PROSPECTS AND CHALLENGES OF NICKEL-RICH LAYERED OXIDE CATHODES

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Project ID #: ES259

OVERVIEW

Timeline

- Project start date: January 2014
- Project end date: September 2015
- 60 % complete

Budget

- Total project funding
  - DOE share: $708K
  - Contractor: $176K
- Funding for FY14
  - $354K
- Funding for FY15
  - $354K

Barriers

- Barriers
  - Energy and power densities
  - Cost
  - Cycle life
- Targets
  - High capacity, long-life Nickel-rich layered oxide cathodes

Partners

- Pennsylvania State University
- Argonne National Lab
- Lawrence Berkeley National Lab
- EC Power

RELEVANCE

Project Objectives

- To develop high-performance nickel-rich layered oxide cathodes for lithium-ion batteries and a fundamental understanding of their structure-morphology-composition-performance relationships

  - To develop high energy density, long cycle life, high tap density nickel-rich layered $Li[Ni_{1-y-z}Co_yMn_z]O_2$ cathodes with Ni > 0.6 that offer a discharge capacity of > 200 mA h g^{-1} with long cycle life

  - To develop concentration-gradient and surface-modified nickel-rich layered oxide cathodes to overcome the limitations of poor cyclability on operating at higher voltages

  - To develop a fundamental understanding of the factors that control the electrochemical performance of nickel-rich layered oxide cathodes

MILESTONES

Month/Year	Milestone
March 2014	Synthesis and characterization of constant-concentration $Li[Ni_{0.7}Co_{0.15}Mn_{0.15}]O_2$ as well as their electrochemical performance (Complete)
June 2014	Demonstrate that Al_2O_3 coating shows improvement on the sample electrochemical performance in terms of both the voltage and capacity fading (Complete)
September 2014	Synthesis and characterization of concentration-gradient $Li[Ni_{1-y-z}Co_yMn_z]O_2$ with considerably enhanced electrochemical performance (Complete)
December 2014	Systematic investigation of the effects of Mn content in $LiNi_{0.8-x}Co_{0.10}Mn_{0.1+x}O_2$ on the structure, morphology, electrochemical performance, and thermal stability (Complete)

APPROACH / STRATEGY

- Develop a firm understanding of the factors controlling the electrochemical performances of nickel-rich layered oxide cathodes and utilize the understanding to develop high-performance cathodes for vehicle batteries

  - Novel low-cost, large-scale synthesis approaches using a continuously-stirred tank reactor to obtain high-performance nickel-rich layered $Li[Ni_{1-y-z}Co_yMn_z]O_2$ cathodes that offer high capacity, high tap density, and long cycle life

  - Precise control of the primary and secondary particle size of the nickel-rich layered oxides and their influence on the electrochemical properties

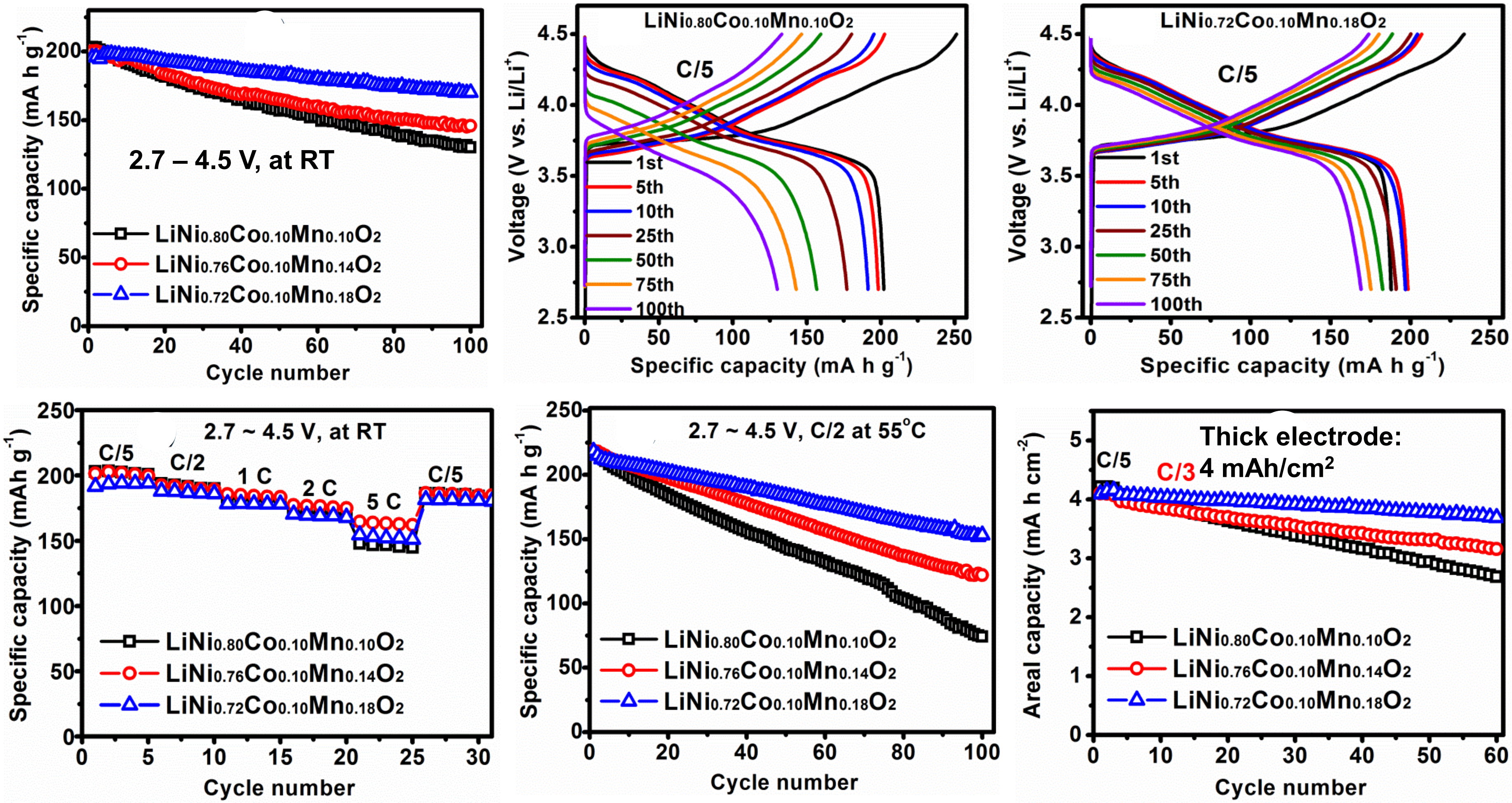
  - Concentration-gradient nickel-rich layered $Li[Ni_{1-y-z}Co_yMn_z]O_2$ cathodes with varying Ni and Mn contents from the interior to the exterior as well as surface coating with Al_2O_3 to enhance the long-term cycling stability

  - Advanced chemical, structural, and surface characterizations
  - In-depth electrochemical characterization and evaluation
  - Understanding the structure-morphology-property-performance relationships

TECHNICAL ACCOMPLISHMENTS AND PROGRESS

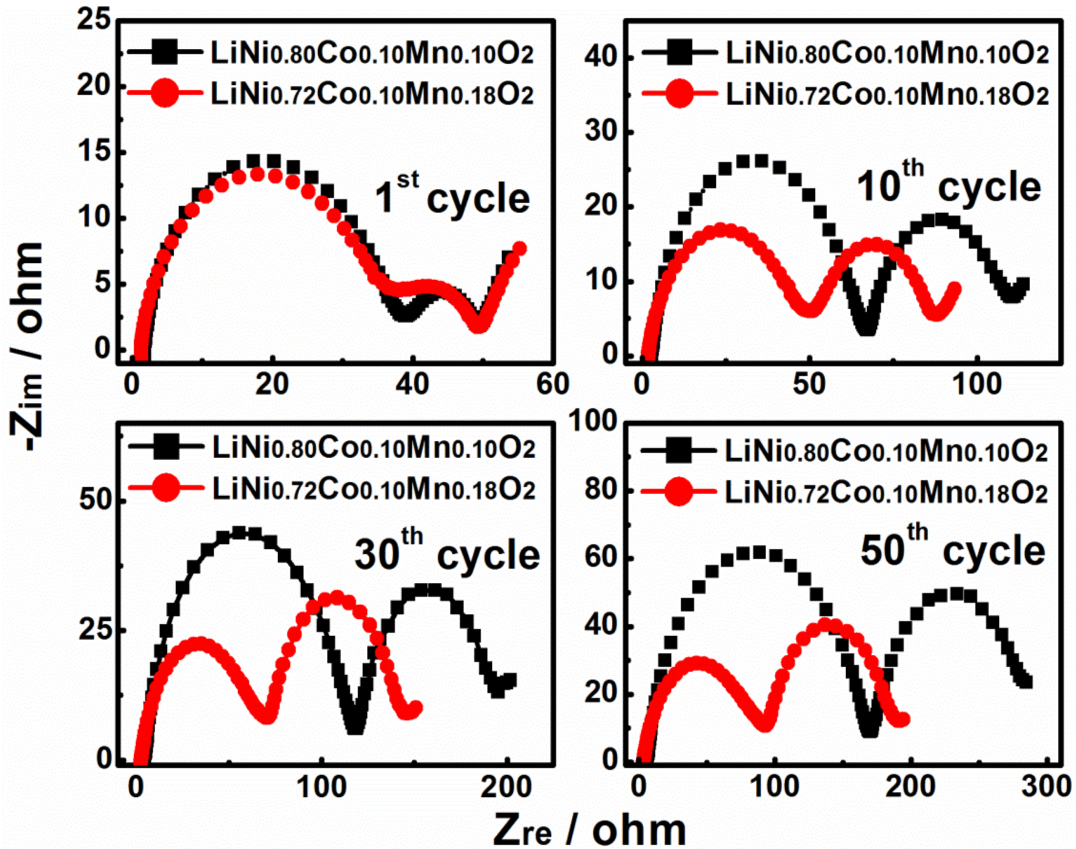
- The synthesis conditions to obtain Ni-rich layered oxide cathodes with different particle sizes have been optimized with a controlled continuously-stirred tank reactor (500 g/batch)
- The effects of Mn substitution for Ni on the structure, morphology, and electrochemical performance of $LiNi_{0.8-x}Co_{0.10}Mn_{0.1+x}O_2$ cathodes have been investigated systematically
- With the optimized synthetic conditions, the Ni-rich $LiNi_{0.7}Co_{0.15}Mn_{0.15}O_2$ cathode with a particle size of ~ 13 μm offers a capacity of around 200 mA h g^{-1} with good cyclability
- A concentration-gradient $LiNi_{0.76}Co_{0.10}Mn_{0.14}O_2$ cathode with a Ni-rich interior and a Mn-rich surface shows superior cyclability compared to the constant-concentration sample
- The capacity and voltage fading during cycling are suppressed by coating the Ni-rich oxides with Al_2O_3

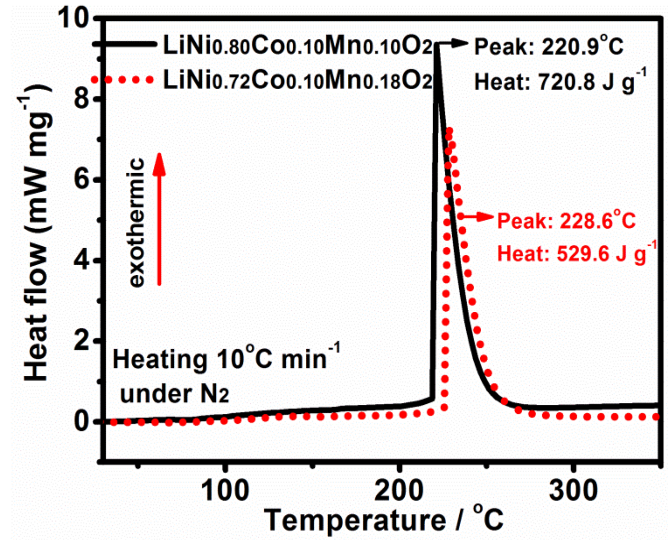
EFFECT OF Mn CONTENT IN Ni-RICH $LiNi_{0.8-x}Co_{0.1}Mn_{0.1+x}O_2$



- The polarization loss (voltage drop) during cycling decreases and capacity retention increases with increasing Mn content

EFFECT OF Mn CONTENT IN Ni-RICH $LiNi_{0.8-x}Co_{0.1}Mn_{0.1+x}O_2$

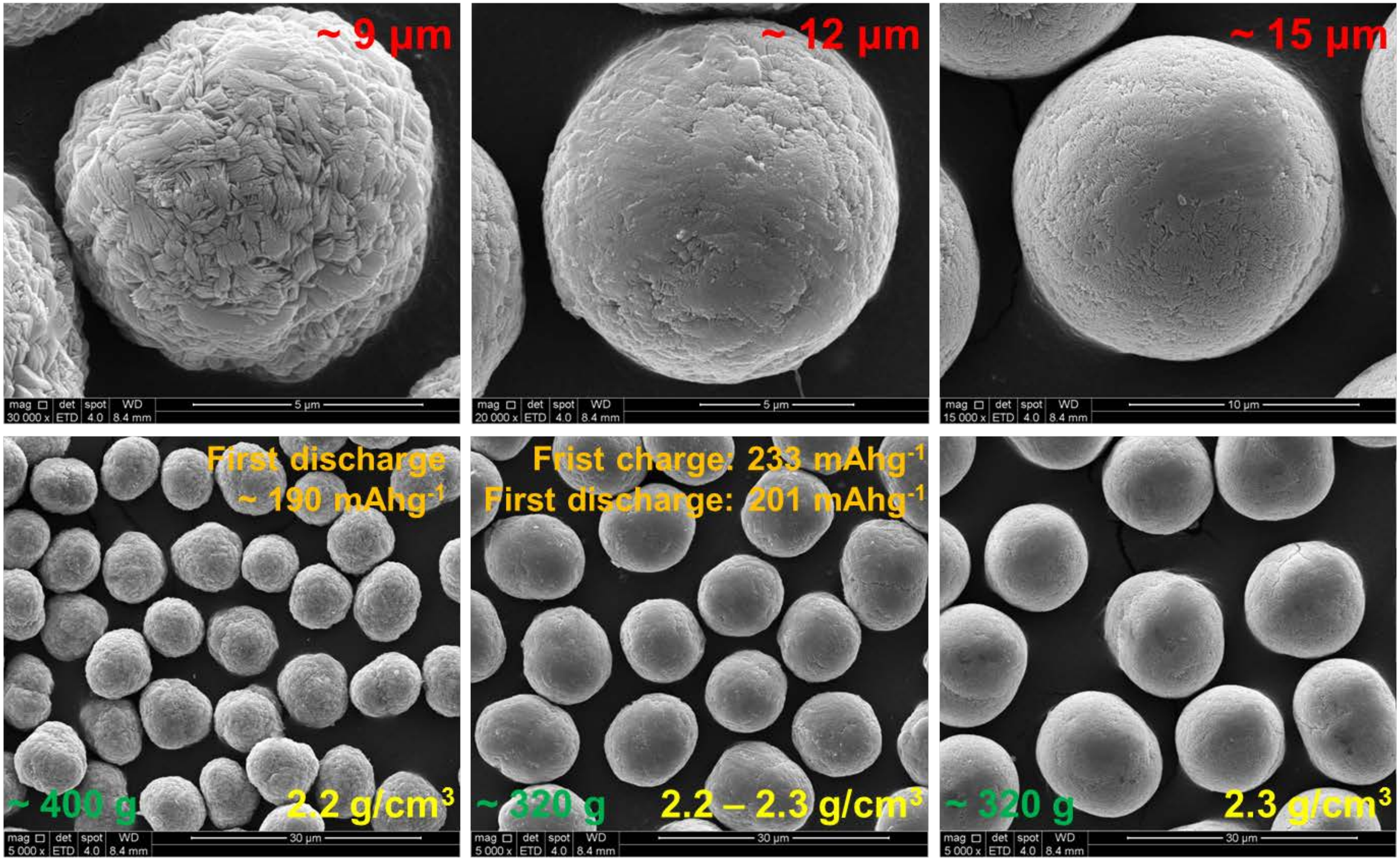




- The exothermic reaction temperature increases and the heat generated decreases with increasing Mn content

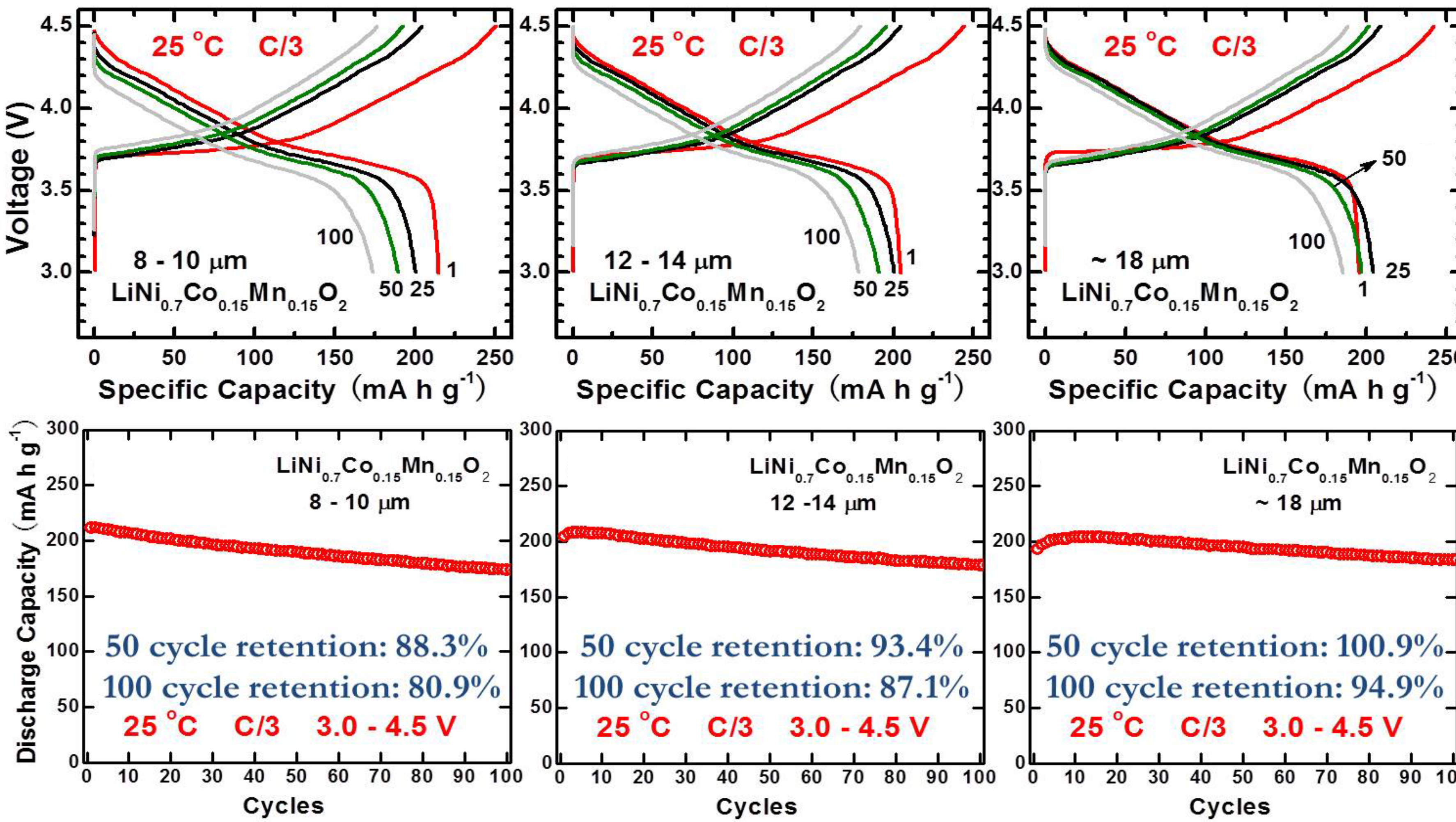
- Only a small difference is observed in the impedance values at early stages of cycling, exhibiting similar surface film resistance and charge-transfer resistance
- Upon cycling, the increase in surface-film resistance and the charge-transfer resistance is smaller for the high Mn-content cathode than for the low-Mn-content cathode

SCALED-UP HYDROXIDE PRECURSORS FOR Ni-RICH OXIDES



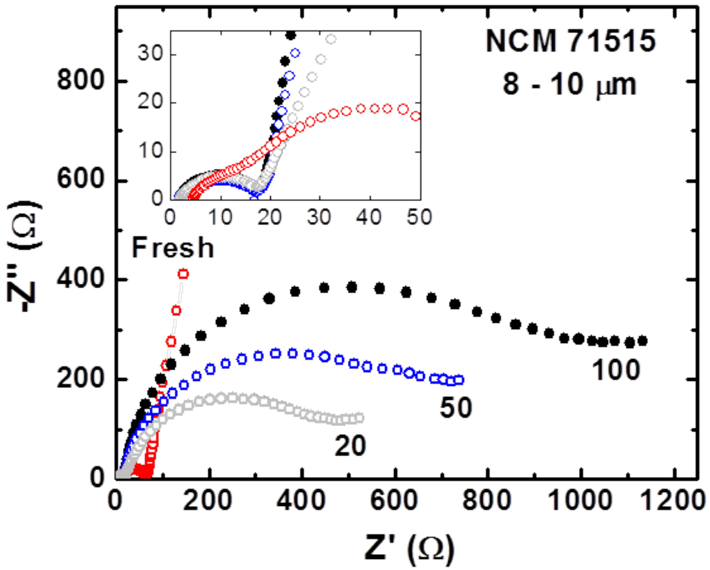
$Li[Ni_{0.7}Co_{0.15}Mn_{0.15}]O_2$ – Product yield per batch: up to 500 – 1000 g

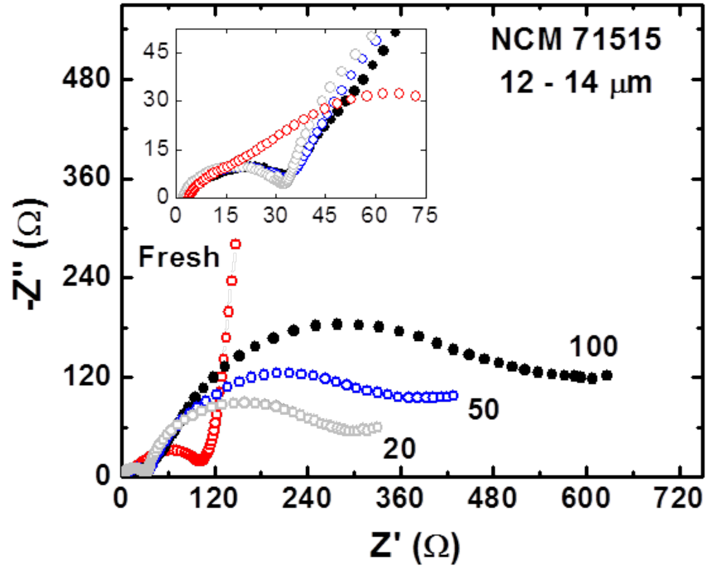
EFFECT OF PARTICLE SIZE IN Ni-RICH LAYERED OXIDES

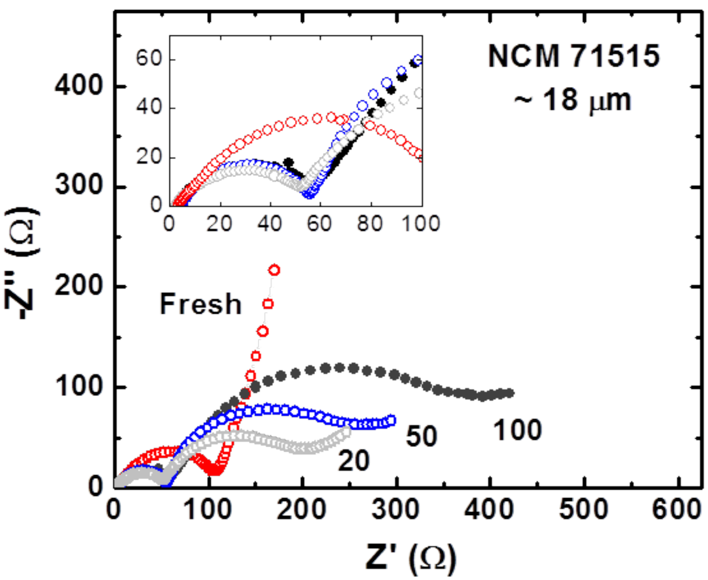


- The polarization loss (voltage drop) during cycling decreases and the capacity retention increases with increasing particle size

EFFECT OF PARTICLE SIZE ON IMPEDANCE EVOLUTION







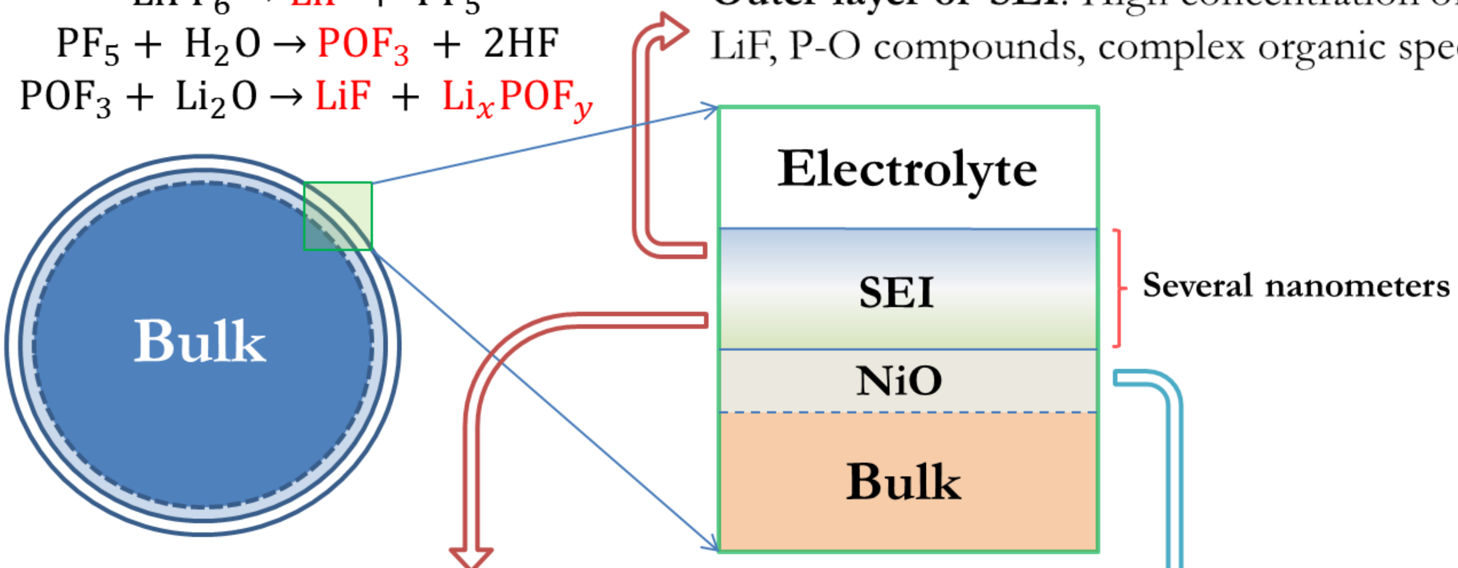
- Overall cathode impedance decreases with increasing secondary particle size
- Charge-transfer resistance is the chief contributor to overall cathode impedance
- Charge-transfer resistance decreases with increasing secondary particle size
- Surface film resistance increases with increasing secondary particle size

SURFACE DEGRADATION OF Ni-RICH LAYERED OXIDES

- Due to electrolyte decomposition and electrode-electrolyte reactivity, the SEI layer is inhomogeneous in chemical composition as a function of depth

$$LiPF_6 \rightarrow LiF + PF_5$$
$$PF_5 + H_2O \rightarrow POF_3 + 2HF$$
$$POF_3 + Li_2O \rightarrow LiF + Li_xPOF_y$$

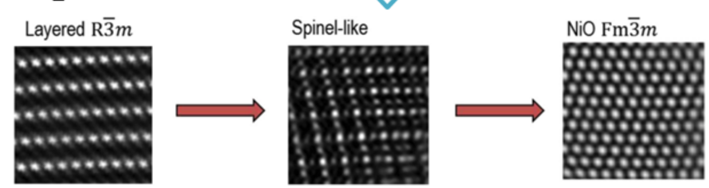
Outer layer of SEI: High concentration of LiF, P-O compounds, complex organic species



Inner layer of SEI: High concentration of LiF and Ni/Co/MnF$_2$

$$LiNi_{1-2x}Co_xMn_xO_2 + 2HF + Li^+ + e^- \rightarrow Li_{1-\delta}Ni_{1-2x}Co_xMn_xO_2 + LiF + 0.5H_2O$$

$$Ni/Co/Mn^{2+}O + 2HF \rightarrow Ni/Co/MnF_2 + H_2O$$



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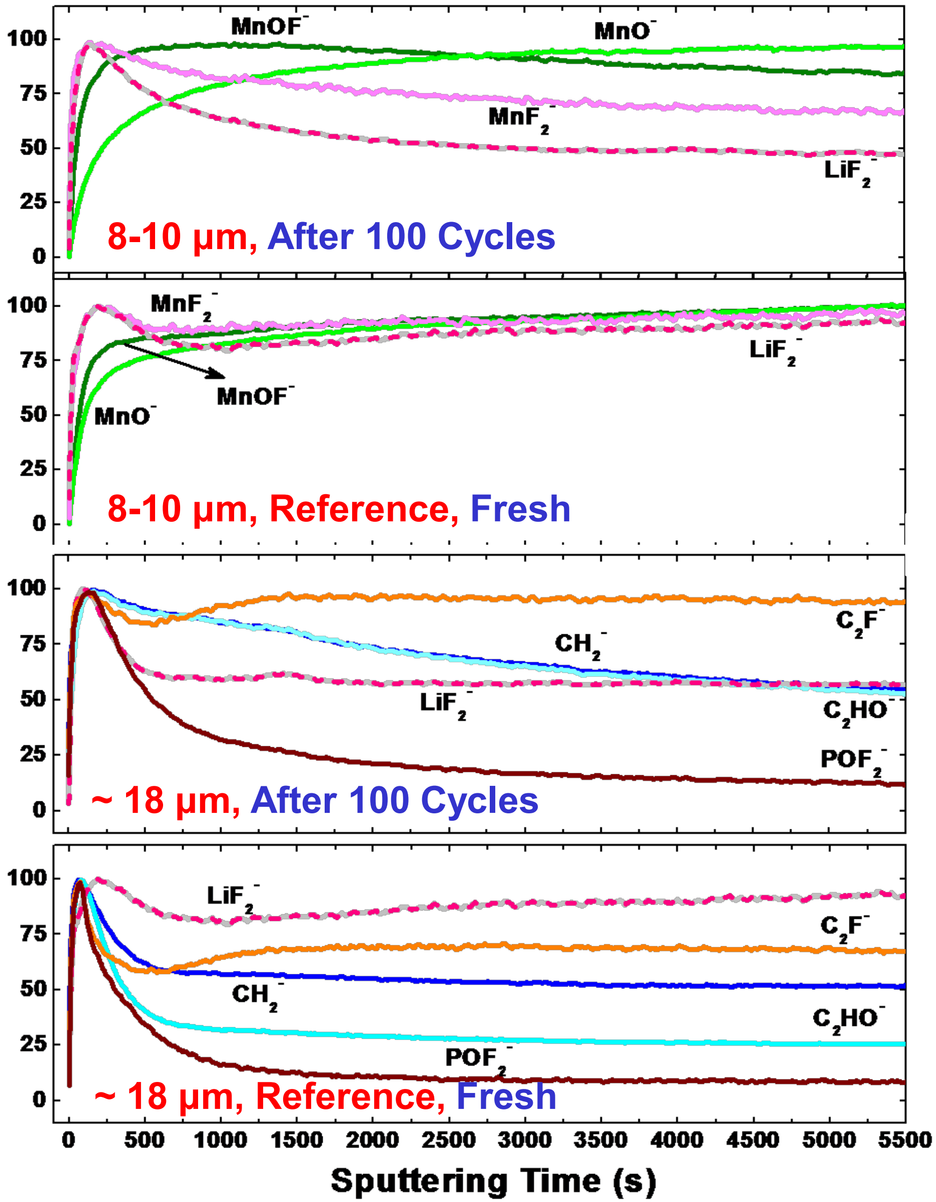
SURFACE DEGRADATION: TOF-SIMS DEPTH PROFILE

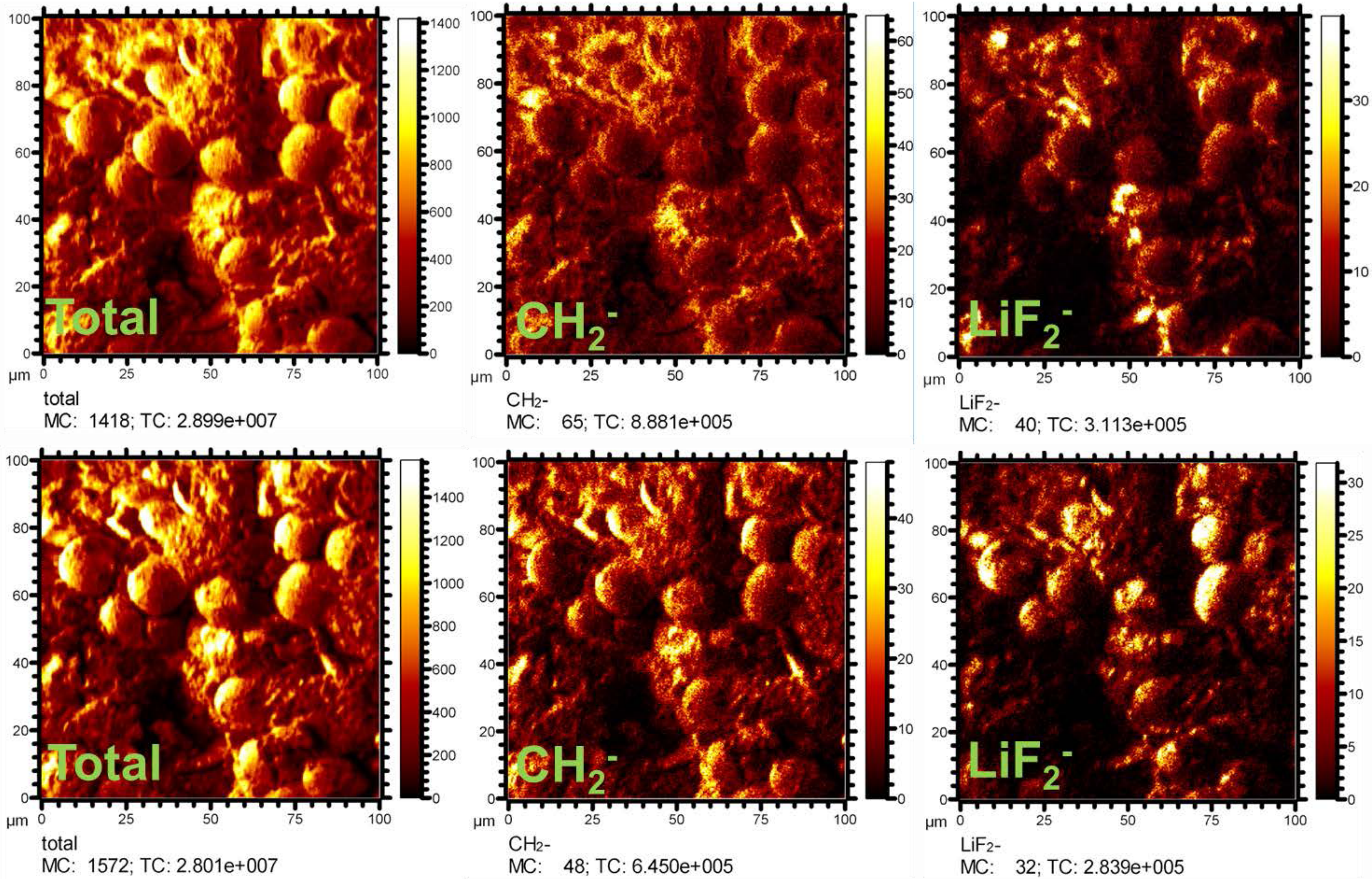


- Even with the fresh sample, small amount of MnF_2 is found on the surface
- An inner layer of SEI (due to HF attack of the active material leading to transition-metal fluorides as well as LiF) is seen with cycled sample

- Even though sample transfer was handled in a glovebox without exposing to air, small surface contamination is still found
- An outer layer of SEI (comprised of complex organic species as well decomposition products from electrolyte salt) is found with the cycled sample

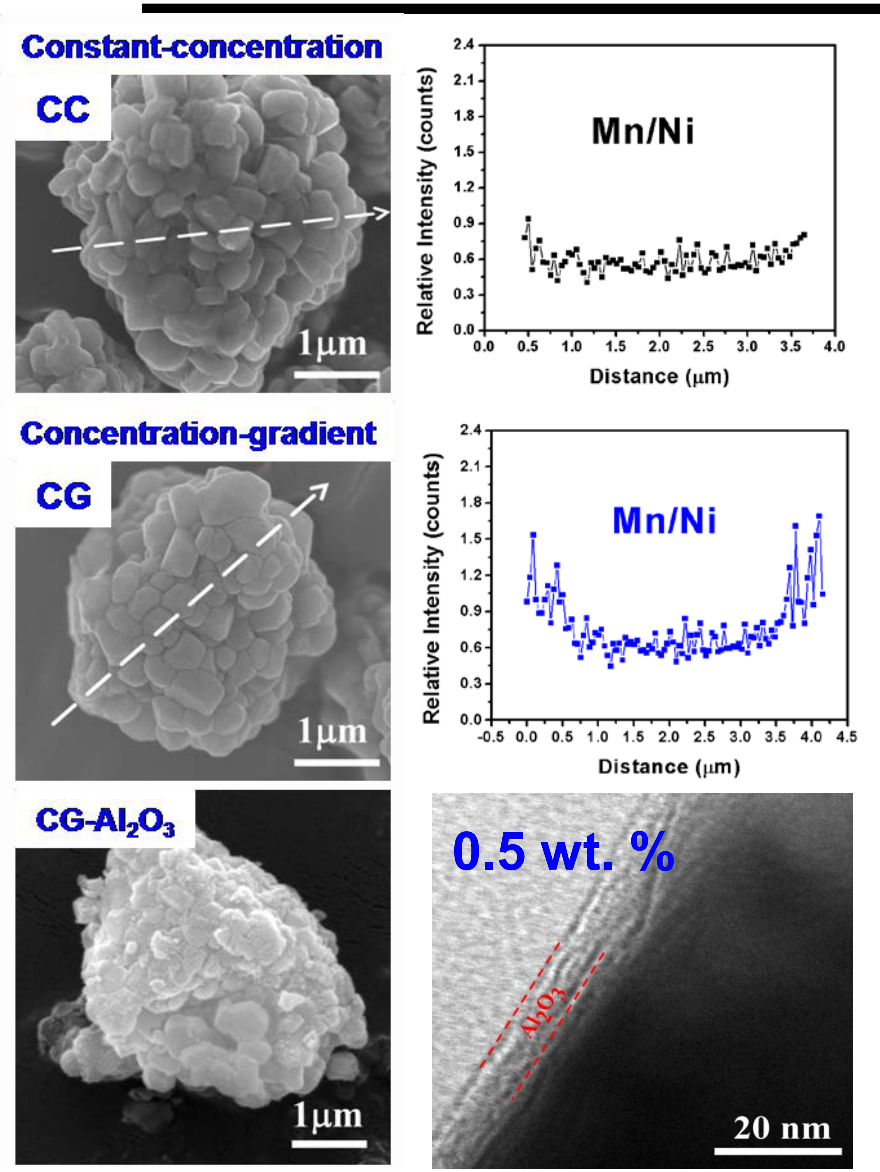
SURFACE DEGRADATION: TOF-SIMS HIGH RESOLUTION MAPPING

~18 µm cycled, 3600s sputtered

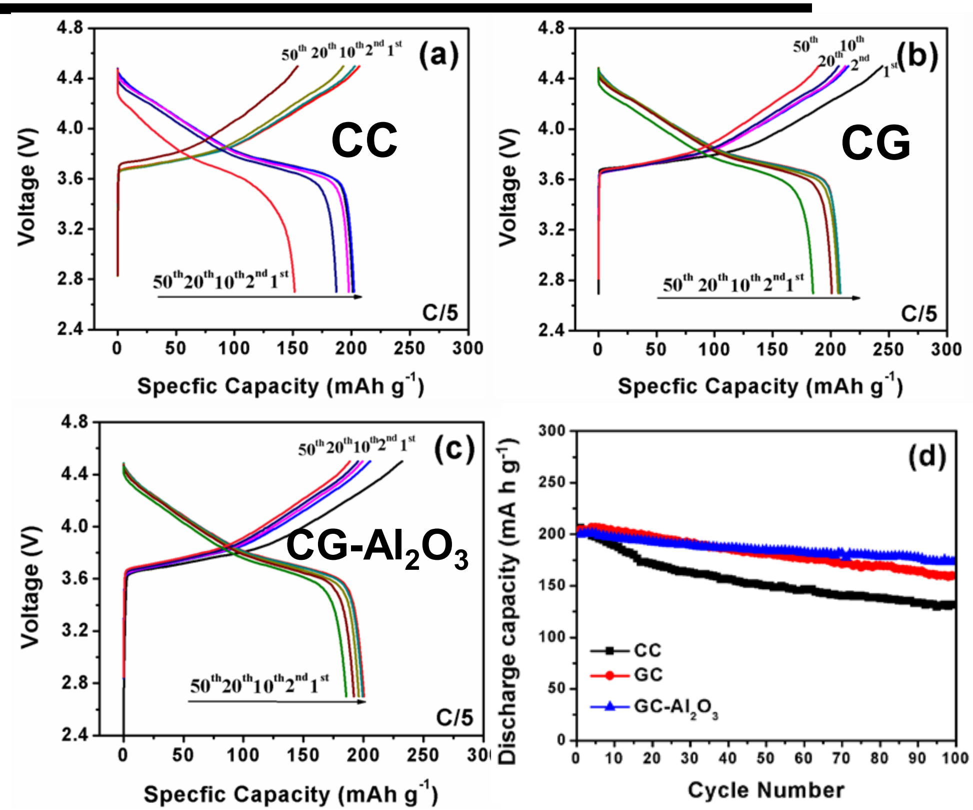


~18 µm cycled, 100s sputtered

Al_2O_3-COATED CONCENTRATION-GRADIENT CATHODES



$LiNi_{0.62}Co_{0.14}Mn_{0.24}O_2$



- Gradual decrease in Ni and increase in Mn contents from interior to surface improves performance
- Surface coating with Al_2O_3 gives further improvement in performance

FY 2014 REVIEWERS' COMMENTS AND RESPONSES

Comment: "it was not very clear if the authors were using a two layer powder, as a cathode powder, with two clear compositions, or a gradient powder"

Response: It is a gradient powder with the composition continuously varying from the interior to the exterior.

Comment: "The scale up of the anode and cathode materials should be better clarified."

Response: We can scale up our cathode materials up to 1000 g in each batch.

Comment: "integrated performance demonstration was less likely"; "the materials capability had been base-lined, but it was not clear that an integrated baseline cell structure had been developed and characterized"

Response: We have sent our cathode electrodes to our partners and more integrated performance data are being collected now.

Comment: **"**the progress with cathode did not seem to be as good"

Response: With the optimized synthesis conditions, we have scaled up the cathode materials to 1 kg per batch, and the new batch of gradient materials show much improved performance in terms of both capacity and cyclability.

COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

- Argonne National Laboratory – Zhengcheng Zhang
  - *Providing us optimized electrolyte compositions to test with Ni-rich cathodes*
  - *Testing our Ni-rich cathodes with optimized high-voltage electrolytes*
- Pennsylvania State University – Donghai Wang
  - *Monthly project discussion to couple the Ni-rich cathodes with other cell components being developed (electrolyte, Si anode, and binder)*
- Lawrence Berkeley National Laboratory – Gao Liu
  - *Monthly project discussion to couple the Ni-rich cathodes with other cell components being developed (electrolyte, Si anode, and binder)*
- EC Power – Rong Kou
  - *Monthly project discussion to couple the Ni-rich cathodes with other cell components to make full cells*

REMAINING CHALLENGES AND BARRIERS

- Our project goal is to achieve a capacity of 220 mA h g^{-1}, and the compositions with Ni, Mn, and Co and the synthesis conditions need to be further optimized to reach this goal by considering the delicate balance/tradeoff among the various factors/parameters
- Capacity and voltage fading have been suppressed, but need to be completely eliminated
- The side reactions involving the formation of a thick solid-electrolyte interphase (SEI) layer, Li/O vacancies due to cation migration, and a surface reconstruction layer (SRL) consisting of spinel-like and/or NiO rock-salt phases are very complicated and need to be completely understood
- Both interfacial reactions and phase transitions need to be considered to realize stable cycling without voltage degradation
- The surface stability of Ni-rich cathodes needs to be optimized

PROPOSED FUTURE WORK

- Evaluate long-term cycle performance (> 500 cycles)
- Evaluate performance at elevated temperatures (55 ^{o}C)
- Make synthesis efforts to increase the capacity to 220 mA h g^{-1}
  - Optimize the preparation conditions of Ni-rich materials by adjusting the co-precipitation process, amount of Li in the firing process, and sintering temperature to reduce the side reactions of cathode surface with electrolyte and maximize the electrochemical performance
  - Optimize the primary and secondary particle size, morphology, and chemical compositions of Ni-rich materials (baseline and concentration-gradient samples)
  - Understand the stabilization mechanisms of concentration-gradient materials
  - Coat the baseline and concentration-gradient samples with other agents like Li_2MnO_3, Li_2ZrO_3, and AlF_3 to improve the electrochemical performance
  - Develop an in-depth understanding of the degradation mechanisms of Ni-rich layered oxides with surface techniques (TOF-SIMS, XPS) and TEM

SUMMARY

- A systematic investigation of the effects of Mn content in $LiNi_{0.8-x}Co_{0.10}Mn_{0.1+x}O_2$ on the structure, morphology, electrochemical performance, and the thermal stability reveals that the cycle life increases with increasing Mn content

- With the optimized synthesis conditions, the Ni-rich $LiNi_{0.7}Co_{0.15}Mn_{0.15}O_2$ cathode materials with different secondary particle sizes have been obtained and their surface degradation and SEI layer formation have been investigated with TOF-SIMS analysis

- Concentration-gradient $LiNi_{0.62}Co_{0.14}Mn_{0.24}O_2$ and $LiNi_{0.76}Co_{0.10}Mn_{0.14}O_2$ cathodes with Ni-rich interior and Mn-rich surface have been synthesized, and they are found to exhibit superior cyclability compared to the constant-concentration samples

- Surface modification of the constant-concentration and concentration-gradient Ni-rich cathodes with Al_2O_3 enhances further the cycle life