Developing a new high capacity anode with long life

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Overview

Timeline
- Start - October 1st, 2008.
- 40%

Barriers
- Barriers addressed
  - Overcome the inherent safety issue of graphite.
  - Extend the cycle life of the lithium-ion battery.
  - Extend the calendar life of the lithium ion batteries

Budget
- Total project funding
  - DOE share: 200K

- Interactions/ collaborations:
  D. Dambournet, I. Belharouak

- Project lead: Khalil Amine
Objectives

- Develop new anode materials that provide very high gravimetric and volumetric energy density for PHEV applications.

- Explore ways for preparing nanosized TiO$_2$ having different structural arrangements.

- Understand the lithium insertion mechanism by which the TiO$_2$ phases can achieve high specific capacity.

- Demonstrate the applicability of TiO$_2$ in full lithium ion cells.
## Milestones

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<tr>
<th>Month/Year</th>
<th>Milestone or Go/No-Go Decision</th>
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| May-09     | - Develop a new synthetic method to prepare nanosized TiO₂ materials.  
             - Understand how to isolate different TiO₂ polymorphs (anatase, rutile, brookite) by tuning the synthesis conditions.  
             - Conduct structural and electrochemical characterizations. |
| Sept-09    | - Investigate alternative routes to prepare specifically the TiO₂ beta form.  
             - Evaluate the electrochemical performance of the TiO₂(B).  
             - Investigate cells based TiO₂ and high capacity cathode materials. |
| Sept-2010  | - Develop a suitable morphology with micron size secondary particles and dense nano-sized primary particles to obtain full capacity of TiO₂ and good rate capability.  
             - Explore further ways to improve the rate capability by means of carbon coating and/or high energy ball milling. |
Approach

- Develop a simple synthesis route to prepare nano-sized TiO$_2$ materials using low cost salts.

- Explore coating TiO$_2$ with nano-sized conductive carbon layers to improve conductivity and increase active particle utilization to achieve high energy.

- Develop a suitable morphology with micron size secondary particles and dense nanosized primary particles to obtain full capacity of TiO$_2$ and good rate capability.
Advantages of TiO$_2$ as anode for lithium batteries

— TiO$_2$ has a potential vs. Li$^0$ (~1.5 V) prevents the plating of metallic lithium at the negative electrode, thus enhancing the safety of the cell.

— TiO$_2$ remains stable after lithium insertion and doesn’t require SEI layer, thus extending the life of the cell.

— TiO$_2$ exhibits relatively high practical capacity (~240 mAh/g), smaller than graphite, but greater than Li$_4$Ti$_5$O$_{12}$.

— TiO$_2$ is non toxic, abundant, and inexpensive.

— TiO$_2$ has different structural arrangements that act as Li-host and display different voltage profiles.
Preparation of TiO$_2$ Anatase by Thermolysis Reaction

**Synthesis:**

- Thermolysis of TiOSO$_4$ oxysulfate in an aqueous medium (T=90°C t=4h).
  - TiOSO$_4$ is a Low cost salt,
  - Contains sulfuric acid which stabilizes the formation of nanoparticles,
  - favors the formation of the Anatase type structure.

X-ray diffraction identifies the formation of TiO$_2$ anatase

Anatase structure

Li insertion
Effect of Additives on the Preparation of TiO$_2$ Anatase

- Additives such as inorganic salts can act as capping agents, structure and morphology directing agents.

Addition of Lithium sulfate prevents the formation of large agglomerate.

Addition of lithium nitrate or chloride decreases the crystallinity (not shown here).

Scanning electron microscopy images
Example of SEM Image of TiO$_2$ Anatase

- Primary crystallite < 20 nm
- Large agglomerates

- TiO$_2$ nano-structured material is obtained
The addition of Li$_2$C$_2$O$_4$ has been proved to be relevant on the preparation of TiO$_2$. The molar ratio $R = [C_2O_4^{2-}]/[Ti^{4+}]$ has a strong influence on the final stabilized phase.

- $R = 2$
- $R = 0.8$
- $R = 0.4$
- $R = 0.2$

XRD of the obtained phases

- Rutile
- Unidentified phase
- Anatase + Rutile

- Oxalate species act as a strong complexing agent and depending of the concentration can stabilized several phases.
Preparation of TiO$_2$ Brookite

- TiO$_2$ Brookite, usually very difficult to prepare, was obtained by a simple preparation route, and has an open structure suitable for lithium insertion.
Electrochemical Properties

Lithium insertion and deinsertion occurs typically at 1.4-1.7 V versus Li⁺/Li as follows: $x\text{Li}^+ + \text{TiO}_2 + xe^- \leftrightarrow \text{Li}_x\text{TiO}_2$

Theoretical capacity value is 335 mAh/g for 1 inserted Lithium per TiO₂

- **Anatase**
- **Brookite**
- **Rutile**

**First discharge profile**

Cell configuration: (80% TiO₂, 10% Super-P, 10% PVdF)
Li metal anode
Rate: C/30 from 1 to 3V
Electrolyte 1.2M LiPF₆ in (3EC:7EMC)

- TiO₂ forms have different voltage profiles and provide specific capacities close to the theoretical ones at low rate
Electrochemical Properties (Continued)

- All TiO₂ forms showed similar capacities, with brookite having the lowest irreversible capacity
Summary

- Developed a new synthetic method to prepare nanosized TiO$_2$ materials.

- Isolated different TiO$_2$ polymorphs (anatase, rutile, brookite) by tuning the synthesis conditions. The case of the Brookite being relevant with the achievement of a very simple way to prepare this metastable phase.

- Structural and electrochemical characterizations have been performed on the materials obtained showing some promising features.
Future works

- Complete the characterization of the prepared TiO$_2$ materials: TEM and further electrochemical characterizations.

- Explore new synthesis route using a CSTR tank reactor that can provide suitable morphology (nano-structured materials with high packing density).

- Explore ways to limit the irreversible capacity loss due to the poor electronic conductivity through the integration of conductive phases
  - Carbon coating and/or
  - high energy ball milling
  - Nano-primary particle inbanded in micron size secondary particles

- Investigate optimum TiO$_2$ with high voltage and capacity cathode materials such as Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$. 