Studies on High Capacity Cathodes for Advanced Lithium-ion Systems

Jagjit Nanda Oak Ridge National Laboratory 17th June 2014

Project ID # ES106

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Overview

<u>Timeline</u>

- Project start date: 1st Oct. 2010
- Project end date: Continuing
- Percent complete: 65%

Barriers

Performance: High energy density for
PEV, 40 mile PHEV, and beyond
Life: More than 5000 deep discharges
(SOC range) over the entire life
Safety: Thermally stable and abuse tolerant

<u>Budget</u>

- Total project funding DOE: \$1,430,000
- Funding received in FY13: \$400K
- Funding for FY14: \$400K

Partners

- Argonne National Laboratory Voltage fade protocol and electrode materials
- Army Research Laboratory Electrolyte additives for high V cathodes
- SSRL, SLAC, Stanford CA. X-ray spectroscopy and imaging
- Lawrence Berkeley National Laboratory
 Interfacial studies
- Tennessee Technical University
 Spectroscopic studies



Project Objectives-Relevance

Develop high energy density lithium-ion electrodes for EV and PHEV applications that meet and/or exceed DOE USDRIVE/USABC target (400 Wh/kg and 600 Wh/L)

- Mitigate technical barriers associated with current high voltage cathode compositions: lithium-manganese rich MNC and Mn-Ni 5V spinel
- Implement new diagnostic techniques to correlate electrode crystal structure and morphology with electrochemical performance
- Develop a mechanistic understanding of how local inhomogeneity leads to cell degradation using state-of-the-art characterization methods
- Design new syntheses of high capacity lithium-ion electrodes and approaches for interface modification



Milestones

Due Date	Description	Status
12/31/2013 (Q1)	Evaluate local SOC inhomogeneity of pristine and cycled LMR-NMC and 5V Mn-Ni spinel	60% complete
03/31/2014 (Q2)	Evaluate the role of high voltage additives on cycle life and performance of LMR-NMC half cells and full cells	Complete Go/No go decision
06/30/14 (Q3)	Determine interfacial charge transfer and area specific impedance at various SOC for LMR-NMC cathodes	In progress
09/30/2014 (Q4)	Local morphology and chemical structure analysis of pristine and cycled LMR-NMC and other high capacity cathodes	In progress



Approach/Strategy-I: Local State of Charge Studies

- Undertake local state-of-charge (SOC) studies on high voltage LMR-NMC electrodes [Li_{1.2}Mn_{0.525}Ni_{0.175}Co_{0.1}O₂]
 - Correlate local structure with electrochemical properties
 - Employ techniques with both high resolution and large field of view
 - Understand and mitigate factors that lead to voltage fade and capacity loss
- Micro-Raman mapping of high voltage cathodes
 - Measure inhomogeneity in state-of-charge with increasing voltage and electrochemical cycling
 - Apply statistical methods for semi-quantitative analysis
- X-ray Imaging and Spectroscopy (XANES)
 - 3D elemental mapping and tomography of pristine and cycled LMR-NMC cathode particles
 - Monitor transition metal (TM) oxidation state, migration, and dissolution which lead to voltage fade



Approach/Strategy-II: Improve Interfacial Stability

- High voltage additives
 - Improve cycle life and interfacial stability
 - Go/No go decision
- Surface Coatings
 - nanometer thick lithium-ion conductor
 - thin electronically conducting layer such as carbon
- Alternative cathode chemistries
 - High capacity (>250 mAh/g) with upper voltage cutoff < 4.4 V
 - Promising candidates include $Li_2M^{\dagger}M^{\dagger}O_2$ (M¹ and M¹¹ = Ni, Cu, or Cr)



← In house system for RF sputtering solid electrolyte coatings on powders

ORNL has developed unique capabilities to coat cathode powders uniformly with excellent thickness control in the nanometer and subnanometer range [AMR-VT 2013 presentation]



Technical Accomplishment Evaluation of High Voltage Additives for LMR-NMC cathodes



High voltage additives have minimal impact on the 1st cycle ICL or short-term capacity retention. Longer-term effects are still under investigation.



Technical Accomplishment Evaluation of High Voltage Additives



Conclusions and next steps

- In some cases additives result in lower capacity retention in subsequent cycles
- Work is in progress to measure impact on long-term voltage fade
- ARL team is working on next generation additives



TXM-XANES reveals change in Mn oxidation state and strong correlation with voltage fade [Li_{1.2}Mn_{0.525}Ni_{0.175}Co_{0.1}O₂]





- Mn oxidation state changes from 4⁺ (green) to 3⁺ (red) as we cycle the cell
- Shift in Mn K edge correlates well with voltage fade as shown by the dQ/dV results (left)



Fay et al. Submitted, 2014

Tomographic reconstruction reveals internal morphologies of cathode particle that can be linked to material degradation such as metal dissolution



We define a dimensionless parameter ϵ to evaluate the change in morphology under electrochemical cycling: $\epsilon = V^{1/3}/S^{1/2}$ (V = volume; S = surface area)

 $\varepsilon_{sphere} = 0.4547$ $\varepsilon_{cube} = 0.4082$ $\varepsilon_{tetrahedron} = 0.3725$ $\varepsilon_{fractal} \sim close to zero$

Proof-of-principle analysis is done for LMR-NMC cathode cycled once (4.9-2.5 V) This method will be used to evaluate the change in particle morphology



Fay et al. Submitted 2014

TXM-XANES monitors changes in LMR-NMC cathode particle morphology under high voltage electrochemical cycling $[Li_{1,2}Mn_{0.525}Ni_{0.175}Co_{0.1}O_2]$



Analysis performed on 60 representative cathode particles

Under continuous high voltage cycling particles change their morphology from near spherical to an elongated geometry. The increase in effective surface area could lead to more surface reactivity with electrolyte especially at oxidizing potentials.



Using TXM-XANES analysis we map the 3D elemental composition of pristine and cycled LMR-NMC cathodes to monitor TM dissolution.



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LMR-NMC Pristine Cathode[Li_{1.2}Mn_{0.525}Ni_{0.175}Co_{0.1}O₂]

3D elemental composition of pristine LMR-NMC cathode particle shows majority Mn-Ni-Co region followed by Mn-Ni region

LMR-NMC Cathode Cycled once (4.9-2.5V)

Cathode particles cycled even once (4.9 - 2.5 V) show a redistribution of TM phases with 8% Mn pure phase

Tomography analysis also yields cross sectional elemental analysis of the LMR-NMC bulk particle

This method can be used to evaluate change in cathode chemical composition or phase segregation under electrochemical cycling.



Transition metal (Mn,Ni,Co) distribution shown for two different LMR-NMC cathode particles cycled once (between 2.5-4.9 V) indicate drop in TM concentration in the surface layer.



1. Distance map showing the variation of TM concentration Mn(blue), Ni(yellow), and Co(red) from the LMR-NMC particle center to surface 2. Cathode particle (top) has different internal morphology compared to bottom. Drop in TM concentration after 1st cycle could also be due to change in particle porosity at the surface due to oxygen vacancies and/or surface reaction

3. All three TM concentration show a relative decrease going from particle center to bulk

4. The results are compared with more local diagnostic tools like high resolution transmission electron microscopy (HRTEM).

(See supplemental slides and AMR-VT 2013)

Work in progress to map the TM concentration for cathodes cycled 50,100 and 200 times





Raman mapping of pristine LMR-NMC electrodes to quantify the distribution of carbon surrounding the active material





Red: Low carbon coverage Green: Intermediate carbon coverage Blue: High carbon coverage

- Pristine (uncycled) electrodes show a variation in carbon coverage
- Differences in the effective electronic wiring are one factor which leads to inhomogeneity in the electrode local state of charge
- This study provides a benchmark for monitoring the carbon distribution and degradation of electrodes under continuous high voltage cycling



Evolution of carbon structure and coverage with cycling of LMR-NMC



cathodes

Carbon becomes increasingly disordered with cycling which is reflected in broader Raman peaks

Disorder may be due to intercalation of PF_6^- at high voltage. This proposed mechanism and its impact on cathode lifetime and performance merits further study





- After 25 cycles most particles are coated with conductive carbon (blue), but a few areas (red) are more exposed
- Green areas show high fluorescence background, likely due to electrolyte decomposition
- Future studies will investigate the effects of long-term cycling on carbon coverage and degradation. Changes in oxide structure will also be monitored.



Screening other high capacity 4 V Li-ion cathode candidates that are not lithium and manganese rich compositions

We synthesize high capacity $Li_2M_x^{i}M_{1-x}^{i}O_2$ compounds. Initial tests with Mⁱ = Cu and $M^{ii} = Ni$



- Masquelier, Chem. Mater. 2005, 17, 4406.
- 2. K. Kang, C-H Chen, B. J. Hwang and G. Ceder, Chem. Mater. 2004, 16, 2685.

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510 mAh/g (2 Li)

Preliminary work elucidating the structure and electrochemical performance of Li₂Cu_xNi_{1-x}O₂ cathodes

Li₂CuO₂

 $Li_2Cu_{0.5}Ni_{0.5}O_2$

- Initial electrochemical studies show capacities >200 mAh/g for Li₂Ni_{0.5}Cu_{0.5}O₂
- Smaller particle size could improve the electrochemical performance
- For Li₂Cu_{0.5}Ni_{0.5}O₂ 1st cycle charge-discharge is substantially different from following cycles
- Major barriers are structural stability and presence of impurity phases

Work in progress

- Phosphate and phosphagene based high voltage electrolyte additives do not have any significant effect on the 1st cycle ICL or short-term voltage fade for LMR-NMC cathodes. Longer-term cycling studies are underway.
- We developed TXM-XANES methods to monitor and evaluate the Mn oxidation state and change in the morphology of LMR-NMC cathode particles under high voltage cycling: The study directly correlates the oxidation state of TM cations to the electrochemical signature of voltage fade as seen in the differential capacity plot.
- Raman imaging/mapping of pristine, charged, and cycled LMR-NMC electrodes measures (i) the structural degradation of the active materials under cycling, (ii) carbon distributions, and (iii) degradation of conductive diluent (carbon) at strongly oxidizing potentials (> 4.5 V)
- We synthesized a new high capacity 4V Li-ion cathode material, Li₂Cu_xNi_{1-x}O₂, with initial capacities exceeding 200 mAh/g

Response to Reviewers Comments-I

Reviewer 3: The reviewer noted that the coating on particles [e.g., atomic layer deposition (ALD) coated on $LiCoO_2$] was shown by many groups to reduce reactivity and improve performance at high voltages. It was not clear how any coating on electrode (versus particles) can reduce reactivity, given that the majority of the high voltage electrode is still in contact with liquid electrolyte.

Response: In our case we coat Lipon on the surface of cathode particles like the ALD method used for $LiCoO_2$. We think the reviewer was confused by one control experiment where we deposited a 50 nm thick Lipon on the LMR-NMC electrode surface to evaluate the performance. In that case the capacity utilization was poor due to higher resistance from the thick Lipon coating.

Reviewer 4:

The reviewer asked whether the results are based on single cell or multiple cells for each coating level. It was difficult to understand how a few nm of coating on the electrode had such a big improvement on cycle life. The reviewer stated that the bulk of the electrode was still in contact with liquid electrolyte at 4.9V, which should result in electrolyte decomposition [and possibly carbon black (CB) decomposition] on long-term cycling, especially at slow rates such as C/10. So, it was surprising that the project team was able to obtain such good cycling data. **Response**: We thank the reviewer for the feedback. We could not present all the data within the scope of the AMR review presentation. Details of the Lipon work and effect of coating are published in 2 journal papers, Journal of Materials Chemistry A, 2013,1,5587–5595 and J. Power Sources, 2014, 249, 509. All our measurements are done on at least 3 coin cells for each given coating thickness to check for reproducibility. The cathode particles are coated by a few nm thick lipon since thicker lipon films increase the electronic resistance.

Response to Reviewers Comments-II

Reviewer 2:

The reviewer reported that there was no follow-up work on the LiPON coated electrode, given the demonstrated good cycle life. The project needs to demonstrate good cycle life performance using LiPON coated electrodes in full cells. The reviewer asked if the LiPON coating on the electrode can be scaled up for manufacturing.

Response : The PI and team at Oak Ridge along with General Motors & LBNL are part of the OVT funded Envia Systems led effort to build high energy PHEV cells. In this project ORNL's task is to coat the surface of Li-rich MNC composite cathodes (Envia material) to improve their interfacial stability. We have plans to increase the coating batches from current 10-100 grams to kilogram scale. As a follow up study we are currently undertaking Mn dissolution studies on Lipon coated versus uncoated LMR-NMC cathodes both at RT and 60 °C under extended cell Cycling.

Reviewer 3:

The reviewer suggested providing more quantitative targets with decision points.

Response: This year's presentation covers more detailed milestones, metrics and go-no go decisions at specific project milestones. For example, if high voltage additives does not reduce the 1st cycle ICL loss and subsequent capacity loss as anticipated we propose alternative mitigation steps.

Collaborations and Coordination with Other Institutions

- High voltage electrolyte additives for 5V cathodes. Army Research Laboratory: Kang Xu
- Quantifying voltage fade using ABR protocol and identify the role of coating. Argonne National Lab: Ira Bloom, Daniel Abraham & Tony Burrell
- Cathode Materials Synthesis: Chris Johnson (Argonne) & Brent Melot (USC)
- Electrode characterization, interfaces, and spectroscopy. Stanford Synchrotron Radiation Light Source, SLAC, CA: Dr. Joy Andrews & Yijin Liu Lawrence Berkeley National Laboratory: Robert Kostecki
- Cell level performance metrics and failure analysis for PHEV & EV cells. Ford Motor Co., Research & Advanced Engineering: Andy Drews
- Micro-Raman studies on high capacity electrodes: Tennessee Tech. University: Andrew Callendar

Remaining Challenges and Barriers

Related to LMR-NMC high voltage cathodes

- Stabilize the structure and composition of LMR-NMC cathode to prevent or suppress voltage fade under continuous high voltage electrochemical cycles (ABR test method)
- Prevent Mn dissolution from the host cathode structure at RT (25 °C) and 60 °C in full cell configuration, tested using ABR method
- Improve the DC-R performance especially in the low SOC region (between 3-3.8 V)

Related to 4V high capacity cathodes : Li₂Mⁱ_xMⁱⁱ_{1-x}O₂; Mⁱ= Cu and Mⁱⁱ is Ni

- Develop new precursors and synthesis method to stabilize Cu disproportionation and prevent NiO formation on the surface
- Stabilize the structure for 2 lithium transfer: Mg or similar dopant suggested
- Improve the transport and interfacial kinetics for better electrochemical capacity retention and cycle life

Future work

- Electrochemical impedance spectroscopy (EIS) studies on high energy cathodes in full cell configuration
 - Temperature and SOC dependence to separate interfacial charge transfer kinetics from passive film (SEI) formation
 - Passive films grows during continuous high voltage cycling leading to impedance rise and cell failure
 - Measurements will use a specially designed three electrode reference cell (from EL-Cell) as shown

Three electrode EL-Cell for EIS studies

- Synthesis and electrochemical characterization of new 4V high capacity lithium-ion cathodes
 - Synthesize materials belonging to the generic class, Li₂MⁱMⁱⁱO₂ and Li₂MⁱMⁱⁱO₃ (Mⁱ and Mⁱⁱ = Ni,Cu,Fe,Cr)
 - Incorporate an isovalent or supervalent dopant that can stabilize the structure when second lithium is extracted
- Continue local SOC and characterization studies on fresh, cycled, and aged high energy electrodes and cells for performance and degradation studies

Publications & Presentations

Journal Publications

- Nanoscale Tomography of High Voltage Lithium-Manganese Rich NMC Composite Cathodes, F. Yang, Y. Liu, S. K. Martha, Z. Wu, J. C. Andrews, G. E. Ice, P. Pianetta, and J. Nanda, Nano Letters, 2014 (under review).
- Role of Surface Functionality on the Electrochemical Performance of Silicon Nanowire Anodes for Rechargeable Lithium Batteries, H. Zhou, J. Nanda, S. K. Martha, R. R. Unocic, H. M. Meyer III, Y. Sahoo, P. Mickiewicz, T. F. Albrecht, ACS Applied Materials & Interfaces, dx.doi.org/10.1021/am500855a (2014).
- Thermophysical Properties of LiFePO4 Cathodes with Carbonized Pitch Coatings and Organic Binders: Experiments and First-Principles Modeling, J. Nanda, S. K. Martha; W. D. Porter; H. Wang; N. J Dudney; M. D Radin; D. J. Seigel, J. Power Sources, 2014, 251, 8-13.
- Effect of Interface Modifications on Voltage Fade in 0.5Li2MnO3•0.5LiNi0.375Mn0.375Co0.25O Cathode Materials, I. Bloom, L. Trahey, A. Abouimrane, I. Belharouak, X. Zhang, Q. Wu, W. Lu, D. P. Abraham, M. Bettge, J. W. Elam, X. Meng, A. K. Burrell, C. Ban, R.Tenet, J. Nanda and N. J. Dudney, *J. Power Sources* (2013), doi:10.1016/j.jpowsour.2013.10.035.
- Electrode Architectures for High Capacity Multivalent Conversion Compounds: Iron (II and III) Fluoride: S.K. Martha, Jagjit Nanda, Hui Zhou, Juan C. Idrobo, Sheng Dai, Sreekanth Pannala, and Nancy J. Dudney, Junjie Wang and Paul V. Braun, RSC Adv., 2014, 4, 6730.
- A Perspective on Coatings to Stabilize High-Voltage Cathodes: LiMn_{1.5}Ni_{0.5}O₄ with Sub-Nanometer Lipon Cycled with LiPF₆ Electrolyte, Y. Kim, N.J. Dudney, M. Chi, S. K. Martha, J. Nanda, G. M. Veith, and C. Liang, J. Electrochem. Soc. 2013 160(5): A3113-A3125.

Conference & Technical meetings

- Local State of Charge Mapping and Analysis of Lithium-Manganese Rich NMC High Voltage Electrodes, J. Nanda, H. Zhou, A. Callendar, R. Ruther, Abstract for ECS Fall Meeting, Orlando, 2014.
- Raman Mapping Study of Inhomogeneity in Lithium-Manganese-Rich Cathode Particles, R. Ruther, A. Callendar, H. Zhou, S. K. Martha and J. Nanda, Gordon Conference on Batteries, Ventura, CA, March 9-14th 2014.
- Nanoscale XANES Tomography of Lithium-ion Electrodes : Bridging between the Chemical State & Morphology, J. Nanda, F. Yang, Y. Liu, J. C. Andrews and S. K. Martha, Gordon Conference on Batteries, CA, March 9-14th 2014 (Invited talk)
- First-principles investigation of the structural changes in Li-rich cathode composites, H. Dixit, W. Zhou J. C. Idrobo J. Nanda and V. Cooper, Spring Meeting, American Physical Society, March 02-07, 2014.
- Confocal Raman Imaging and Spectroscopy of Energy Storage Materials, J. Nanda, 10th Symposium of Confocal Raman Imaging Ulm, Germany, Sept 30th-2nd Oct. 2013 (Invited talk).

Technical backup slides

Technical Accomplishment Uncycled or pristine LMR-NMC; $Li_{1.2}Mn_{0.525}Ni_{0.175}Co_{0.1}O_2$ showed majority hexagonal; R3m structure & minority monoclinic phase for the Li_2MnO_3 component

With Wu Zhou and Juan Carlos ORNL (2012 unpublished)

LMR-NMC materials cycled 200 times between 4.9- 2V showed majority spinel like phase in the particle bulk

- FFT image can be indexed to the spinel phase along the [121] zone axis
- Suggests that structural changes could be a bulk driven process
- Increase TM metal at the surface . Ni is relatively higher. Mn and Co follow the same spatial pattern

