

High Energy, Long Cycle Life Lithium-ion Batteries for EV Applications

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Project ID: ES212

Overview

Timeline

- Project Start – Oct. 01 2013
- Project End – Sep. 30 2015
- Overall % Complete: **65%**
 - FY 2015 % Complete: 30%

Barriers

- Energy/power density
- Cycle and calendar life
- Battery component compatibility
- Abuse Tolerance

Budget

Total project funding: \$2,425 K

- DOE share: \$1,940K
 - Contractor share: \$485K
- FY 2014: \$1,243K
FY 2015: \$1,182K

Partners

- UT-Austin (Arumugam Manthiram, subcontract)
- EC Power (subcontract)
- Argonne National Lab (Zhengcheng Zhang, collaboration)
- Lawrence Berkley National Lab (Gao Liu, collaboration)

Relevance

Develop a **lithium-ion battery system** with high energy density, high power density, and good cycle life, and safe operation for EV applications.

Project scope

Design of full lithium-sulfur cell:

- Layered Oxide Cathode – high energy/power, stable
- Advanced Silicon Alloy-carbon Anode – high energy/power, stable
- Functional Binder – Improve cyclability
- Electrolyte – stabilize electrodes and improve safety

Performance targets

2.5 Ah cells

330 Wh/kg (770 Wh/L)

1600 W/L

Cycle life 500+ cycles

Excellent safety characteristics

Project Milestones - I

- Scale up the state of the art anode and cathode synthesis (completed)
- Delivery of baseline cells (completed)
- Si-carbon anode with 1500 mAh/g capacity, 95% capacity retention after 100 cycles at C/3, coulombic efficiency >99% (completed)
- Surface-coated, Ni-rich layered oxide cathode with 190 mAh/g capacity, 95% capacity retention after 100 cycles at C/3 (completed)
- Si-carbon anode with 1900 mAh/g capacity, 95% capacity retention after 300 cycles at C/3, coulombic efficiency >99.9% (completed)
- Surface-coated, Ni-rich layered oxide cathode with 220 mAh/g capacity, 95% capacity retention after 300 cycles at C/3 (in progress)

Project Milestones - II

- Scale to 50g batches of advanced anode and cathode (completed)
- Demonstrate 2.5 Ah prismatic cells with: Energy density of: 250 Wh/kg (700 Wh/l); Power density of 1200 W/l with energy density > 150 Wh/kg; Cycle test of: 95% capacity retention in 300 cycles at C/3 and 1C; and Cell self-discharge rate of < 1%/day (in progress)
- Complete delivery of 12, 2.5 Ah prismatic cells to DOE with the following specifications: Energy density of 330 Wh/kg (770 Wh/l); Power density of 1600 W/l with energy density > 200 Wh/kg; Cell self-discharge rate of < 0.3%/day; Cycle test of 95% capacity retention in 500 cycles at C/3 and 1C (in progress)

Approach / Strategy

- **Si-alloy carbon composite anodes**

- Design micro-sized Si/Si alloy-carbon anodes composed of nanoscale building blocks to enable both good electrochemical performance and high tap density
- Construct conductive network at the electrode level to achieve high areal capacity

- **Functional binders**

- Prepare conductive and cross-linked binders to form interpenetrated conductive network to accommodate volume change of Si and improve integrity of Si electrodes

- **Nickel-rich layered oxide cathodes**

- Control the composition, microstructure, and morphology through novel synthesis and processing approaches
- Condition the surface to suppress aggressive reaction with the cathode surface

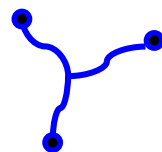
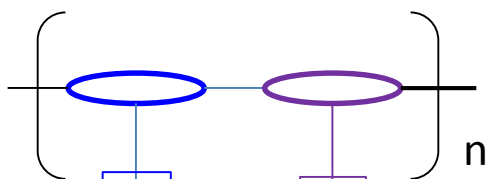
- **Electrolytes**

- Develop novel fluorinated electrolytes and additives to stabilize the anode SEI, prevent electrolyte reaction at the cathode surface
- Improve cell safety by enhancing high temperature stability and decreasing flammability

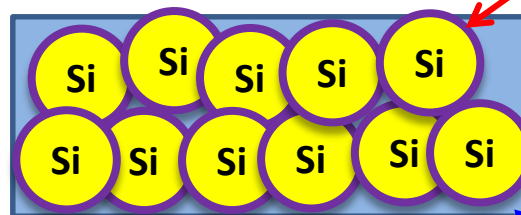
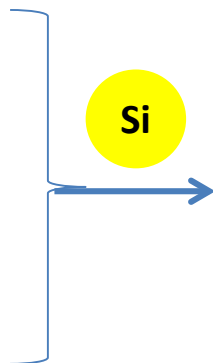
Technical accomplishments

I. Advanced polymer binder

Block I Block II



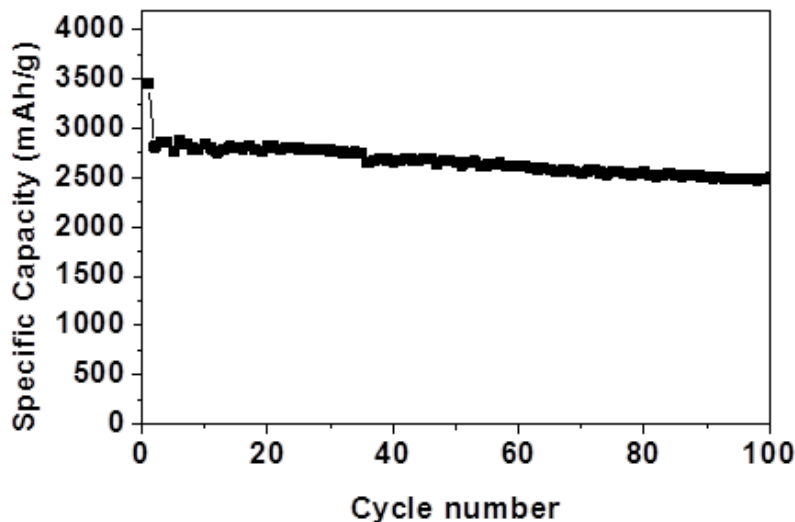
Cross-linker



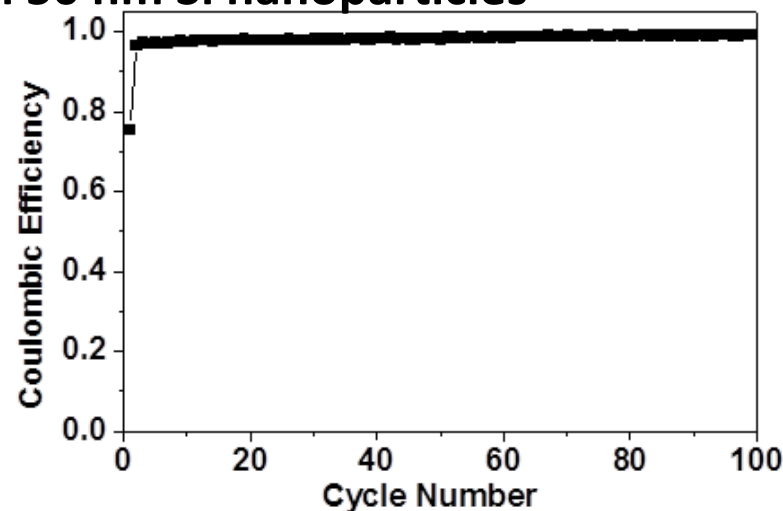
Coating on Si particles
to mediate interface

Rigid 3D network

Performance of commercial 50 nm Si nanoparticles

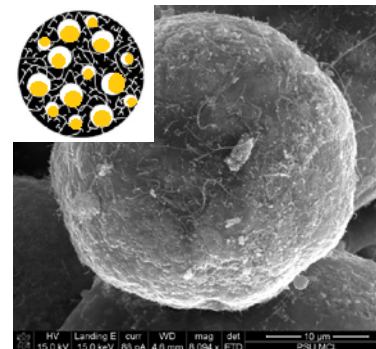
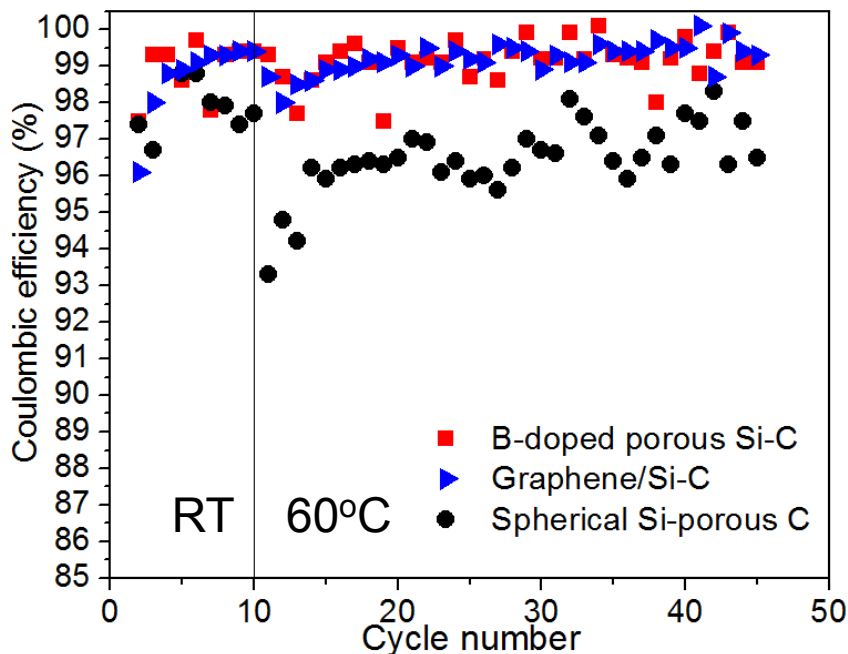
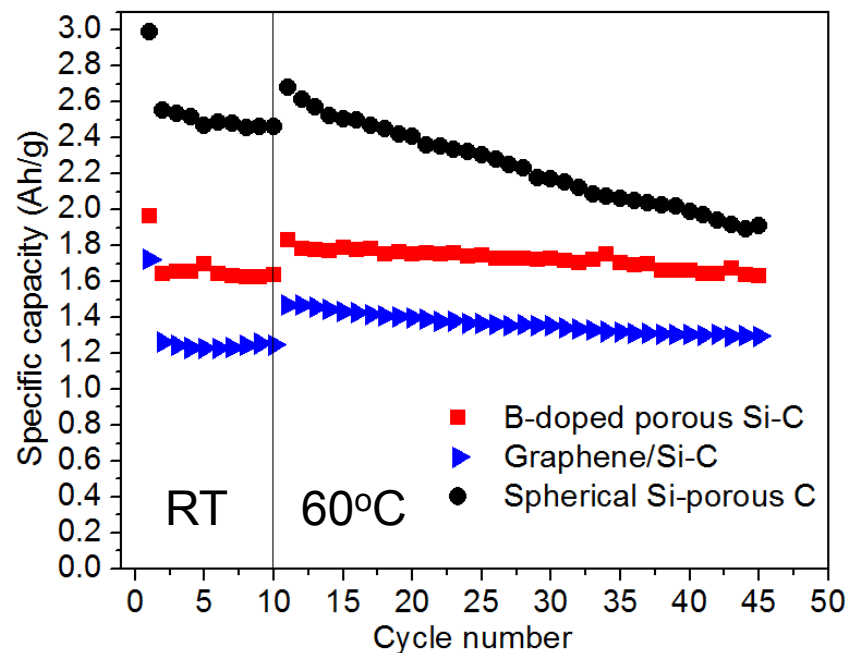


Good cycling stability

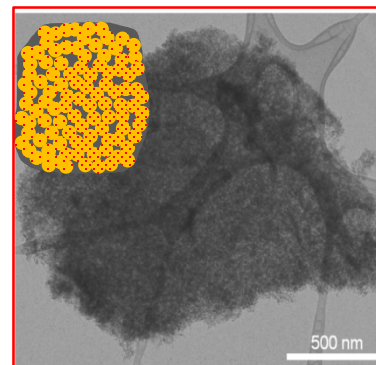


High efficiency

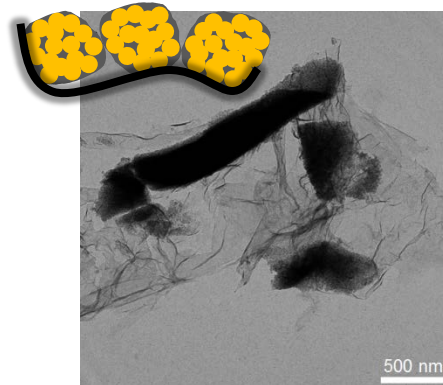
II. Material development and scale up



- High capacity
- Fast fading
- Low CE



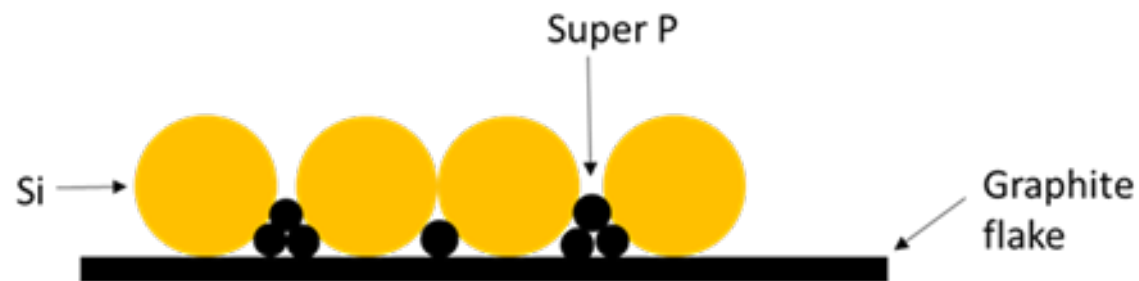
- Medium capacity
- Stable cycling
- High CE



- ▶ Low capacity
- ▶ Stable cycling
- ▶ High CE

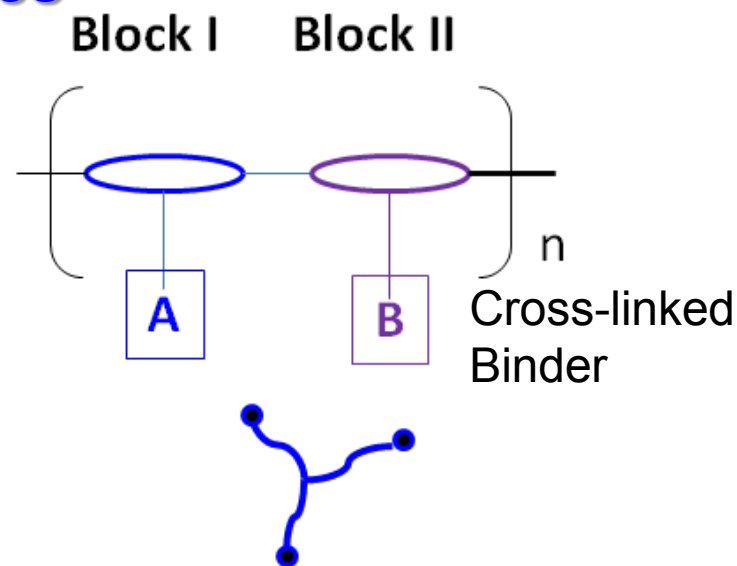
The B-doped porous Si-C anode materials
scale up to 50 gram

III. Fabrication of Si/graphite electrodes

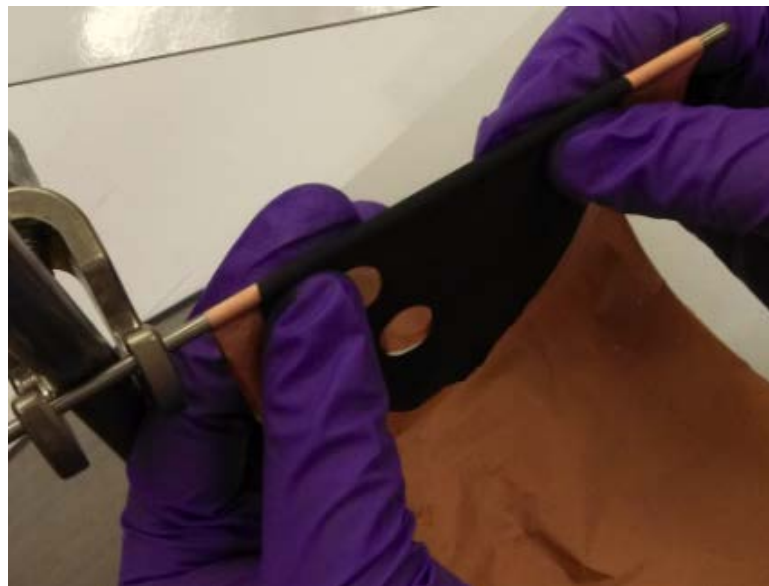


Rational design of electrode with conductive network

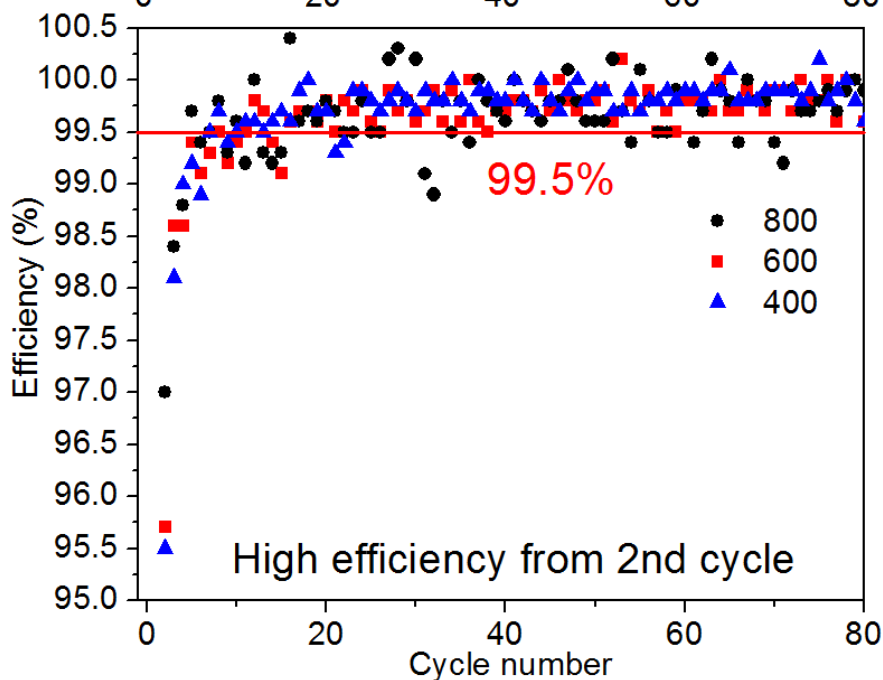
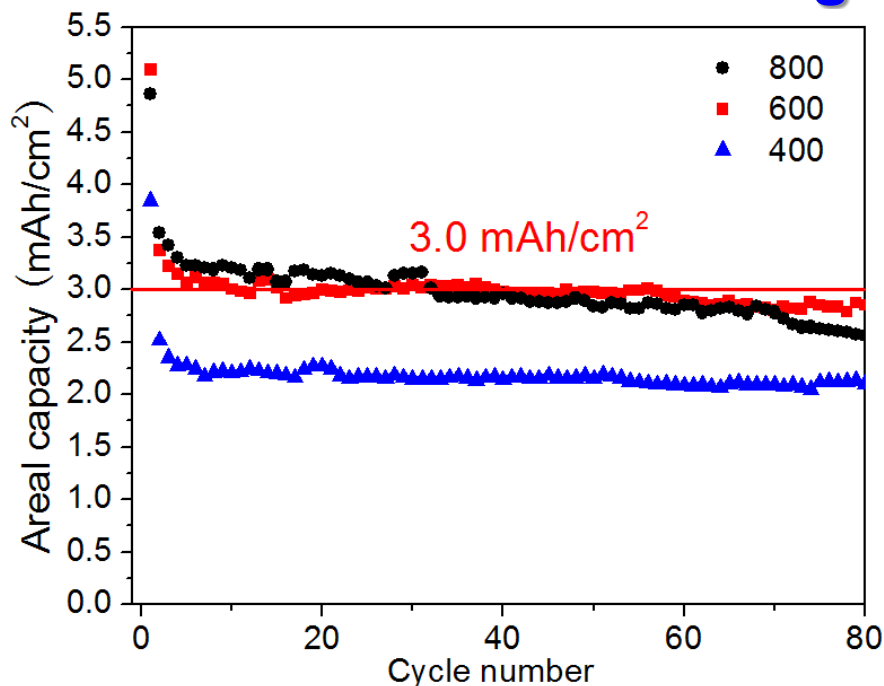
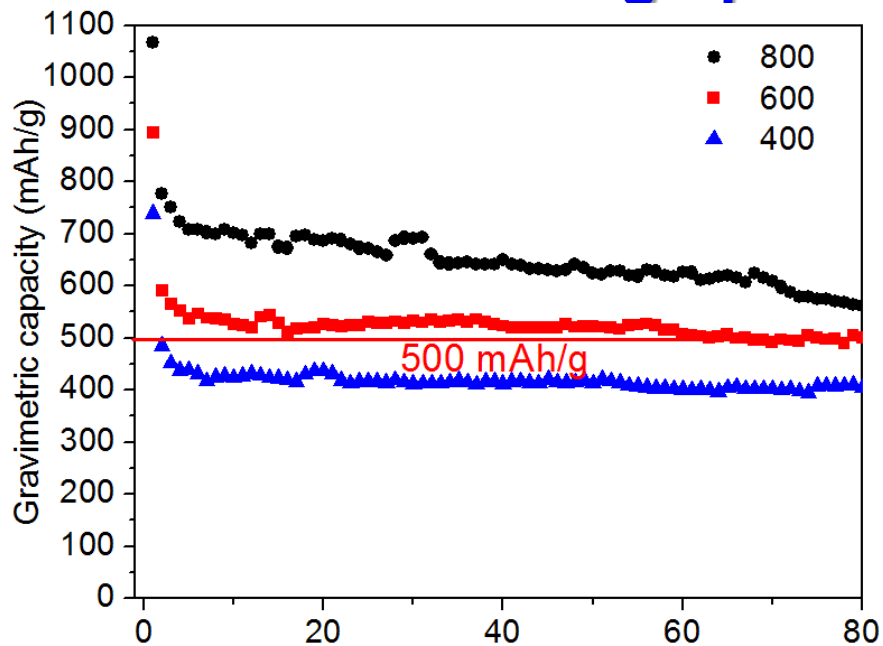
Uniform coating



Cross-linker
High flexibility



III. Fabrication of Si/graphite electrodes—half cell testing



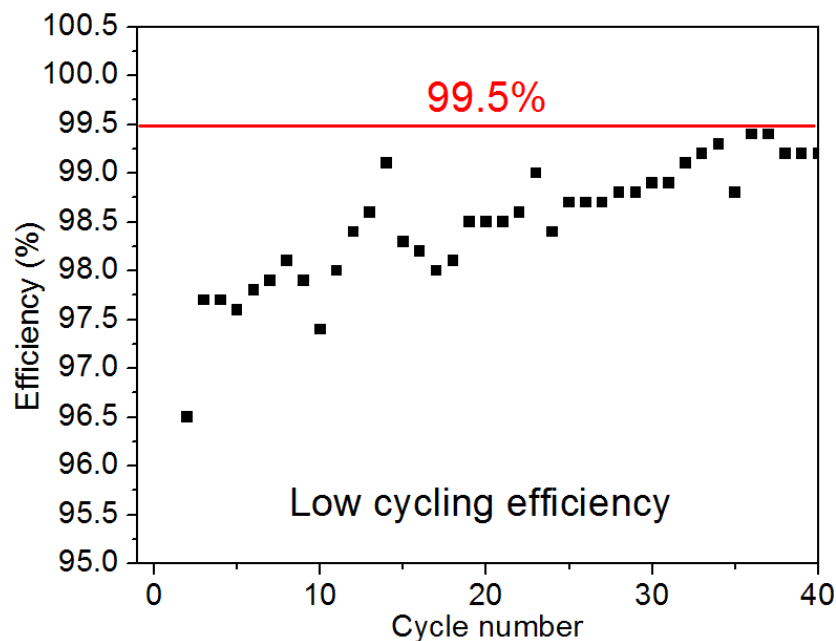
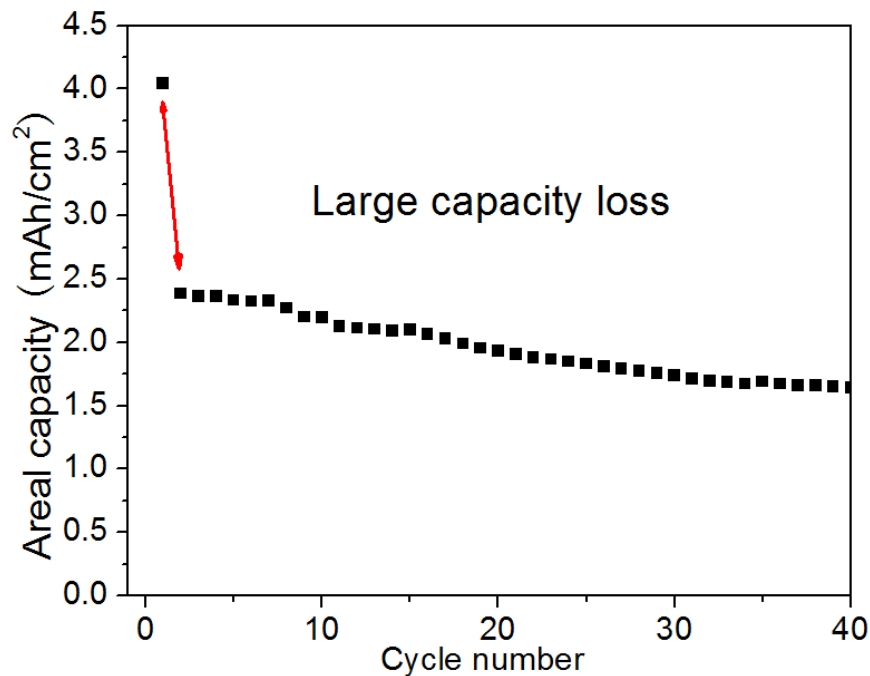
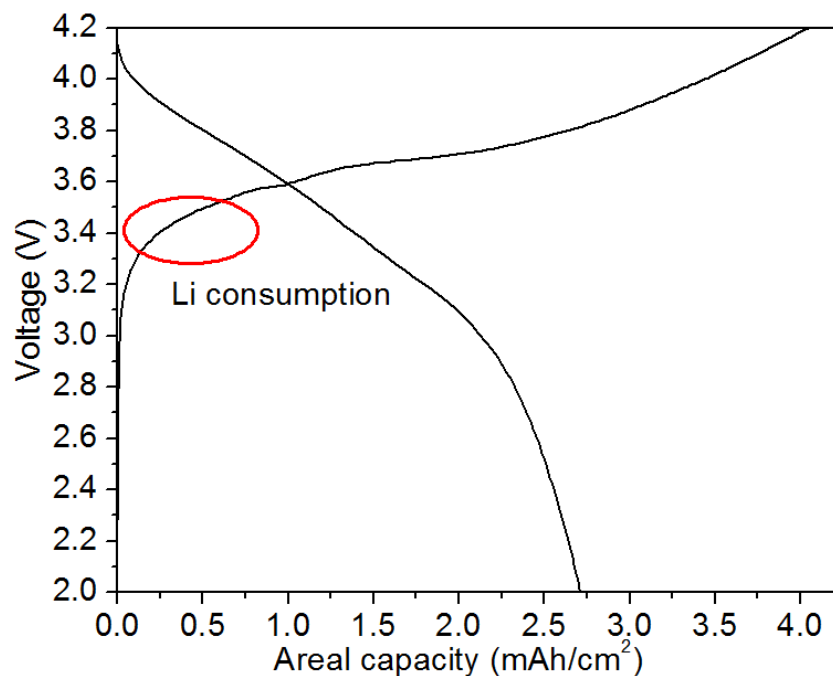
1st cycle efficiency: >72%

Average efficiency after 1st cycle: >99.6%

Gravimetric capacity > 500 mAh/g
(based on whole electrode)

Areal capacity: 1st cycle ~5 mAh/cm²
stable > 3.0 mAh/cm²

III. Fabrication of Si/graphite electrodes—full cell testing



Coupled with NCM cathodes

1st cycle efficiency: 67%

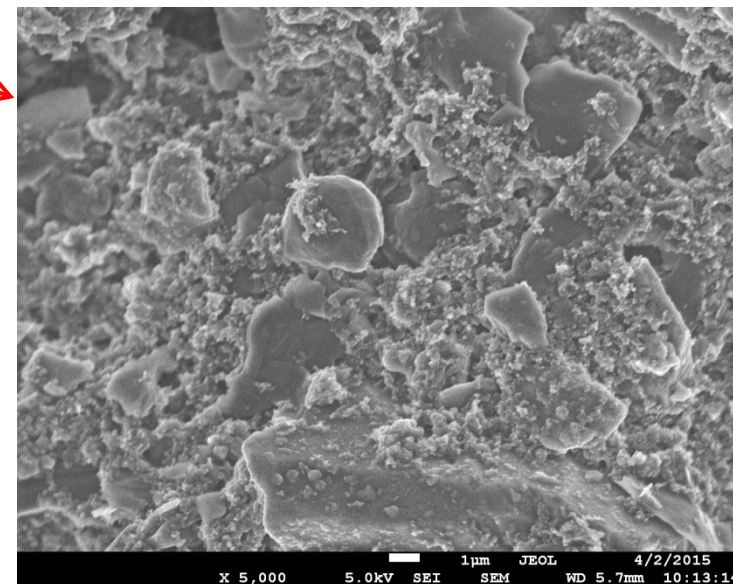
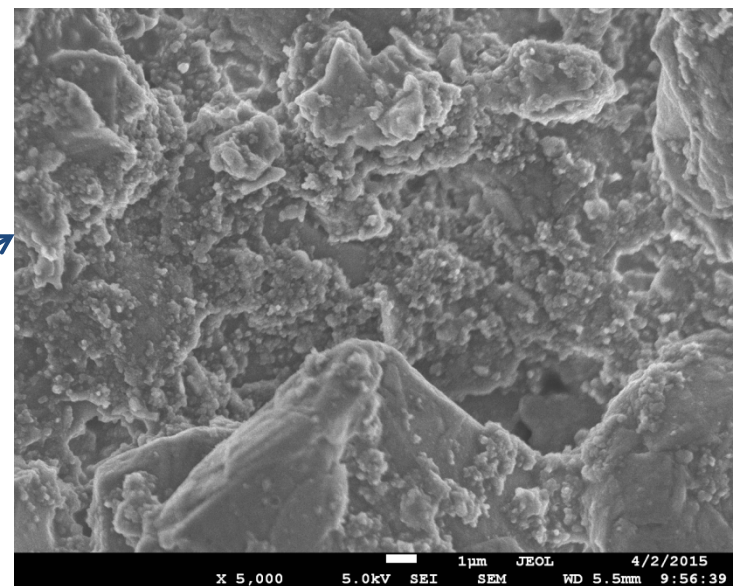
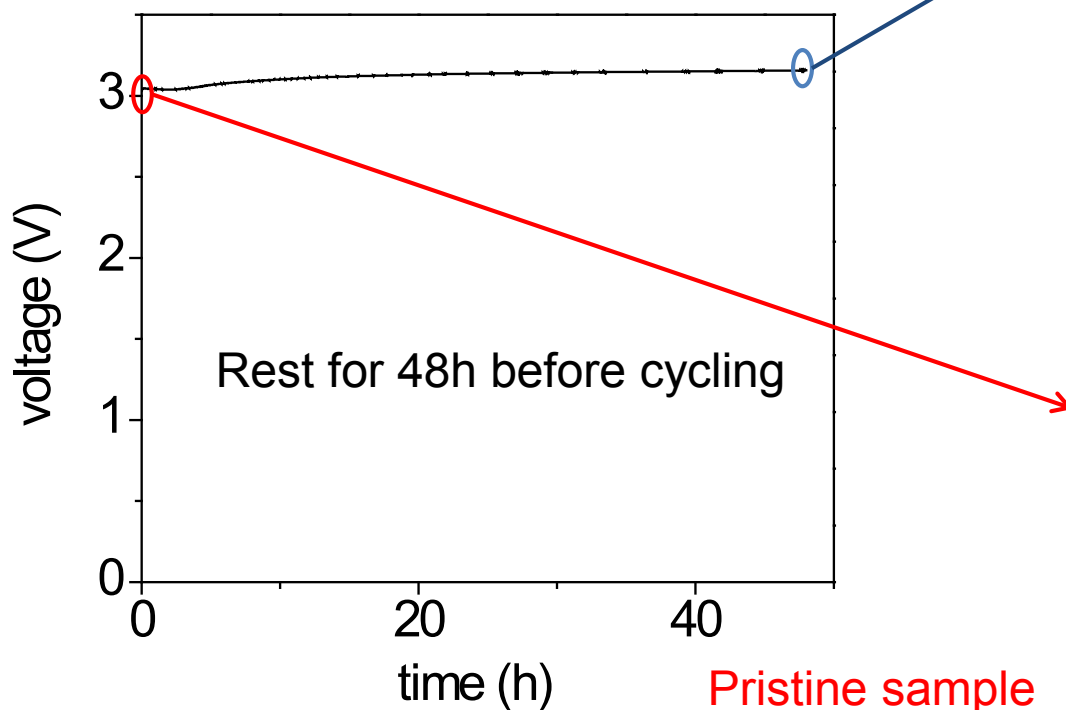
Average efficiency after 1st cycle: 98.5%

Cycling is not stable

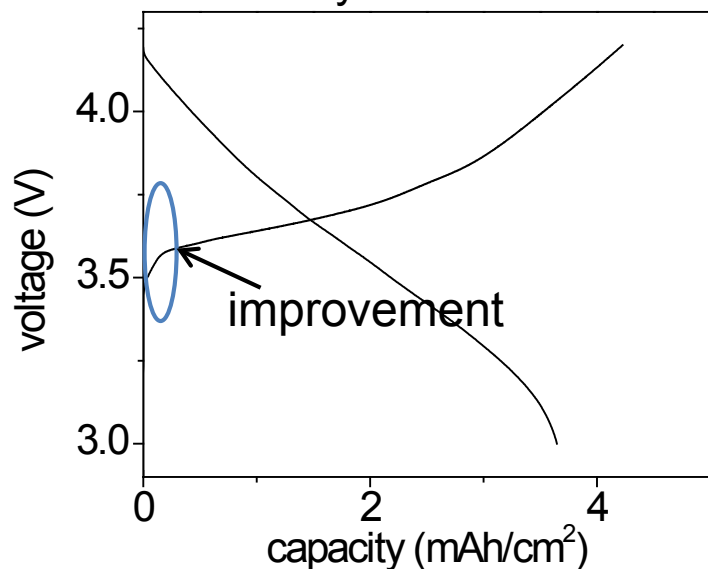
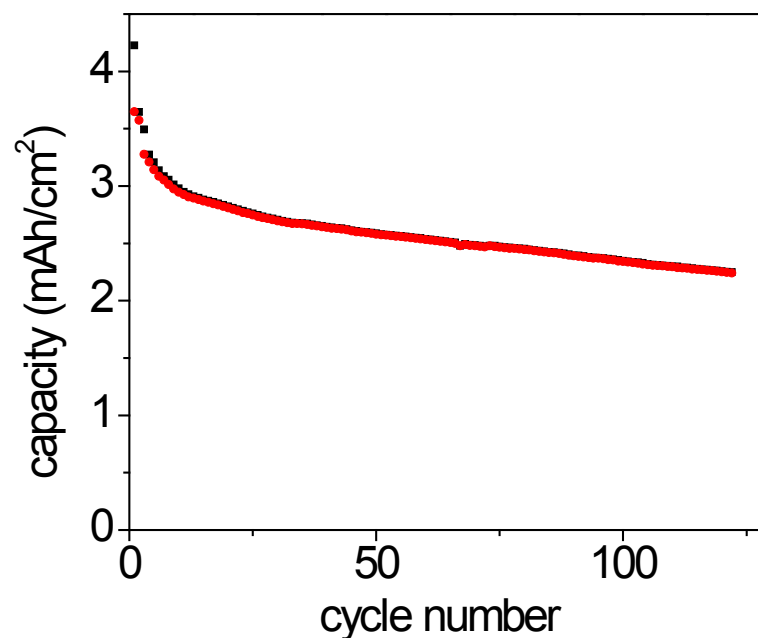
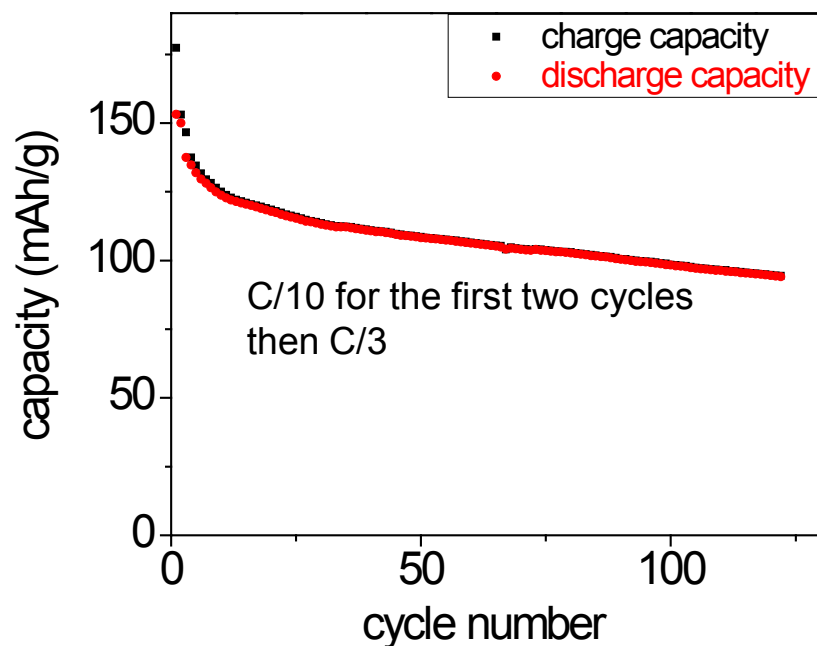
IV. Prelithiation of Si/graphite electrodes

Si-graphite/NMC full cell with SLMP prelithiation

Sample after prelithiation
Before cycling



IV. Cycling Performance of Full Cell of Prelithiated Si/graphite Anode and NCM Cathode

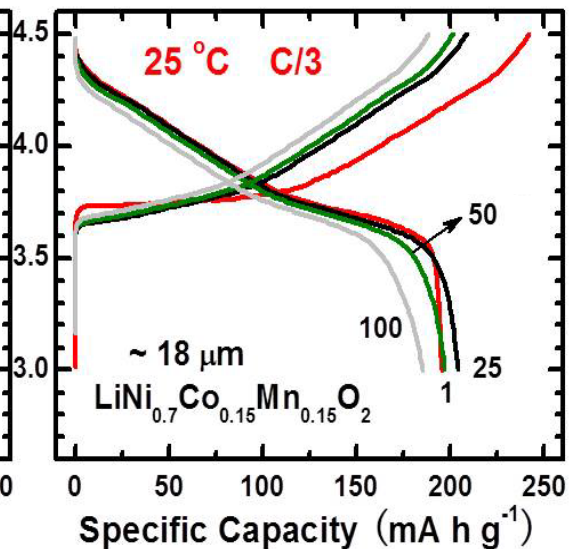
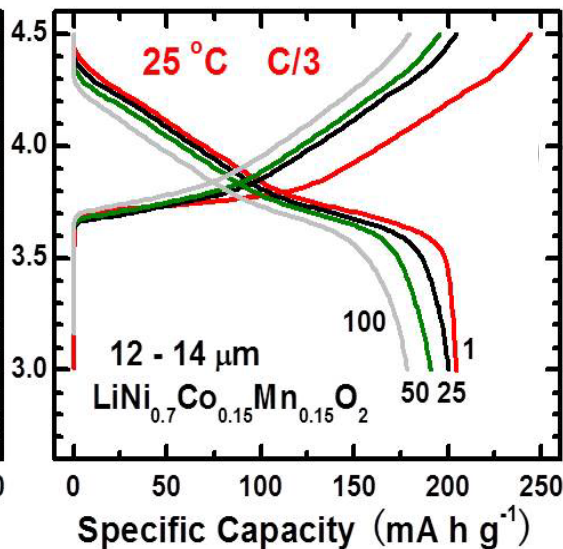
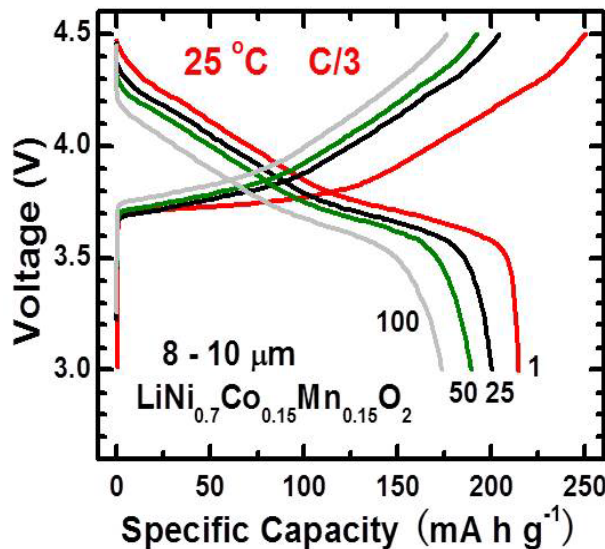
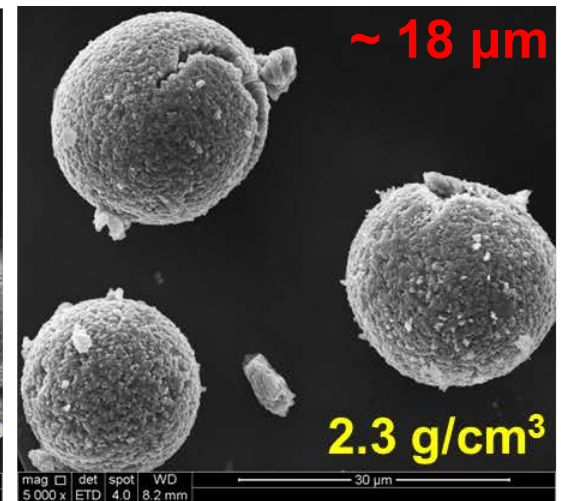
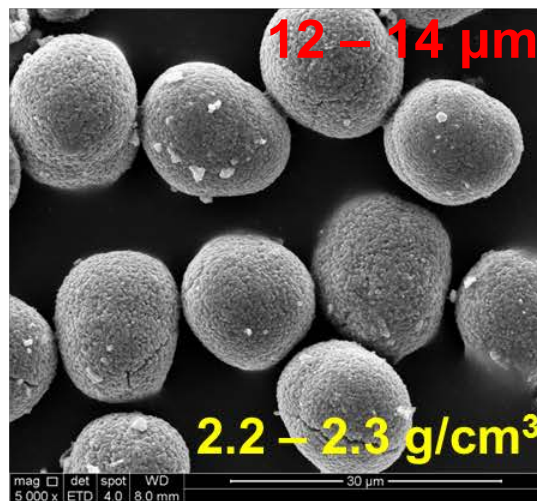
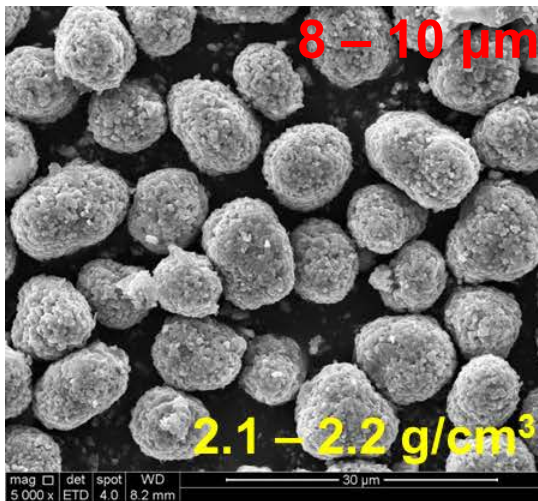


Improved efficiency
1st cycle efficiency: 86.32%
100th cycle efficiency: 99.81%
Improved cycling stability

1st cycle voltage profile

V. Layered Oxide Cathodes

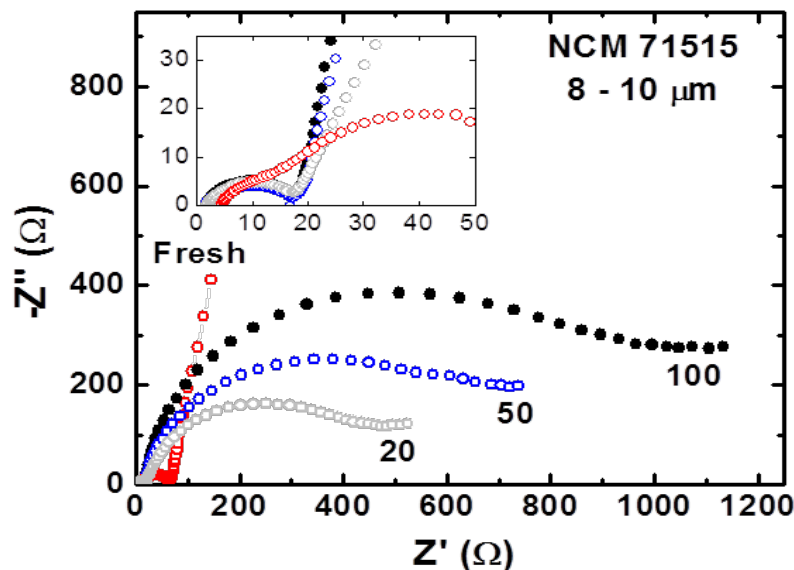
Secondary Particle Size Effect: Cell Performance



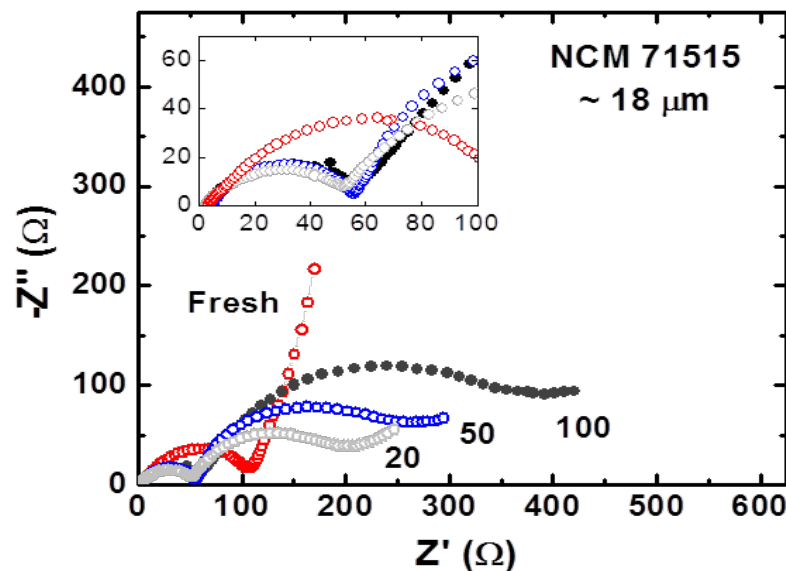
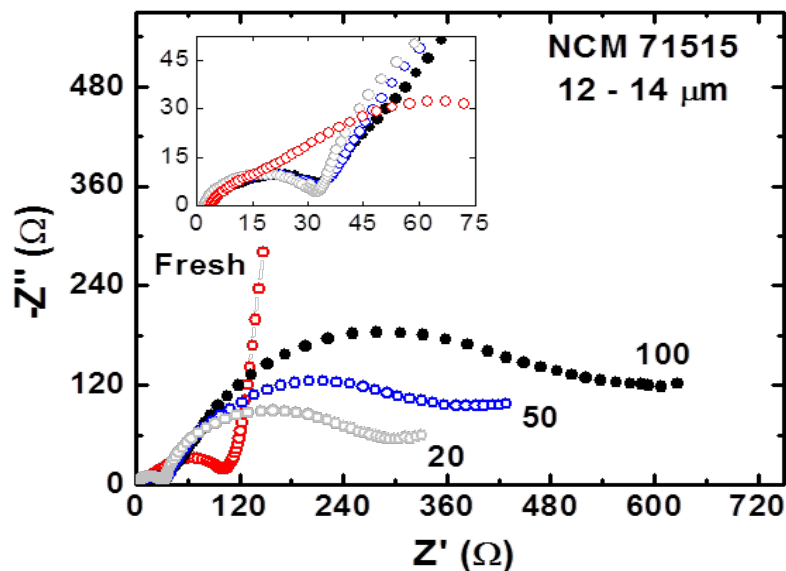
Capacity and voltage fading are suppressed with increasing secondary particle size

V. Layered Oxide Cathodes

Secondary Particle Size Effect: Impedance Evolution

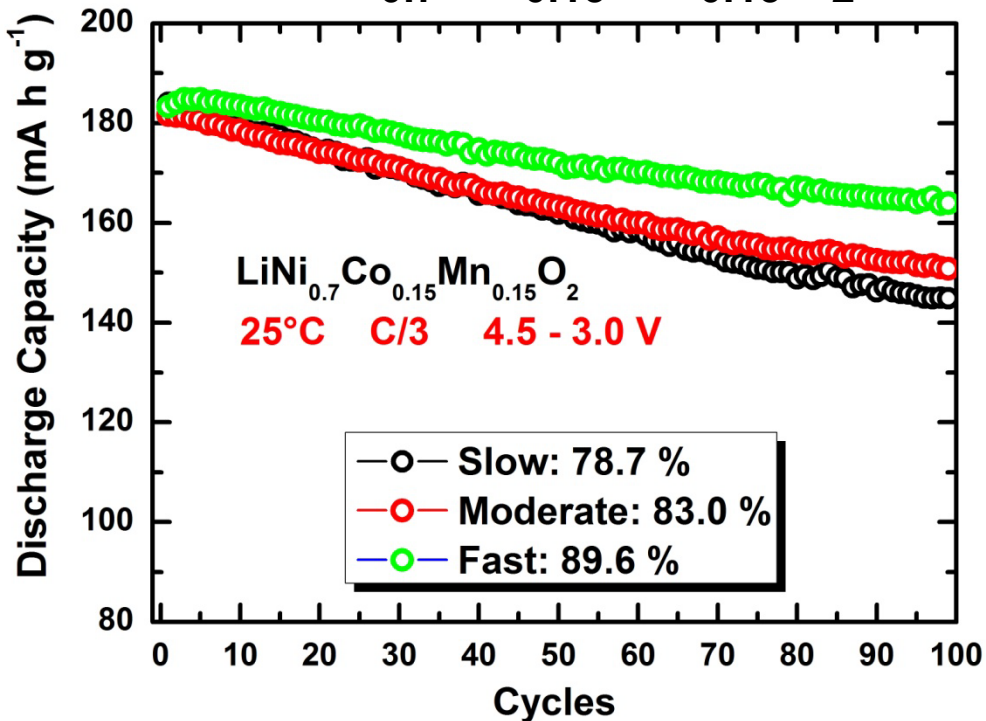


- Overall cathode impedance decreases with increasing secondary particle size
- Charge-transfer resistance is the chief contributor to overall cathode impedance
- Charge-transfer resistance decreases with increasing secondary particle size
- Surface film resistance increases with increasing secondary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

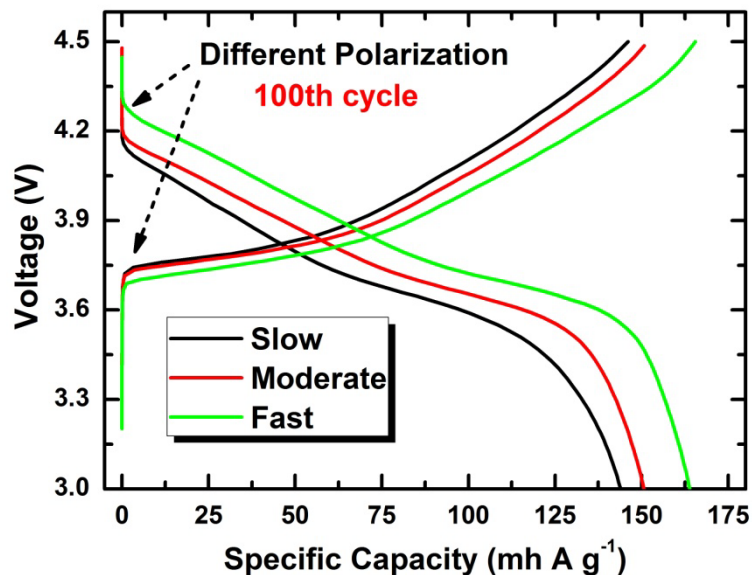
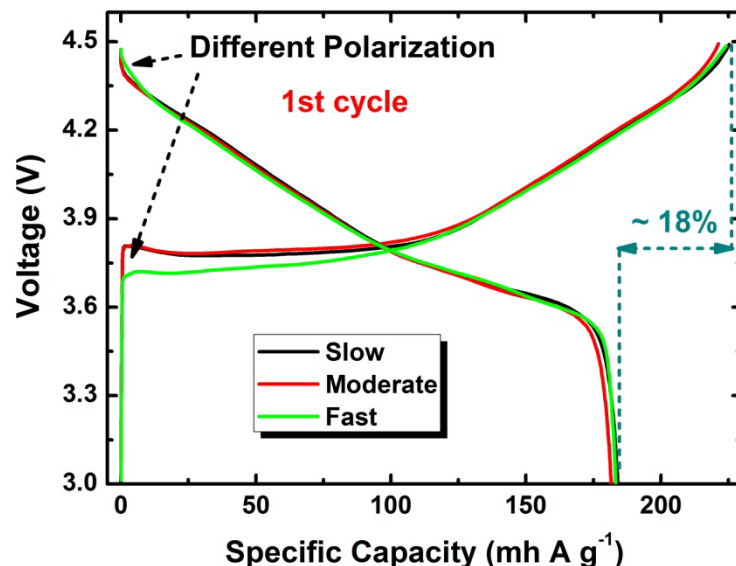


V. Layered Oxide Cathodes

Cooling Rate Effects on Electrochemical Performance

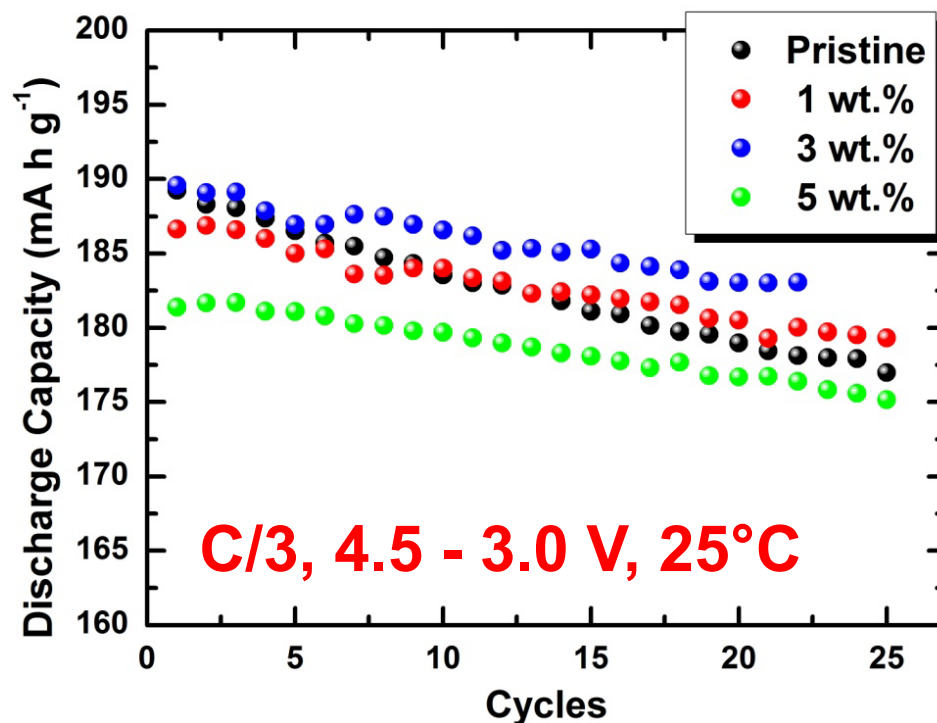
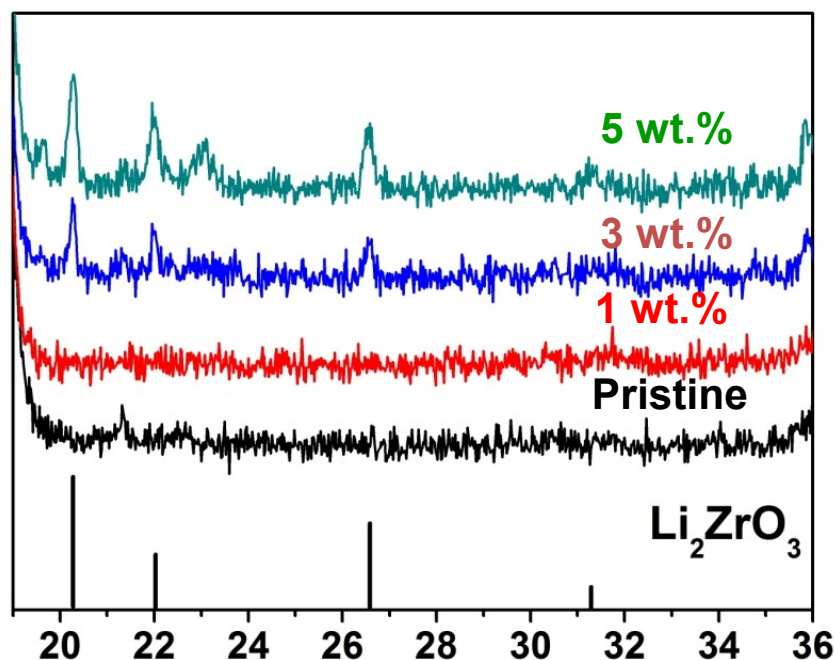


- Faster cooling rate shows lower initial capacity but superior cyclability
- The superior cyclability may be ascribed to the lower polarization during cycling



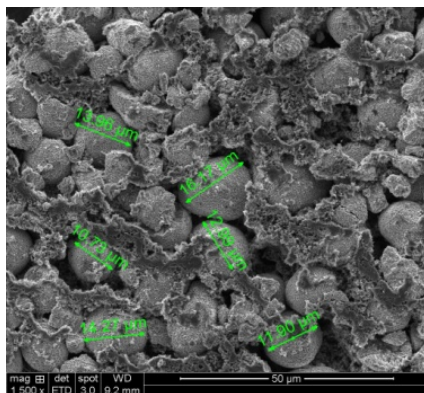
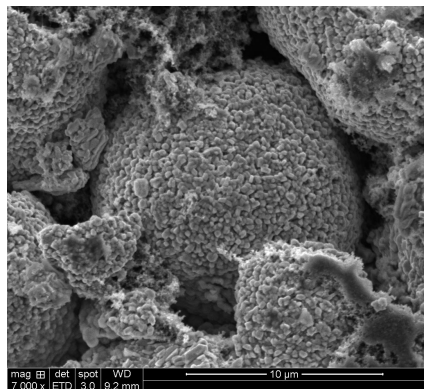
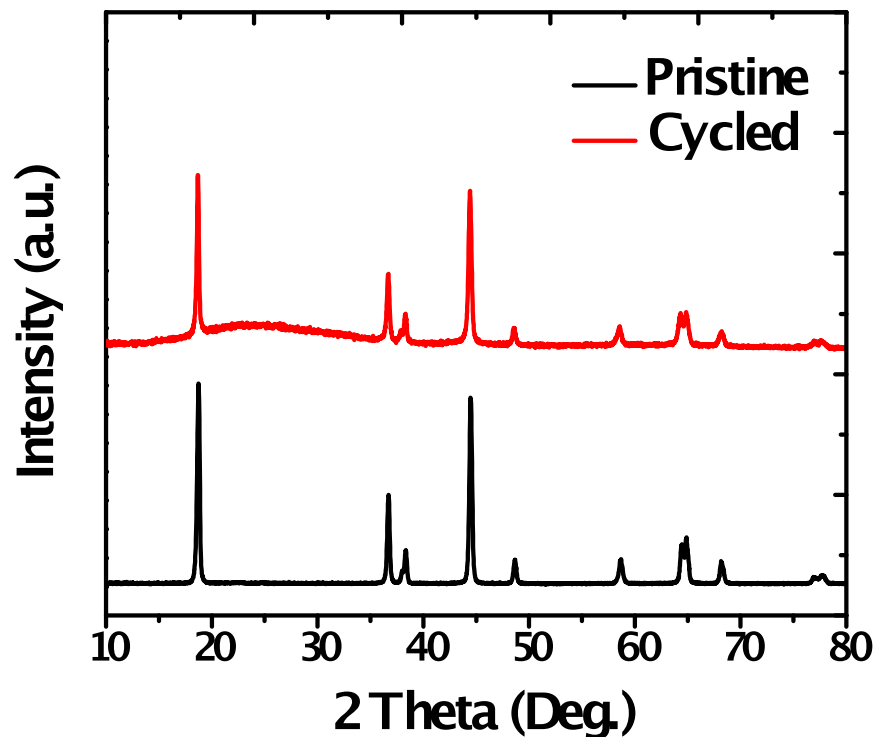
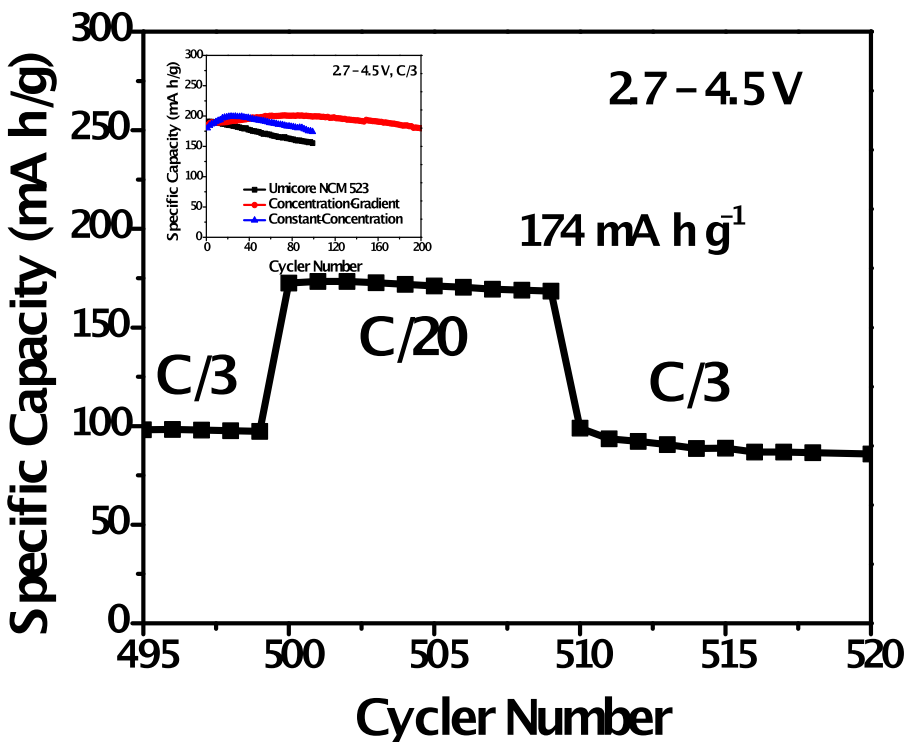
V. Layered Oxide Cathodes

Li_2ZrO_3 -coated $\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$



- Li_2ZrO_3 -coated $\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ materials are prepared by co-precipitation method
- 3 wt.% Li_2ZrO_3 coating shows best performance compared to other samples

Concentration-Gradient Materials (After 500 cycles)



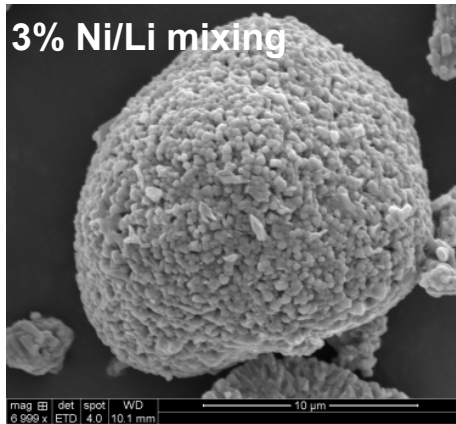
- After 500 cycles, capacity can reach 174 mA h g⁻¹ on lowering to C/20 rate , but < 100 mA h g⁻¹ when changed back to C/3
- Ex-situ XRD and SEM show no notable changes compared to the pristine sample
- Not good cyclability at high C-rate?

After 520 cycles

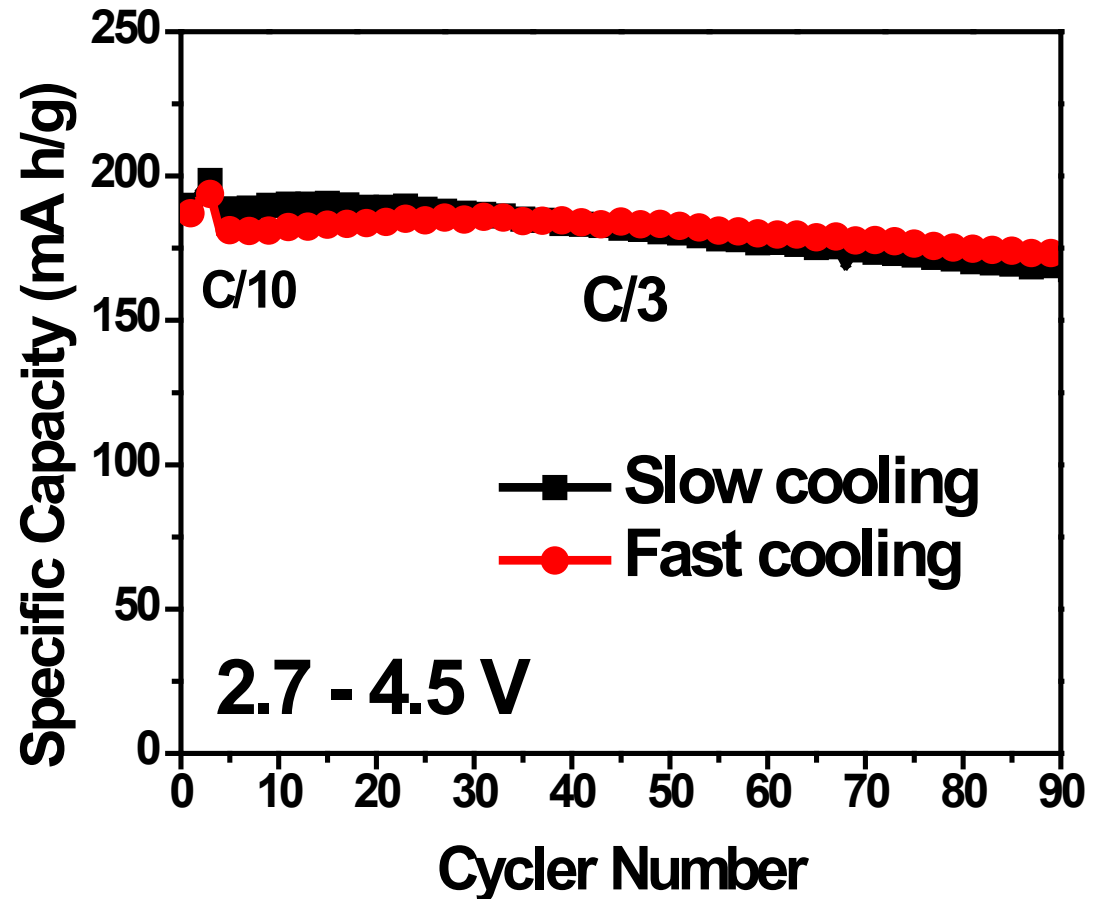
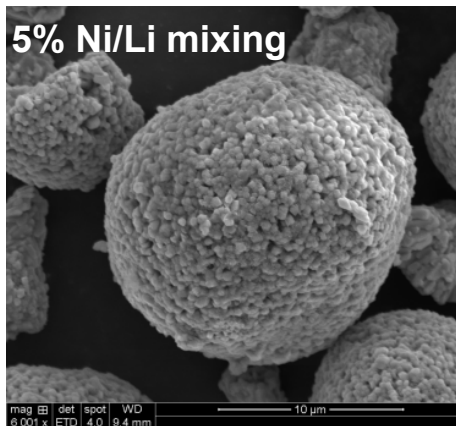
V. Layered Oxide Cathodes

Quenching CG sample to Improve Cyclability

Slow cooling



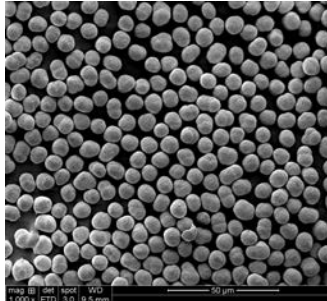
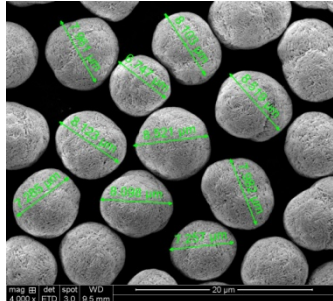
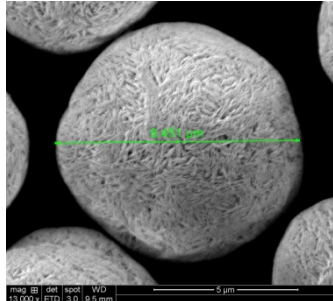
Fast cooling



➤ No notable changes in morphology can be found with different cooling rates, but faster cooling rate results in a higher mix rate of Ni/Li, but superior cyclability

V. Layered Oxide Cathodes

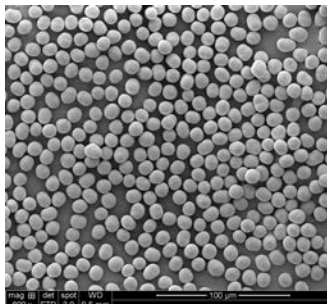
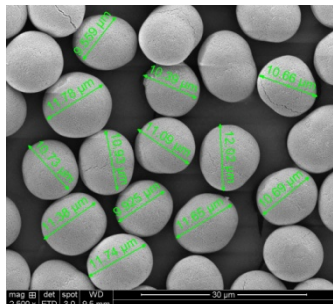
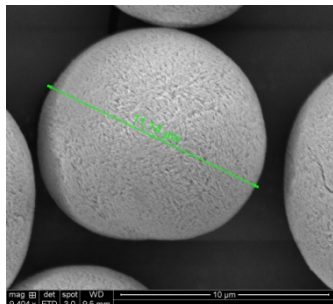
New Batch: Precursors



Sample A: 8 μm

ICP: Ni:Co:Mn = 0.9 : 0.1 : 0

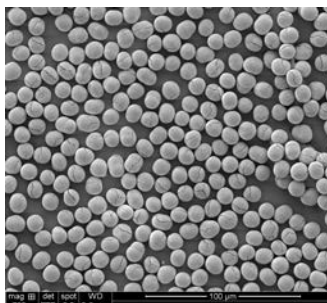
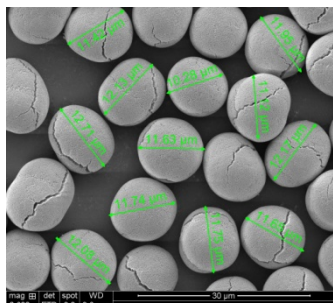
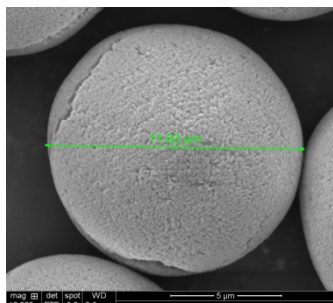
Tap density: 2.08 g/cm³



Sample B: 11 μm

ICP: Ni:Co:Mn = 0.78:0.1:0.12

Tap density: 2.12 g/cm³



Sample C: 11-12 μm

ICP: Ni:Co:Mn = 0.76:0.1:0.14

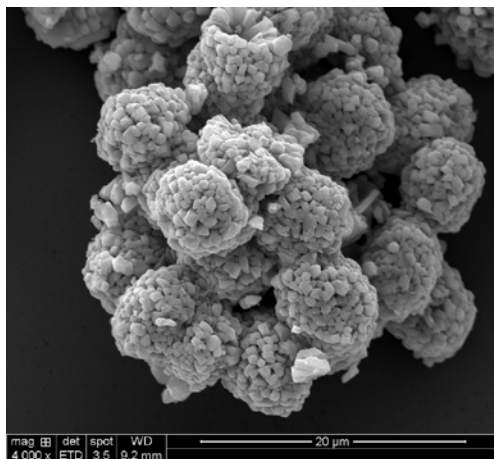
Tap density: 2.15 g/cm³

- Uniform Ni-rich precursors with spherical shape have been prepared from 8 to 12 μm; tap density increases with increasing secondary particle size

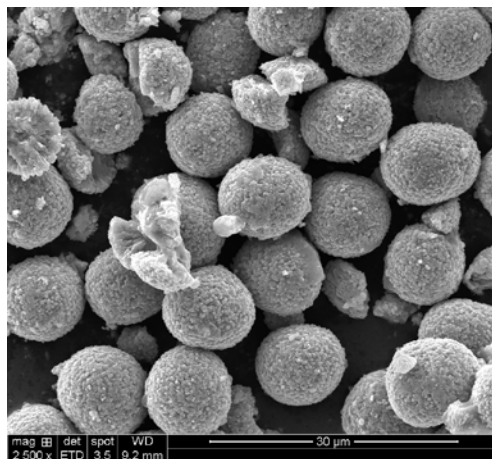
V. Layered Oxide Cathodes

New Batch: Gradient Cathode

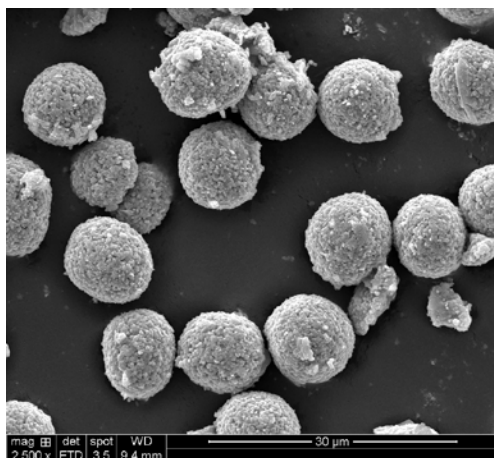
Sample A: 7-8 μm



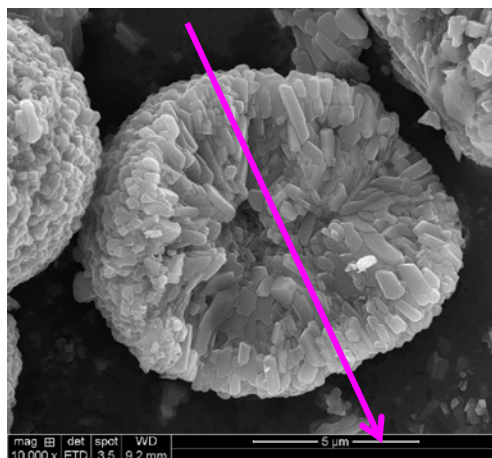
Sample B: 10-11 μm



Sample C: In Air

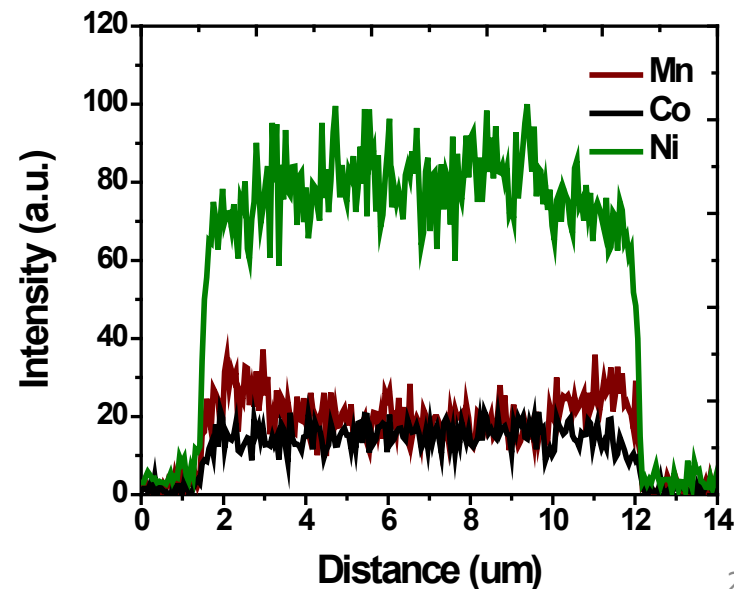
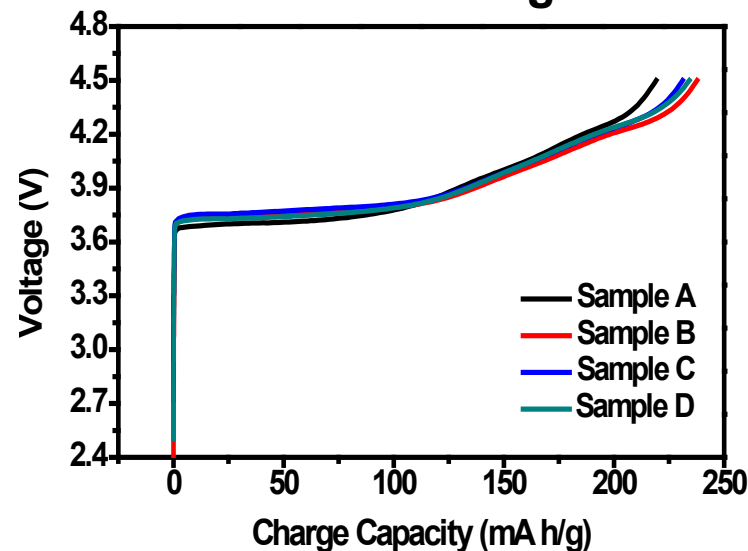


Sample D: In O_2



11-12 μm

First Charge



V. Layered Oxide Cathodes

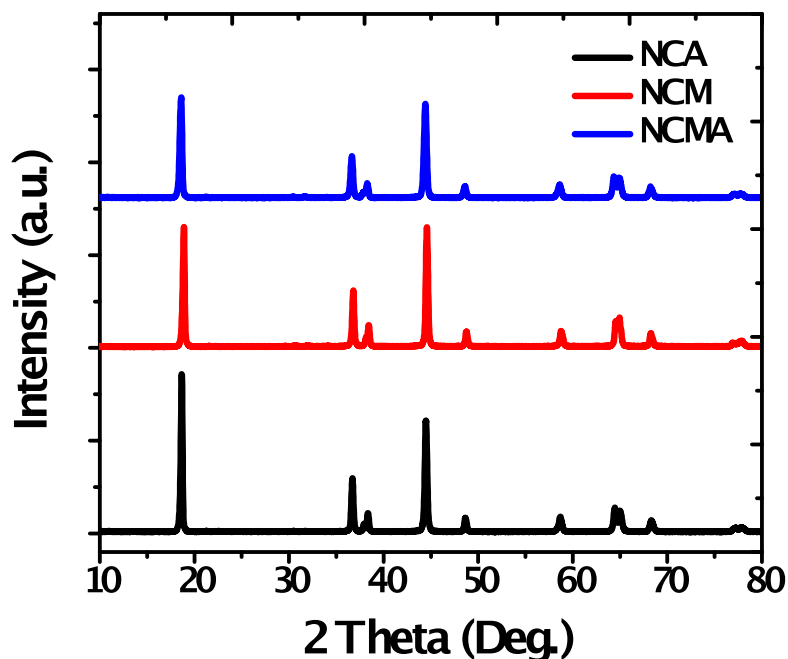
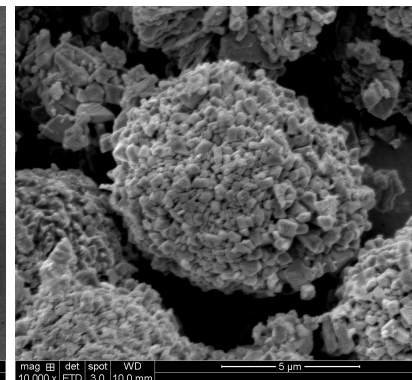
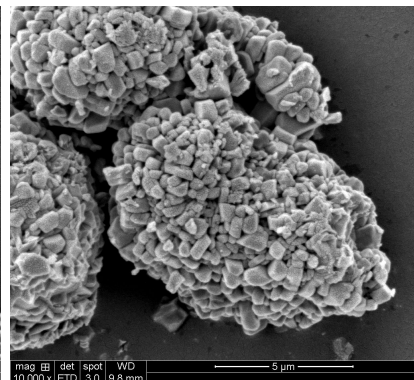
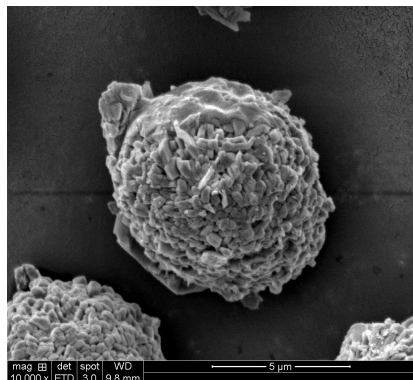
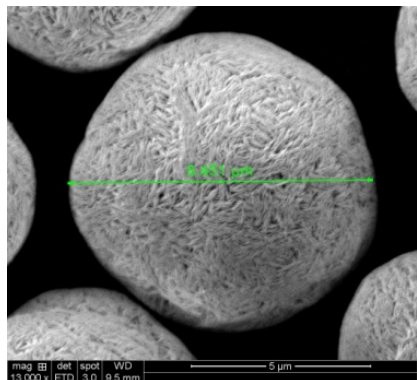
Al or/and Mn Doping in NC Precursor

$\text{Ni}_{0.9}\text{Co}_{0.1}(\text{OH})_x$: NC

LNCA

LNCM

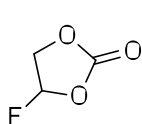
LNCMA



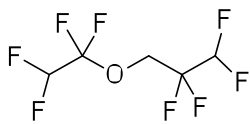
- Spherical morphology can be maintained with different doping elements and procedures (7 - 8 μm)
- The ratio of (003)/(104) decreases from NAC to NCMA, and then to NCM, indicating a better layered structure for LNCA sample

VI. Electrolyte Additive for Ni-Rich Cathode

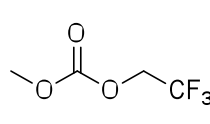
Stabilization of Ni-Rich Cathode Surface



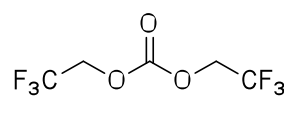
FEC



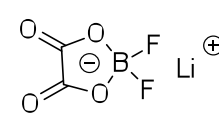
FEPE



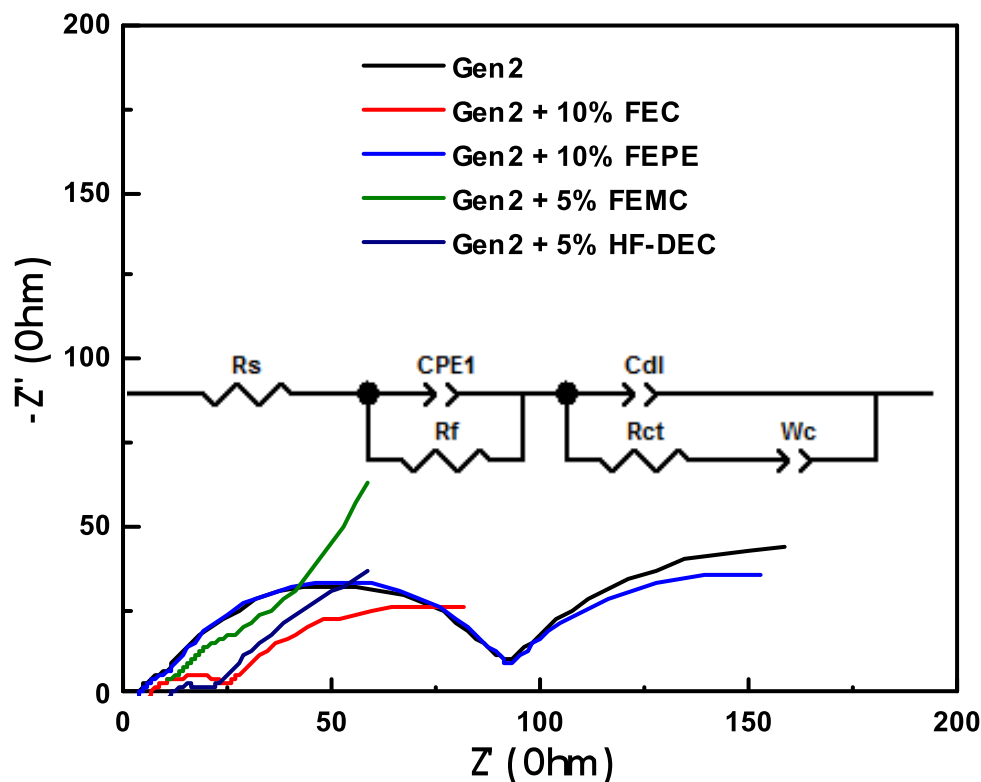
FEMC



HF-DEC



LiDFOB

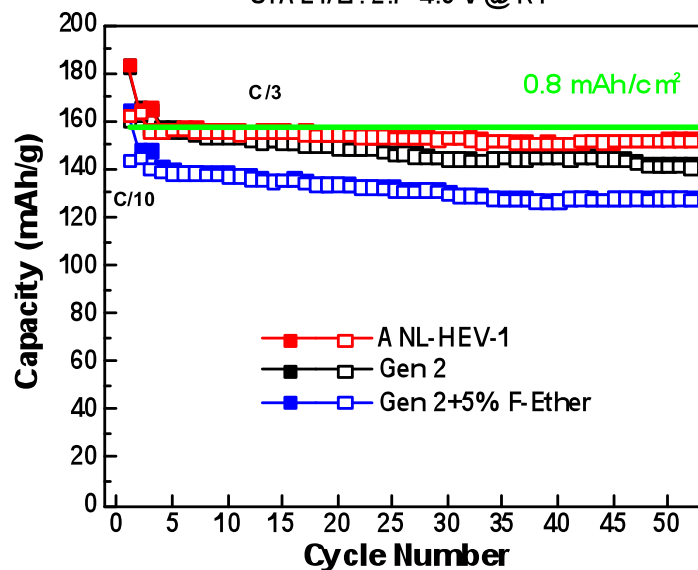


Cell with different electrolyte	Loading (mg/cm ²)	R_s (Ohm)	R_f (Ohm)	R_{ct} (Ohm)
Gen2	27.2	3.52	27.49	88.93
Gen2+10% FEC	27.9	6.45	12.12	27.41
Gen2+10% FEMC	28.1	6.446	8.502	22.15
Gen2+10% FEPE	27.9	3.765	23.3	88.73
Fluorinated Electrolyte	26.8	11.88	5.25	54.09

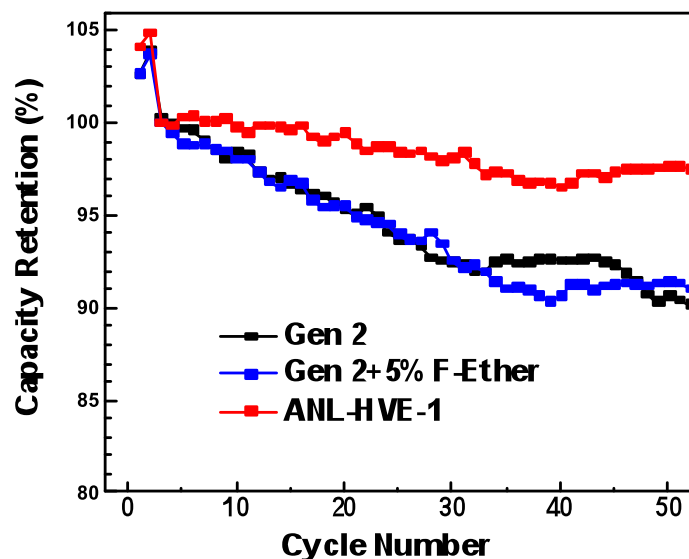
VI. Electrolyte Additive for Ni-Rich Cathode

High Voltage Fluorinated Electrolyte

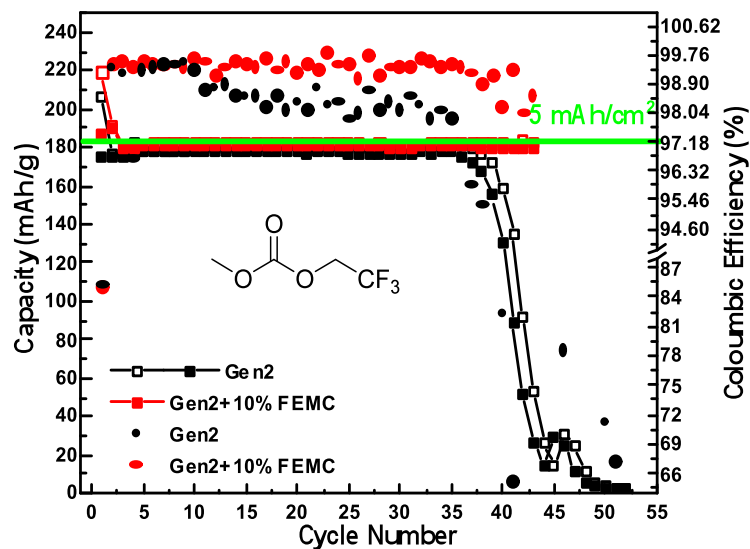
UTA E1/Li: 2.7~4.5 V @ RT



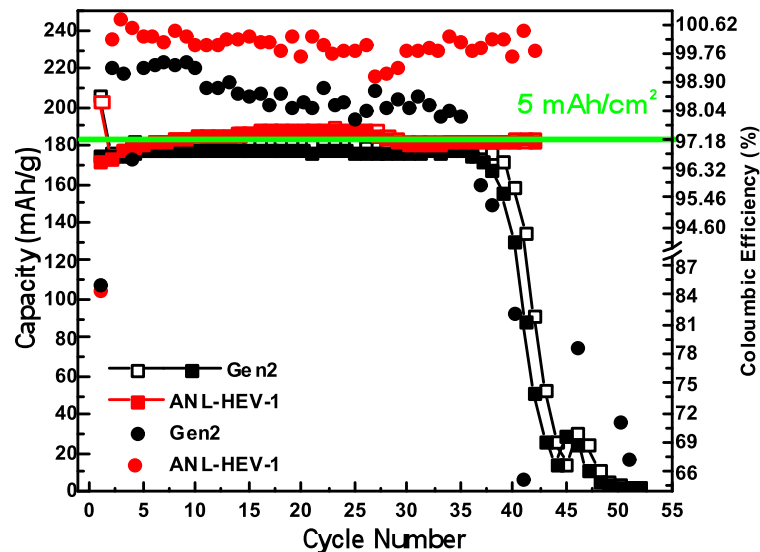
UTAE1/Li: 2.7~4.5 V @ RT



UTAE/Li: 2.7~4.5 V

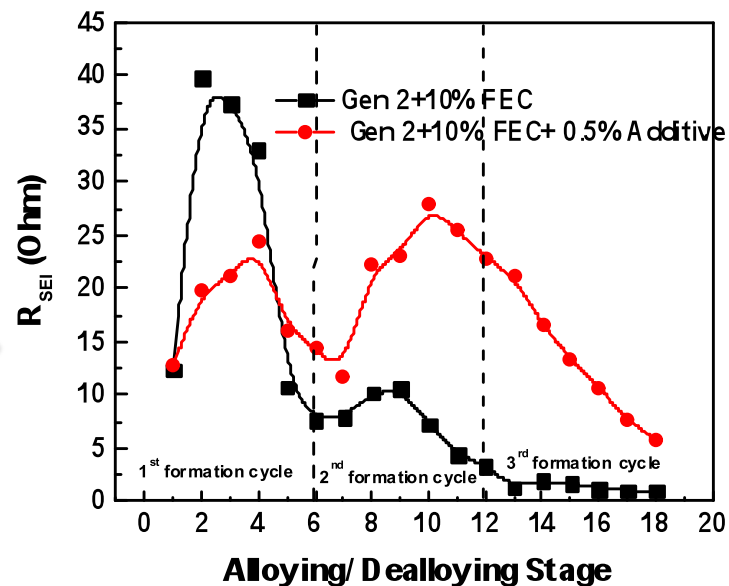
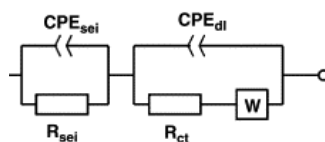
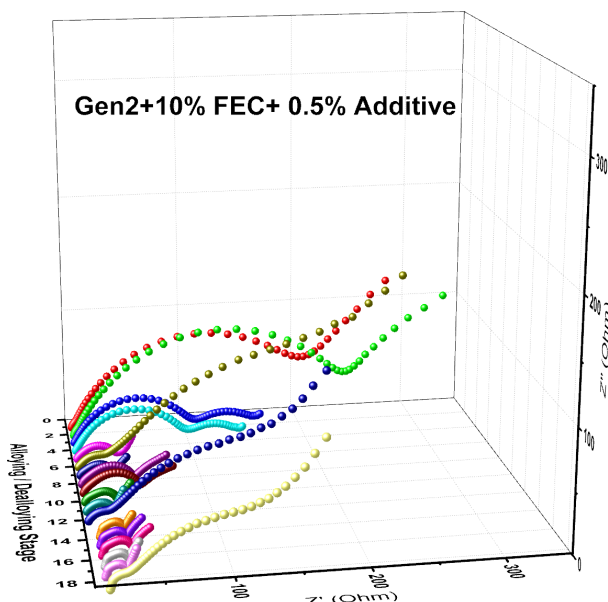
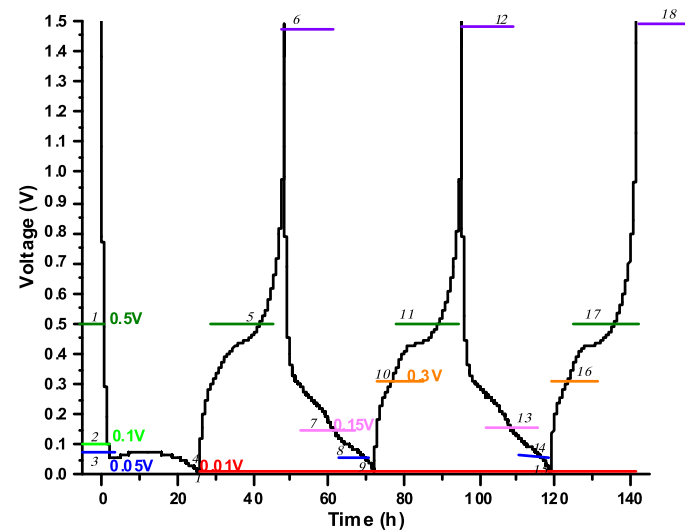
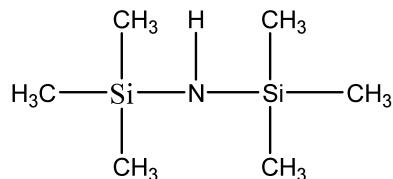
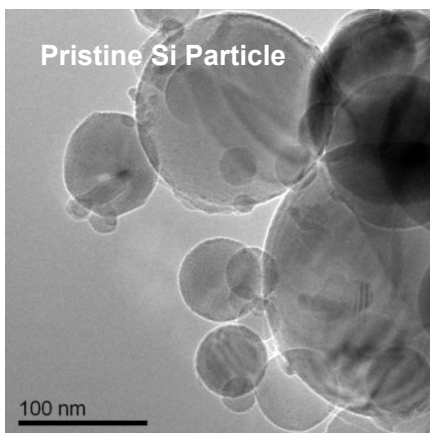


UTAE/Li: 2.7 ~ 4.5 V



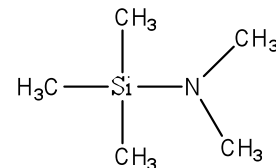
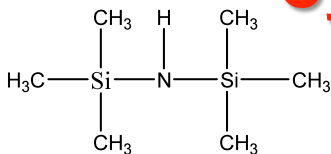
VI. Electrolyte Additive for Si Anodes

Impedance Evolution During Formation Cycles

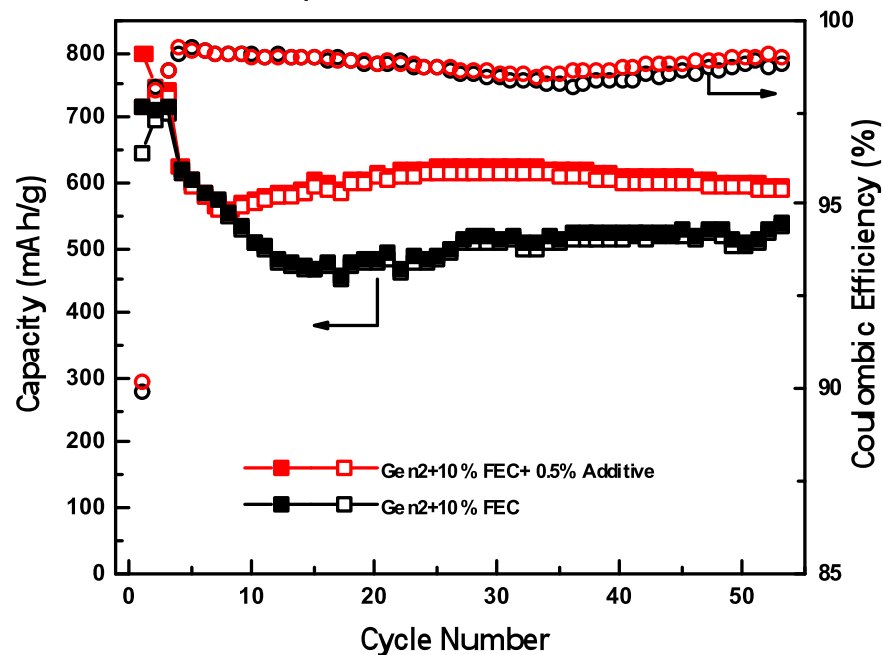


VI. Electrolyte Additive for Si Anodes

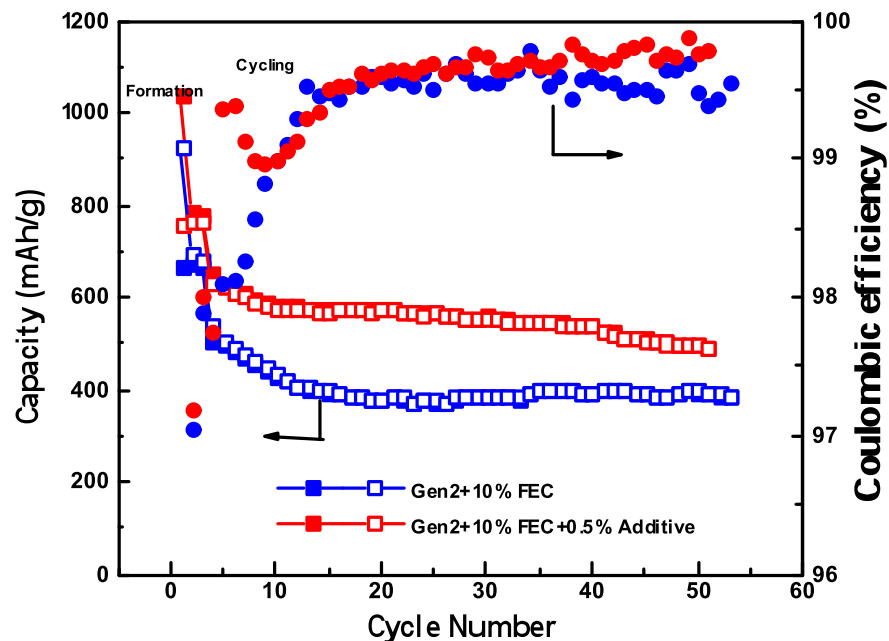
Cycling Performance



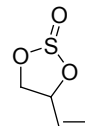
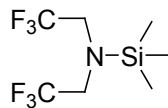
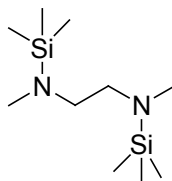
Composite Si Anode from CAMP



PSU Si Anode



More electrolyte additives under investigation:



Response to Reviewer Comments

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 reviewer explained that it was not clear on what strategies were implemented for minimizing the first irreversible capacity loss.”

Response: We have used prelithiation method to significantly increase the 1st cycle efficiency of Si anode as evidenced by the comparison of full cell performance.

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

- Working with EC Power on pouch cells development and testing.
- Working with Argonne National Laboratory on concurrent high voltage electrolyte development and testing.
- Working with Lawrence Berkeley National Laboratory on conductive binders development and testing.
- Independent testing of prismatic cells is being conducted by Idaho National Lab.

Remaining Challenges and Barriers

- Key challenges in anode are improving the 1st cycle efficiency and cycling efficiency and cycling stability of Si/Si alloy - carbon anodes at high mass loading.
- The cyclability of Ni-rich cathodes needs to be improved while keeping the capacity above 200 mAh/g by appropriate surface control.
- New electrolyte is desired to further improve the surface stability of high voltage high capacity cathode and the cycling stability of high capacity anode with good compatibility for an extended cycle life.

Proposed Future Work - I

- Optimize the composition and structure of electrodes to further improve cycling stability and energy density.
- Optimize the prelithiation approach to improve the efficiency and cycling stability of the newly optimized Si/Si alloy-carbon electrodes.
- Investigate the compatibility of new binder with Si/Si alloy-carbon micro-size particles.
- Present works focuses on coin cell. The SLMP prelithiation method for larger piece of anode is being developed at LBNL.
- Continue co-precipitation synthesis to control the primary particle size of gradient and constant-concentration samples to further improve the electrochemical performance and study their structure-morphology-performance relationships.

Proposed Future Work - II

- Explore alternative surface modification methods (Li_2MnO_3 , AlF_3) to further improve the performance of the samples.
- Battery performance confirmation for the new prepared gradient sample and Al/Mn doped samples.
- Improve the slurry coating/calendaring to reduce the electrode polarization for thick electrodes and full cells.
- Further explore tailored electrolytes and additives for individual $\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ cathode and silicon anode.
- Further explore tailored electrolytes and additives for individual layered oxide cathode and silicon anode.

Summary - I

- Advanced binder enables uniform and flexible Si-based electrodes.
- Si/graphite based electrodes exhibit good cycling stability with capacities $> 500 \text{ mAh/g}$ and $> 3 \text{ mAh/cm}^2$ and cycling efficiency $> 99.5\%$.
- The prelithiation approach enable improved 1st cycle efficiency and allows full cell performance that reaches 3 mAh/cm^2 at C/3 based on the Si-based anodes.
- Cell performance, morphology, and impedance evolution for the baseline $\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ with different secondary particle size has been systematically investigated. These products can be scaled up to 500 – 1000 g per batch.
- Faster cooling rate shows superior cyclability for both constant-concentration and concentration-gradient materials.
- Concentration-gradient sample with Ni-poor and Mn-rich surface give superior cyclability compared to the Umicore and constant-concentration samples, but poor stability at high C-rate.

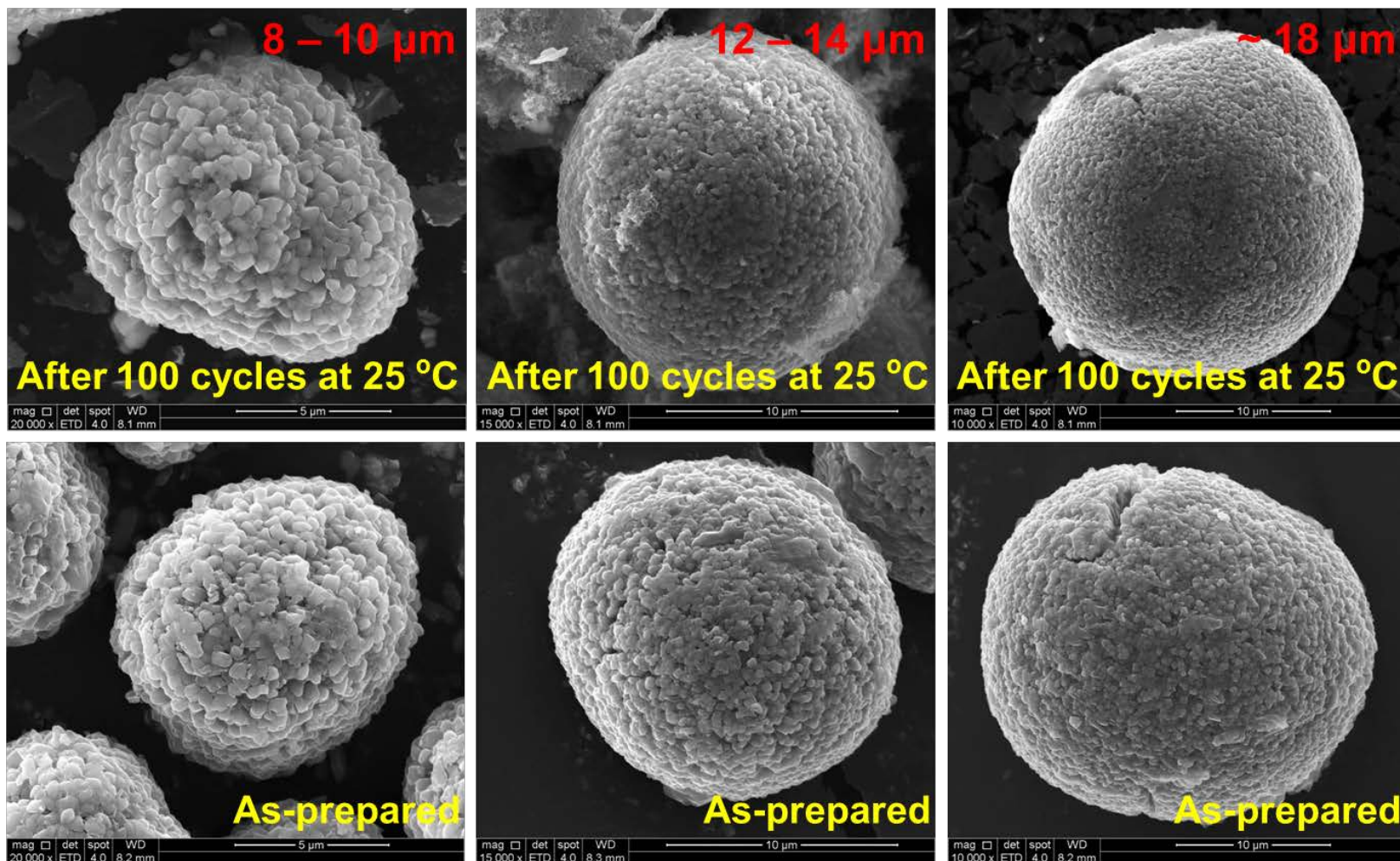
Summary - II

- Controlled secondary particle size of around 12 μm has been prepared to further improve the electrochemical performance.
- NCA, NCM and NCMA cathode materials have been obtained by Al or/and Mn doping.
- New electrolyte and additives were investigated to stabilize the interphase of the $\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ cathode.
- $\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2/\text{Li}$ cell using electrolyte with fluorinated carbonate as solvent/co-solvent showed low interphasial impedance and good capacity retention.
- Electrolyte additive with Si-N skeleton forms a less resistant SEI on the surface of silicon anode.

Technical Back-Up Slides

IV. Layered Oxide Cathodes

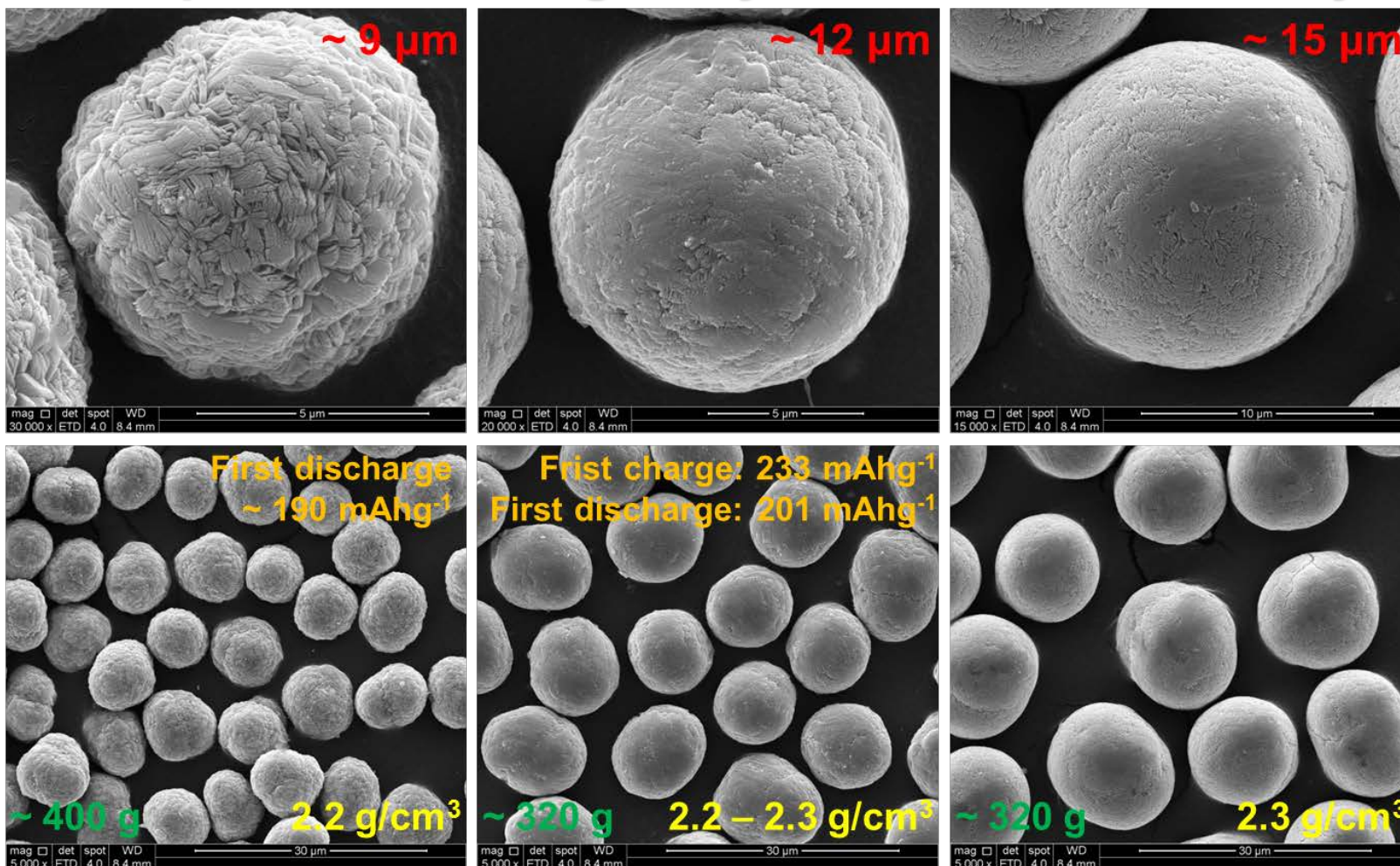
Secondary Particle Size Effect: Morphology Evolution



After cycling, no notable changes in morphology were found

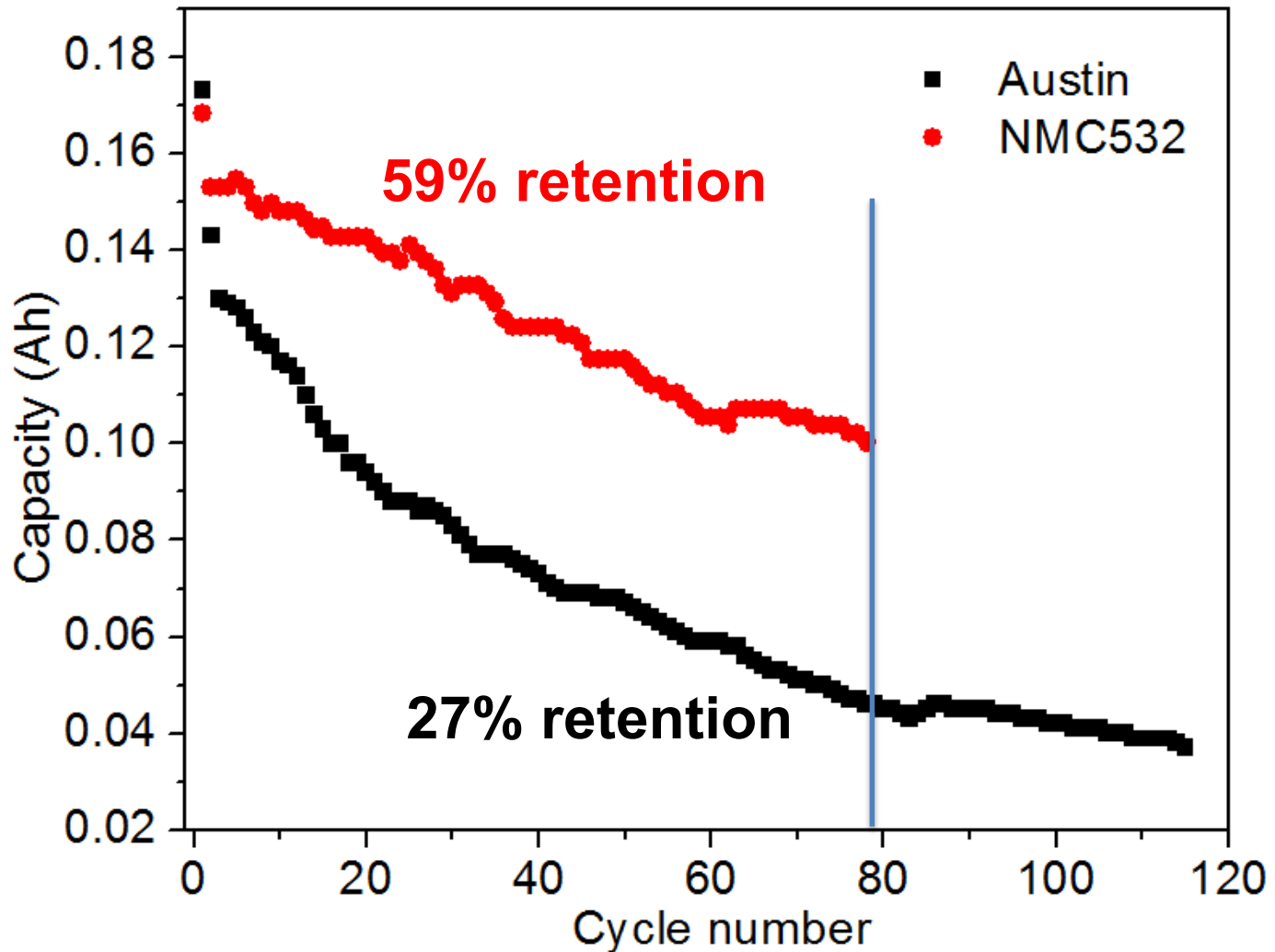
IV. Layered Oxide Cathodes

Scaled-up Manufacturing of Hydroxide Precursors by CSTR



- Product yield per batch: up to 500 – 1000 g
- Future direction: higher Ni; possibly replacing Mn with Al

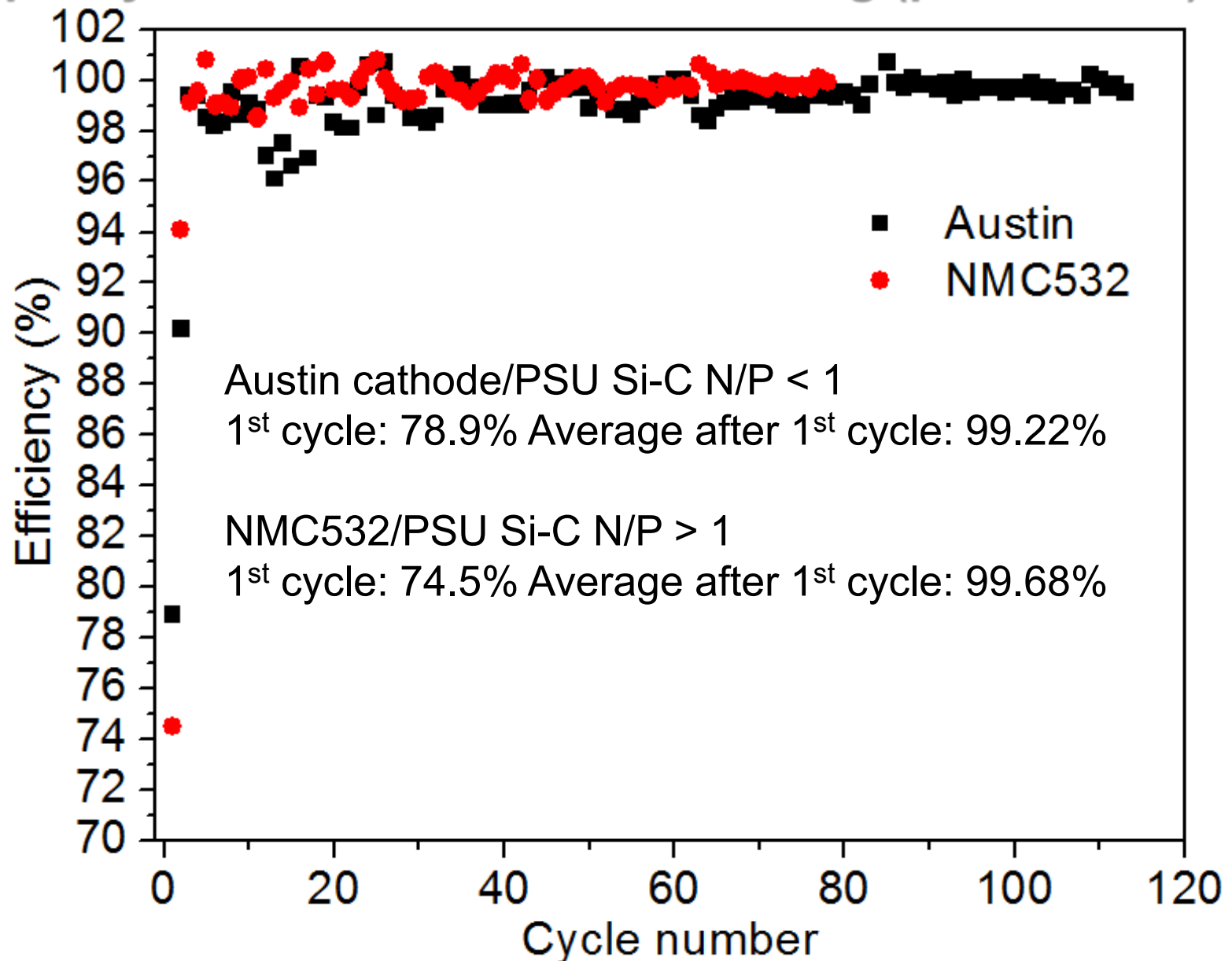
High quality Si electrodes—full cell testing (pouch cells)



Austin cathode/PSU Si-C N/P < 1
NMC532/PSU Si-C N/P > 1

Design capacity 0.2 Ah
C/3, 2.5-4.2 V, 10% FEC/EC/DEC

High quality Si electrodes—full cell testing (pouch cells)



Publication and Presentation

Publications:

8. Min Ling, Yanan Xu, Hui Zhao, Xingxing Gu, Jingxia Qiu, Sheng Li, Mingyan Wu, Xiangyun Song, Cheng Yan, Gao Liu, and Shanqing Zhang, Dual-functional gum arabic binder for silicon anodes in lithium ion batteries. *Nano Energy*, **2015**, 12, 178-185.
9. Hui Zhao, Neslihan Yuca, Ziyang Zheng, Yanbao Fu, Vincent S. Battaglia, Guerfi Abdelbast, Karim Zaghim, and Gao Liu. High capacity and high density functional conductive polymer and SiO anode for high-energy lithium-ion batteries. *ACS Applied Materials & Interfaces*. **2015**, 7(1), 862-866.
10. Min Ling, Hui Zhao, Xingcheng Xiao, Feifei Shi, Mingyan Wu, Jingxia Qiu, Sheng Li, Xiangyun Song, Gao Liu, and Shanqing Zhang. Low cost and environment-benign crack-blocking structure for long life and high power Si electrodes in Lithium ion batteries. *J. Mater. Chem. A*, **2015**, 3, 2036-2042.
11. Song, J. X., Zhou, M. J., Yi, R., Xu, T., Gordin, M. L., Tang, D. H., Yu, Z. X., Regula, M., Wang, D. H. Interpenetrated Gel Polymer Binder for High Performance Silicon Anode in Lithium-ion Battery. *Advanced Functional Materials* 2014, 24, 5904.
12. Yi, R., Zai, J. T., Dai, F., Gordin, M. L., Wang, D. H. Dual Conductive Network-Enabled Graphene/Si-C Composite Anode with High Areal Capacity for Lithium-ion Batteries. *Nano Energy* 2014, 6, 211.

Publication and Presentation

Presentations in Materials Research Society meeting, 2015 Spring, San Francisco

1. Toward a Better Understanding of the Surface Effect through the Design of Binders in Lithium Sulfur Battery, Oral presentation, Presenter (Guo Ai)
2. Side-Chain Conducting and Phase-Separated Polymeric Binders for High-Performance Silicon Anodes in Lithium-Ion Batteries. Oral presentation, Presenter (Hui Zhao)
3. Toward Practical Application of Functional Conductive Polymer Binder for a High-Energy Lithium-Ion Battery Design. Oral presentation, Presenter (Hui Zhao)
4. Mesoporous Silicon-Carbon Hybrid Li-Ion Anode Materials toward Practical Applications, Oral presentation, Presenter (Donghai Wang)

Presentations in TMS 2015 Spring, Orlando, FL

1. Structured Micro-sized Si-C Composites as Li-ion Anodes, Oral presentation, Presenter (Donghai Wang)