Studies on High Voltage Lithium Rich MNC Composite Cathodes

Project ID: ES106

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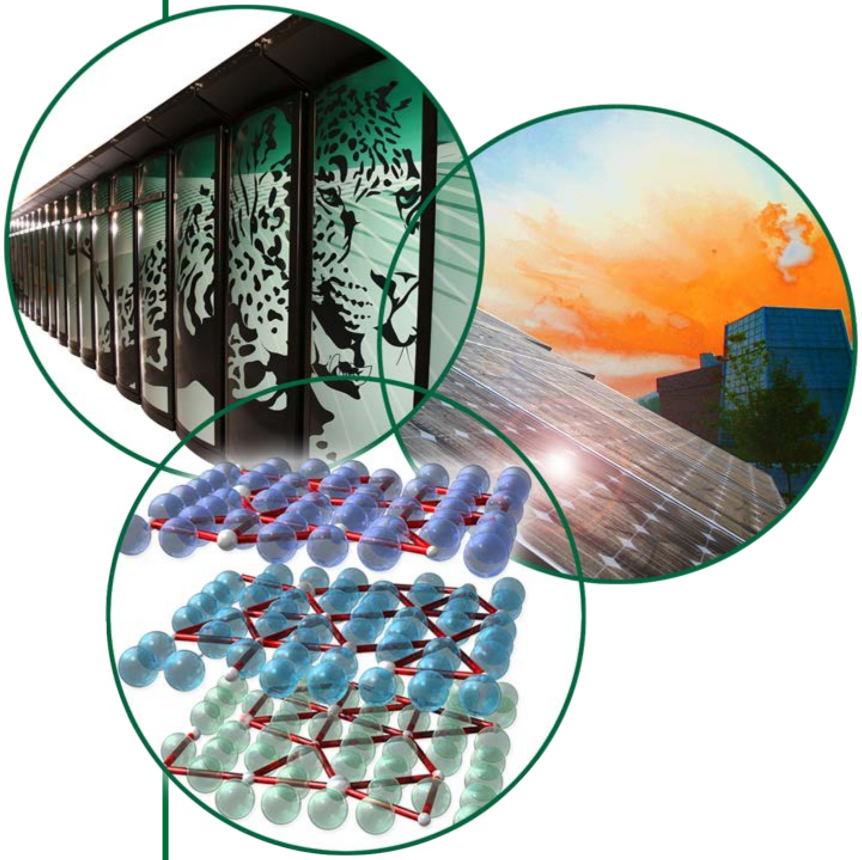
Oak Ridge National Laboratory



DOE Annual Merit Review
OVT- Energy Storage
May 9th 2012
Arlington VA

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U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Overview

Timeline

Project Start Date :
10/1/2011 (FY2012)
Percentage Complete : 65%

Budget

FY 2011 : 400K
FY 2012 : 400K

Barriers

Cycle life and Capacity fade
Rate Performance
Surface Degradation and
Structural changes

Collaborators

Dr. S. K. Martha
Dr. Ray Unocic
Dr. Nancy Dudney
Dr. Gabriel Veith

Industrial partners

Ford Motor Co.
Research and Innovation Center
Andy Drews
Raji Chandrasekaran
Dawn Bernardi

Toda America Inc.
Mr. Toyoji Sugisawa

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Objectives/Relevance

- ❖ Improve the current *state-of-the art* Li-ion cathode materials to achieve overall USABC EV energy density of 300 Wh/L (long-term) at C/3 and beyond.

- ❖ Improve the rate performance of high energy Li-ion cathode material to have a overall P/E ratio of 2:1 or higher.

- ❖ Address/mitigate cycle life issues at a full cell level arising from high voltage/energy Mn rich Cathodes.

- ❖ Investigate Lithium-ion transport limiting cases resulting in power and capacity fade.

Approach/Strategy

- Perform electrochemical performance benchmark of high voltage lithium-rich MNC composite cathodes.
- Address the issue of voltage suppression in lithium-rich composition induced by structural changes upon continuous electrochemical cycling.
- Improve the rate performance of high voltage lithium-rich MNC composite cathode using chemical and physical coating methods.
- Screening of suitable anode and electrolyte additives (for Lithium-rich cathode) for full cell assembly.

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Programmatic Milestones

FY 2011

Task 1: Electrochemical benchmarking of Li-rich MNC from Toda

Subtask 1.1 : Electrochemical performance of Excess Lithia Compositions from Toda Inc.

Subtask 1.2 : Improving the rate performance using 1.5 wt% carbon fiber additives

Progress/Status : 100% 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 $LiCoNiAlO_2$ *(Gen-2) Electrodes*

Subtask 2.2 Local in situ SoC studies of a full cell (NCA-Graphite) under various cycling protocols.

Progress/Status : 100 % Completed (in collaboration with Ford Motor Co.)

Task-3: *In situ* - Raman studies on high energy density Li-ion cathodes

Progress/Status : 100 % Completed

FY 2012

Task 1 Factors affecting cycle life of high-voltage Li-rich MNC

Subtask 1.1 Improving the electronic conductivity

Subtask 1.2 Impedance and surface analysis of cycled electrodes

Progress/status : 70% complete (in Li-half cells)

Task 2 : Improving the rate performance of Li-rich MNC

Subtask 2.1: Coating with LIPON and Al_2O_3

Subtask 2.2 : Electrochemical study of coated Li-rich MNC

Progress/status : 60% complete

Task 3 : Addressing the voltage suppression (loss in energy) in high voltage Li-rich MNC

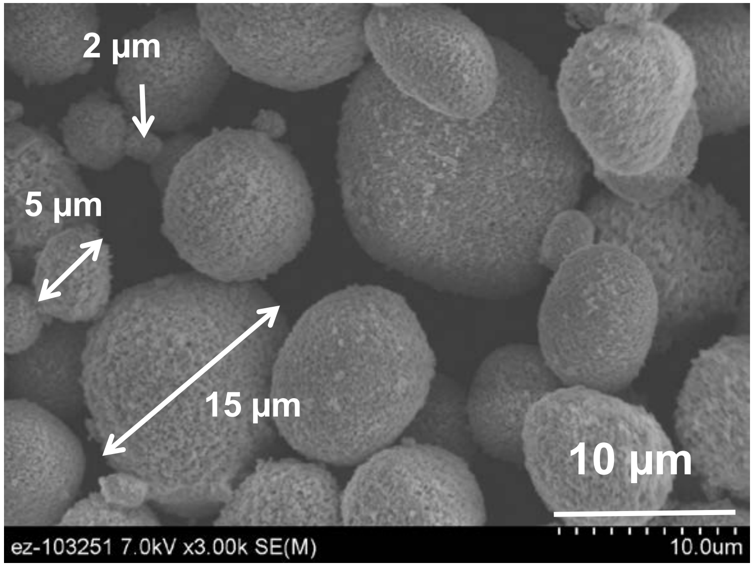
Subtask 3.1 Structure-electrochemical performance correlation as a function of high voltage cycling.

Subtask 3.2 High resolution electron microscopy (STEM) and EELS studies. (work under progress)

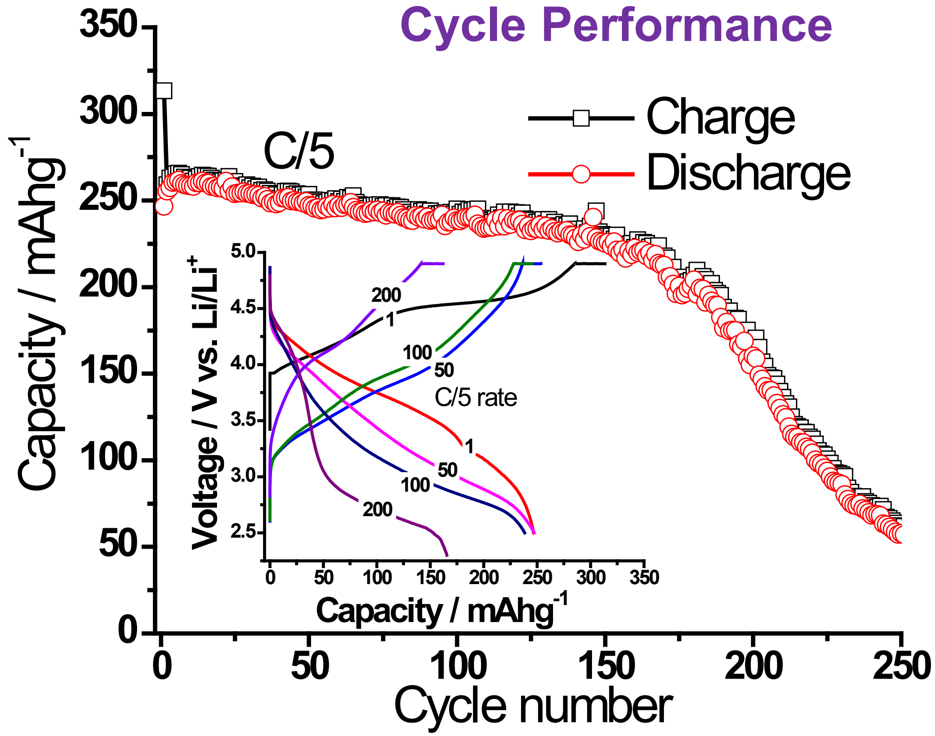
Performance of pristine electrode cycled between (4.9-2.5 V) versus Li
Electrolyte : 1.2 M $LiPF_6$ in EC : DMC (1:2 wt./wt.)

Technical Progress and Accomplishment

Particle Morphology



Cycle Performance



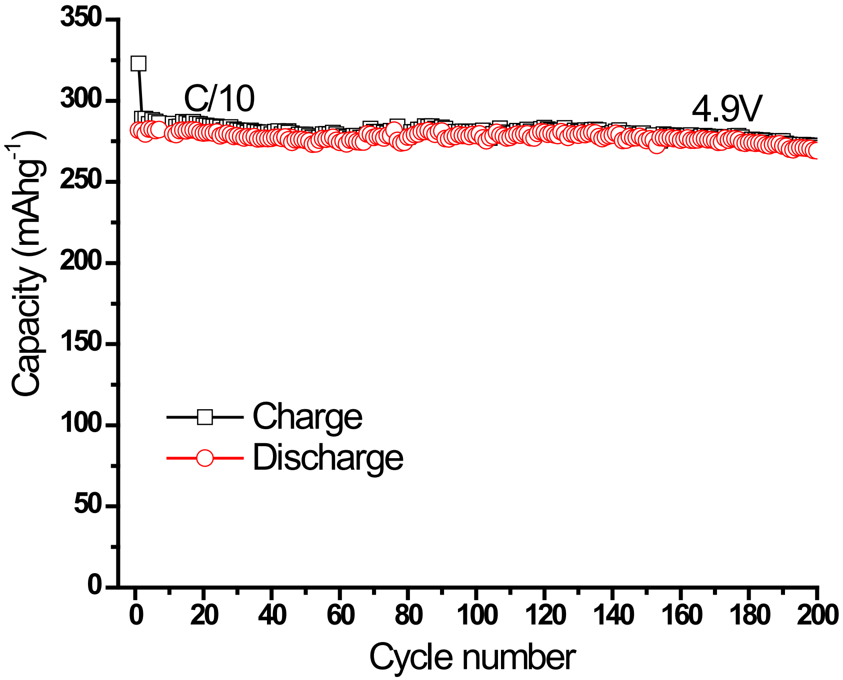
Summary

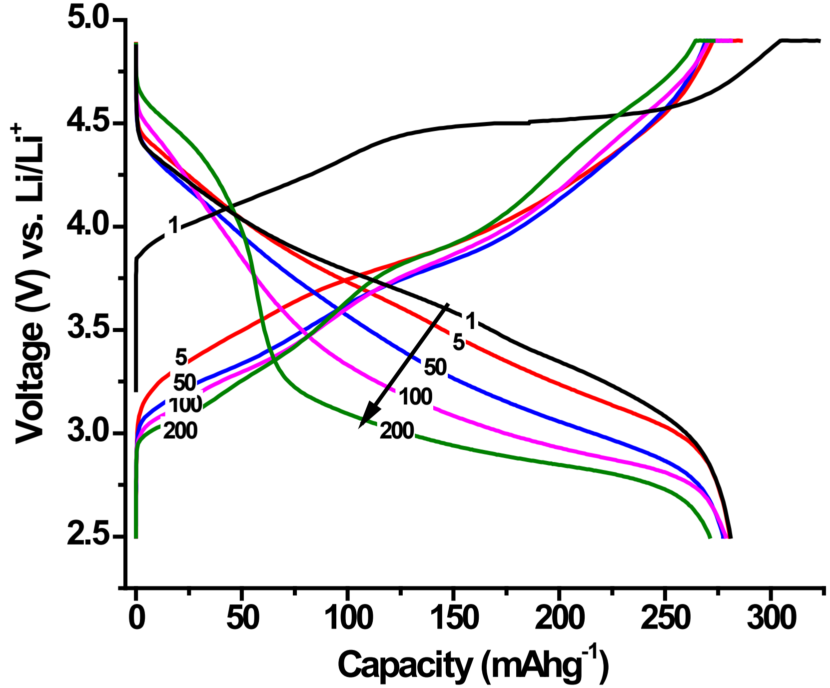
- 1st cycle irreversible capacity loss (ICL) = 18-20% (cycled to 4.9 V)
- Rapid drop in capacity after 120-150 cycles
- Continuous voltage plateau drop with cycling
- Clear appearance of low voltage plateau at below 3 V

Materials Supplier Toda America Inc.

Cycle life performance of 1.5 wt % Carbon nanofiber(CNF) added electrode
Electrolyte: 1.2 M $LiPF_6$ in EC:DMC (1:2 wt./wt.); (4.9-2.5 V versus Li)

Technical Progress and Accomplishment





Summary

- Only 3.5 % capacity loss when cycled > 200 times
- CNF addition improves the capacity retention by improving the electronic conductivity
- We still notice voltage suppression as a function of charge-discharge
- Increase in rate performance using CNF (2011 merit review).

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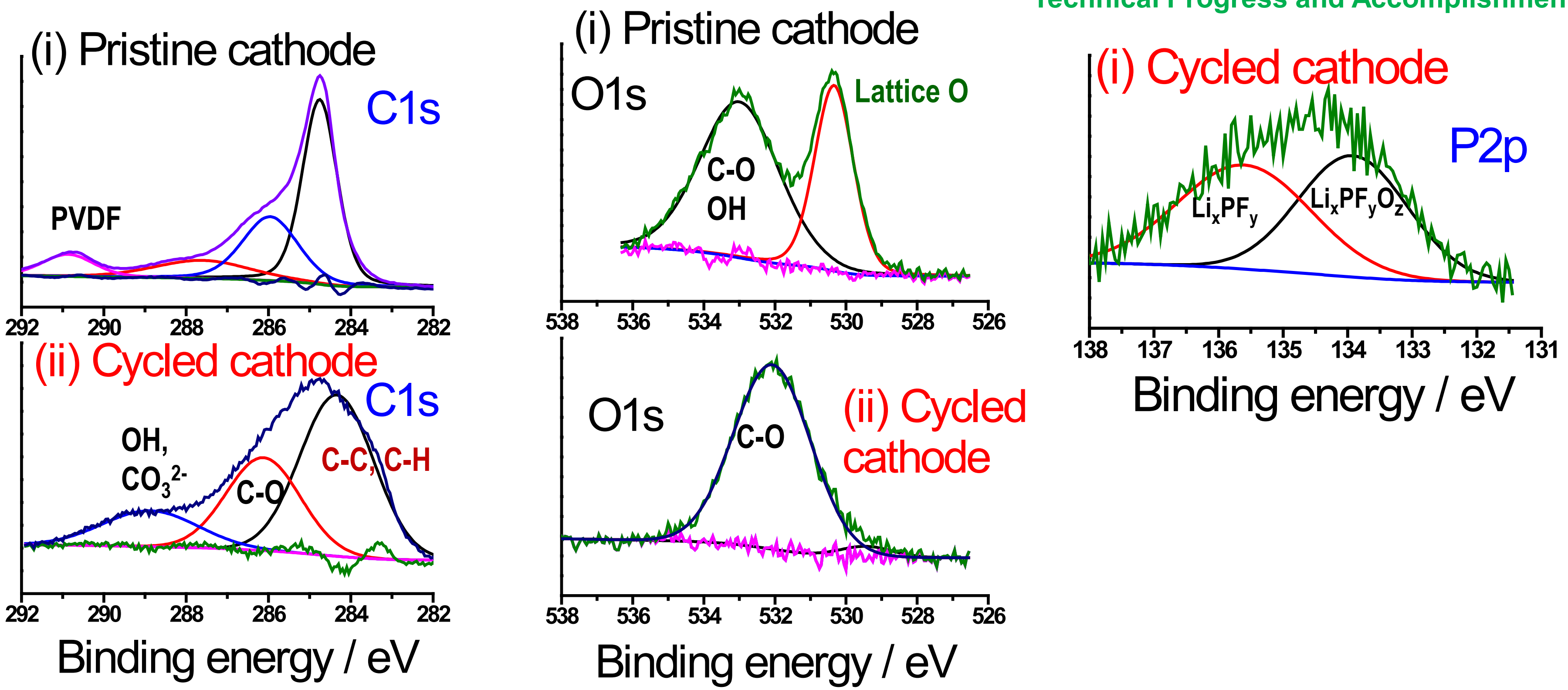
Surface Passivation film due to high voltage cycling: X-Ray Photoemission Spectroscopy

Technical Progress and Accomplishment



Summary

❖**C1s and O1s pristine cathode**: Presence of surface films such as Li_2CO_3, and hydroxides (-OH), which is a residue from the synthesis precursors, or a product of reactions between CO_2 and moisture from atmosphere with Li-rich MNC

❖**C1s and O1s cycled cathode** : Formation of $ROCO_2Li$, $(ROCO_2)_y$ M, ROLi and $(RO)_x$ M surface species.

- **P2p:** Formation of salt-based products such as Li_xPF_y and $Li_xPO_yF_z$

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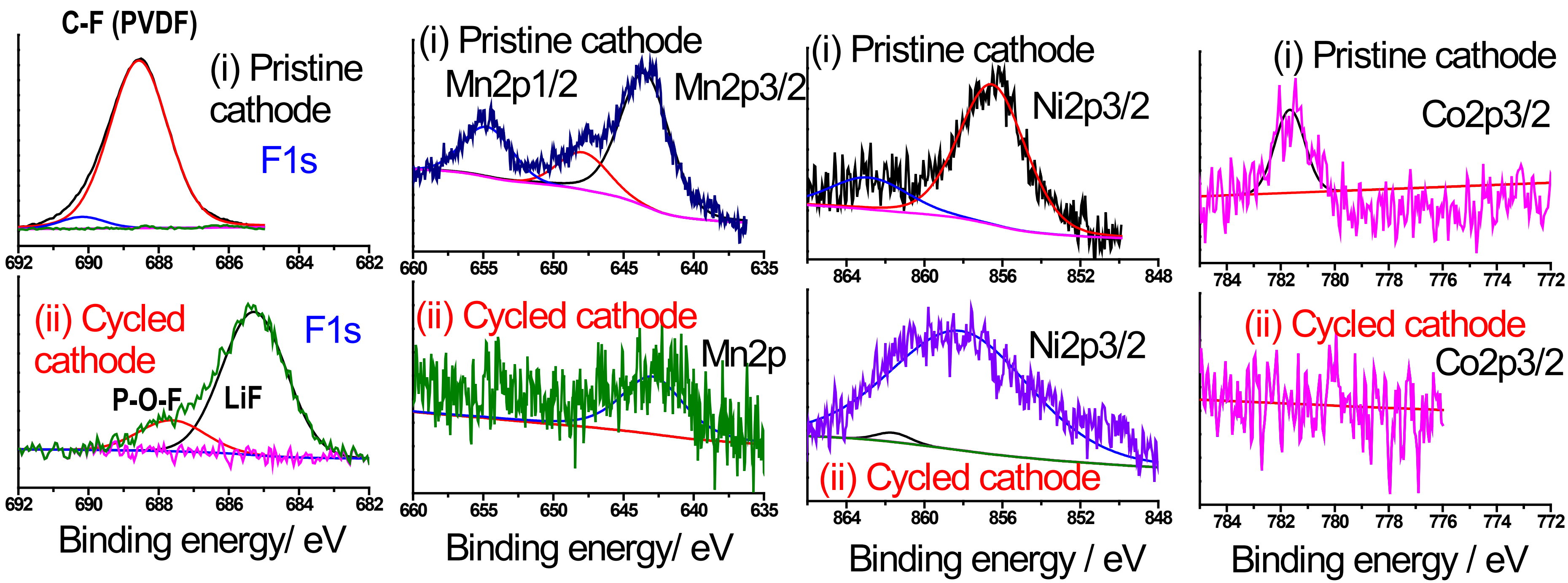
Surface Passivation film due to high voltage cycling: X-Ray Photoemission Spectroscopy

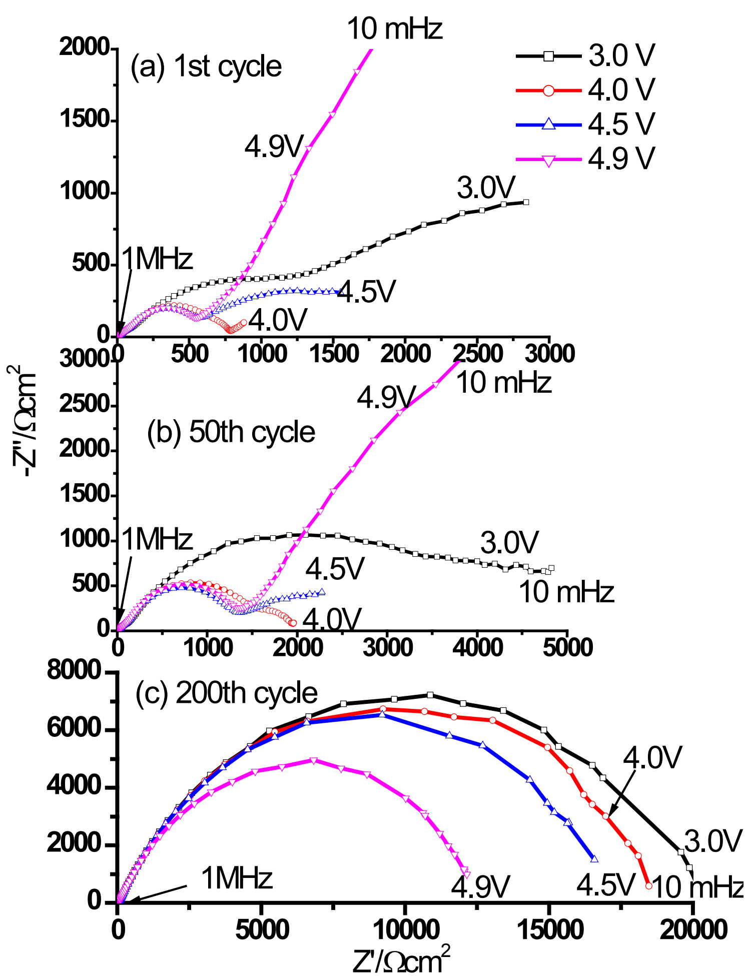
Technical Progress and Accomplishment

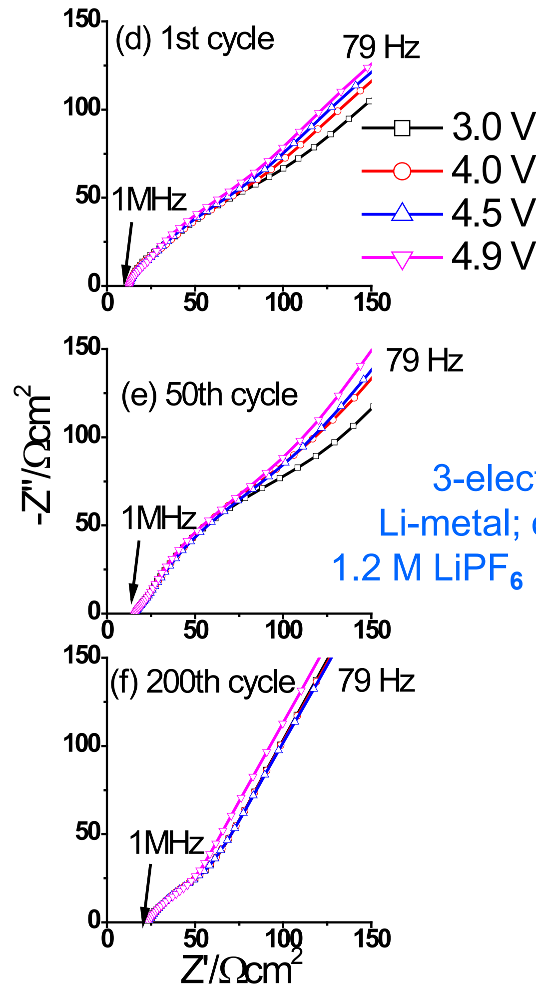


- **F1s:** Oxygen reacts with acidic HF forms surface fluorides (LiF, MF_x).
- **Metal signals:** Weak features of Mn and Ni signal with no appreciable $Co2p_{3/2}$ feature.
- The Ni $2p_{3/2}$ Binding energy region overlaps with F auger line.
- It is possible that for cycled electrodes, the relatively thick surface film layer screens most of the surface transition metal signals.

EIS Study at Different State of Charge

Technical Progress and Accomplishment





3-electrode configuration
Li-metal; counter and reference
1.2 M $LiPF_6$ in EC: DMC (1:2 wt/wt)

- **EIS spectra dependent on electrode SOC.**
- **Growth of surface passivation film as a function of cycling.**
- **Possible cause for Capacity fade.**

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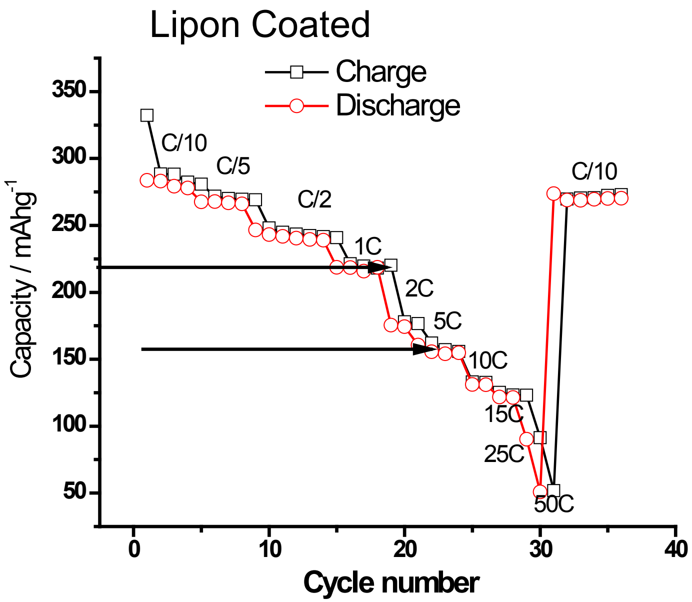
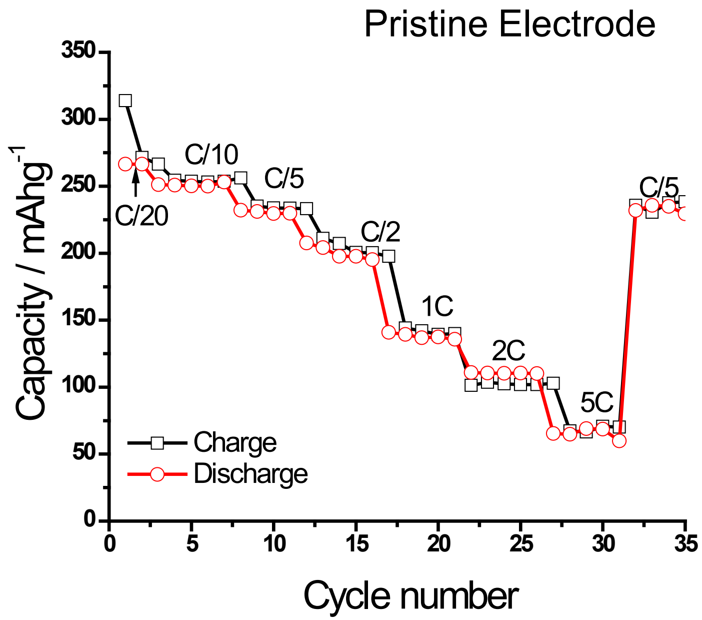
Improving the Rate Performance of Li-rich MNC

Coating a few nanometer layer of Lithium Phosphorus Oxynitride (LIPON)-I

Technical Progress and Accomplishment





Summary

- Excellent improvement in rate performance by LIPON Coating
- LIPON was coated using RF magnetron sputtering method
- XPS results (not shown) show evidence of LIPON films on surface.
- LIPON coating not conformal; can vary from few nanometer to tens of nanometer

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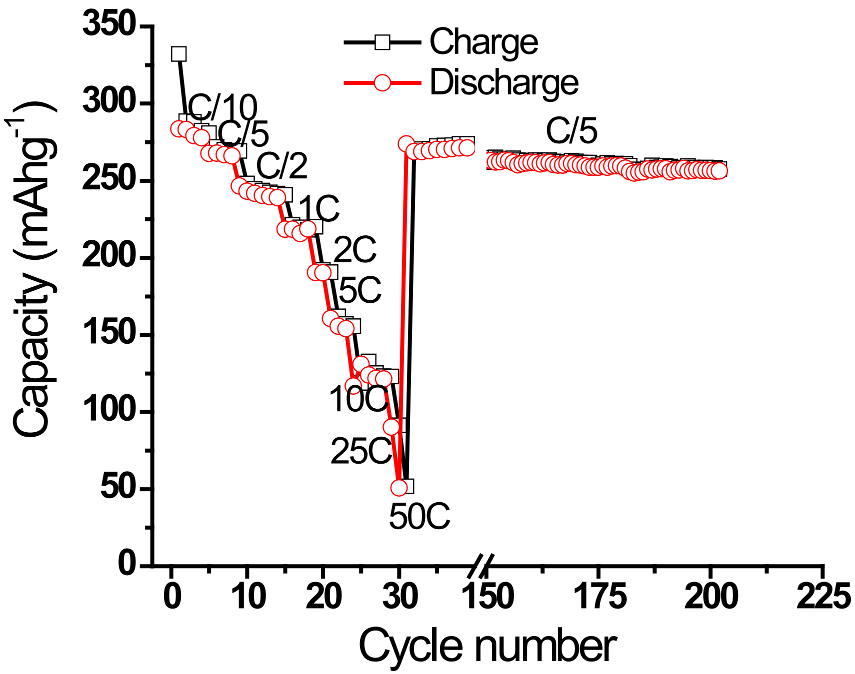
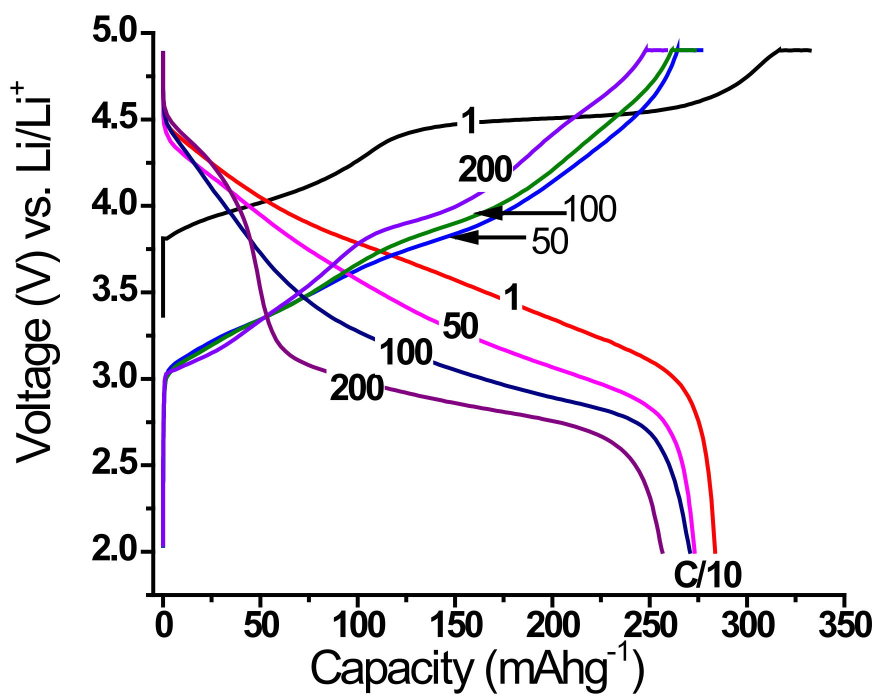
Improving the Rate Performance of Li-rich MNC

Coating a few nanometer layer of Lithium Phosphorus Oxynitride (LIPON)-II

Technical Progress and Accomplishment





Summary

- LIPON coating maintains excellent rate capability and capacity retention.
- Coating of LIPON could not prevent voltage suppression as shown above.
- The origin of voltage suppression point to bulk structural changes.
- Thick LIPON coating (> 10 nm) affects capacity utilization due to their highly insulating nature.

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First cycle irreversible capacity loss (ICL)as a function of depth of charge (SOC) and coating

Positive active material $Li_{1.2}Mn_{0.525}Ni_{0.175}Co_{0.1}$	Applied voltage vs. Li/Li^+	% of irreversible capacity	Discharge capacity (mAh/ g)
Conventional Li-rich MNC LIPON coated Li-rich MNC	4.6 V	15	210
		13-14	225 (240 after 8 cycles)
Conventional Li-rich MNC CNF added Li-rich MNC	4.8 V	21 18	235 (250 after 8 cycles) 253 (~270 after 10 cycles)
Conventional Li-rich MNC	4.9 V	18-19	275
1-2 nm LIPON coated Li-rich MNC 200 nm LIPON coated Li-rich MNC electrode surface		14 19	283 245-255
1.5% CNF added Li-rich MNC		16-18	283
1% Al_2O_3-coated Li-rich MNC		17	230

Summary

- Li-rich MNC cycled above 4.5 V has a higher 1st cycle ICL due to Li_2MnO_3 activation.
- 5% reduction in 1st cycle ICL loss when coated with 1-2 nm LIPON
- First cycle ICL is a function of depth of charge.

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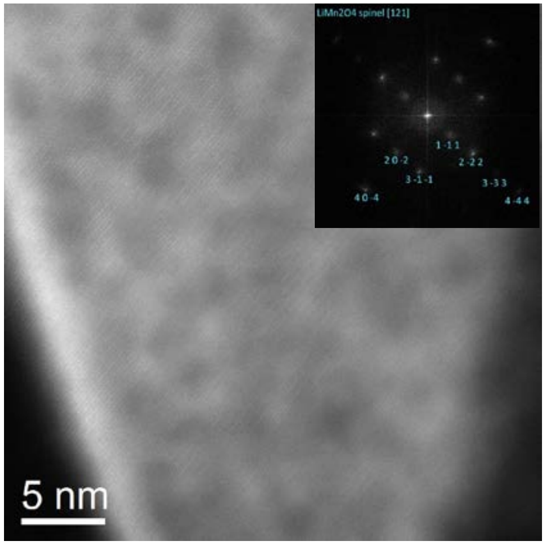
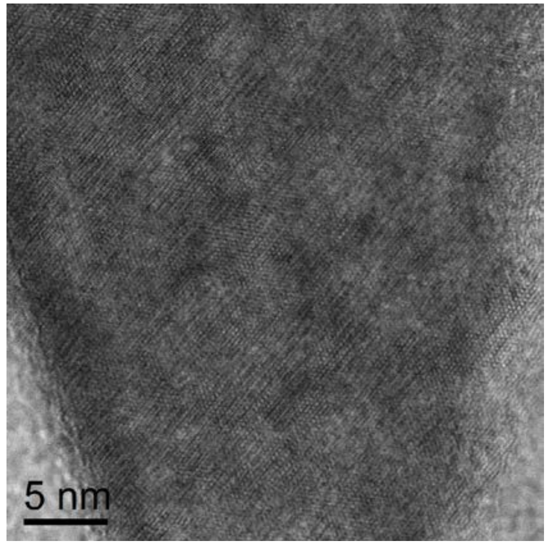
Structure-property correlation : Origin of Voltage Suppression in High Voltage Li-rich MNC

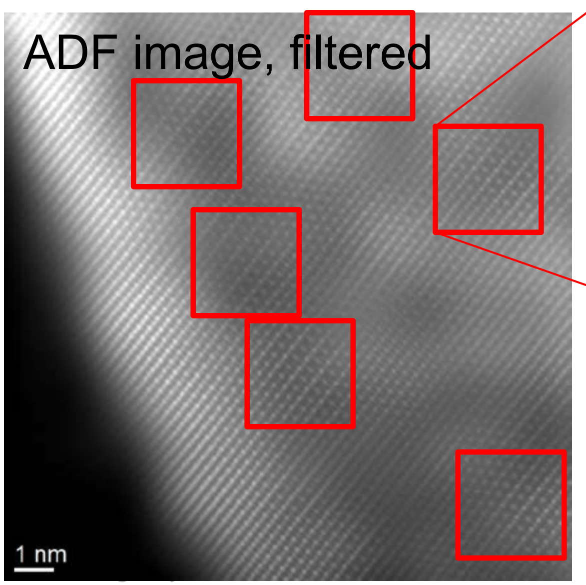
High Resolution Electron Microscopy and EELS Studies of Cycled : $Li_{1.2}Mn_{0.525}Ni_{0.175}Co_{0.1}$

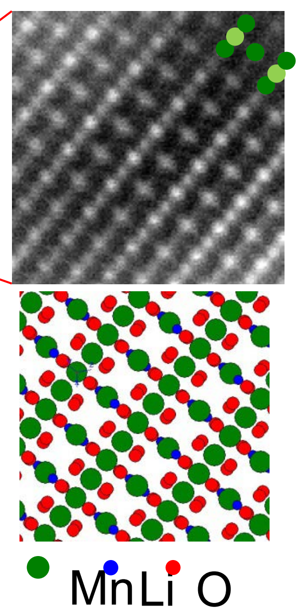




Cycled 150 times to 4.9 V

Summary





- The particle shows diffraction pattern that matches spinel [121] zone axis, but with different intensity distribution
- In standard spinel [121], the (4,0,-4) and (4, -4, 4) are the most intense diffraction. The intensity redistribution may be due to formation of solid solution of different transition metal cations in the Mn sites.
- ADF & BF image show nanometer sized domains in cycled samples

Work in Progress

Future Work

- Electrochemical benchmarking of full cells using high voltage Li-rich MNC as cathode and AR-12 Graphite (from Conoco-Philips) in pouch cell format.

- Development of a high energy density (> 400 Wh/Kg and 600 Wh/L) using Lithium-rich MNC and silicon-carbon fiber anodes developed at ORNL.

- Local SOC Raman mapping of cycled or degraded Li-rich MNC Electrodes from industry

- Study the role of PF_6 anion intercalation effect in carbon/graphitic additives in high voltage cathodes.

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Collaboration

Industrial Partners

- Research and Innovation Center, Ford Motor Co. collaboration in the area of in-situ characterization, cell level modeling and design specification.

- Toda America Inc. materials supplier for high energy cathodes

- Conoco-Philips : High capacity carbon anode for lithium-ion.

Army Research Laboratory

Dr. Kang Xu : High Voltage Electrolyte additives for advanced Li-ion

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Acknowledgments

Mr Tien Duong and David Howell, Energy Storage Team, Office of Vehicle Technologies, EERE, DOE.

Electron Microscopy work supported by SHaRe user facility, ORNL

ORNL Team/Collaborators

Drs. Sreekanth Pannala, Juan Carlos Idrobo, Wu Zhou, Wally Porter, C. K. Narula, Wyatt Tenhaeff, Josh Phil, Claus Daniel, Ronald Graves, Karen More