Application of *In Situ* XAFS: Structural study of lithium intercalation in battery materials

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Introduction

The emergence of portable telecommunication, computer equipment and ultimately hybrid electric vehicles (HEV) has created a substantial interest in manufacturing rechargeable batteries that are less expensive, non-toxic, operate for longer time, small in size and weigh less.

Li-ion batteries are taking an increasing share of the current rechargeable battery market. Due to their high energy and power density they are also poised to be used for HEV applications.

Current technology uses $LiCoO_2$ as cathode and a graphitic carbon-based anode . Cobalt is toxic and is expensive. Development of new cathode material based on Mn, Fe or Ni is of considerable interest.

Nanostructured cathode materials for rechargeable lithium batteries:

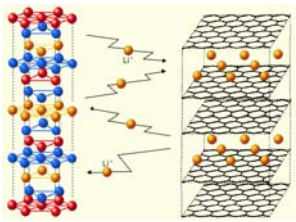
- Wide variety of choices: meta-stable compositions, structures, morphologies accessible
- Enormous kinetic advantages: short diffusion lengths, better utilization of active material capacity → Higher specific capacities at practical rates
- Lack of long-range-order: suppression/alteration of phase transformations → better reversibility and capacity retention upon cycling

–Major Challenge: Characterizing the structural phenomena behind the observed electrochemical properties

A fundamental understanding of the mechanism of charge compensation and structure is important in tailoring materials with desirable properties.

Li-ion Battery: Chemistry

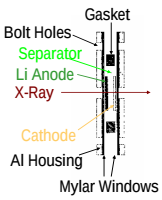
Cathode Anode



Charge: Li ions deintercalated from cathode

Discharge : Li ions intercalated into cathode

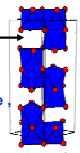
Spectroelectrochemical Cell for *In Situ* XAFS



Nanocrystalline Fe_2O_3

[Publication: Chem. Mater. 18, 423-434 (2006)]

- Hexagonal structure (R-3C) with 1/3rd of octahedral sites vacant
- Can lithium be put into this structure?



Yes, Li^+ goes to face shared octahedral site but …

In microcrystalline α-Fe_2O_3

Strong repulsion from neighboring Fe ions

Hexagonal → Cubic transformation for ~0.1 Li insertion

Kinetic limitations to intercalation

Poor reversibility due to phase transformation

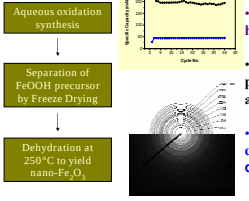
$xLi + hex\text{-}Fe_2O_3 \rightarrow cubic\text{-}Li_xFe_2O_3$ (for x ~ 0.1)

Literature:

Structural aspects : Thackeray et al. , 1981

Nano-Fe_2O_3 : Tarascon et al. , 2003

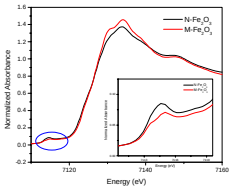
Nano-Ferric Oxide: Synthesis and Electrochemistry



- Nano Fe_2O_3 delivers very high capacity
- TEM and XRD indicate presence of nanometric anisotropic crystallites
- All rings in electron diffraction correspond to α-Fe_2O_3

$FeCl_2 + NaOH + NaOCl \rightarrow FeOOH \xrightarrow{\Delta} Fe_2O_3$

Nano-Fe_2O_3 Vs Micro-Fe_2O_3 (Hematite)

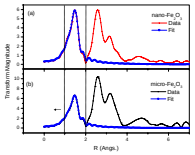


- Edge positions similar
- Increased pre-edge intensity for nano-Fe_2O_3.

Enhanced pre-edge intensity seen in system where Fe (III) has tetrahedral or pentahedral coordination with oxygen

Strongly suggests that surface Fe atoms are under-coordinated

XANES findings similar to those of Chen et al., 2002



Micro: 3 Fe-O @ 1.93 Å, 3 Fe-O @ 2.09 Å

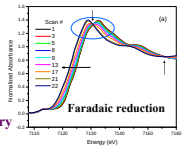
Nano: 3 Fe-O @ 1.93 Å, 1.5 Fe-O @ 2.08 Å

Selective reduction of long Fe-O bond in nano-sample

⇒ under-coordinated Fe.

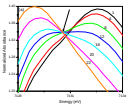
Medium range local structure of nano-Fe_2O_3 (determined from Fe-Fe correlations) similar to hematite

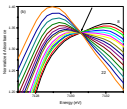
Nano Fe_2O_3 : First discharge and phase behavior

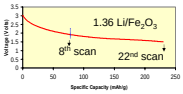


Systematic reduction in the oxidation state of Fe

Edge position of fully discharged sample consistent with $Fe^{2.3+}$







- Well defined isosbestic points for scans 8-22
- Scan 1-7 do not go through the same common point
- Two phase behavior during scans 8-22
- Similar results from PCA of EXAFS

⇒ Li-rich phase created at expense of Li-poor phase

- Accounts for relatively flat voltage profile during scans 8-22
- Absence of isosbestic points during scans 1-7

⇒ topotactic insertion of Li and/or presence of intermediate local structures

Nanocrystalline Li_2MnO_3

[Publication: Chem. Mater. 17, 3850-3860 (2005)]

Microcrystalline samples known to be electrochemically inactive

Nanocrystalline materials shows surprisingly high reversible intercalation capacity of 0.87 Li/Mn

Excellent capacity retention measured over 50 cycles

Monoclinic, rock-salt structure (C2/m)

Closely related to layered $LiCoO_2$:$Li(Li_{1/3}Mn_{2/3})O_2$

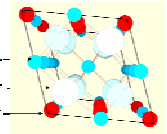
Alternating layers of Li and $Li_{1/3}Mn_{2/3}$

Li cannot be "extracted" from Li_2MnO_3

- Mn already in 4+ ox. state
  - →cannot be charged further

Li cannot be "intercalated" into Li_2MnO_3

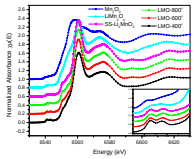
- Octahedral sites are all filled
- Vacant tetrahedral sites share faces with cations → repel Li^+

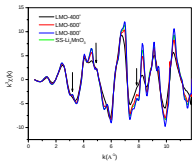


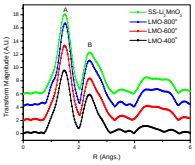
Li_2MnO_3

Structure of sol-gel Li_2MnO_3

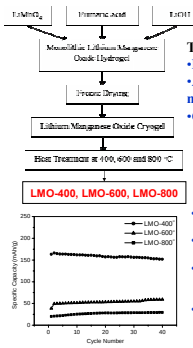
- Pre-edge, main-edge shapes and position of sol-gel samples matches well with solid-state Li_2MnO_3
- FT also shows good correspondence between sol-gel and solid-state samples
- Higher frequency EXAFS oscillations strongly suppressed in nanocrystalline LMO-400
- EXAFS analysis shows strong similarity of sol-gel samples to Li_2MnO_3 and distinct difference when compared to other Mn(III,IV) compounds







Nano-Li_2MnO_3: Synthesis and Electrochemistry



TEM and SAED LMO-400

- Nanocrystalline structure evident
- All rings correspond to rock-salt, monoclinic Li_2MnO_3
- Crystallites of size ≈ 5nm

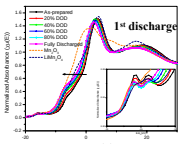
LMO-400 electrochemistry

Specific capacity ≈ 200 mAh/g

Intercalation of 0.87 Li/Mn

- Surprisingly high intercalation capacity
- Excellent charge-discharge reversibility
- Good reproducibility in charge discharge curves and over different cycles
- Indicates very good structural reversibility

LMO-400 redox mechanism and structural reversibility



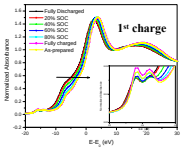
In situ discharge:

Capacity = 191 mAh/g

Expected Mn ox. state = 3.17+

Edge position lies between $LiMn_2O_4$ ($Mn^{3.5+}$) and Mn_2O_3 (Mn^{3+})

Evidence of Faradaic reduction during discharge



In situ charge:

Faradaic oxidation observed during charge

Excellent reversibility in terms of edge-position and shape

Core structure maintained during cycling and excellent structural reversibility evident in EXAFS. XAFS data consistent with electrochemistry.

Summary

Nano-Fe_2O_3

- Medium range structure same as microcrystalline hematite (Fe-Fe correlations, XRD,SAED)
- The average Fe atom is under-coordinated in the Fe-O shell; possibly due to surface effects.
- Faradaic reduction/oxidation of discharge and charge
- Distinct two phase behavior only after x=0.47; $Li_{0.47}Fe_2O_3$
- Excellent electrochemical and structural behavior exhibited by product (cubic Li-Fe-O) formed after first discharge

Nano-Li_2MnO_3

- LMO-400, a nanocrystalline Li_2MnO_3-like compound shows surprising electrochemical capacity of up to 200 mAh/g
- Shows big contrast to microcrystalline Li_2MnO_3 which is electrochemically *inactive*
- XAFS and SAED of LMO-400 sample indicate strong similarity of the Mn-O framework structure to that of Li_2MnO_3
- Reversible Faradaic processes occurring during discharge and charge
- XAFS and electrochemical data show excellent reversibility of the LMO-400 structure through charge discharge cycling

XAFS measurements carried out at 20-BM, PNC-XOR. PNC-XOR facilities at the Advanced Photon Source, and research at these facilities, are supported by the US DOE Office of Science Grant No. DEFG03-97ER45628, the University of Washington, a major facilities access grant from NSERC, Simon Fraser University and the Advanced Photon Source. Use of the Advanced Photon Source is also supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-Eng-38. Work at Rutgers University supported by the NSF Industry/University Collaborative Research Program on Ceramic and Composite Materials at Rutgers University/Penn State University/University of New Mexico and by the Office of Naval Research.

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