OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT or CONTRACT: N00014-98-WX-20379-AA

PR Number 98pr02708-00

X-RAY ABSORPTION STRUCTURAL AND ELECTROCHEMICAL INVESTIGATIONS OF NOVEL MATERIALS FOR ADVANCED BATTERIES AND ULTRACAPACITORS

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Contract/Grant Number: N00014-98-WX-20379-AA
Contract/Grant Title: X-RAY ABSORPTION STRUCTURAL AND ELECTROCHEMICAL INVESTIGATIONS OF NOVEL MATERIALS FOR ADVANCED BATTERIES AND ULTRACAPACITORS

Principal Investigator: Azzam N. Mansour
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E-mail Address: MansourAN@crbesmtp.dt.navy.mil http address:

a. Number of papers submitted to refereed journals, but not published: __3__
b. + Number of papers published in refereed journals (for each, provide a complete citation): _1__

A. N. Mansour, C. A. Melendres, and J. Wong "In Situ X-ray Absorption Spectroscopic Study of Electrodeposited Nickel Oxide Films During Redox Reactions", J. Electrochem Soc. **145**, 1121 (1998).

c. + Number of books or chapters submitted, but not yet published: __0__
d. + Number of books or chapters published (for each, provide a complete citation): __0__
e. + Number of printed technical reports/non-refereed papers (for each, provide a complete citation): __3__

M. Balasubramanian, C. A. Melendres, A. N. Mansour, and S. Mini, " X-Ray Absorption Spectroscopy Studies of Electrochemically Deposited Thin Oxide Films", in Application of Synchrotron Radiation to Materials Science, Vol. 524, 1998, Proceedings of MRS, April 1998, San Francisco, CA.

A. N. Mansour and C. A. Melendres, "In Situ X-Ray Absorption and Electrochemical Studies of Anodically Deposited Nickel Oxide Thin Films, The Electrochemical Society Extended Abstracts, Volume 98-1, abstract 28, San Diego, CA, 3-8 May 1998.

C. A. Melendres, M. Balasubramanian, A. N. Mansour, S. Mini, "X-Ray Absorption Spectroscopy Studies of the Structure of Electrodeposited Metal Oxide Films and Some Applications", The Electrochemical Society Extended Abstracts, Volume 98-1, abstract 265, San Diego, CA, 3-8 May 1998.

f. Number of patents filed: __1__
g. + Number of patents granted (for each, provide a complete citation): __0__
h. + Number of invited presentations (for each, provide a complete citation): __0__
i. + Number of submitted presentations (for each, provide a complete citation): __2__

A. N. Mansour and C. A. Melendres, "In Situ X-Ray Absorption and Electrochemical Studies of Anodically Deposited Nickel Oxide Thin Films, The 193rd Meeting of the Electrochemical Society, San Diego, CA, 3-8 May 1998.

C. A. Melendres, M. Balasubramanian, A. N. Mansour, S. Mini, "X-Ray Absorption Spectroscopy Studies of the Structure of Electrodeposited Metal Oxide Films and Some Applications", , The 193rd Meeting of the Electrochemical Society, San Diego, CA, 3-8 May 1998.

j. + Honors/Awards/Prizes for contract/grant employees (list attached): __0__
(This might include Scientific Society Awards/Offices, Selection as Editors, Promotions, Faculty Awards/Offices, etc.)

k. Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this PR number: __0__
Graduate Students: __0__
Post-Doctoral Associates: __0__
including the number of,
Female Graduate Students: __0__
Female Post-Doctoral Associates: __0__
the number of
Minority* Graduate Students: __0__
Minority* Post-Doctoral Associates: __0__
and, the number of
Asian Graduate Students: __0__
Asian Post-Doctoral Associates: __0__

l. + Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)

NLPP Matching Fund Program of NSWC ($80.0K).

EOY Report - PART II

a. Principal Investigator: Azzam N. Mansour

b. Telephone Number: (301)227-4451 Fax number: (301)227-4461

c. Cognizant ONR Program Officer: Dr. Richard T. Carlin

d. Program Objectives:

- Synthesize and characterize the chemistry and structure of a new class of tin-based amorphous oxides suitable for use as anode material in rechargeable Li-ion batteries. Provide a fundamental understanding of the intercalation mechanism of Li in this type of anode material during redox reactions.

- Examine the evolution of the electronic and atomic structure of electrodeposited nickel oxide thin films on graphite substrates and $LiNiO_2$ cathode materials during electrochemical oxidation and reduction reactions

- Establish structure-property relationships, which can be used as a guide to enhance the energy and power densities as well as stability of batteries and ultracapacitors.

e. Significant results:

- Successfully prepared a tin-based amorphous oxide with nominal composition $Sn_{1.0}B_{0.56}P_{0.40}Al_{0.42}O_{3.47}$ and confirmed the amorphous nature of this compound by x-ray diffraction and x-ray absorption spectroscopy measurements.

- Measured changes in the local structure of Sn as a function of Li insertion and removal during charge and discharge over the voltage range 0.14-2.5 vs. Li/Li^+ by x-ray absorption spectroscopy under in situ conditions.

- Demonstrated that nickel in electrochemically deposited nickel oxide thin films can be cycled between oxidation states of 2 and 4 during charge and discharge and can be used for fabrication of ultracapacitors.

- Demonstrated that redox process for $LiNiO_2$ cathode material in non-aqueous electrolyte is associated with oxidation of Ni^{2+} to Ni^{3+}.

- Our results also indicate that structural integrity, and hence good cycle life, of Li_xNiO_2 cathode material is maintained if cycled in the range $0.45<x<1$.

f. Summary of plans for next year:

- Continue investigating the chemistry and structure of tin-based amorphous oxides in order to determine the composition range over which the material is amorphous in nature.
- Determine the composition for which the Li storage capacity is optimized.
- Examine the reaction mechanism of Li with tin-based amorphous oxides using X-ray Absorption Spectroscopy under in situ conditions.
- Examine the morphology and composition homogeneity of tin-based amorphous oxides with Scanning Electron Microscopy and Energy Dispersive Spectroscopy.
- Examine in more details structural integrity of $LiNiO_2$ cathode materials upon lithium removal and insertion.

X-Ray Absorption and Electrochemical Investigations of Novel Materials for Advanced Batteries and Ultracapacitors

Azzam N. Mansour, Naval Surface Warfare Center

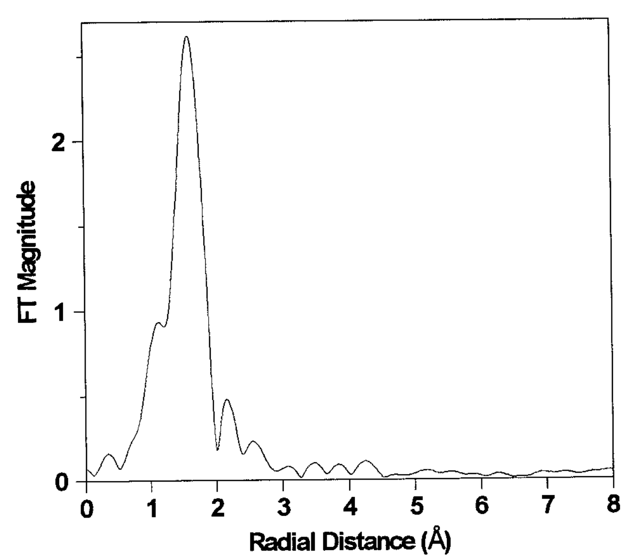
Technological Issues:

•A need to increase the energy and power densities as well as cycle life for energy conversion and storage devices such as batteries and ultracapacitors.

Objectives:

•Synthesize and characterize the structure and morphology of tin-based composite oxide (TCO) material.
•Provide a fundamental understanding of the reaction mechanism of Li with TCO during redox reactions
•Examine the evolution of the electronic and atomic structure of electrodeposited nickel oxide thin films and $LiNiO_2$ cathode material during redox reactions.

FT of Sn EXAFS for Tin-Based Composite Oxide (TCO)



Approach:

•X-ray absorption spectroscopy coupled with electrochemical techniques for in situ structural and chemical state studies.
•X-ray diffraction to determine phase purity of the material.
•Scanning electron microscopy for morphological studies.

Accomplishments:

•Synthesized and confirmed the amorphous nature of TCO material.
•Measured the x-ray absorption spectra of TCO material as a function of Li content during redox processes.
•Established the oxidation state and local structure of Ni for electrodeposited nickel oxide thin films and $LiNiO_2$ material.

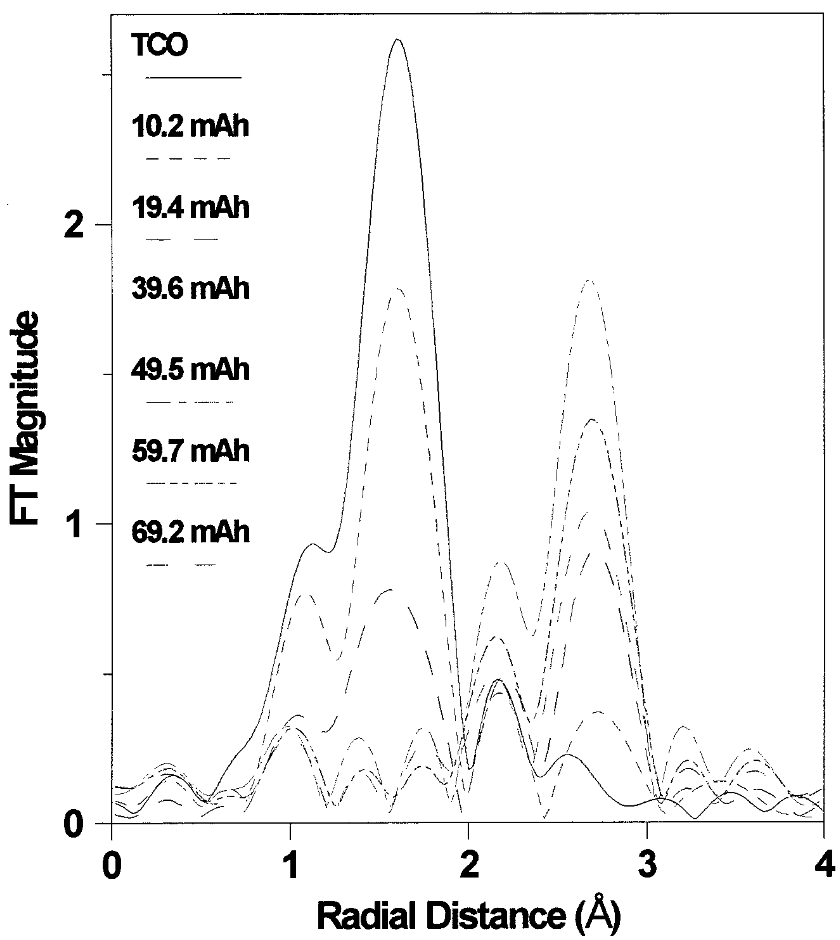
Impact and transition:

•Development of novel materials for advanced rechargeable Li-ion batteries and nickel based ultracapacitors.
•Applications include electric vehicle, portable computers, submarines, unmanned underwater vehicles.

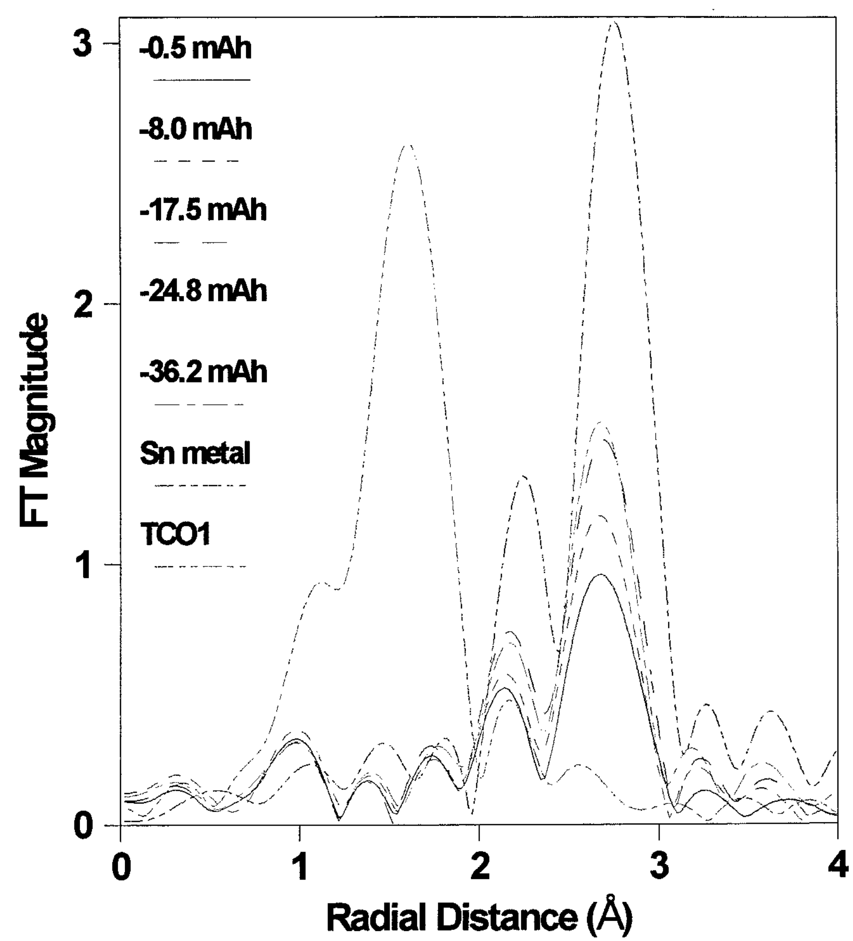
Fourier Transforms of Tin-Based Composite Oxide (TCO) as a Function of State of Charge During Charge (Left) and Discharge (Right)

Azzam N. Mansour, Naval Surface Warfare Center

FT of Sn EXAFS vs. State of Charge for TCO



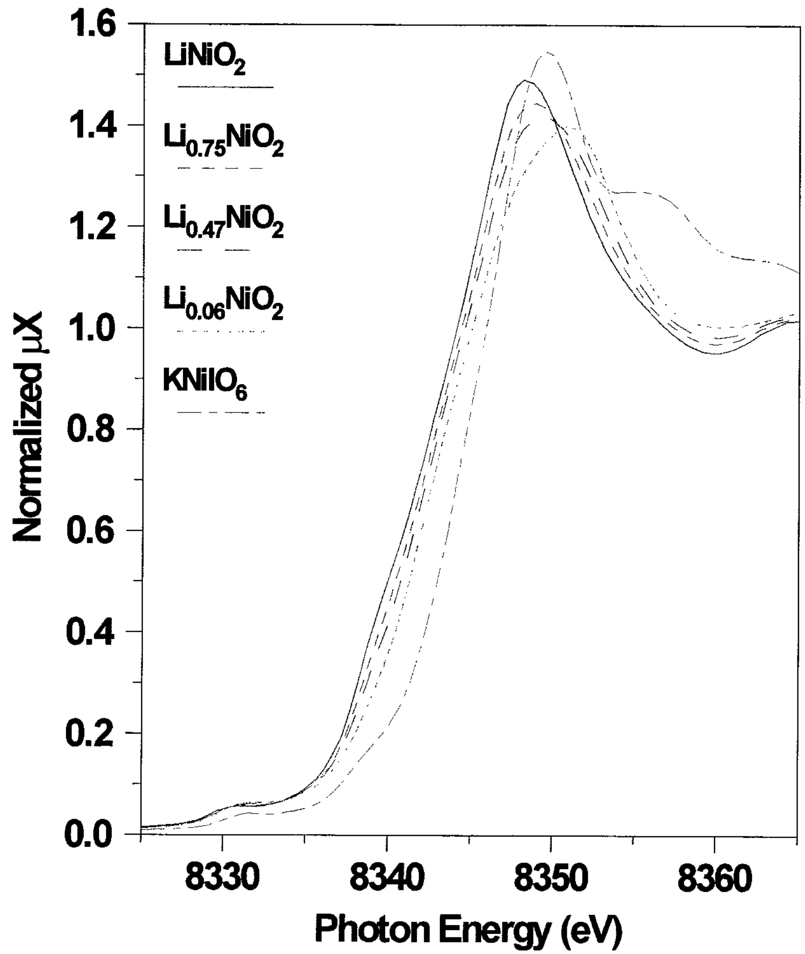
FT of Sn EXAFS vs. State of Discharge for TCO



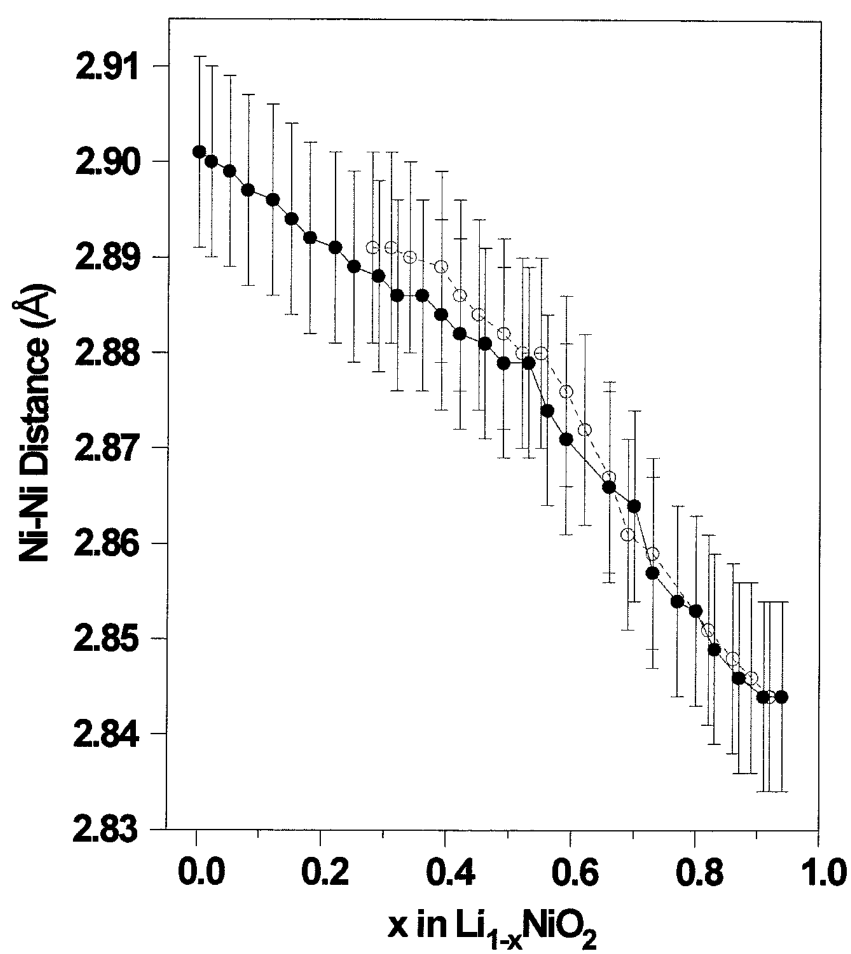
In Situ X-Ray Absorption Studies of $LiNiO_2$ Cathode Material During Redox Reactions

Azzam N. Mansour, Naval Surface Warfare Center

XANES of Ni vs. State of Charge for Li_xNiO_2



Ni-Ni Distance vs. State of Charge for Li_xNiO_2



X-Ray Absorption and Electrochemical Investigations of Novel Materials for Advanced Batteries and Ultracapacitors

Azzam N. Mansour, Naval Surface Warfare Center

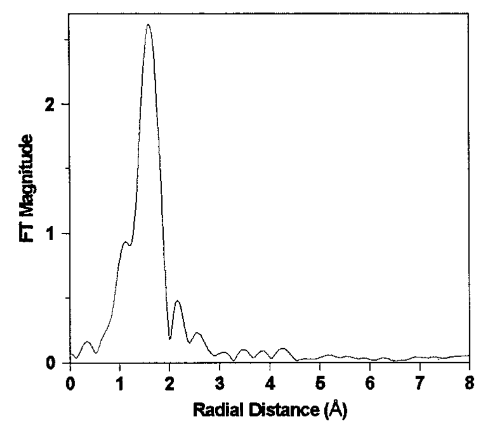
Technological Issues:

- A need to increase the energy and power densities as well as cycle life for energy conversion and storage devices such as batteries and ultracapacitors.

Objectives:

- Synthesize and characterize the structure and morphology of tin-based composite oxide (TCO) material.
- Provide a fundamental understanding of the reaction mechanism of Li with TCO during redox reactions
- Examine the evolution of the electronic and atomic structure of electrodeposited nickel oxide thin films and $LiNiO_2$ cathode material during redox reactions.

FT of Sn EXAFS for Tin-Based Composite Oxide (TCO)



Approach:

- X-ray absorption spectroscopy coupled with electrochemical techniques for in situ structural and chemical state studies.
- X-ray diffraction to determine phase purity of the material.
- Scanning electron microscopy for morphological studies.

Accomplishments:

- Synthesized and confirmed the amorphous nature of TCO material.
- Measured the x-ray absorption spectra of TCO material as a function of Li content during redox processes.
- Established the oxidation state and local structure of Ni for electrodeposited nickel oxide thin films and $LiNiO_2$ material.

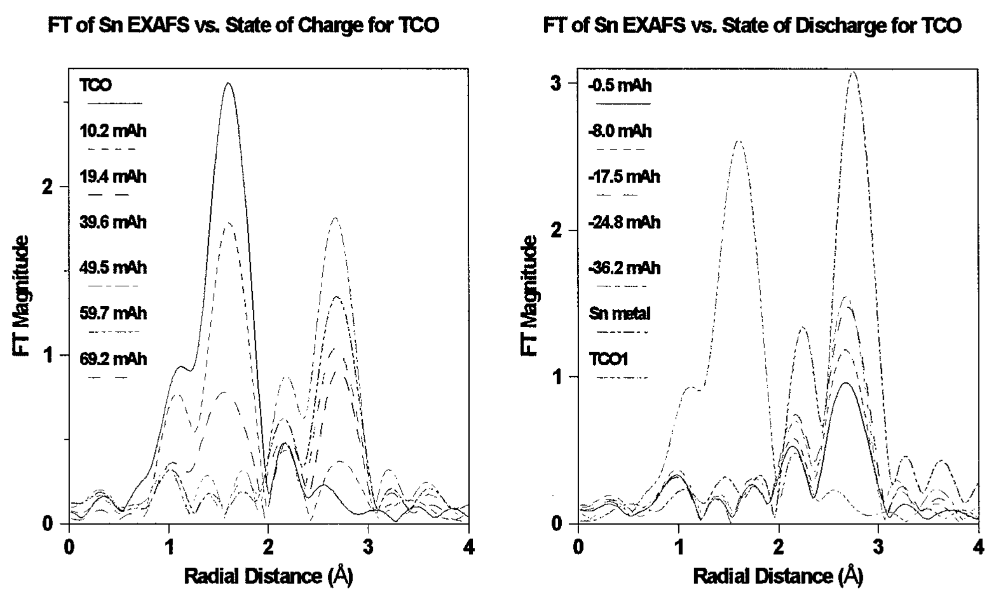
Impact and transition:

- Development of novel materials for advanced rechargeable Li-ion batteries and nickel based ultracapacitors.
- Applications include electric vehicle, portable computers, submarines, unmanned underwater vehicles.

The Fourier transform shown here is for a tin based composite oxide material with nominal composition of $Sn_{1.0}B_{0.56}P_{0.40}Al_{0.42}O_{3.47}$. It displays a single peak, which corresponds to Sn-O bonds. The lack of contributions from higher coordination spheres confirms the amorphous nature of tin-based composite oxide material (TCO). TCO is a candidate for Lithium-ion batteries.

Fourier Transforms of Tin-Based Composite Oxide (TCO) as a Function of State of Charge During Charge (Left) and Discharge (Right)

Azzam N. Mansour, Naval Surface Warfare Center

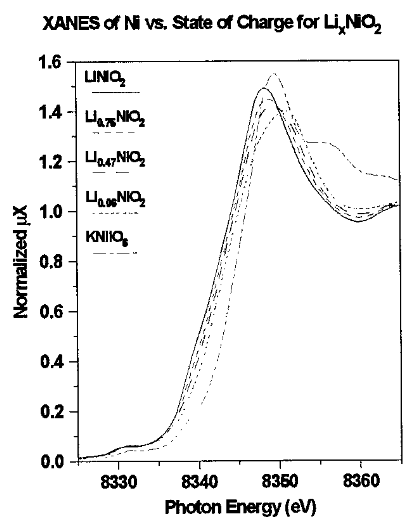


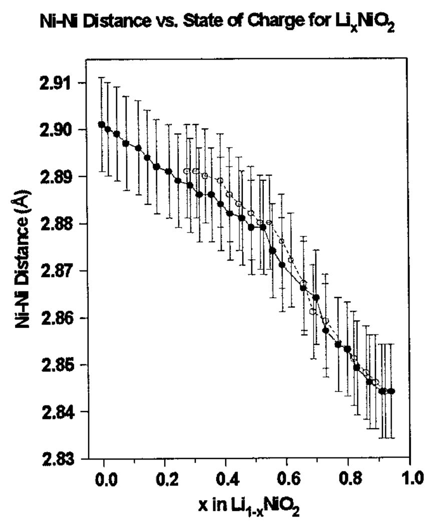
These Fourier transforms were collected to provide insight into the reaction mechanism of Li with TCO material during redox reactions in non-aqueous electrolyte. They are for a TCO electrode (0.0985 g of TCO) charged and discharged at a rate of 35.6 mA/g over the voltage range 0.14-2.5 V (vs. Li/Li^{+}). The Fourier transforms (left) were taken during the charge cycle (i.e., Li insertion) and show that the perturbation in the local structure initially, manifest itself as a reduction in the amplitude of the first peak, which corresponds to Sn-O interactions. The amplitude of this peak decreases and then a second peak, which corresponds to Sn-Sn interactions, emerges after 25 mAh of charge passed.

The Fourier transforms on the (right) were taken during the discharge cycle (i.e., Li removal) and clearly show that the original structure of the material is not restored upon discharging the material.

In Situ X-Ray Absorption Studies of $LiNiO_2$ Cathode Material During Redox Reactions

Azzam N. Mansour, Naval Surface Warfare Center





The x-ray absorption near edge structure (XANES) clearly show that upon oxidation of $LiNiO_2$, the oxidation state of nickel changes from roughly +2 in the fully discharged state to +3 in the fully charged state. This is consistent with the hypothesis that the charge compensating mechanism in $LiNiO_2$ is due to holes residing on the oxygen atoms.

The data on the right hand side show the distance of the second coordination sphere of Ni-Ni contributions as a function of state of charge during the charge cycle (solid circle) and discharge during the discharge cycle. The data show that the rate of distance contraction is slower in the range x = 0-0.55 than that in the range 0.56-1.0. This implies that $LiNiO_2$ electrodes should be cycled between $LiNiO_2$ and $Li_{0.45}$ NiO_2 for enhanced cycle life.