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Developing a new high capacity anode with long life

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Argonne National Laboratory

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U.S. Department of Energy

THE UNIVERSITY OF CHICAGO

Office of Science U.S. DEPARTMENT OF ENERGY

A U.S. Department of Energy laboratory managed by The University of Chicago

Overview

Timeline

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

Budget

- Total project funding
  - DOE share: 200K

Barriers

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

- 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

Month/Year	Milestone or Go/No-Go Decision
May-09	- Develope a new synthetic method to prepare nanosized TiO_2 materials. - Understande how to isolate different TiO_2 polymorphs (anatase, rutile, brookite) by tuning the synthesis conditions. - Conduct structural and electrochemical characterizations.
Sept-09	- Investigate alternative routes to prepare specifically the TiO_2 beta form. - Evaluate the electrochemical performance of the TiO_2(B). - Investigate cells based TiO_2 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 TiO_2 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^o (~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 $Li_4Ti_5O_{12}$.

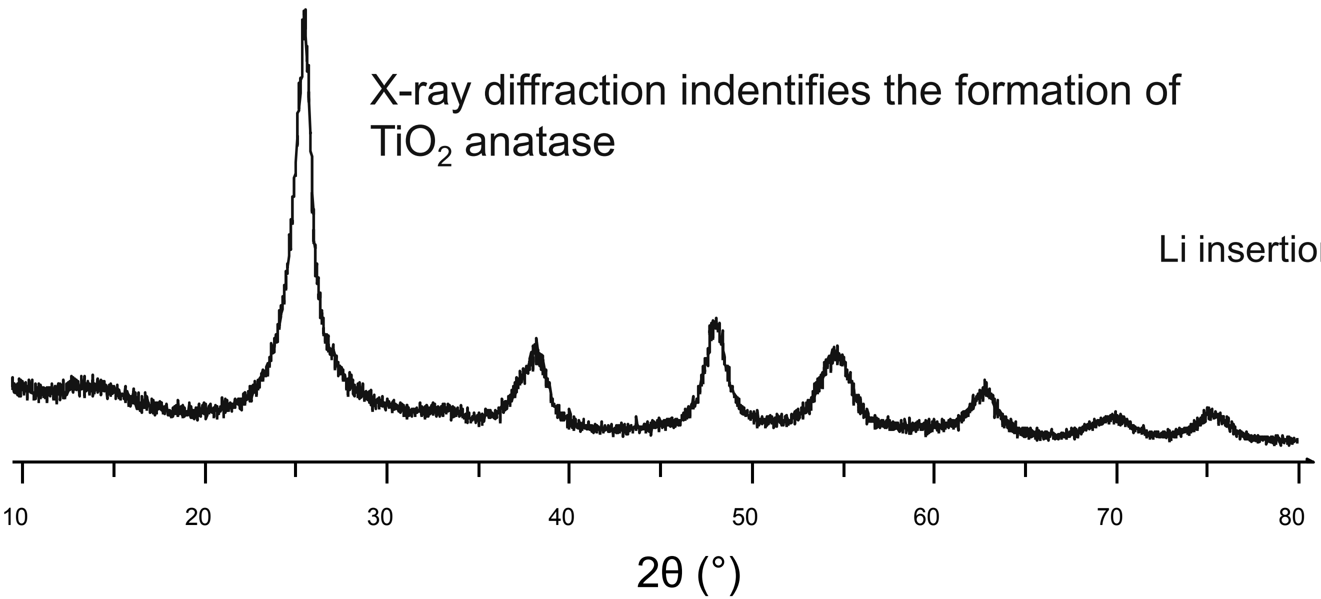
– TiO_2 is non toxic, abundant, and inexpensive.

– TiO_2 has different structural arrangements that act as Li-host and display different voltage profiles.

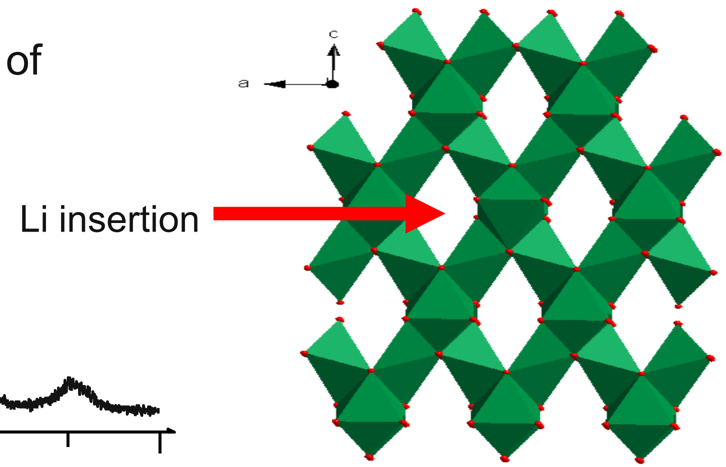
Preparation of TiO_2 Anatase by Thermolysis Reaction

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,
  - favorizes the formation of the Anatase type structure.

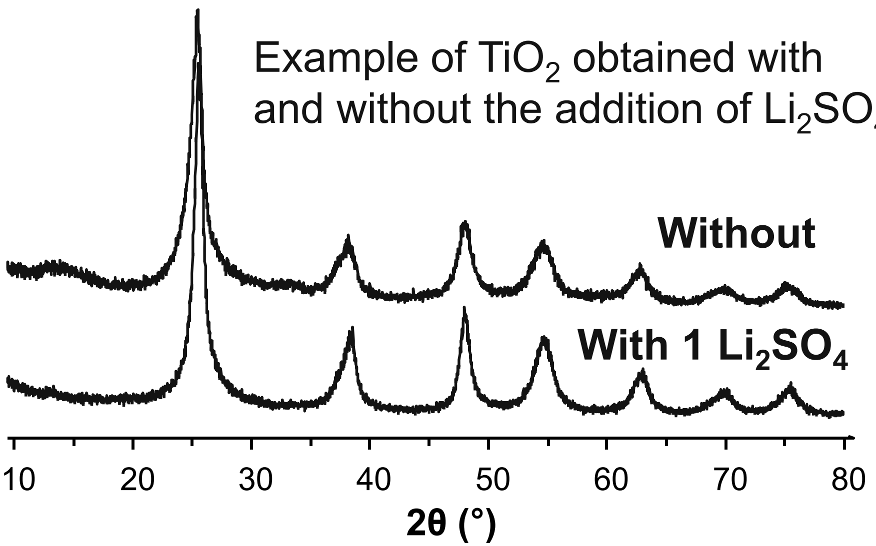


Anatase structure

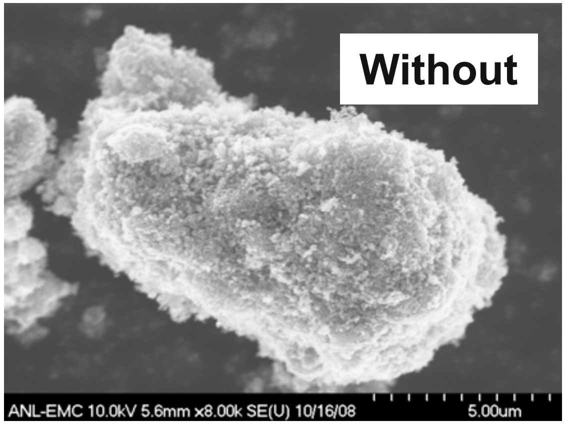


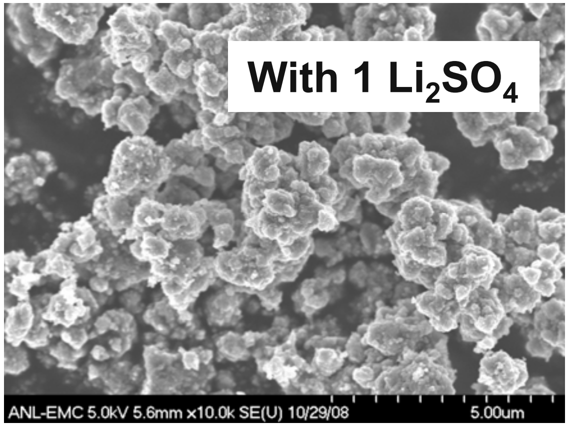
Effect of Additives on the Preparation of TiO_2 Anatase

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



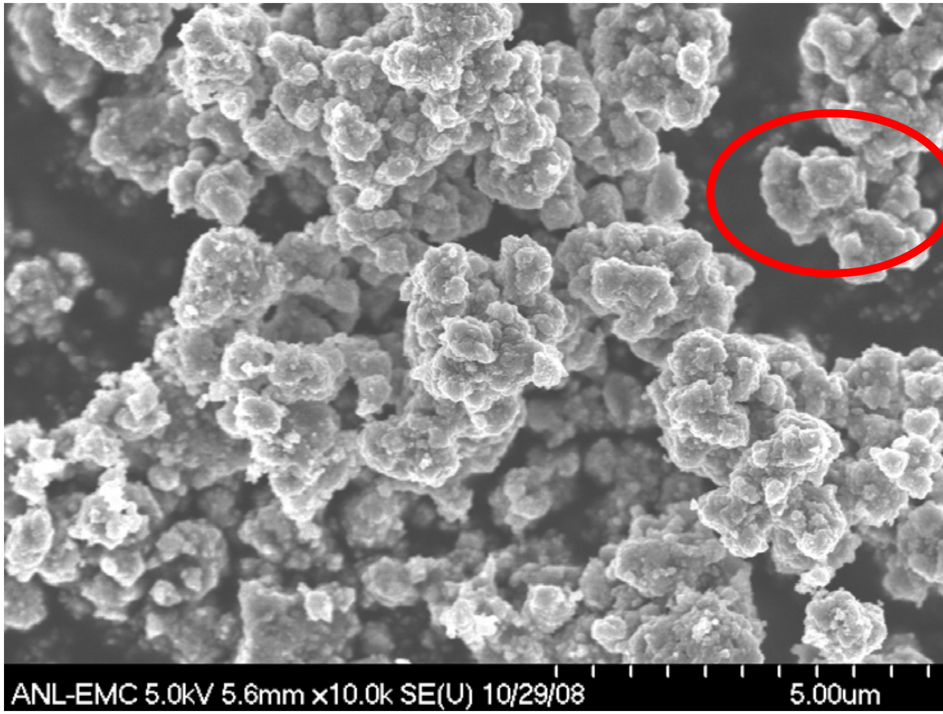
- Addition of Lithium sulfate prevents the formation of large agglomerate.
- Addition of lithium nitrate or chloride decreases the crystallinity (not shown here).



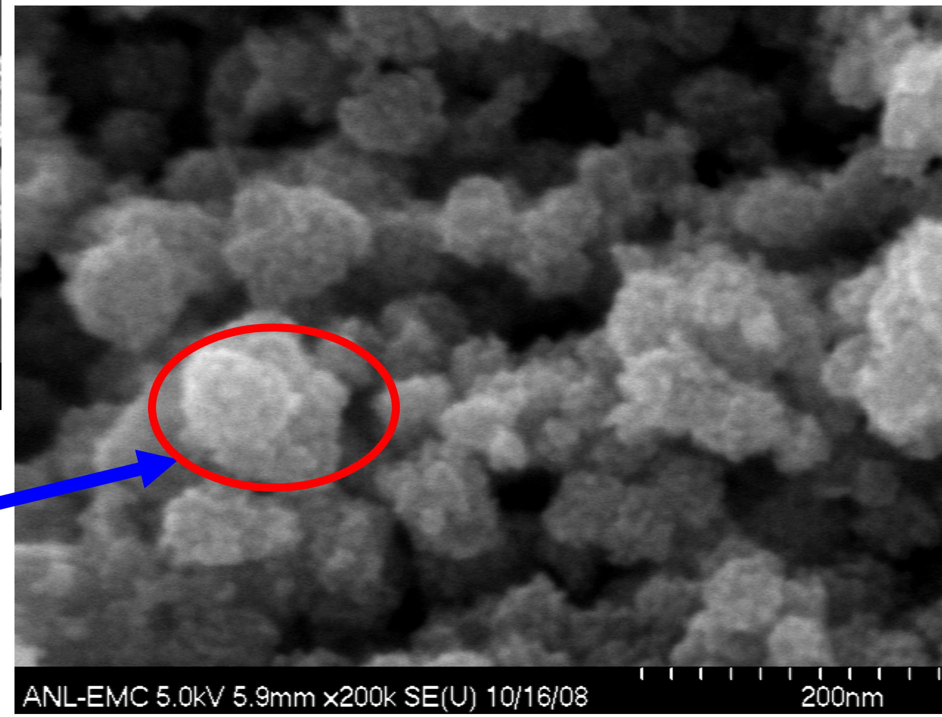


Scanning electron microscopy images

Example of SEM Image of TiO_2 Anatase



Large agglomerates



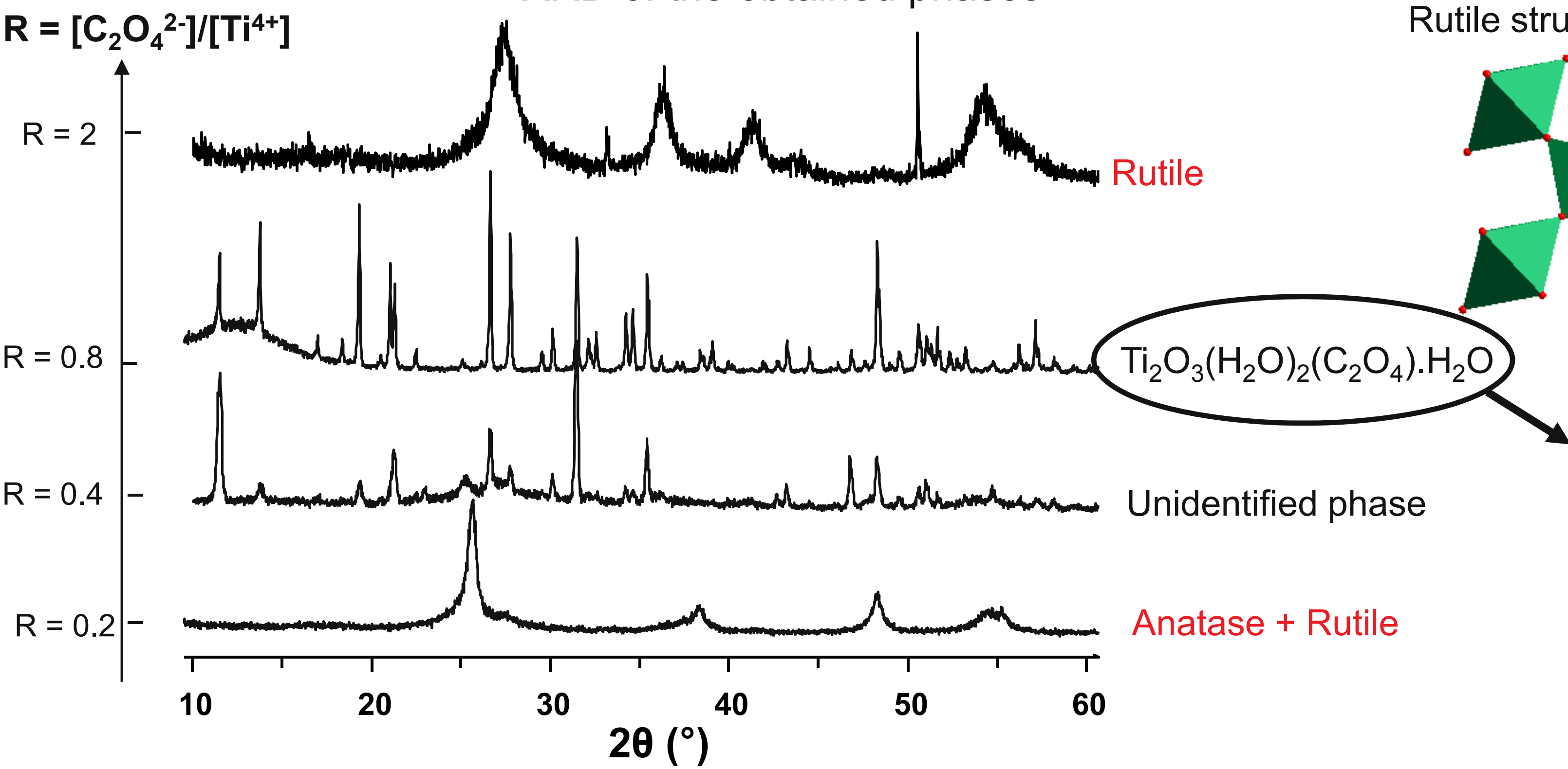
Primary crystallite < 20 nm

- TiO_2 nano-structured material is obtained

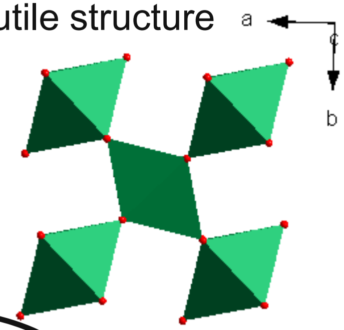
Effect of Oxalate Group on the Preparation of TiO_2

The addition of $Li_2C_2O_4$ 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.

XRD of the obtained phases



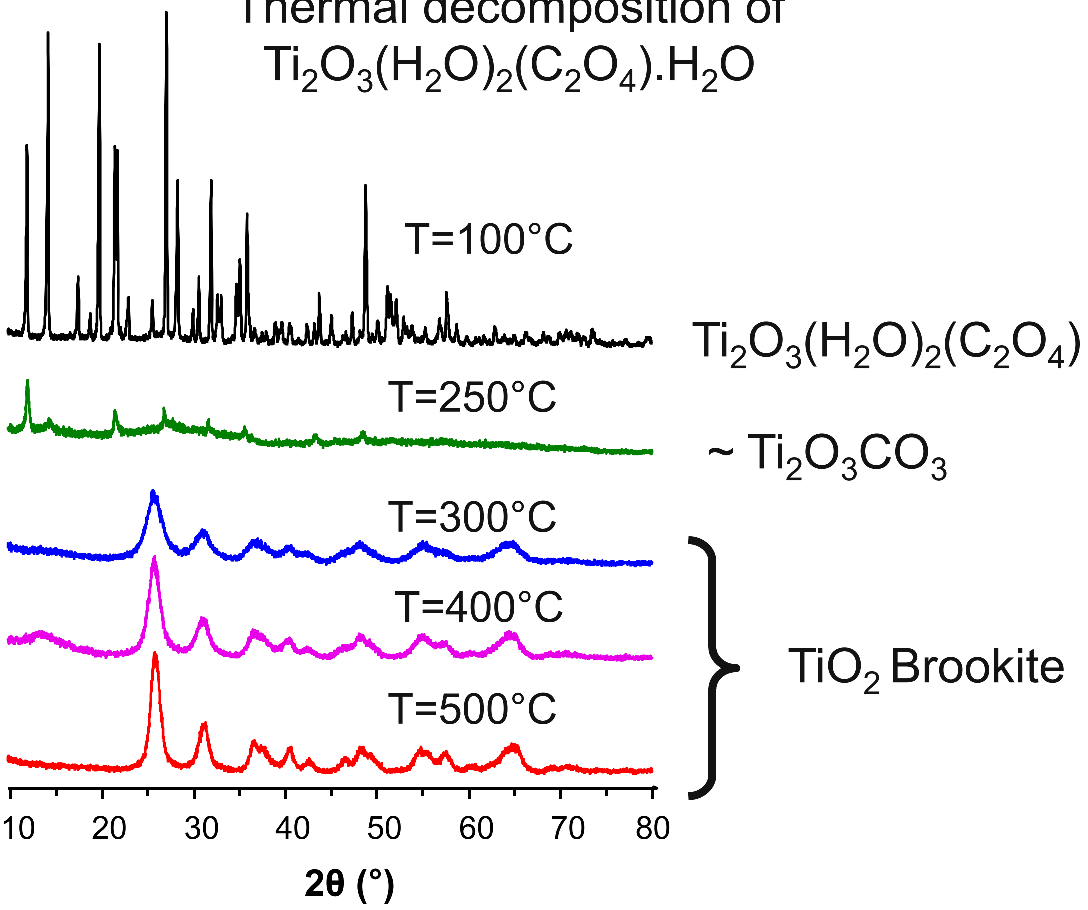
Representation of the Rutile structure



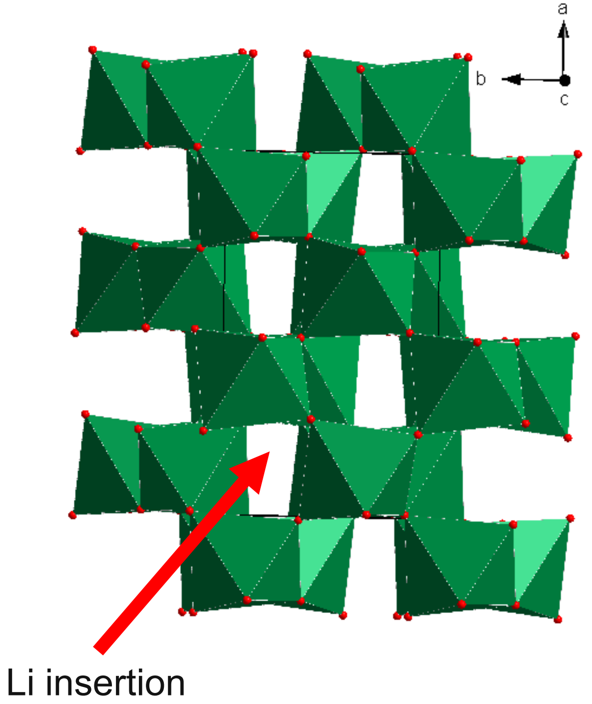
- Oxalate species act as a strong complexing agent and depending of the concentration can stabilized several phases

Preparation of TiO_2 Brookite

Thermal decomposition of $Ti_2O_3(H_2O)_2(C_2O_4).H_2O$



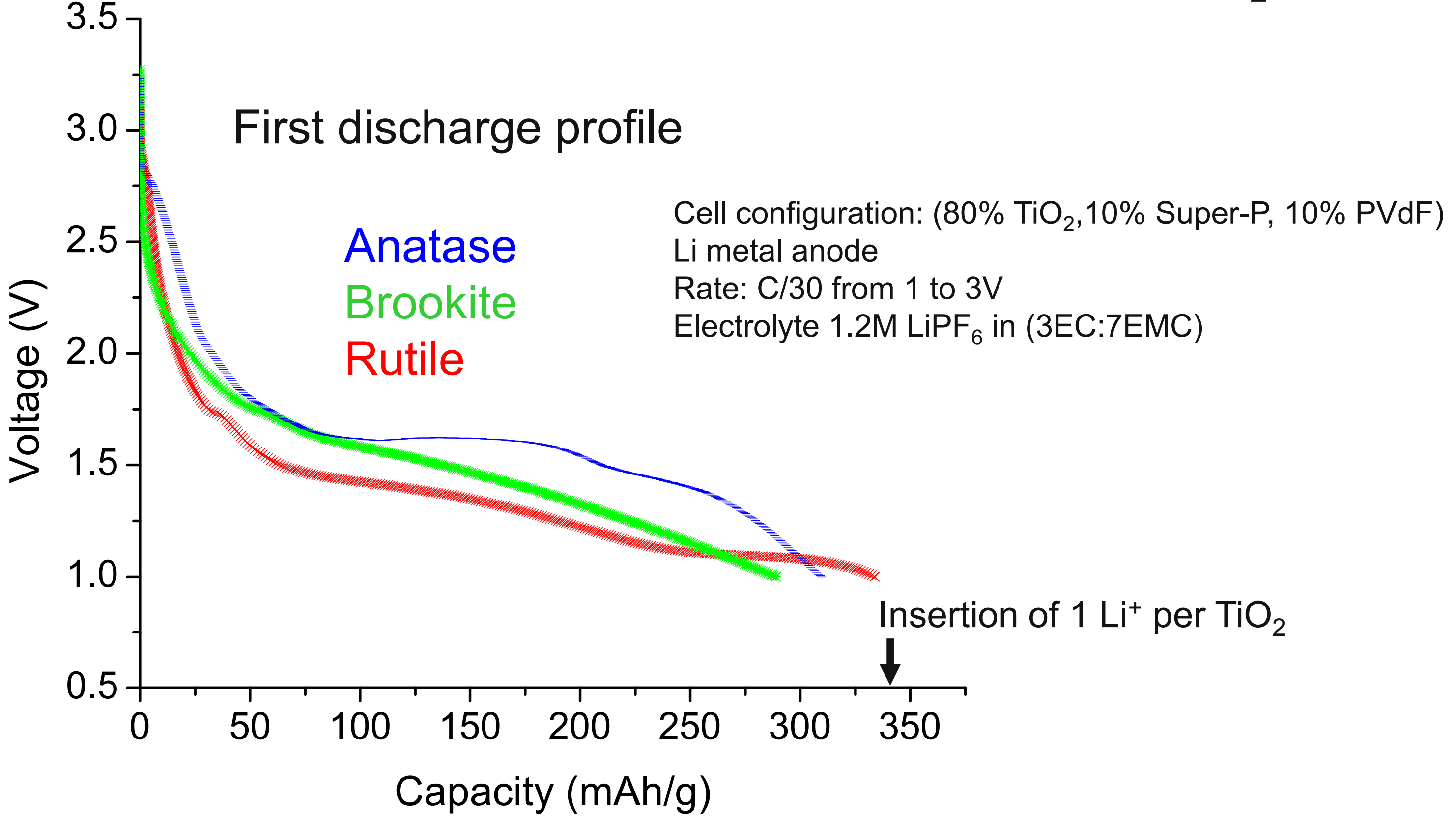
Representation of the Brookite structure



- TiO_2 Brookite, usually very difficult to prepare, was obtained by a simple preparation route, and has an open structure suitable for lithium insertion

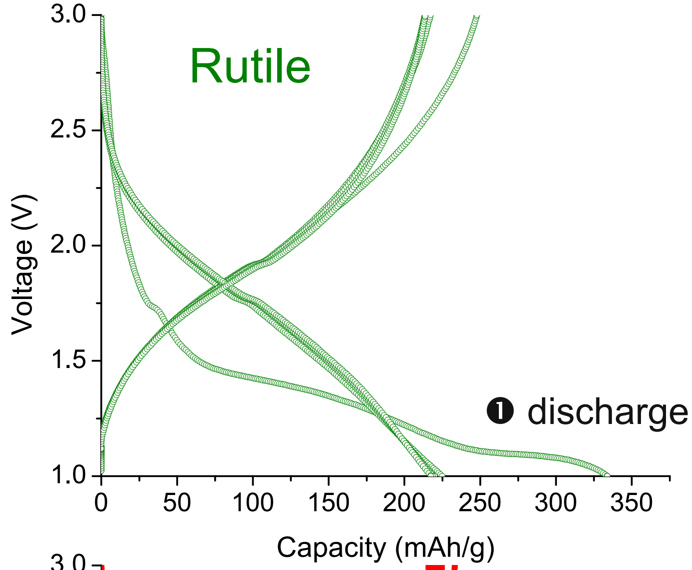
Electrochemical Properties

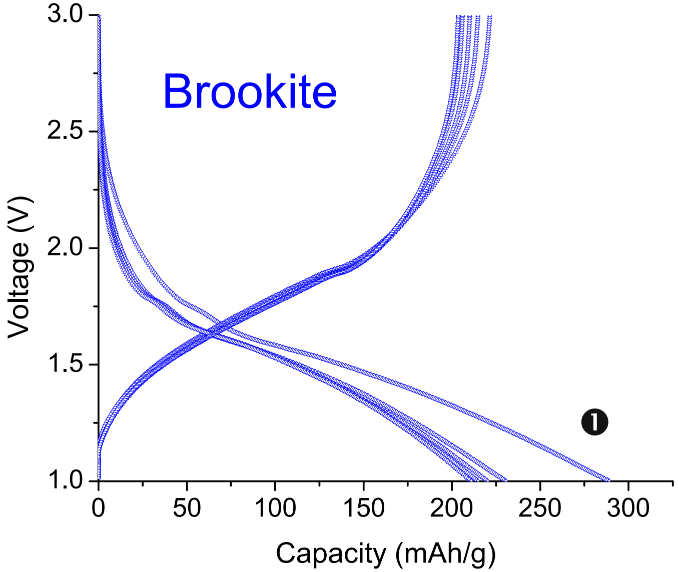
Lithium insertion and deinsertion occurs typically at 1.4-1.7 V versus Li^+/Li as follows: $xLi^+ + TiO_2 + xe^- \leftrightarrow Li_xTiO_2$
Theoretical capacity value is 335 mAh/g for 1 inserted Lithium per TiO_2

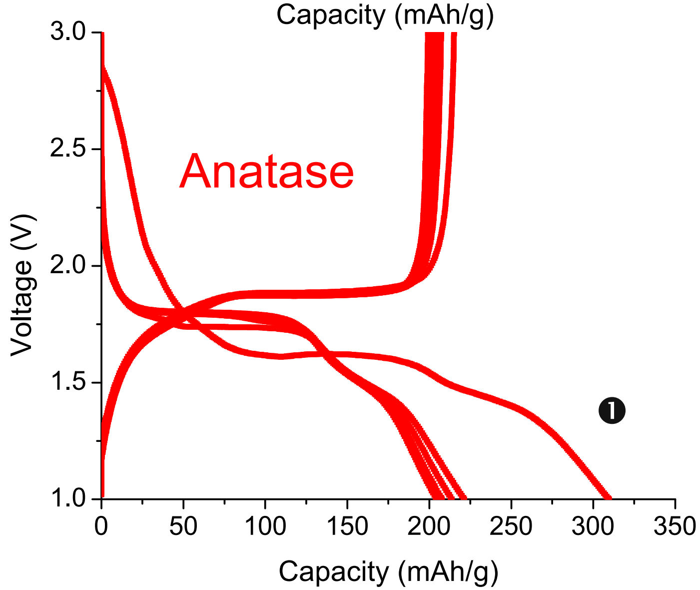


- TiO_2 forms have different voltage profiles and provide specific capacities close to the theoretical ones at low rate

Electrochemical Properties (Continued)







- All TiO_2 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 $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$.