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).
- 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$_2$M$_6$Ti$_6$O$_{14}$ ($M=\text{Ba, Sr, 2Na}$) materials were selected based on the following criteria:
  - High-potential anodes ($\sim 1.4V$) can provide long life & better safety because they don’t require an SEI layer.
  - Anodes possess lower potentials than Li$_4$Ti$_5$O$_{12}$ (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$_4$Ti$_5$O$_{12}$.
  - 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 $\text{MLi}_2\text{Ti}_6\text{O}_{14}$ ($\text{M}=\text{2Na, Ba, Sr}$) compounds. *(Completed)*

- Comparative studies between $\text{Ba/SrLi}_2\text{Ti}_6\text{O}_{14}$ and $\text{Na}_2\text{Li}_2\text{Ti}_6\text{O}_{14}$ 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$_2$Ti$_6$O$_{14}$ Materials

- Development of a sol-gel process to prepare MLi$_2$Ti$_6$O$_{14}$ materials.

- Sol gel method was found to be adequate to prepare pure and well crystallized Na$_2$Li$_2$Ti$_6$O$_{14}$, SrLi$_2$Ti$_6$O$_{14}$ and BaLi$_2$Ti$_6$O$_{14}$ compounds.
- Solids consist of 500 nm primary particles that agglomerate in larger particles. Ba$_2$Li$_2$Ti$_6$O$_{14}$ showed larger agglomerates which had a negative impact on power & capacity of the material.
Rationales behind the selection of $\text{MLi}_2\text{Ti}_6\text{O}_{14}$ type structure

- $[\text{TiO}_6]$ framework
  - 11-fold coordinated position

- $[\text{LiO}_4]$ positions
  - 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

- Vacant sites suitable for Li ions
- Insertion of 2Li$^+$ ions per unit formula

- $\text{MLi}_2\text{Ti}_6\text{O}_{14}$ materials possess a 3D type structural framework with crystallographic vacant sites that can host lithium ions.
- $\text{Ba/SrLi}_2\text{Ti}_6\text{O}_{14}$ display additional vacant sites compared to $\text{Na}_2\text{Li}_2\text{Ti}_6\text{O}_{14}$. 
• Both Na$_2$Li$_2$Ti$_6$O$_{14}$ and SrLi$_2$Ti$_6$O$_{14}$ display an average voltage lower than Li$_4$Ti$_5$O$_{12}$, i.e. 1.25V (Na) and 1.4V (Sr).
• SrLi$_2$Ti$_6$O$_{14}$ showed higher capacity than Na$_2$Li$_2$Ti$_6$O$_{14}$. 
Cycling and Rate Capability

- Good cycling with high coulombic efficiency.
- Reversible insertion of 3Li$^+$ in SrLi$_2$Ti$_6$O$_{14}$ and 2Li$^+$ in Na$_2$Li$_2$Ti$_6$O$_{14}$
- SrLi$_2$Ti$_6$O$_{14}$ anode showed superior rate capability, i.e. 92-mAh/g capacity under a 5C rate.
Optimization of $\text{SrLi}_2\text{Ti}_6\text{O}_{14}$ Anode

Modified Sol-gel method improved the electrochemical properties of $\text{SrLi}_2\text{Ti}_6\text{O}_{14}$

- Improved cycling under at 1C rate.
- Retention of more than 100mAh/g at 5C rate.
Preliminary Evaluation of SrLi$_2$Ti$_6$O$_{14}$/LiMn$_2$O$_4$ Cell

Rate capability

[Graph showing voltage (V) vs. anode capacity (mAh/g) for different rates: C/5, C/2, and 2C]

- Good rate capability.
- Comparable HPPC results to Li$_4$Ti$_5$O$_{12}$/LiMn$_2$O$_4$
Summary

- New sol-gel synthesis was successfully applied to prepare high purity MLi$_2$Ti$_6$O$_{14}$ new anode materials.

- Lithium ion insertion mechanisms in MLi$_2$Ti$_6$O$_{14}$ (M = Sr, Ba, 2Na) have been fully understood. Particularly, it was found that SrLi$_2$Ti$_6$O$_{14}$ material exhibits additional vacant sites available for lithium insertion.

- SrLi$_2$Ti$_6$O$_{14}$ shows promising properties in terms of capacity, cyclability, and rate capability.

- Full cells with LiMn$_2$O$_4$ cathode were found to deliver stable capacity and good rate capability.
Future Works

- Optimization of the full cells $\text{SrLi}_2\text{Ti}_6\text{O}_{14}/\text{LiMn}_2\text{O}_4$ design and evaluation of electrochemical properties for HEV applications.

- In-situ structural characterizations of $\text{SrLi}_2\text{Ti}_6\text{O}_{14}$ with BNL (Dr. Yang).

- Investigate the pulse-discharge and charge performance of designed cell based on $\text{SrLi}_2\text{Ti}_6\text{O}_{14}$ anode through hybrid pulse power characterization (HPPC test).

- Enable the high power performance of $\text{MLi}_2\text{Ti}_6\text{O}_{14}$ through new synthesis method and/or through nano-carbon coating.

- Investigate the potential use of $\text{Na}_2\text{Li}_2\text{Ti}_6\text{O}_{14}$ 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 TiO₂ Brookite material. *(Completed)*

- Mechanistic investigation of the formation of nano-structured TiO₂ Brookite. *(Completed)*

- Electrochemical characterizations and investigation of the lithium insertion mechanism in TiO₂ 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:
       \[
       \text{Ti}_2\text{O}_3(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)\cdot \text{H}_2\text{O}
       \]
    2. Thermal decomposition (<400$^\circ$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.

- 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.
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.
Material was prepared by a scalable high-energy ball milling.

Material has high packing density (1.7 g/cm³).

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 TiO₂ 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 TiO₂ 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
- P.J. Chupas, Advanced Photon Sources, Argonne
- H. Kang, Northwestern University