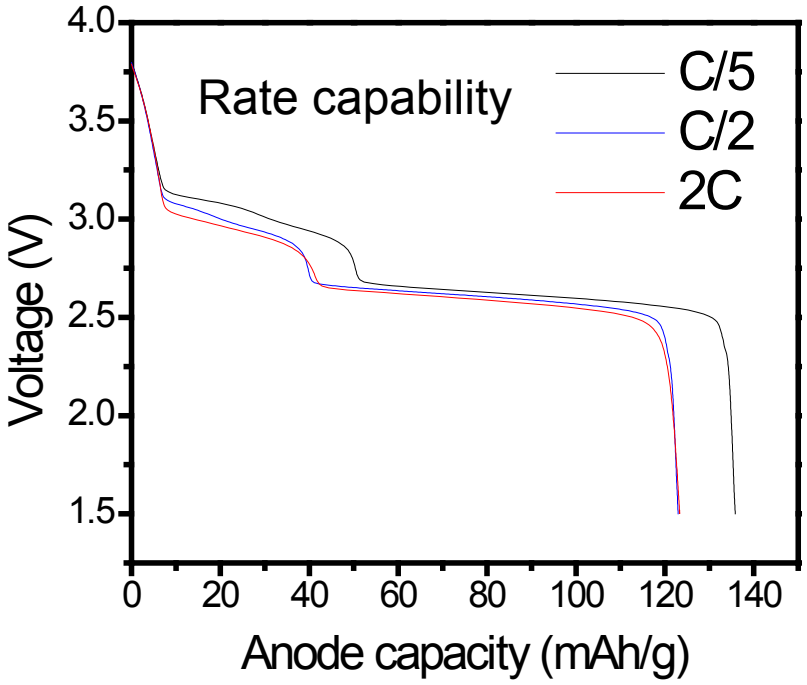


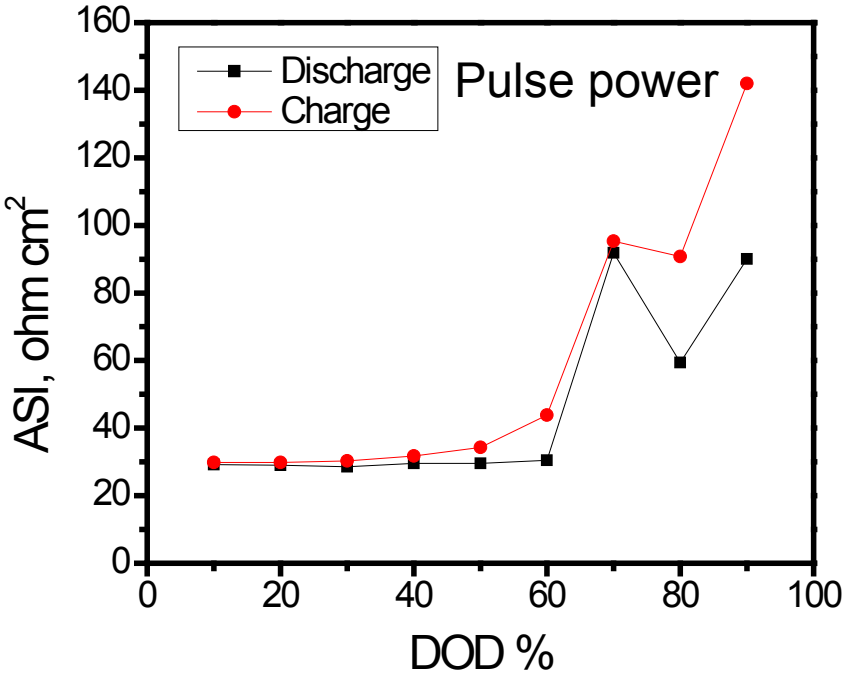


Modified Sol-gel method improved the electrochemical properties of $SrLi_2Ti_6O_{14}$

- Improved cycling under at 1C rate.
- Retention of more than 100mAh/g at 5C rate.

Preliminary Evaluation of $SrLi_2Ti_6O_{14}/LiMn_2O_4$ Cell





Preliminary results on anode-limited cell configuration :

- Good rate capability.
- Comparable HPPC results to $Li_4Ti_5O_{12}/LiMn_2O_4$

Summary

- New sol-gel synthesis was successfully applied to prepare high purity $MLi_2Ti_6O_{14}$ new anode materials.
- Lithium ion insertion mechanisms in $MLi_2Ti_6O_{14}$ (M = Sr, Ba, 2Na) have been fully understood. Particularly, it was found that $SrLi_2Ti_6O_{14}$ material exhibits additional vacant sites available for lithium insertion.
- $SrLi_2Ti_6O_{14}$ shows promising properties in terms of capacity, cyclability, and rate capability.
- Full cells with $LiMn_2O_4$ cathode were found to deliver stable capacity and good rate capability.

Future Works

⇨ Optimization of the full cells $SrLi_2Ti_6O_{14}/LiMn_2O_4$ design and evaluation of electrochemical properties for HEV applications.

⇨ In-situ structural characterizations of $SrLi_2Ti_6O_{14}$ with BNL (Dr. Yang).

⇨ Investigate the pulse-discharge and charge performance of designed cell based on $SrLi_2Ti_6O_{14}$ anode through hybrid pulse power characterization (HPPC test).

⇨ Enable the high power performance of $MLi_2Ti_6O_{14}$ through new synthesis method and/or through nano- carbon coating.

⇨ Investigate the potential use of $Na_2Li_2Ti_6O_{14}$ as high power anode (operating voltage is around 1.25V).

⇨ Investigate the safety and stability (vs. electrolyte, gazing issue) of these materials.

Second Project
Development of a high capacity and long life anodes

Milestones FY May 09 – May 10: High capacity and long life anodes

- Development of a new synthesis method to prepare nano-structured, high surface area and high packing density TiO_2 Brookite material. (*Completed*)

- Mechanistic investigation of the formation of nano-structured TiO_2 Brookite. (*Completed)*

- Electrochemical characterizations and investigation of the lithium insertion mechanism in TiO_2 Brookite. (*Completed)*

- Development and optimization of high capacity and long life silicon-based composite anodes. (*On going)*

- Investigation of silicon-based-anode/cathode cells as high-energy density and long life cell systems. *(On going)*

Development of a unique synthesis method for TiO_2

- **Unique way to prepare a metastable TiO_2 brookite with suitable morphology**

  - Low cost synthesis (2-step process)
    1. Aqueous precipitation of a titanium oxalate:
       $Ti_2O_3(H_2O)_2(C_2O_4).H_2O$
    2. Thermal decomposition (<400°C) to form TiO_2 brookite.

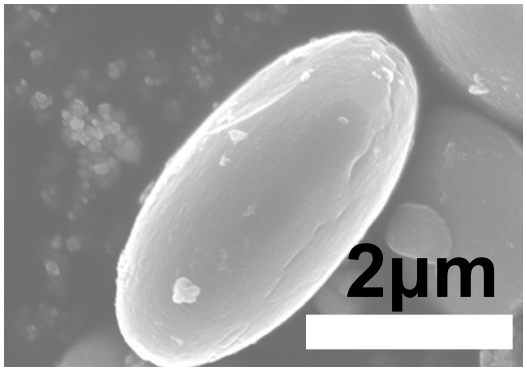
  - The process allows the monitoring of the morphology and size of particles, by tuning the synthesis parameters (concentration, duration time…).

  - Morphology does not change after thermal treatment.

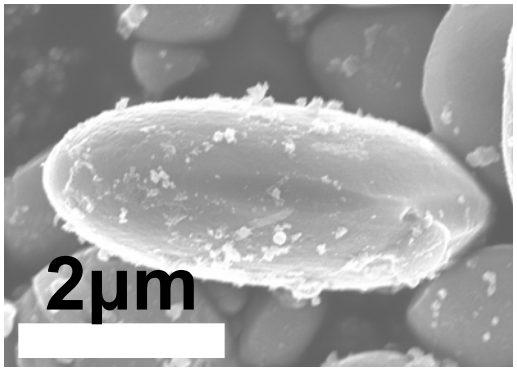
  - The obtained TiO_2 material is nano-structured, has high surface area (~400 m^2/g), but high packing density which can increase the volumetric energy density at the cell level.

Key features of the prepared TiO_2 Brookite.

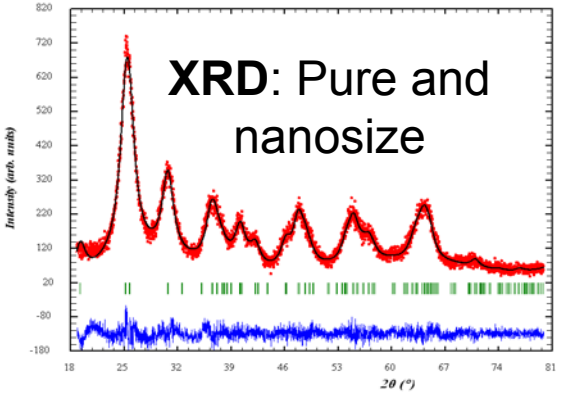
Precursor $Ti_2O_3(H_2O)_2(C_2O_4).H_2O$



T=300-400°C



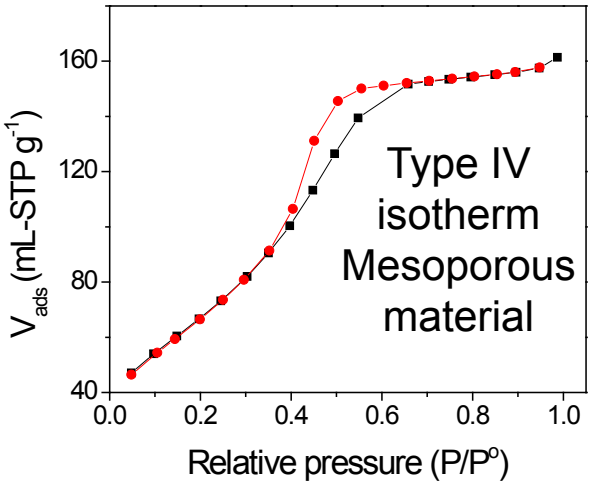
TiO_2 Brookite



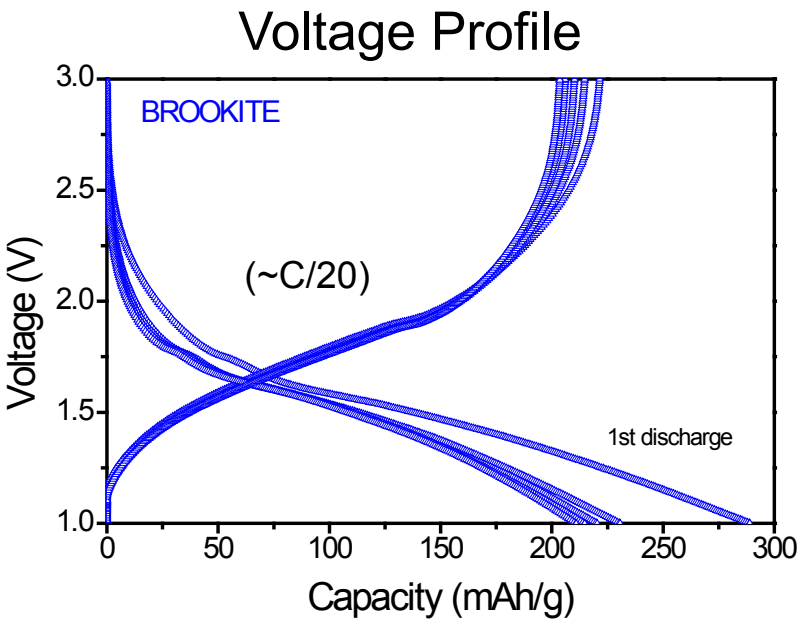
- Morphology of the precursor is retained.
- Nanosize particle and phase purity.
- High packing density can be achieved, up to 1.2 g/cc
- Easier electrode fabrication.

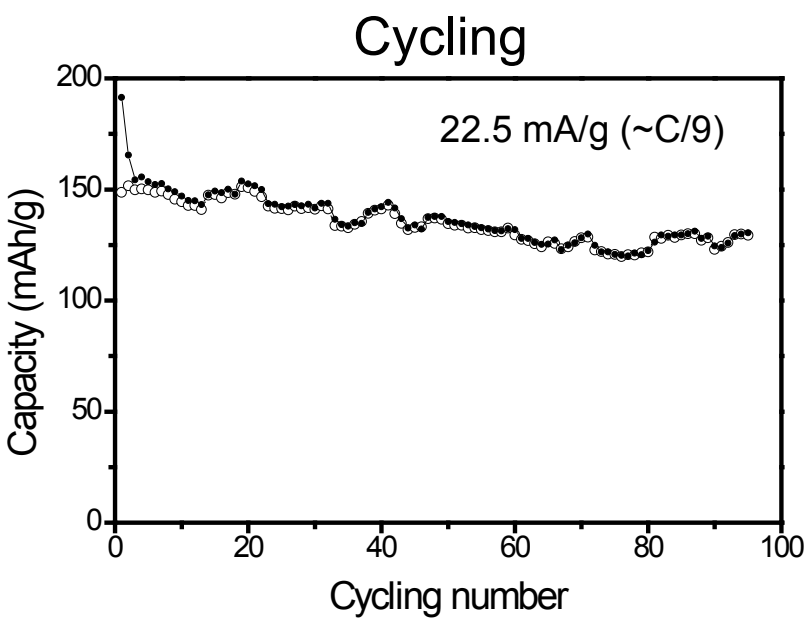
- Mesoporous material with very high surface area (up to 400 m^2/g)
- Combination of nano-sized domains embedded in micro-sized particles having high surface area but high packing density.

N_2 isotherm



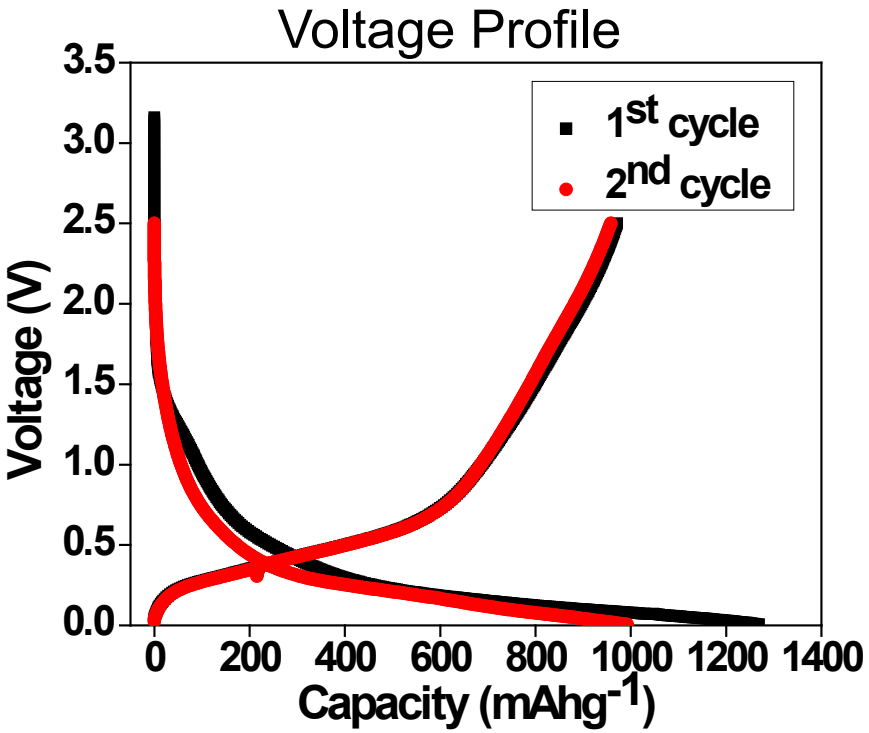
Electrochemical Properties of Li/TiO_2

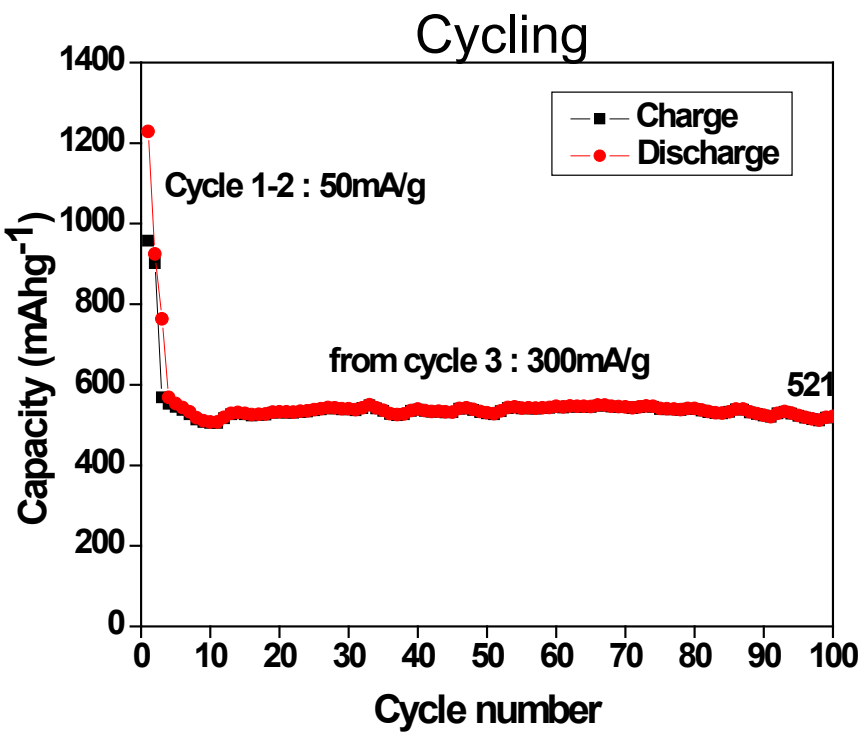




- X-ray PDF analysis has confirmed the stability of the Brookite structure after lithiation.
- Because of the insulating character of TiO_2 Brookite, the material delivered a low capacity at high rate.
- Carbon coating experiments are underway to improve the electronic conductivity of the material.

Development of a New Silicon- Composite Based Anode





- Material was prepared by a scalable high-energy ball milling.
- Material has high packing density (1.7g/cm^3).
- The anode shows very promising results in terms of capacity, low irreversible loss and good cycle life.

Summary and Future Work

- Nano-structured, high surface area and high packing density TiO_2 Brookite has been made through an innovative and first time reported method.

- X-ray PDF analysis has confirmed the stability of the Brookite structure after lithiation.

- Electrochemistry of the prepared TiO_2 Brookite has been shown to be under the project's goals. Nevertheless, ways to improve the electrochemical performances can be applied.

- High capacity and long life anode has been developed based silicon-composite system.

- Future work will mainly focus on these new Silicon composite anode to further increase the capacity while maintaining good cycle life and low irreversible loss.

- Investigate the performance of silicon composite in a full cell configuration and further explore ways to reduce the irreversible loss (collaboration with FMC using stabilized lithium metal powder)

Collaborations

- X.Q. Yang (BNL) (structural studies of TiO_2 and silicon composite anode) Composite
- A. Tressaud & A. Demourgues (ICMCB, Bordeaux, France)
- FMC corporation
- Y. Sun, Center of Nanoscale material at Argonne
- PJ. Chupas, Advanced Photon Sources, Argonne
- H. Kang, Northwestern University