Project ID: bat416

Cobalt-Free Cathode Materials and Their Novel Architectures

P. I.: Dr. Y. Shirley Meng

University of California, San Diego

June 11th, 2019

Overview

Timeline

- October 1st, 2018
- September 30th, 2021
- Percent complete: 10%

Barriers

- Barriers addressed
  - electrolyte decomposition at high voltage
  - LNMO surface instability
  - poor rate performance for thick electrodes

Budget

- Total project funding
  - US$ 2,500,000 (20% non-federal matching)
- Funding received in FY18
  - US$ 0
- Funding for FY19
  - US$ 834,000 (matching non-federal US$ 209,000)

Partners

- Interactions/ collaborations
  - University of Texas, Austin
  - Lawrence Berkeley National Lab
  - Maxwell Technologies
  - Army Research Laboratory

Relevance and Project Objectives

Overall Objectives:

- The objective of this project to research, develop, and demonstrate a spinel type $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) electrode and novel electrolyte formulation for use in next-generation Li-ion batteries (LIB).

Objectives in this Period:

- Large batch (~kg) of initial LNMO material and establish baseline electrochemistry of LNMO in full cells.
- Novel electrolyte for LNMO cycling at high voltage with graphite anode will be identified.
- Surface modification of LNMO cathode will be applied and characterized through series of techniques.

Project Impact:

- Our proposed cathode is 100% free of cobalt and its novel architecture will have porosity less than 20% and designed tortuosity for high rate capability. Our innovative, solvent-free, dry- electrode process will be applied. At the cathode level we will reach more than 600 Wh/kg with the possibility of reaching an areal loading of at least 4 mAh/cm^2 for the delivered pouch cells.

Milestones

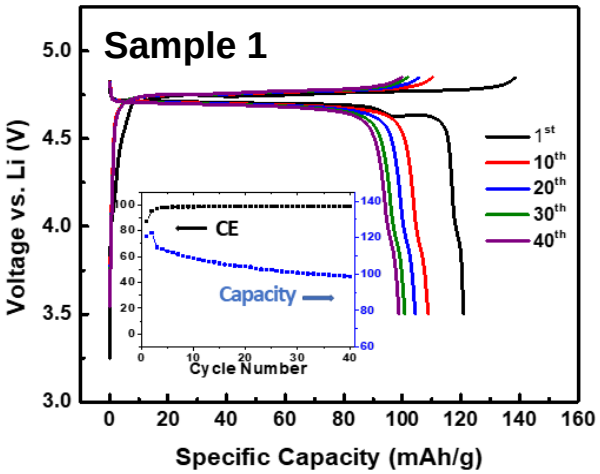
- Large batch production of LNMO cathode (Dec.-18).
  – Complete
- Baseline electrochemistry of LNMO cathode (Mar.-19).
  –Complete
- Identification of novel electrolyte for LNMO under high voltage cycling and Improvement of modified LNMO cathode (June-19).
  – On track
- LNMO thick electrode (at least 3 mAh/cm2 per side) delivers 600 Wh/kg (cathode level) with capacity retention >80% at C/3 rate for 300 cycles in full cell with graphite anode (Go/No Go Decision).
  – On track

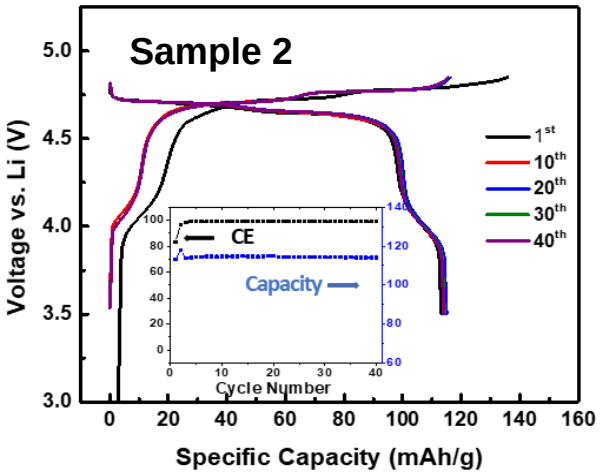
Approach

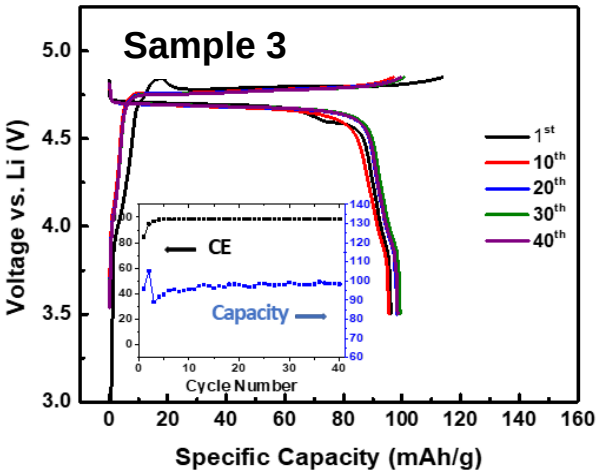
- Novel electrolytes screening from Dr. Kang Xu in ARL; As an un-funded partner of this proposal, the ARL team led by Kang Xu will provide support in electrolyte and additive materials.
- Innovative synthesis of high tap density LNMO; Various approaches for the high-voltage spinel cathode materials, such as concentration gradient structures, and elemental doping, which will be applied in this project.
- Thick electrode architecture cell prototyping; Maxwell's dry coated battery electrode offers extraordinary benefits particularly at high loading weights.
- In addition, we will develop a series of characterization techniques such as ex-situ X-ray photoelectron spectroscopy (XPS), ex-situ cryogenic transmission electron microscopy (cryo-TEM), ex-situ cryogenic focused ion beam microscope (cryo-FIB) and in situ time-of-flight secondary-ion mass spectrometry (TOF-SIMS).

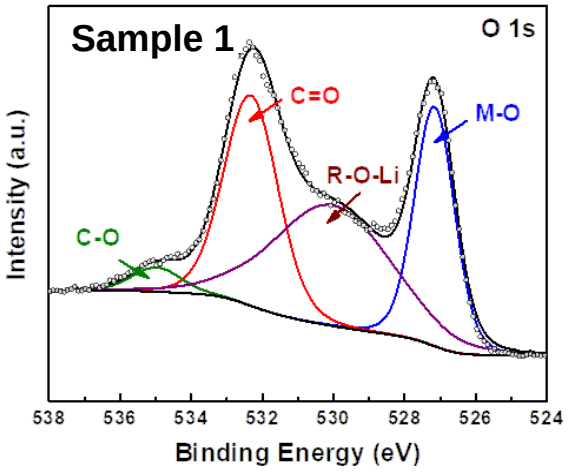
Accomplishment to Date FY 19

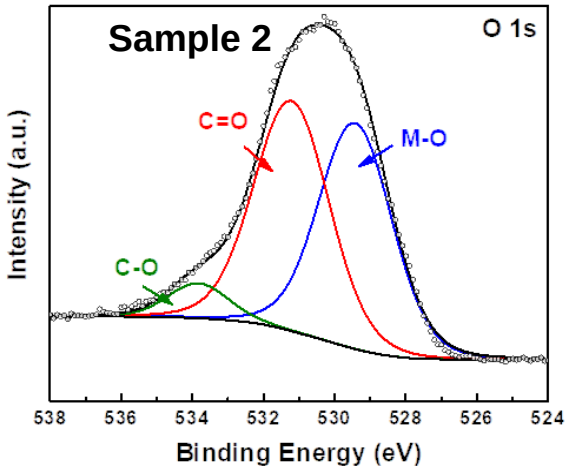
Baseline electrochemistry of LNMO cathode materials

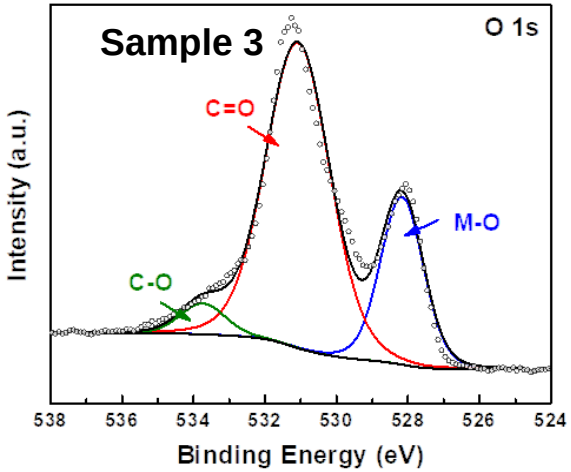










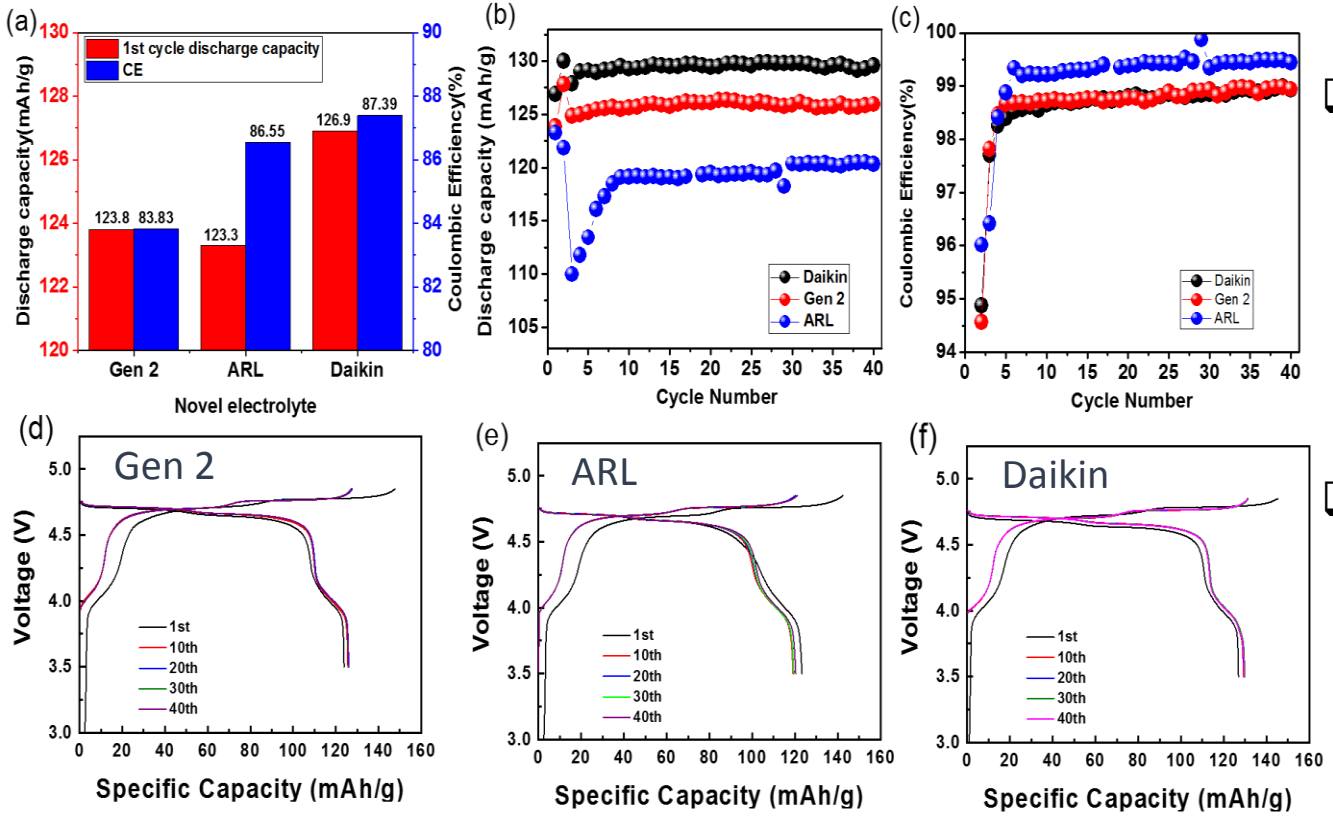


- Sample 2 exhibits the best cycling performance and does not have surface contamination as shown in XPS. This sample will serve as baseline cathode for novel electrolyte screening.

Accomplishment to Date FY 19

Baseline electrochemistry of LNMO cathode materials with novel electrolyte

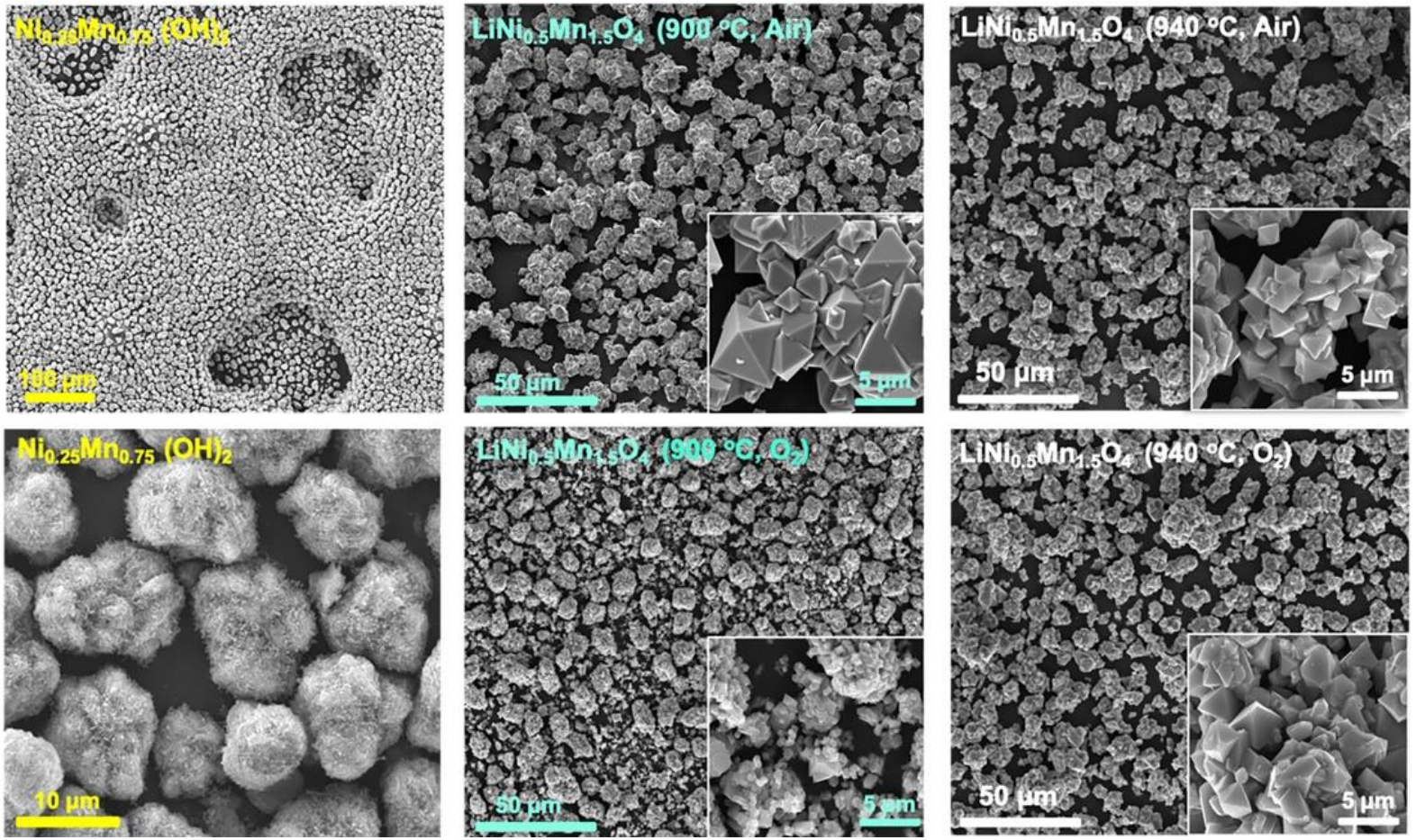
Aberration	Chemical composition	Supplier
Gen 2	1M of $LiPF_6$ in EC/EMC=3:7 wt%	Gotion Corporation
ARL	1M of $LiPF_6$ in FEC/DMC=1:4 wt%	Army Research Laboratory
Daikin	1.2 M of $LiPF_6$ FEC/EMC/fluoroether = 2:6:2 wt% + 1% PS	Daikin Industries Ltd



- Daikin electrolyte delivers discharge capacity of 129 mAh/g and stable cycling performance at the voltage range of 3.5-4.85 V;
- Daikin electrolyte is the most promising candidate among the three electrolytes.

Accomplishment to Date FY 19

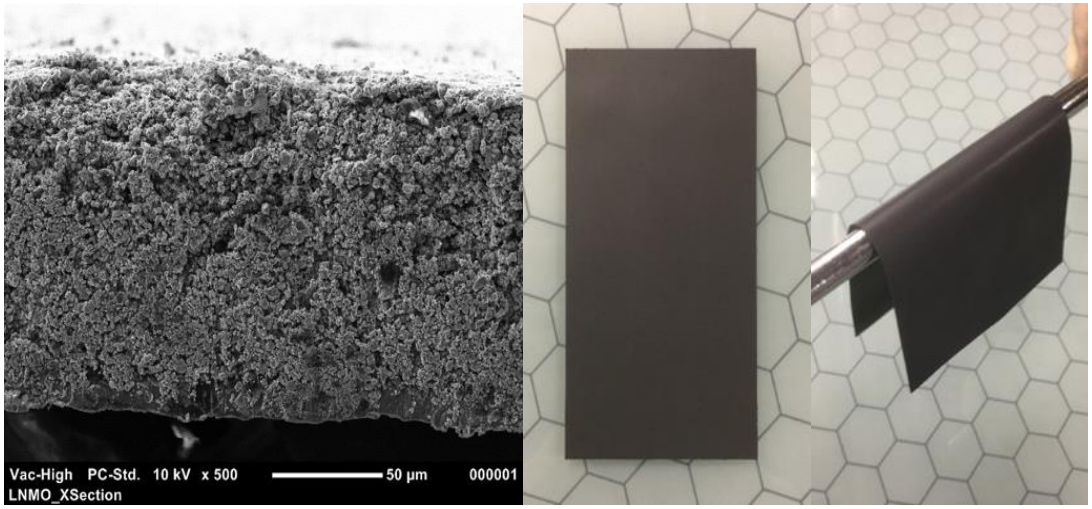
Large batch production of LNMO cathode

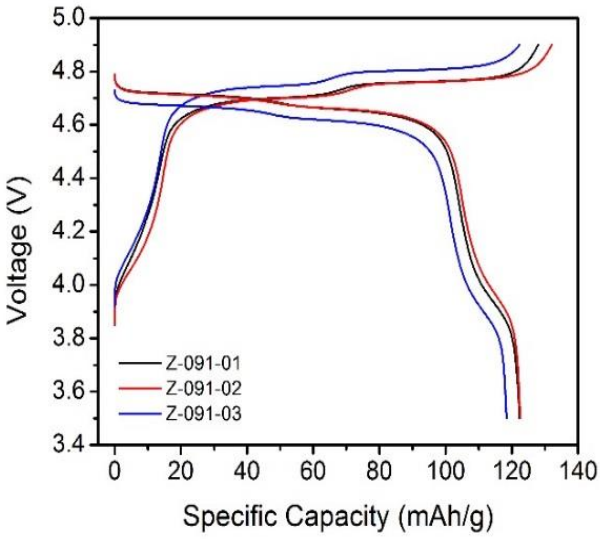


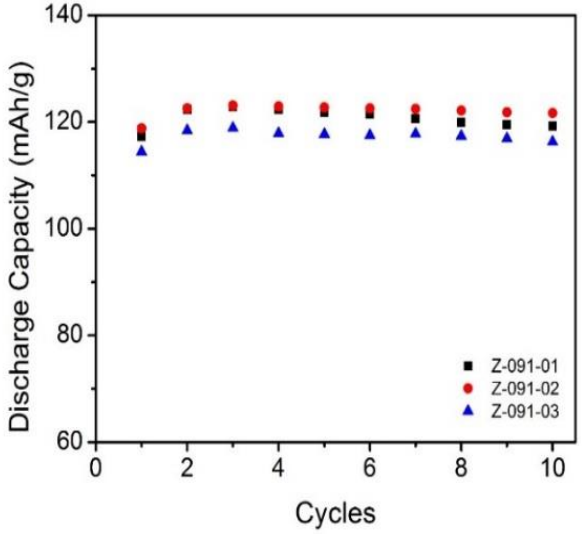
- UT Austin has synthesized > 1 kg of $Ni_{0.25}Mn_{0.75}(OH)_2$ hydroxide precursor by coprecipitation in a 10 L tank reactor, with SEM micrographs depicted in SEM. The calcination temperature and lithium concentration has been optimized as well.

Accomplishment to Date FY 19

Baseline dry processability of LNMO and electrochemical performance



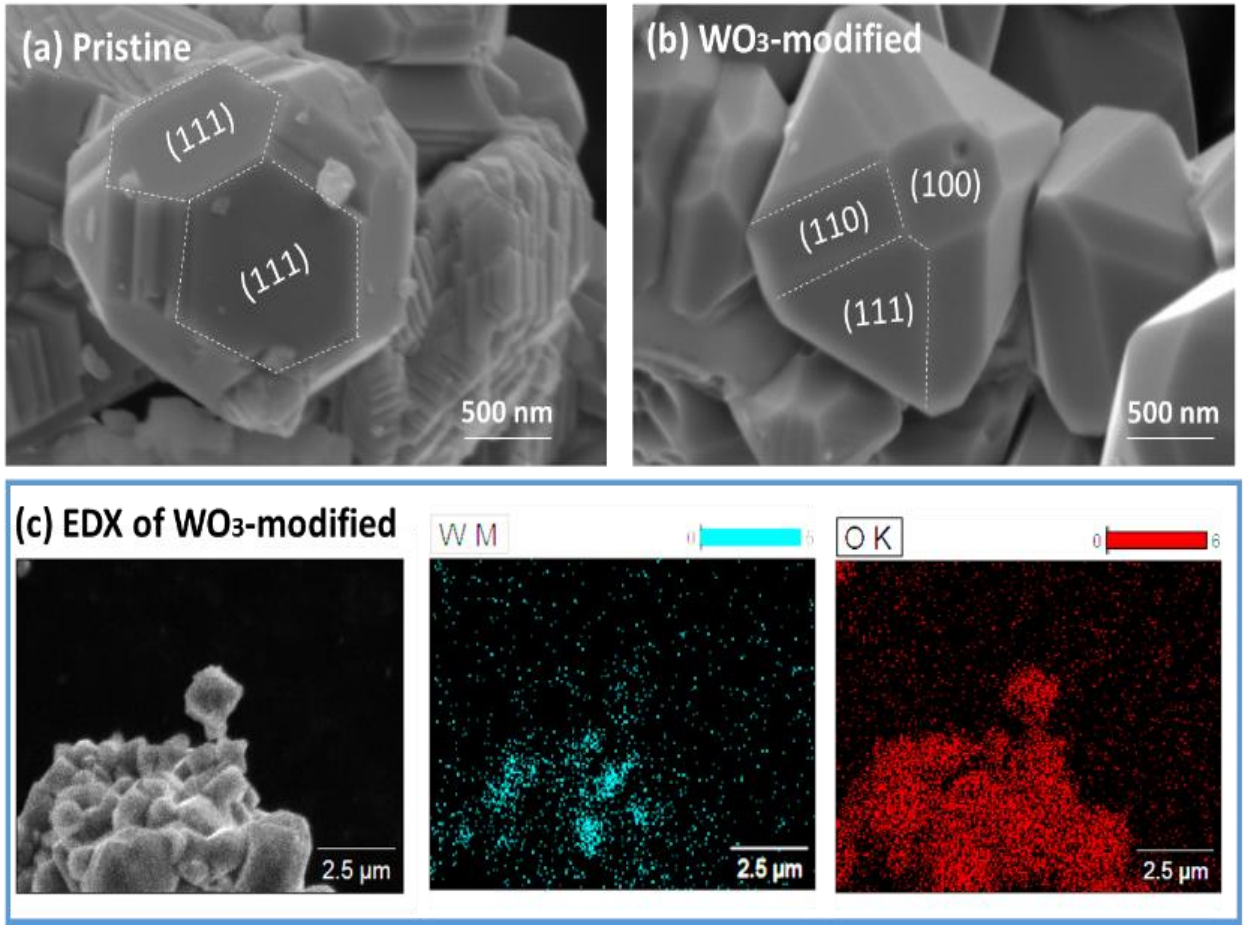




- We have successfully dry coated thick electrodes and demonstrated their initial electrochemical results using baseline LNMO powders.
- The fabricated dry electrode is about 115 microns in thickness and has a loading of approximately 30 mg/cm^2 (2.61 g/cc).
- Initial cycling retention is quite stable.

Accomplishment to Date FY 19

Surface modified LNMO cathode materials



- To reduce surface charge transfer resistance formed during high voltage cycling, WO_3 surface-modified LNMO cathode were prepared through a facile and cost-effective mixing and annealing process.
- The fraction of the {110} facets, exhibiting the most open channels for fast lithium diffusion, increases substantially after W cation modification.

Responses to Previous Year Reviewers' Comments

No reviewer comments are available from previous year review on this project.

Collaboration and Coordination with Other Institutions

Dr. Arumugam Manthiram
University of Texas, Austin

Dr. Vincent Battaglia
Lawrence Berkeley National Lab

Dr. Hieu Duong
(Maxwell Technologies)

Dr. Kang Xu
(Army Research Lab)

Dr. Ich Tran (XPS)
Irvine Materials Research Institute

Remaining Challenges and Future Research

Remaining Challenges:

- Further modification is needed for LNMO cathode to achieve energy density target.
- Atomistic-level Interactions between the electrolyte and the electrode after cycling at high voltages need to be characterized of modified LNMO materials with novel electrolytes.

Future Research:

- Electrochemistry testing of surface modified LNMO cathode with novel electrolyte system.
- Thick dry electrodes optimization to further improve the cycling retention in full cell format using the recommended 4.3 V cutoff voltage by LBNL.
- STEM/ EELS Characterization on modified LNMO single particle using novel electrolyte.
- Investigation of LiTDI as a water scavenging additive to prevent LiPF6 hydrolysis and associated secondary reactions with FEC based electrolyte.

Any proposed future work is subject to change based on funding levels

Summary

- Three baseline LNMO cathodes from different suppliers were systematically compared from both materials properties and electrochemical performances.
- Three novel electrolytes were received and tested, where Daikin electrolyte is the most promising candidate to achieve the final objective.
- Temperature and atmosphere for firing the LNMO cathode has been optimized based on large batch synthesized $Ni_{0.25}Mn_{0.75}(OH)_2$ hydroxide precursor.
- Dry coated thick electrodes have been prepared and their initial electrochemical performance has been improved.