Development of High-Energy Cathode Materials

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Pacific Northwest National Laboratory

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Project ID #ES056

Overview

Timeline

- Start date: Oct. 2015
- End date: Sept. 2018
- Percent complete: 25%

Barriers addressed

- Low energy/high cost
- Limited cycle life
- Safety

Budget

- Total project funding: $1.2M
  - DOE share: 100%
- Funding for FY16: $400k

Partners

- SUNY Binghamton
- Argonne National Laboratory
- Brookhaven National Laboratory
- Army Research Laboratory

Relevance/Objectives

- Synthesize Ni-rich $LiNi_xMn_yCo_zO_2$ (NMC) cathode materials using controlled co-precipitation method.
- Improve the discharge capacity and stability of NMC cathode materials at higher charge voltage.
- Use advanced characterization techniques to understand the stability of NMC cathode materials at high charge cutoff voltages.

Milestones

FY15

- ✓ Identify appropriate synthesis step to enhance the homogeneous cation distribution in the lattice LMR cathode and demonstrate 200 cycling with less than 10% energy loss. (March 2015) **Completed**
- ✓ Develop the surface treatment approaches to improve the stability of high energy cathode at high voltage conditions. (June 2015) **Completed**
- ✓ Demonstrate high voltage operation of traditional NMC with 180 mAh/g capacity and less than 20% in100 cycles. (Sept. 2015) **Completed**

FY16

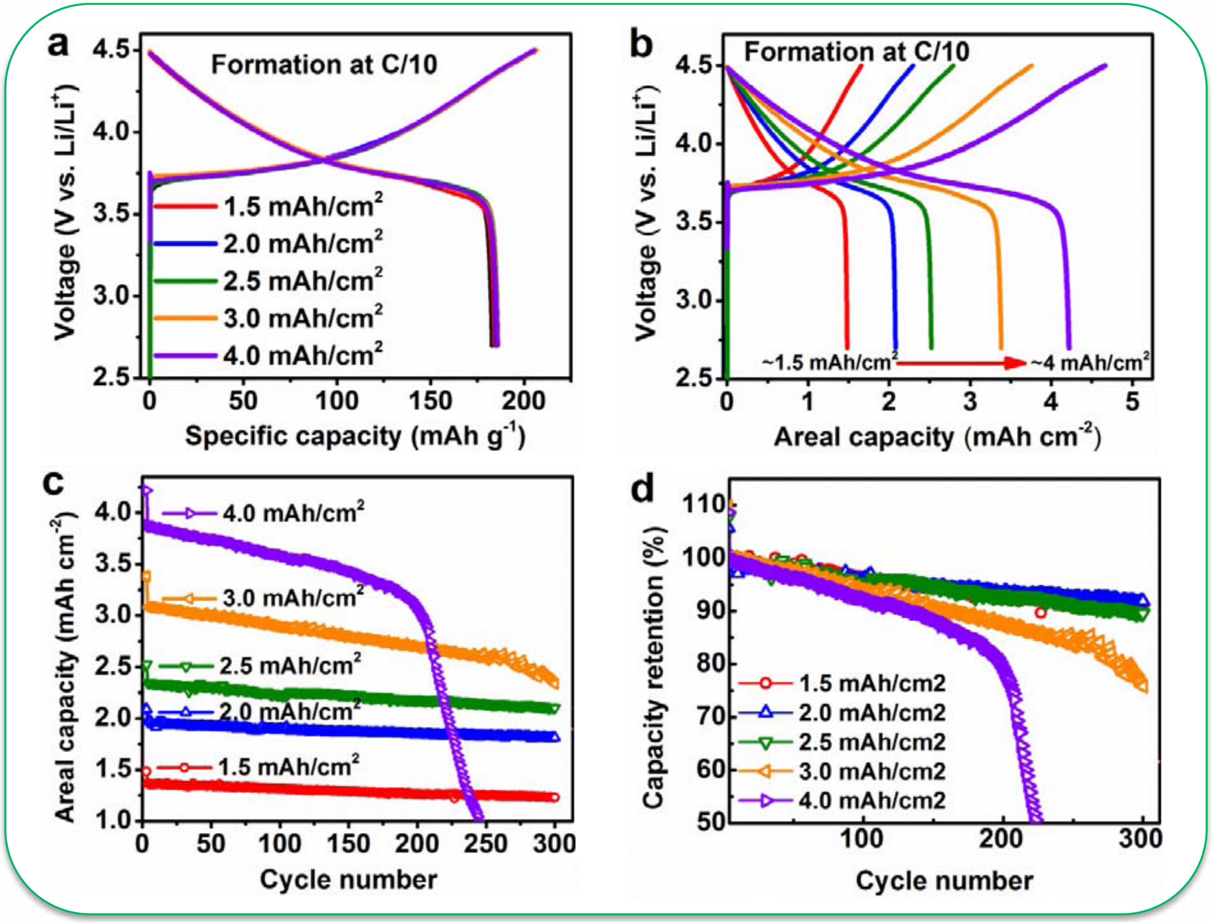
- ✓ Identify NMC candidates that can deliver 190 mAh g^{-1} at high voltages. (Dec. 2015) **Completed**
- ✓ Complete multi-scale quantitative atomic level mapping to identify the behavior of Co, Ni, and Mn in NMC during battery charge/discharge. (March 2016) **Completed**
- ✓ Optimize charge voltage based on the correlation between structure stability and capacity of NMC. (June 2016) **Completed**
- ✓ Optimized compositions of NMC materials to achieve improved electrochemical performance. (Sept. 2016) **On going**

Approach

1. Use controlled co-precipitation method (continuously stirred tank reactor) to synthesize the Ni-rich NMC cathodes with high specific discharge capacity.
2. Optimize the composition, particle size, and micro structure of NMC cathode to enhance the high voltage stability of NMC cathode materials.
3. Use advanced microscopic characterizations to investigate the capacity degradation mechanism of NMC cathodes charged to high voltages.

Technical Accomplishments

High Voltage Operation of NMC Cathode Electrodes with Different Areal Capacities



Performances of **Li/NMC333** cells. 2.7 ~ 4.5 V.

C/3 charge, 1C discharge after 3 formation cycles at C/10.

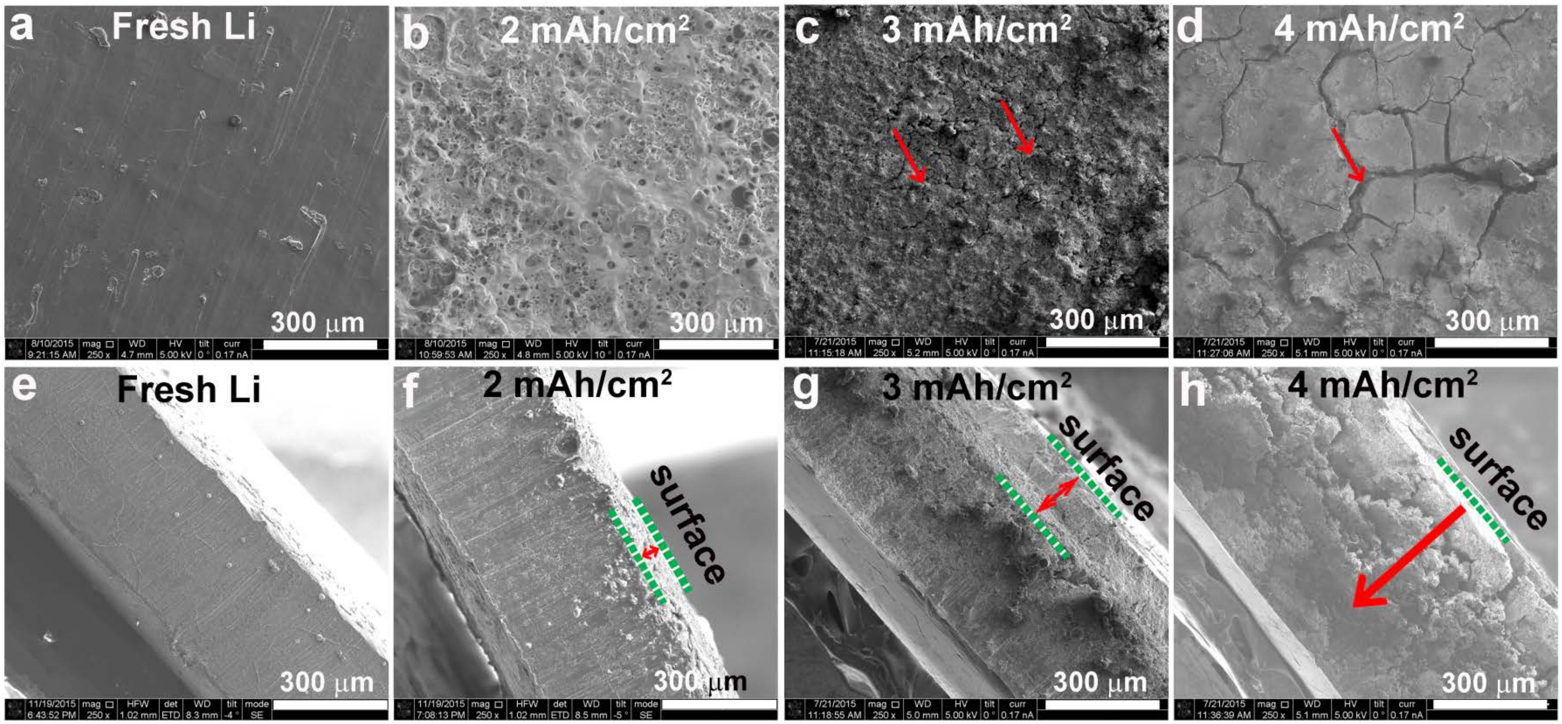
NMC333 exhibits a capacity > 180 mAh g^{-1} at charge cutoff 4.5 V.

- ➢ Increasing electrode loading shortens the cycle life of NMC cathode when tested in Li/|NMC half cells.

Technical Accomplishments

High Voltage Operation of NMC Cathode Electrodes with Different Areal Capacities

Li metal anode retrieved from Li/NMC cells after 300 cycles

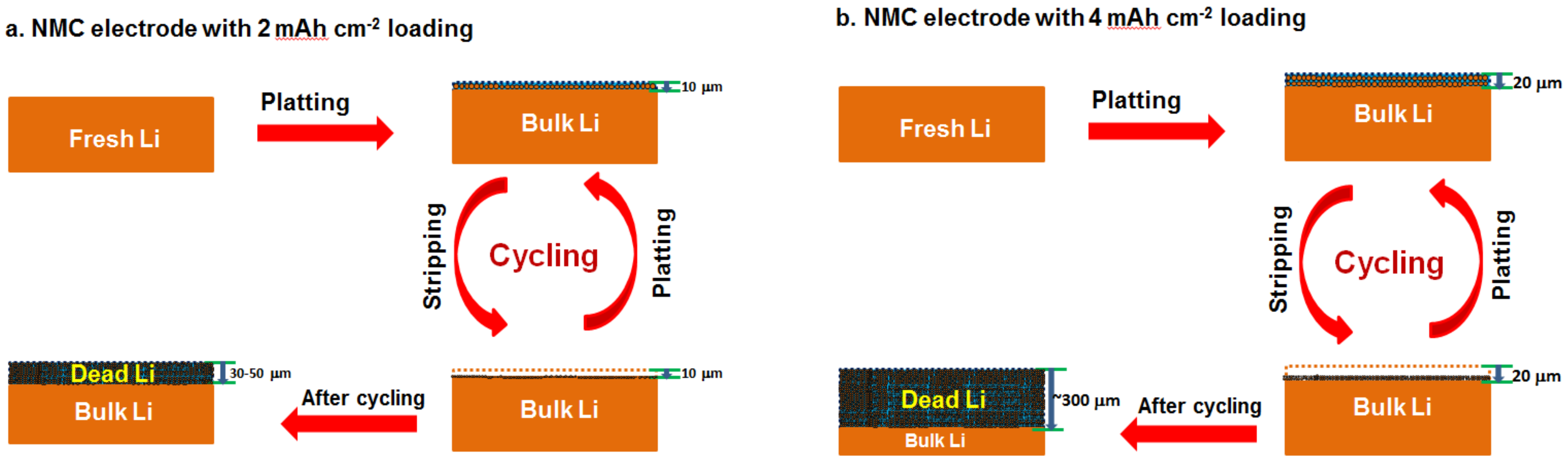


- Serious cracks and porous/loose lithium was observed for electrode with 4 mAh cm^{-2} loading (~ 22 mg active material per cm^2) after cycling.

Technical Accomplishments

High Voltage Operation of NMC Cathode Electrodes with Different Areal Capacities

Degradation mechanism of lithium metal cells using NMC electrodes with different areal capacity loadings

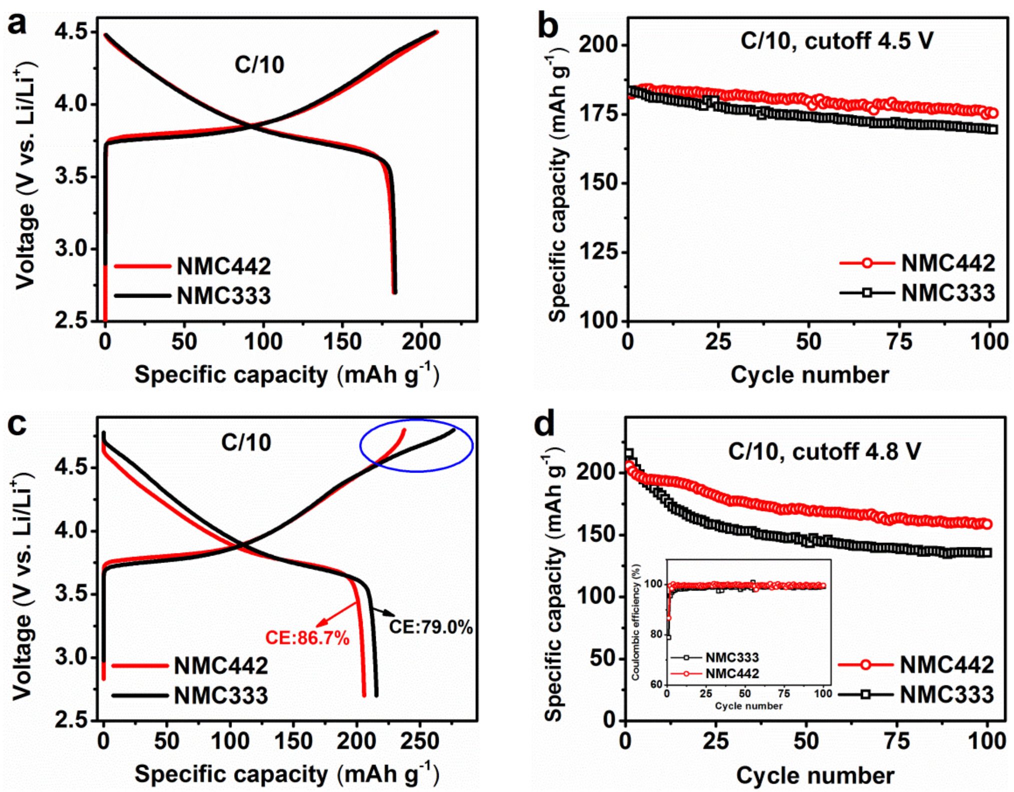


- Higher NMC loading requires thicker lithium to be cycled in each charge/discharge process.
- ➢ Higher current density for lithium deposition resulted in accelerated corrosion of lithium metal anode.

Technical Accomplishments

Capacity Degradation Mechanism of NMC materials at High Charge Cutoff voltages

Ni-rich/Mn-rich NMC is more stable than Co-rich NMC at deep delithiation



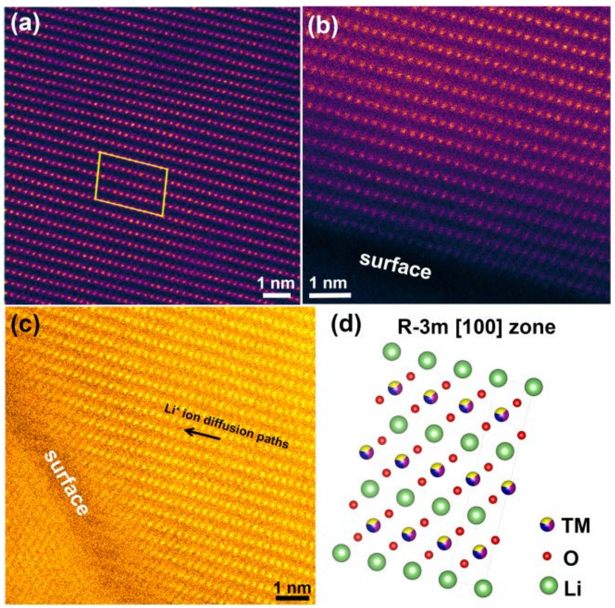
Electrolyte:
1 M $LiPF_6$ in EC-DMC

- Co-rich NMC333 showed large initial capacity loss and poor cycling stability.
- ✓ NMC442 showed better cycling performance at charge cutoff 4.5 and 4.8 V.

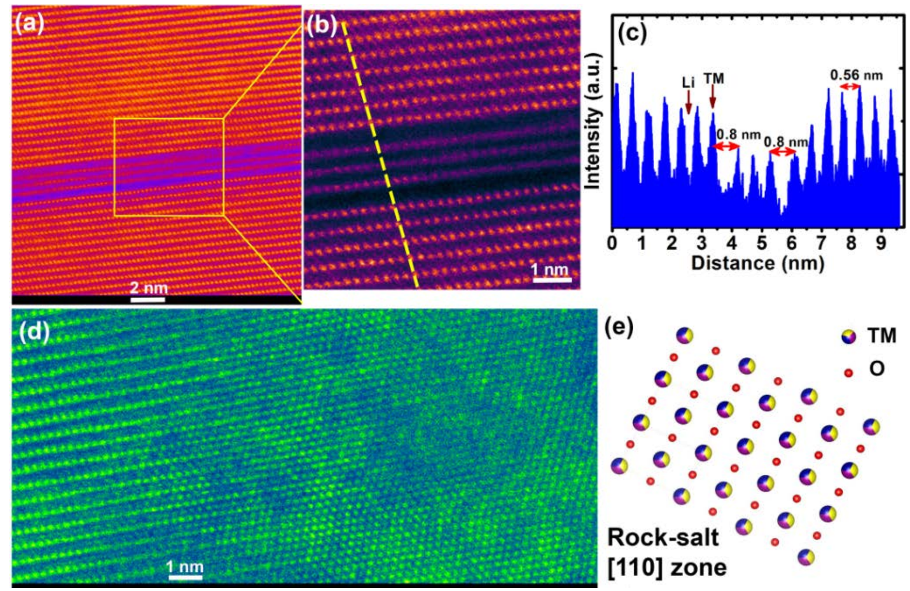
Technical Accomplishments

Crystal structure evolution of NMC333 (cut-off at 4.8 V)

STEM images of NMC333 before cycling



STEM images of NMC333 after 100 cycles at 2.7 ~ 4.8 V



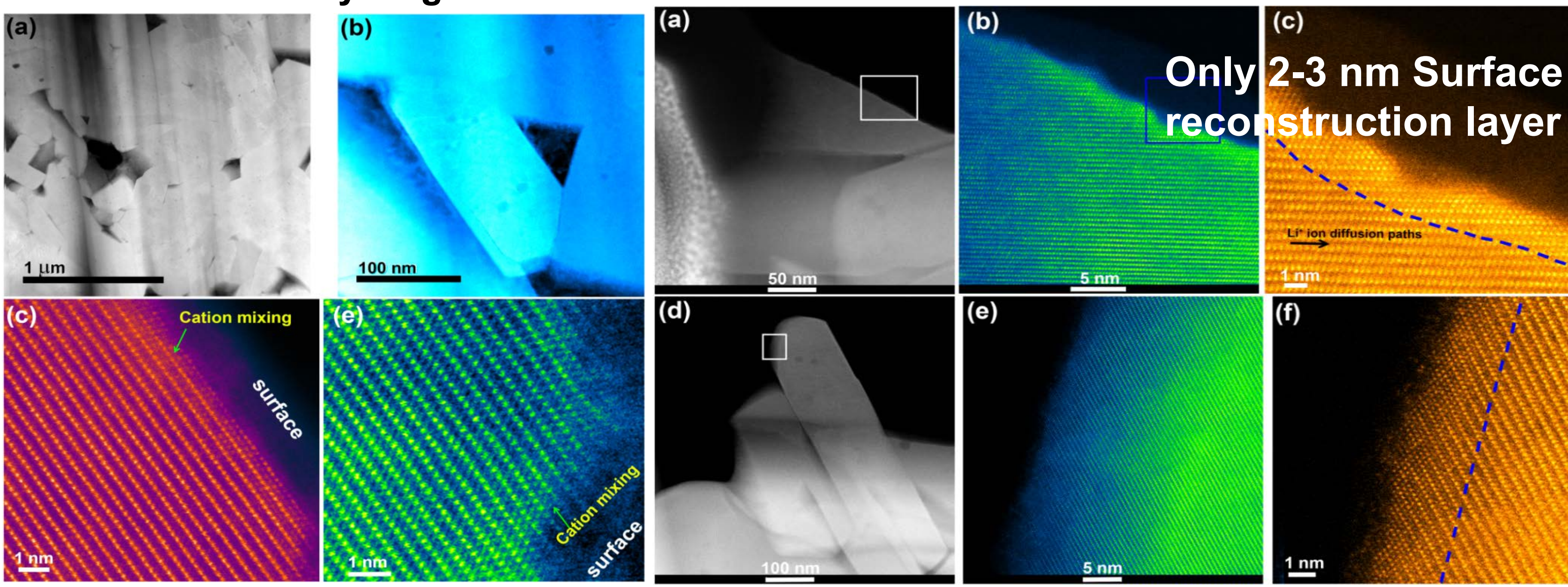
- Pristine NMC333 showed well defined layered structure without cation mixing observed.
- Stream formation & Lattice expansion

➢ NMC transforms from layered to disordered rock-salt structure (10 – 15 nm thick) after cycled at high voltage (4.8V)

Technical Accomplishments

Crystal structure evolution of NMC442 (cut-off 4.8 V)

STEM images of NMC442 before cycling | **STEM images of NMC442 after 100 cycles at 2.7 ~ 4.8 V**

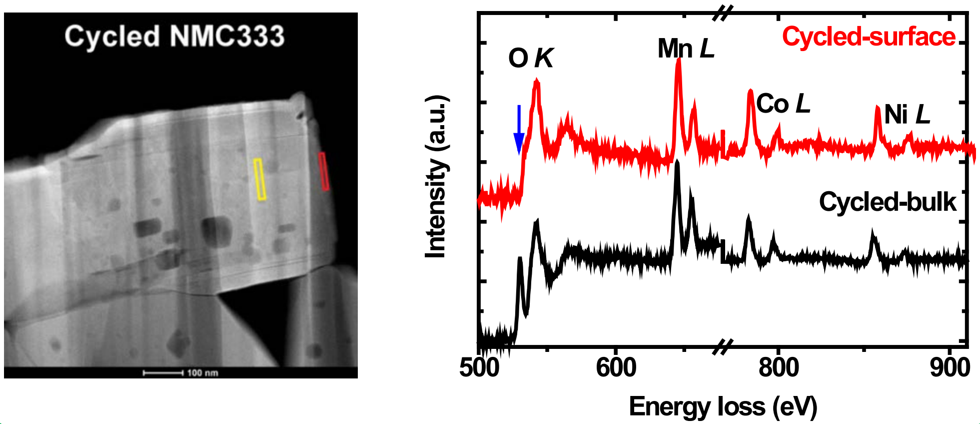


- ○ Pristine NMC442 shows slight cation mixing due to the higher Ni content.
- ✓ NMC442 demonstrates much better structural stability during cycling, exhibits reduced phase transformation from layered to disordered rock-salt phase as compared with NMC333.

Technical Accomplishments

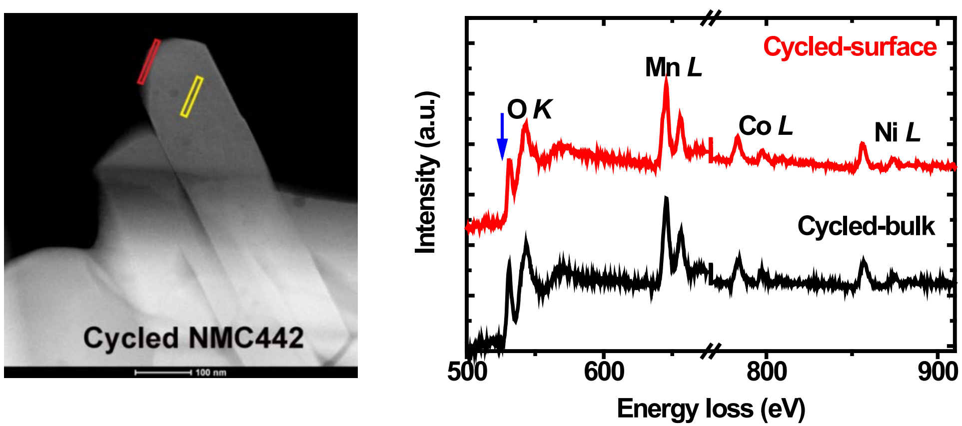
Capacity Degradation Mechanism of NMC materials at High Charge Cutoff voltages

NMC333 after 100 cycles at 4.8 V cutoff



- For NMC333, the disappearance of oxygen pre-edge peak after charged to high voltages.

NMC442 after 100 cycles at 4.8 V cutoff

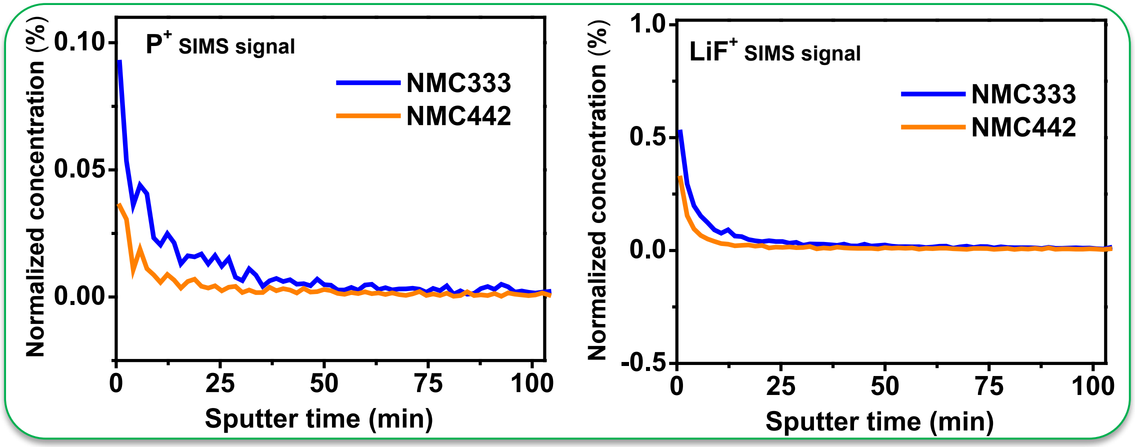


- For NMC442, the oxygen pre-edge peak is better maintained, suggesting a superior crystal structural stability when charged to high voltages.

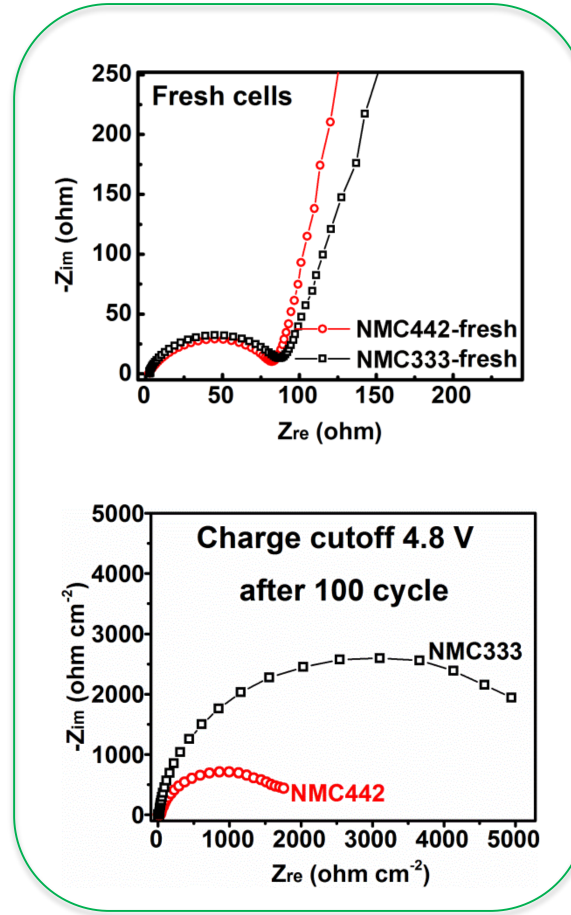
Technical Accomplishments

Interfacial characterization (NMC333 vs. NMC442)

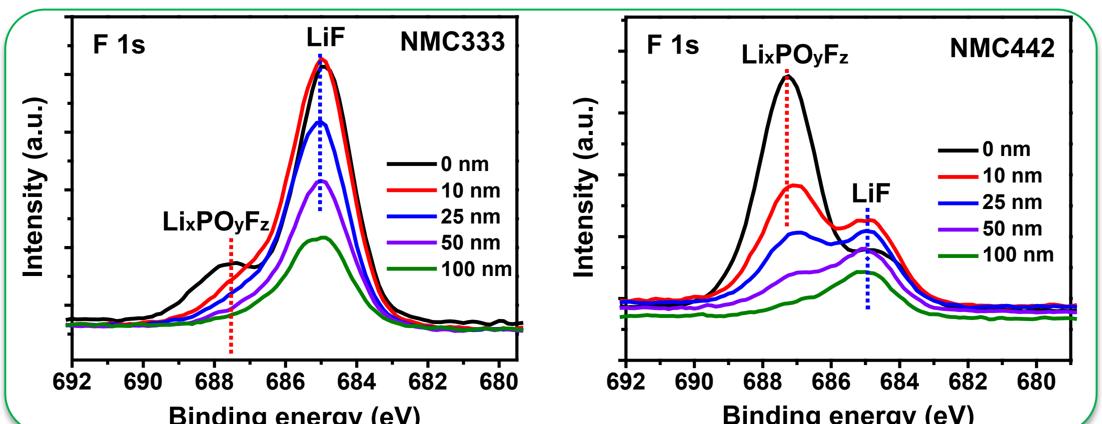
TOF-SIMS



EIS



XPS

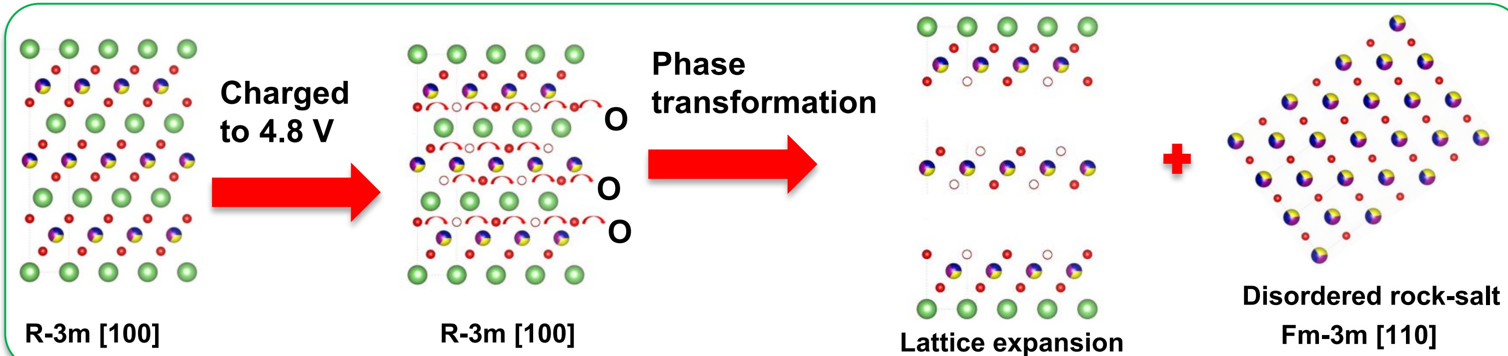


- ○ Cycled NMC333 leads to the formation of large amount of LiF on the surface.
- ➢ Cycled NMC442 exhibits a much smaller impedance than NMC333.

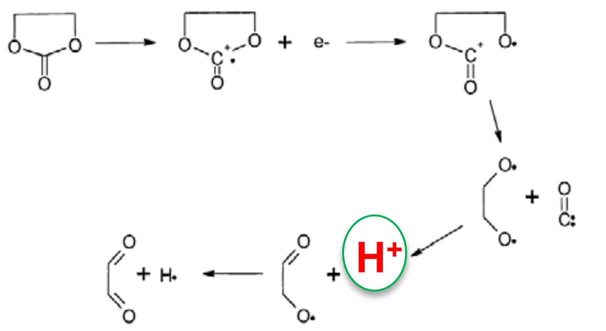
Technical Accomplishments

Capacity fading mechanism at high charge cut-off voltages

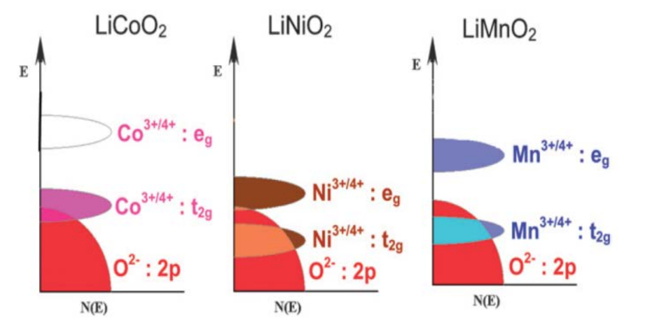
✓ **Oxygen removal and structural changes**



✓ **Acidic specie generation at high voltages,**
Co catalytic effects?



P. G. Bruce et al. / Chem. Mater., 2003, 15, 1984



A. Manthiram et al. / Energy Environ. Sci., 2008, 1, 621

- **Significant overlap between $Co^{3+/4+}$ t_{2g} band and O^{2-}: 2p band → easy oxygen removal**

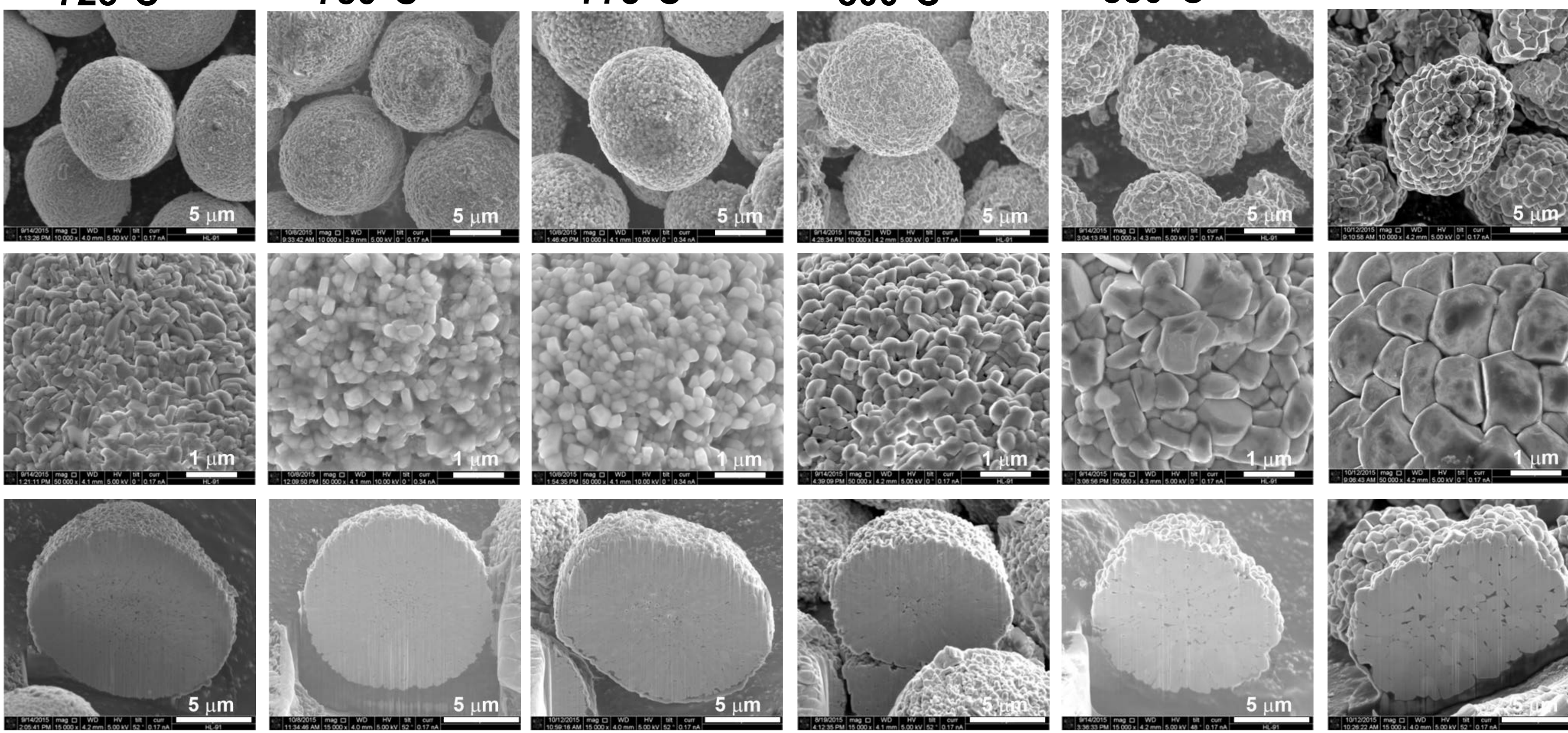
➢ Both the crystal structural and interfacial instability resulted in the fast capacity fading of NMC333 material at charge cutoff 4.8 V.

Technical Accomplishments

The Effects of Calcination Temperature on the Structure of Ni-rich NMC materials

SEM images of Ni-rich NMC material: $LiNi_{0.76}Mn_{0.14}Co_{0.10}O_2$ before cycling

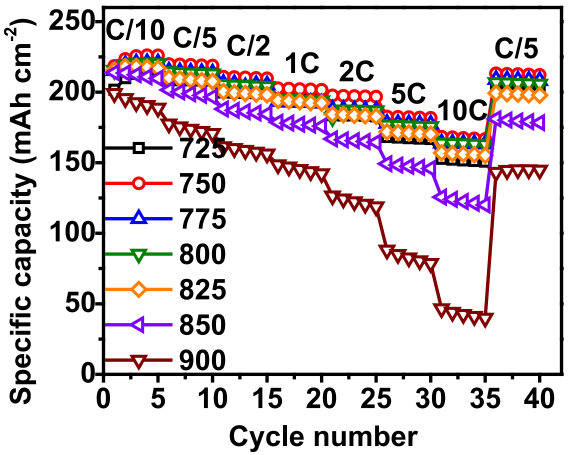
725°C | 750°C | 775°C | 800°C | 850°C | 900°C

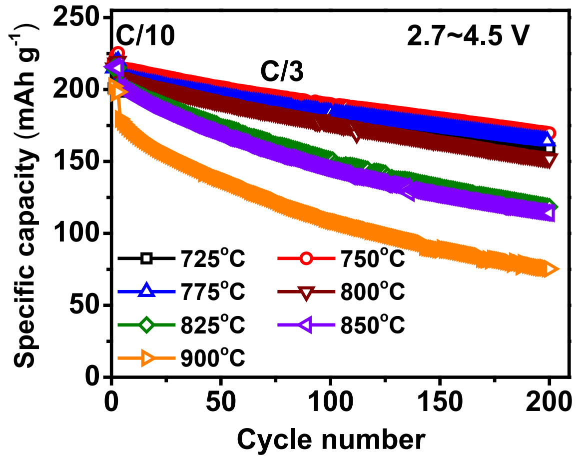


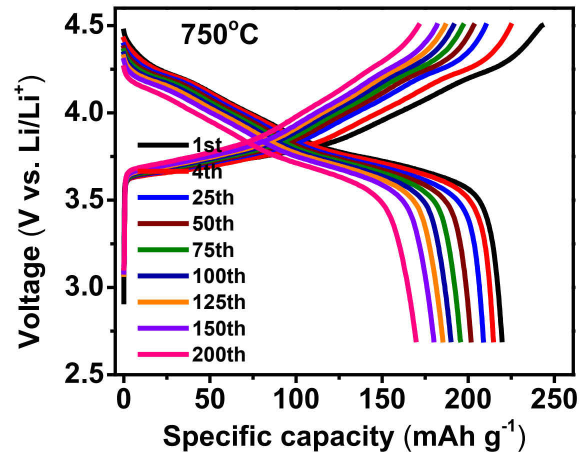
- ➢ **Higher calcination temperature leads to significant growth of primary particles and void space inside particles.**

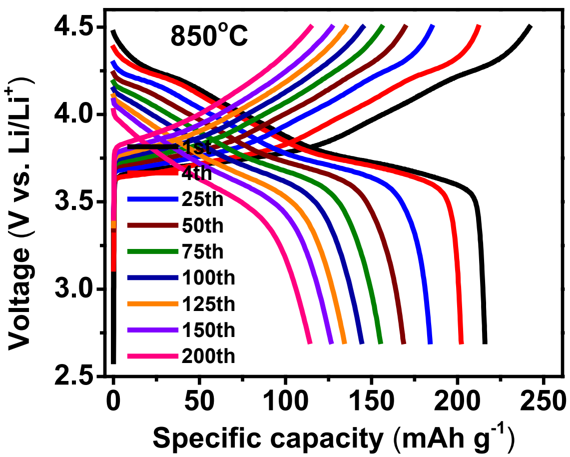
Technical Accomplishments

The Effects of Calcination Temperature on the Performances of Ni-rich NMC materials









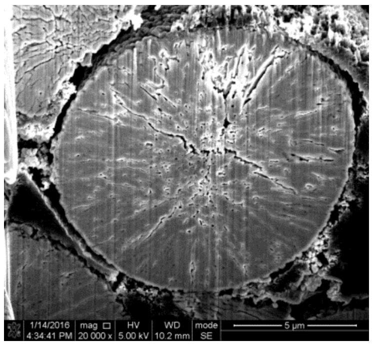
- The Ni-rich material prepared at 750^{o}C exhibit the best rate capability (delivering164 mAh g^{-1} at 10C rate) and best cycling stability (capacity retention of 79% after 200 cycles).

Technical Accomplishments

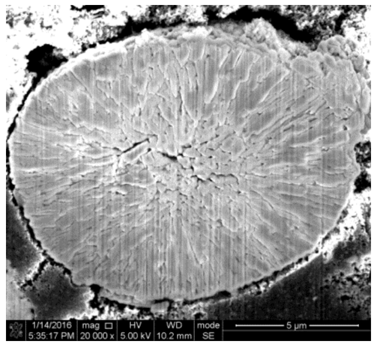
The Effects of Calcination Temperature on the Structure of Ni-rich NMC materials After Long Term Cycling

SEM images of Ni-rich NMC material: $LiNi_{0.76}Mn_{0.14}Co_{0.10}O_2$ after 200 cycles

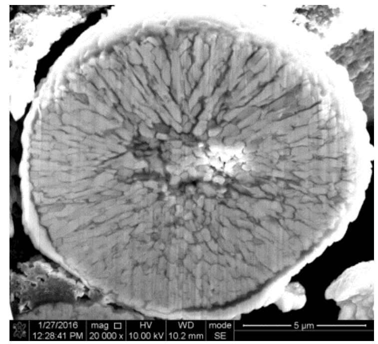
725°C



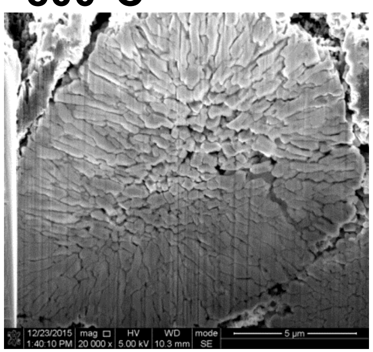
750°C



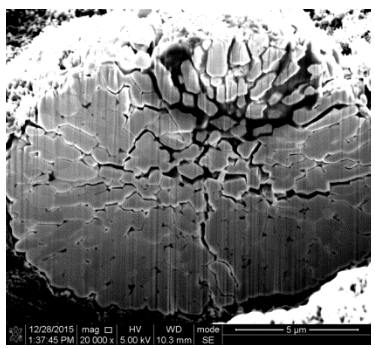
775°C



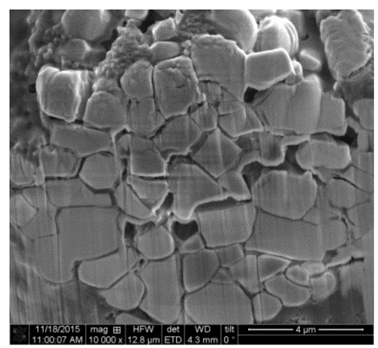
800°C



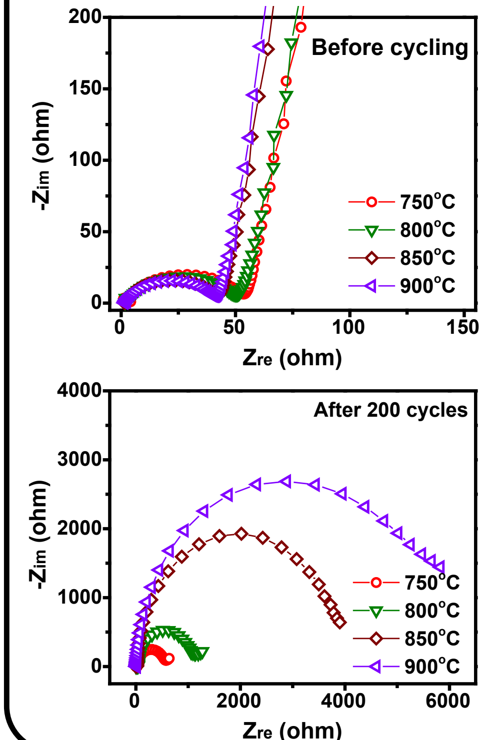
850°C



900°C



Impedance evolution

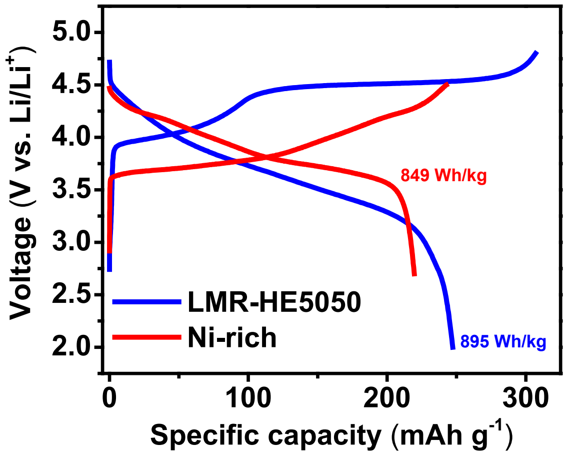


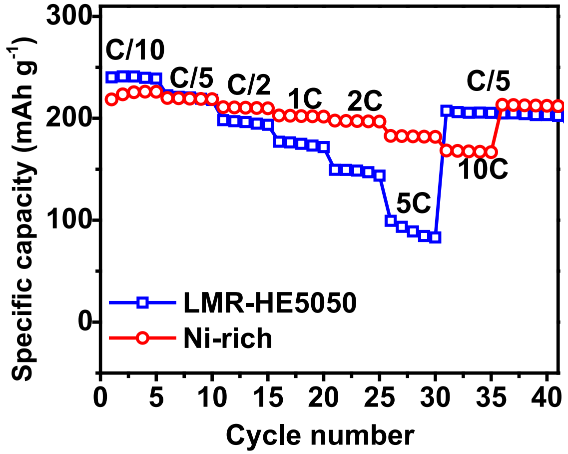
- ➢ The fast capacity degradation of material prepared at high temperature is ascribed to the increase of internal strain formation, particle crack, and rapid built-up of charge transfer resistance.

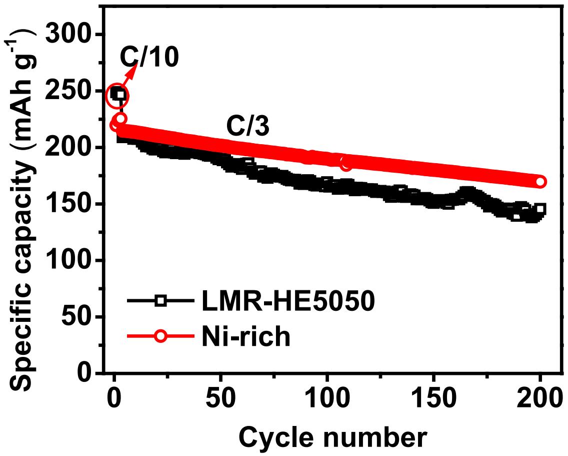
Technical Accomplishments

The Effects of Calcination Temperature on the Performances of Ni-rich NMC materials

Comparison between Ni-rich and Li-rich cathode materials







- Ni-rich NMC cathode exhibits an energy density comparable to those of LMR cathode when charged to 4.5V.
- Ni-rich NMC showed superior rate and cycling performance as compared to LMR cathode.

Collaboration and Coordination with Other Institutions

Partners:

- Argonne National Laboratory: Provide LMR/NMC cathode and standard anode materials for testing.
- Brookhaven National Laboratory: *In situ* XRD on electrode materials.
- Army Research Laboratory: electrolytes and additives
- SUNY Binghamton: Materials characterizations.

Remaining Challenges and Barriers

- Long-term cycling stability of traditional NMC cathode materials at high charge cut-off voltages needs to be further improved.
- Ni-rich cathode materials deliver much higher discharge capacity (200~220 mAh g^{-1}), but their thermal stability still need to be improved.

Proposed Future Work

- Use advanced characterization techniques to investigate the behavior of Co, Ni, and Mn in NMC cathode materials during battery charge/discharge.

- Identify the optimum charge cutoff voltage based on the achievable discharge capacity and its correlation with the structural stability of different NMC cathode materials.

- Optimize the compositions and interfacial stability of Ni-rich NMC cathodes to enable their high discharge capacity ($\geq$ 200 mAh g^{-1}) at acceptable charge cut-off voltages and enhance their long-term cycle life.

- Using gradient structure and surface coating to improve the safety feature of Ni-rich NM cathodes.

Pacific Northwest NATIONAL LABORATORY

Summary

1. High voltage operation of NMC333 cathode electrodes
   - 180 mAh/g capacity and less than 20% loss in 100 cycles were obtained at a charge cutoff 4.5 V.
   - The degradation of lithium metal anode should be carefully considered with increase of electrode loading to higher than 2 mAh cm^{-2}, especially at high rate.

2. Capacity degradation mechanism of NMC cathode materials was revealed at high charge cutoff voltages
   - The Composition (Ni, Co, Mn) showed significant effects on the performances of NMC materials at high charge cutoff voltages.
   - NMC442 cathode cycled at a high charge cut-off of 4.8 V exhibits much less cavity, strain/streams formation, smaller layered to rock-salt phase transformation and a much thinner SEI layer formation, leading to much stable cycling than NMC333.

3. The effects of calcination temperature on the performances of Ni-rich NMC cathode materials
   - Calcination temperature had significant effects on the electrochemical performances of Ni-rich cathode $LiNi_{0.76}Mn_{0.14}Co_{0.10}O_2$ (optimum temperature at ca. 750^{o}C) .
   - Higher temperature resulted in drastic growth of primary particles, which largely increased the lithium ion diffusion length, strain built-up and crack formation during battery cycling, leading to poor rate capability and fast capacity fading.

Acknowledgments

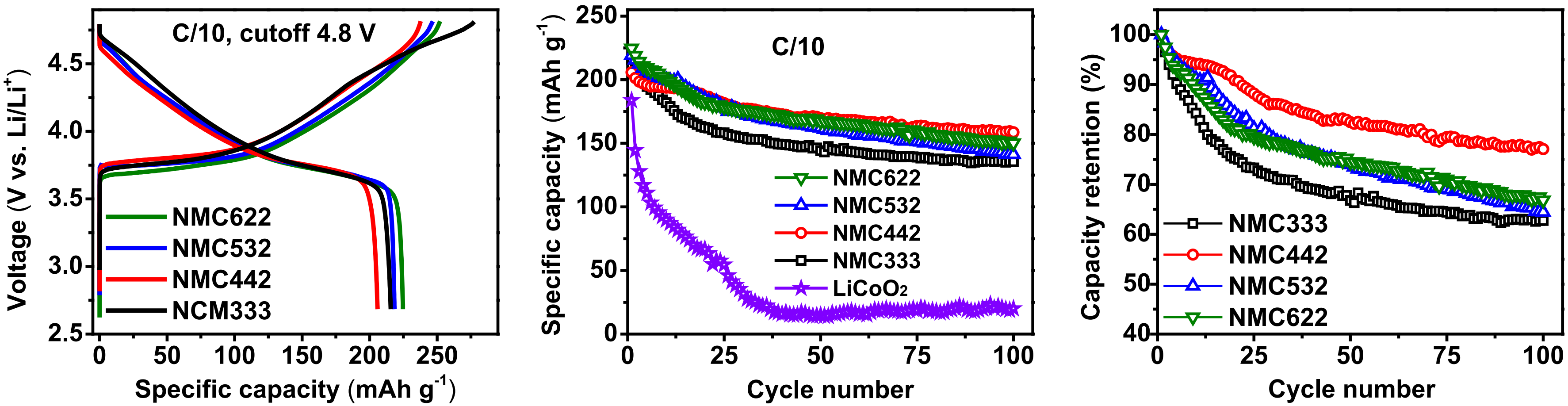
- ✓ Support from the DOE/OVT/BMR program is greatly appreciated.
- ✓ Team Members: Pengfei Yan, Wu Xu, Sookyung Jeong, Samuel Cartmell, Chongmin Wang, Jun Liu

Technical Backup Slides

Technical Accomplishments

Capacity Degradation Mechanism of NMC materials at High Charge Cutoff voltages

Cycling performances of NMC at high charge cutoff 4.8 V

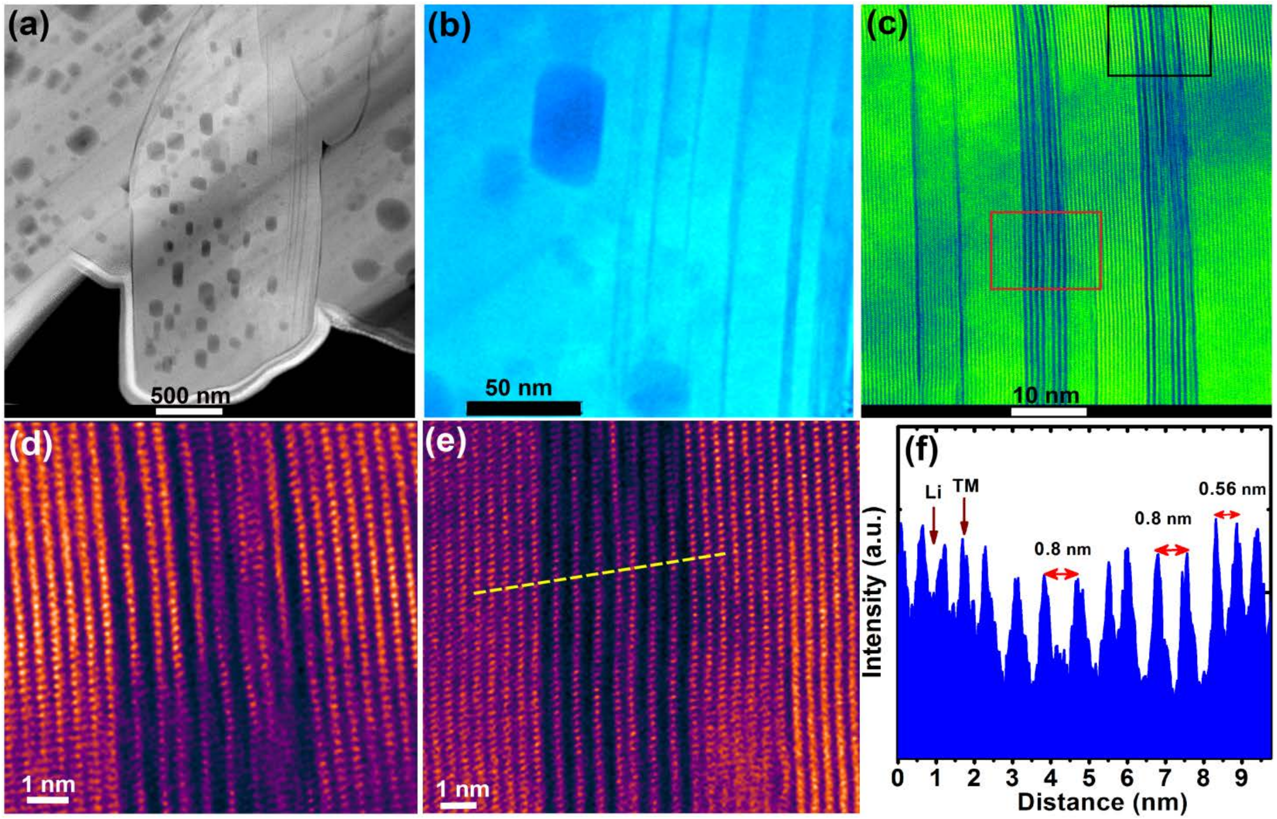


- Mn-rich NMC442 shows the best cycling performance due to the superior structural stability.
- Co-rich NMC333 shows poorest cycling stability, which is ascribed to the structural instability at deep delithiation in the presence of high content of Co.

Technical Accomplishments

Crystal structure evolution of NMC333 (cut-off 4.8 V)

STEM images of NMC333 after 100 cycles at 2.7 ~ 4.8 V



- Cycled NMC333 material show more & deeper Cavities, stream formation, and significant lattice expansion.