Studies on the Local State of Charge (SOC) and Underlying Structures in Lithium Battery Electrodes

Jagjit Nanda
Oak Ridge National Laboratory

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Overview

Timeline
Project Start Date: 10/1/2010 (FY2011)
Percentage Complete: 65%

Barriers
Cycle life and Capacity fade
Rate Performance
SEI Stability
Surface Degradation and Structural changes

Budget
FY 2010: 230K
(June Fin Plan: Capital request)

FY 2011: 400K

Collaborators/Partners
Dr. S. K. Martha
Post Doctoral Researcher

Non funding partners

Ford Motor Co.
Dawn Bernardi
Raji Chandrasekaran
Andy Drews
Ann O'Neill
Jeffrey Remillard

Toda Inc
Mr. Toyoji Sugisawa
Project Objectives

• Correlate local electrode and interfacial properties at sub-micron level to the macroscopic electrochemical performance.

• Investigate local inhomogeneity, composition, structural changes during lithiation-delithiation of high energy lithium electrodes.

• Dynamical/in situ studies for spatio-temporal mapping of commercial electrodes subjected to stress/abuse.
Programmatic Milestones

Task 1: Electrode Fabrication and Electrochemical Testing

Subtask 1.1: Electrochemical performance of Excess Lithia Compositions from Toda Inc.
Progress/Status: Work in progress (70% complete)

Task 2: Ex-situ SoC analysis of commercial and Laboratory Fabricated High Energy Cathodes

Subtask 2.1 Local SoC Analysis of Commercial fresh and degraded LiCoNiAlO₂ (Gen-2) Electrodes
Progress/Status: Completed (in collaboration with Ford Motor Co.)

Subtask 2.2 Local SoC studies of high energy Lithium Rich compositions
Progress/Status: Work in progress

Task-3 In-situ SoC and Structural Studies at Cell Level

Subtask 3.1 Development of in-house fabricated optical Raman Cell in “edge” configuration
Progress/Status: Work in progress
Confocal Micro Raman–AFM Setup

Confocal x-y spatial resolution ~ 350 nm
Confocal along depth (z) ~ 700 nm
Excitation Laser 532 nm
Silicon

532 nm Excitation
Grating 600 lines/mm
50X

Excess Lithia Composition

Si 1st and 2nd order peak
Task-1 Electrochemical Performance of $\text{Li}_{1.2}\text{Mn}_{0.525}\text{Ni}_{0.175}\text{Co}_{0.1}$

Two types of composition
1. Conventional slurry 85% active mass - 7.5% each of PVDF and C-black
2. Instead of 7.5% C-black - 1.5% Carbon fiber and 6% Carbon black

C/10 rate - 25 °C
Operating voltage = 2.5V-4.9V

Capacity / mAh g\(^{-1}\)

Charge - Graphite fiber
Discharge - Graphite fiber
Charge - 85-7.5-7.5
Discharge - 85-7.5-7.5

Voltage / V vs. Li/Li\(^+\)

1.5% graphitic fiber
1.5% graphitic fiber
85-7.5-7.5
85-7.5-7.5
Rate Performance

Materials Supplier Toda Inc.
Discharge Capacity: Comparison

1.5% Carbon fiber

Conventional
Task-2 Local State of Charge Concept

Electrode

Secondary particle

Primary particle

Edge

LiNi$_{0.80}$Co$_{0.15}$Al$_{0.05}$O$_2$ (NCA)

LiNi$_{0.33}$Co$_{0.33}$Mn$_{0.33}$O$_2$ (NCM)

xLi$_2$MnO$_3$ (1-x)LiMO$_2$ (Excess Lithia compounds)
Raman Modes of LiMO$_2$ ($M = \text{Co, Ni, Cr}$)

**Charged NCA cathode (3.77V)**

- **$A_{1g}$** – oxygen atoms vibrate in opposite directions parallel to c-axis
- **$E_g$** – oxygen atoms vibrate alternately in opposite directions parallel to Li and transition metal planes.
- **SOC proportional to** $\frac{A_{475 \text{ cm}^{-1}}}{A_{550 \text{ cm}^{-1}}}$ (Kostecki)
Micro-Raman Mapping

NCA

Carbon

SoC Map
Carbon Coverage

[Graph showing Raman spectra for different conditions]
Severely Degraded Electrodes

100 % SOC
45 °C; 22% SOC swing
Spatial anode maps of $A_{D1}/A_G$ -- greater value, more graphite disorder (damage)
Histogram Analysis: SoC

Reference band surface:
- Intensities < 90 filtered out
- Average: 1.30, 0.24

Degraded band cathode surface:
- Average: 1.42, 0.26

Reference band cathode cross-section:
- Average: 0.96, 0.26

Degraded band cathode cross-section:
- Average: 1.51, 0.70

SoC
Ex-situ Raman Spectra of $\text{Li}_{1.2}\text{Mn}_{0.525}\text{Ni}_{0.175}\text{Co}_{0.1}\text{O}_2$

Ratio of Raman peaks of M-O vibrations changes upon lithiation/delithiation
Micro Raman Imaging of Pristine $\text{Li}_{1.2}\text{Mn}_{0.525}\text{Ni}_{0.175}\text{Co}_{0.1}$

Video Image

Integrated Carbon Peaks

Integrated M-O Peaks
3D Imaging of Lithium in porous Carbon Electrodes: Neutron Radiography

2D Neutron Imaging Reconstructed Radiographs of Li distribution (Li$_2$O$_2$) in Foam Matrices (from coarse to thin matrix)

3D Li distribution (Li$_2$O$_2$) in coarser carbon foam matrix

Nanda, Bilheux et al. Unpublished 2011
Summary and Conclusion

- Good columbic efficiency and capacity of Li$_{1.2}$Mn$_{0.525}$Ni$_{0.175}$Co$_{0.1}$
- Stable cycling (> 100 cycles) without high voltage additives and
- Addition of graphitic fibers improves the capacity retention and rate.
- Raman analysis provides spatial information about the electrode SoC at various cycling conditions.
- Statistical analysis of degraded electrodes.

Work in Progress

- \textit{In situ} Raman studies of Excess Lithia compositions
- High Resolution Electron Microscopy of Excess Lithia compositions at various lithiation stages (SoC).
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ORNL Team/Collaborators