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

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Project ID: ES212

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Overview

Timeline

- Project Start – Oct. 01 2013
- Project End – Sep. 30 2015
- Overall % Complete: **25%**
  - FY 2014 % Complete: 40%

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

- EC Power (subcontract)
- Argonne National Lab (Zhengcheng Zhang, collaboration)
- Lawrence Berkley National Lab (Gao Liu and Vincent Battaglia, 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 and Fabrication of a lithium-ion 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

- Scale up the state-of-the-art anode and cathode synthesis (in progress)
- Delivery of baseline cells (in progress)
- 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 (in progress)
- Si-carbon anode with 1900 mAh/g capacity, 95% capacity retention after 300 cycles at C/3, coulombic efficiency >99.9% (in progress)
- Surface-coated, Ni-rich layered oxide cathode with 220 mAh/g capacity, 95% capacity retention after 300 cycles at C/3 (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 crosslinked binders to form interpenetrated conductive network to accommodate volume change of Si and improve integrity of Si electrodes

- **Nickel-rich layered oxide cathodes**

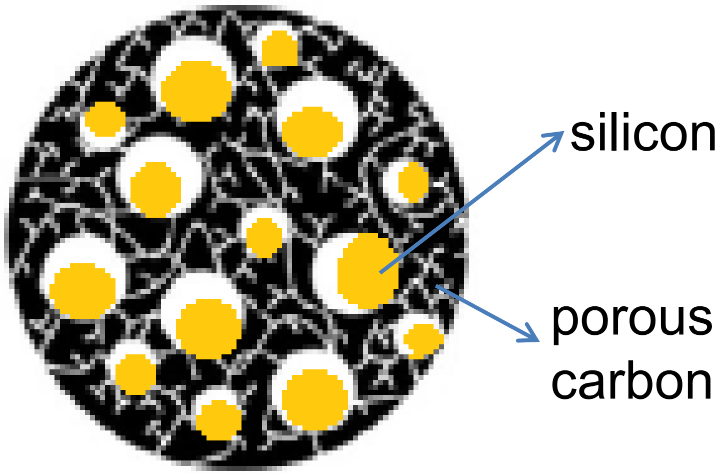
  - Control the composition, microstructure, and morphology through novel synthesis and processing approaches
  - Condition the surface to suppress aggressive reaction with the cathode surface

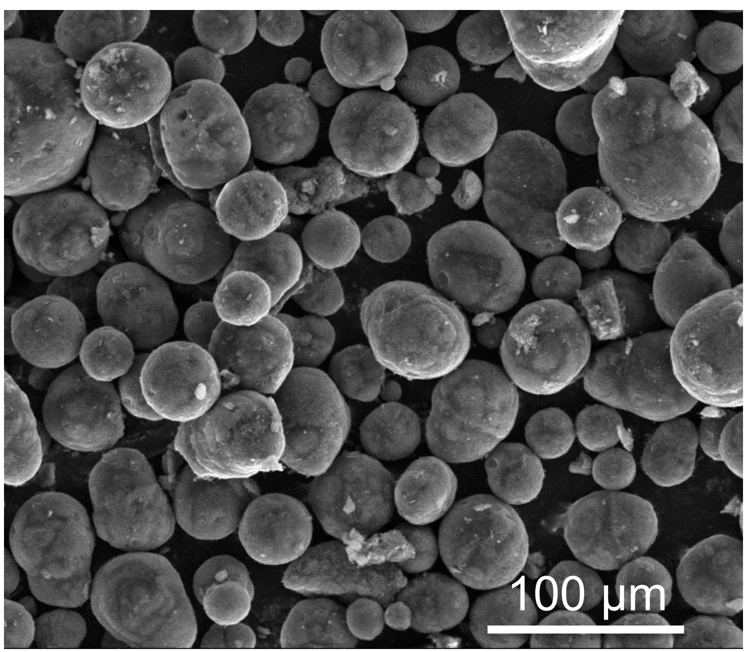
- **Electrolytes**

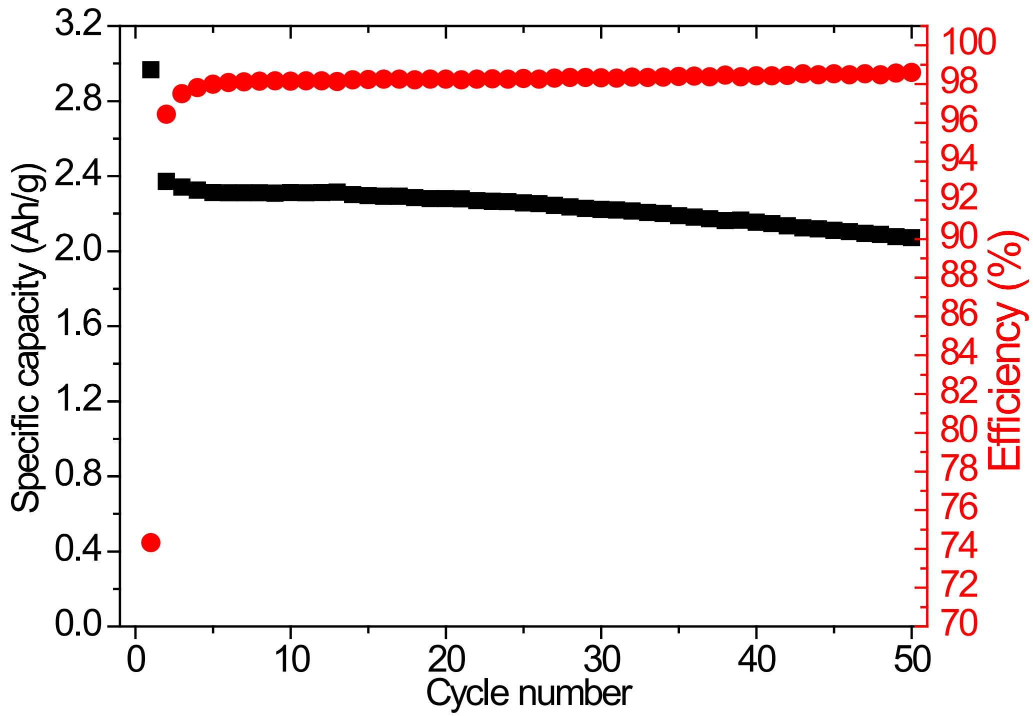
  - Develop novel fluorinated electrolytes and additives to stabilize the anode SEI, prevent electrolyte reaction at the cathode surface
  - Improve cell safety by enhancing high temperature stability and decreasing flammability

Technical accomplishments

I. Micro-sized Spherical Si-porous C composite



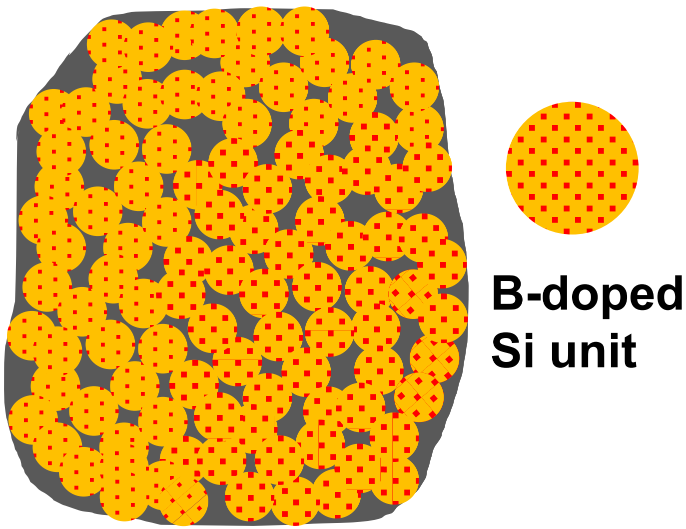


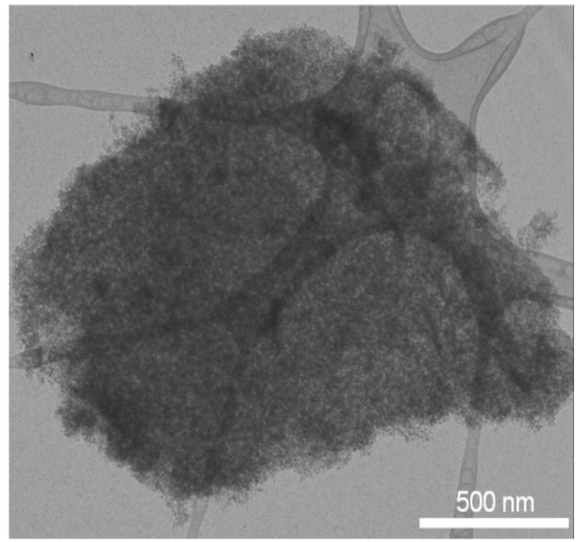


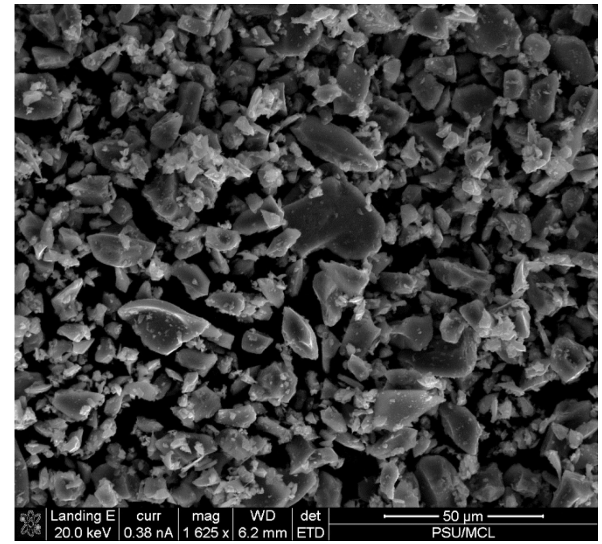
Bottom-up synthesis using commercial Si nanoparticles

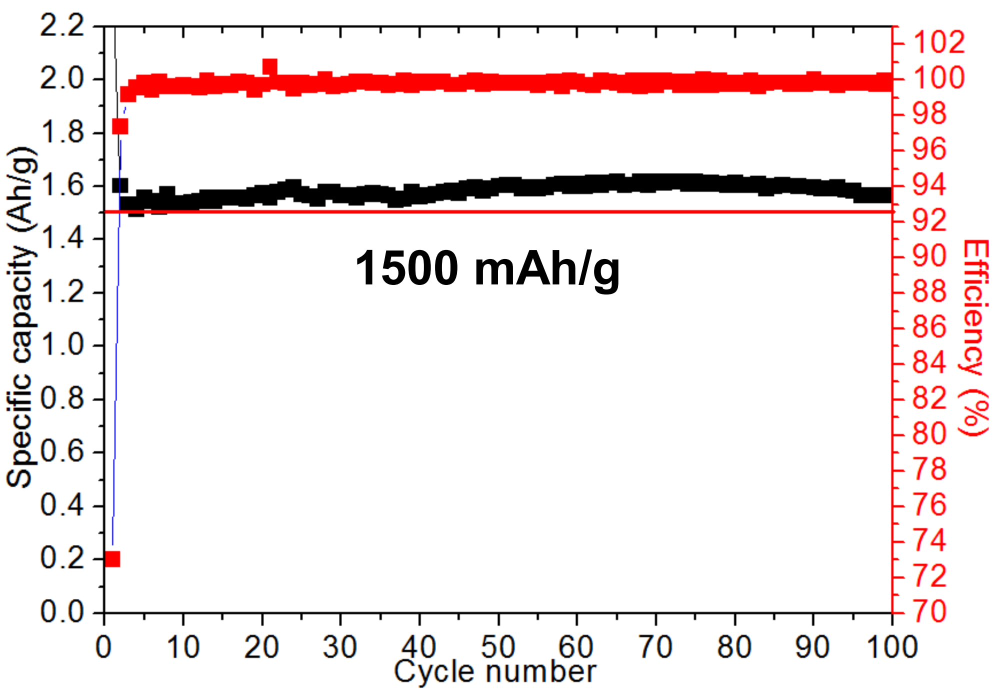
- Micro-sized
- Spherical particles
- High capacity
- High tap density >1 g/cm^3

II. Scale up Boron-doped Porous Si-C Composite



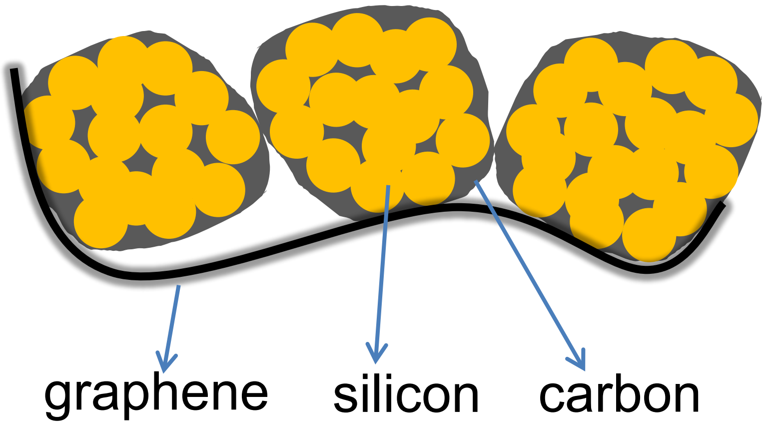


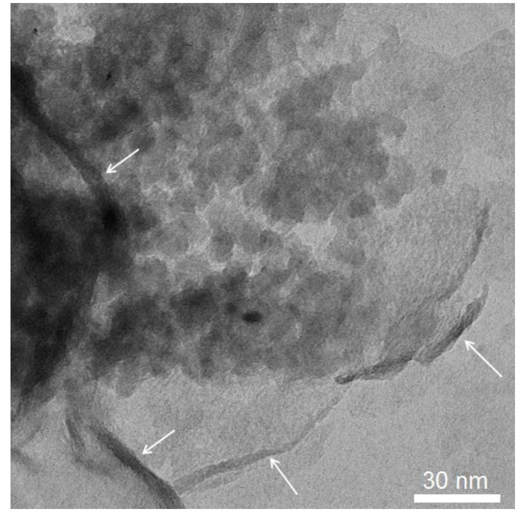


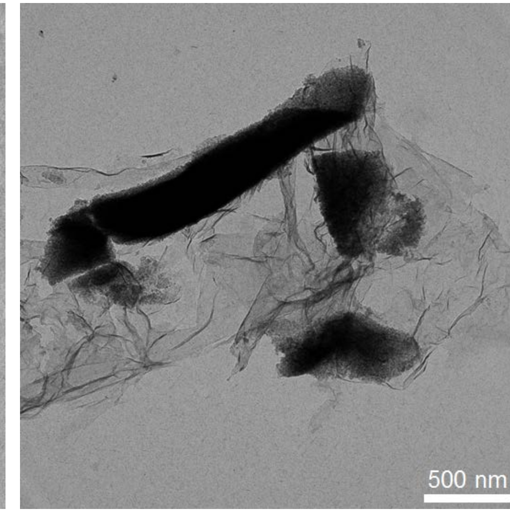


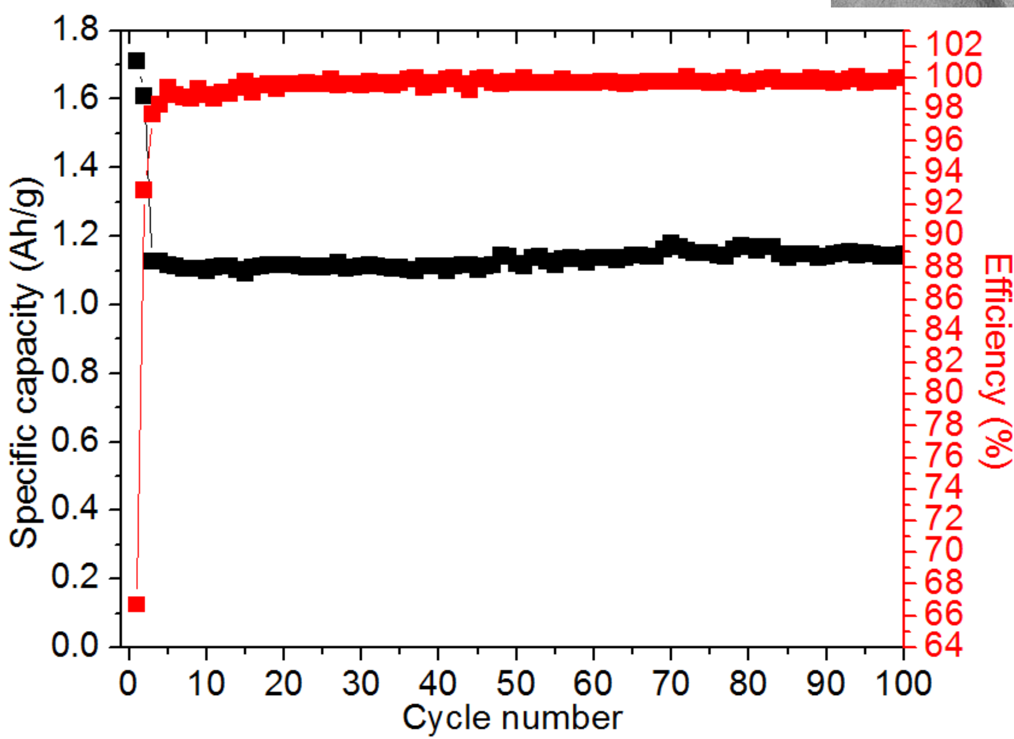
- Large-scale production
- Micro-sized
- B doping improves conductivity
- Good cyclability
- High tap density 0.8 g/cm^3

III. Dual Conductive Network-Enabled Graphene/Si-C Composite









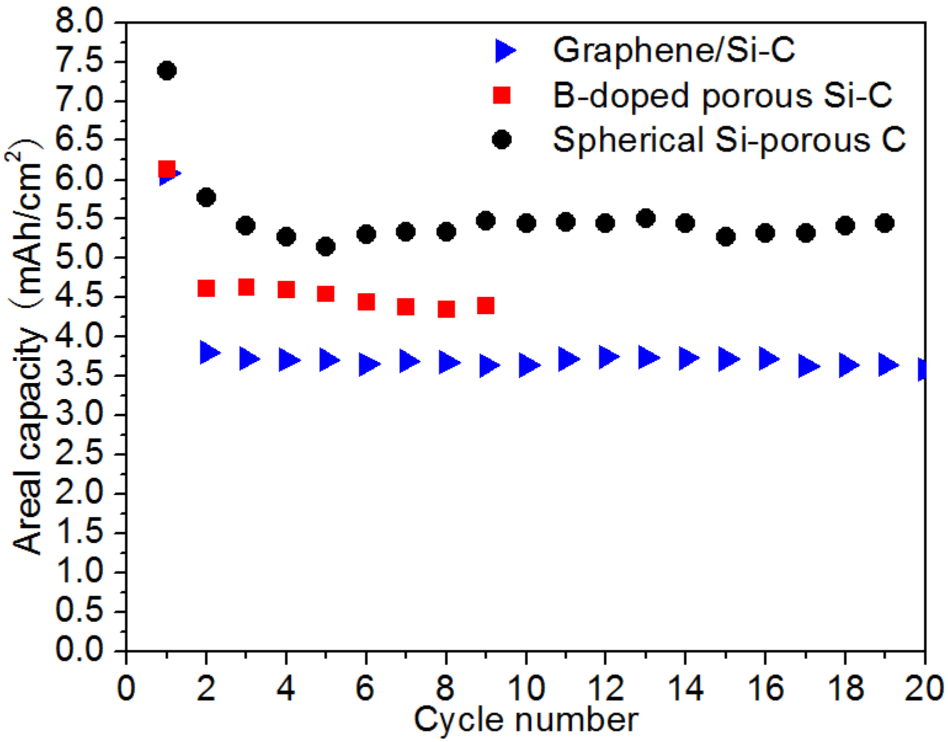
- Micro-sized
- Conductive network among particles
- Good cyclability
- High tap density 0.8 g/cm^3

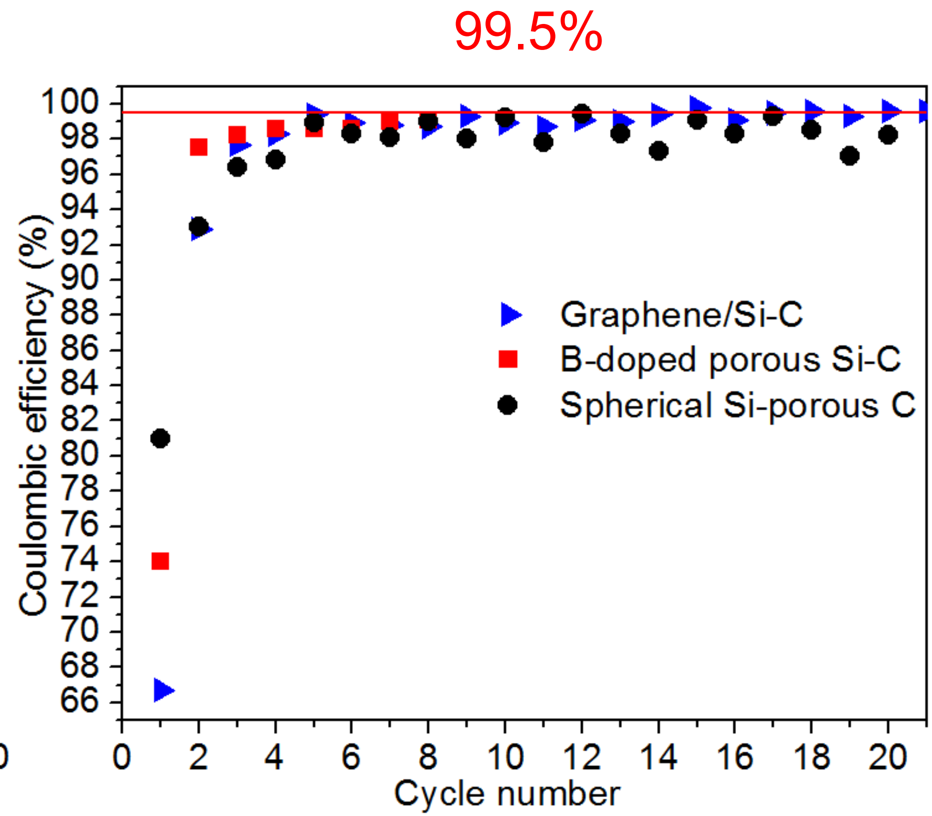
IV. High Areal Capacity Electrodes

Gravimetric capacity → Materials

↓ ?

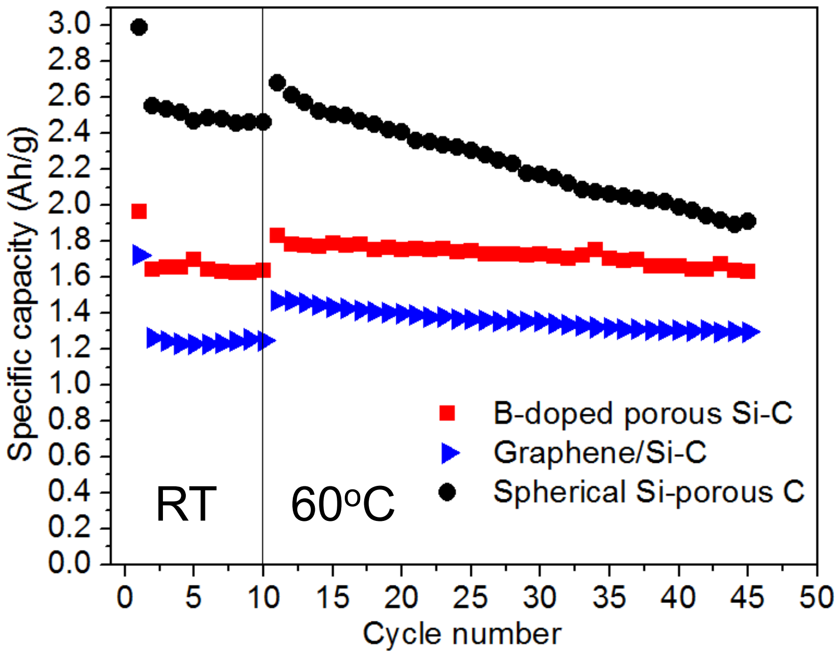
Areal capacity → Electrodes

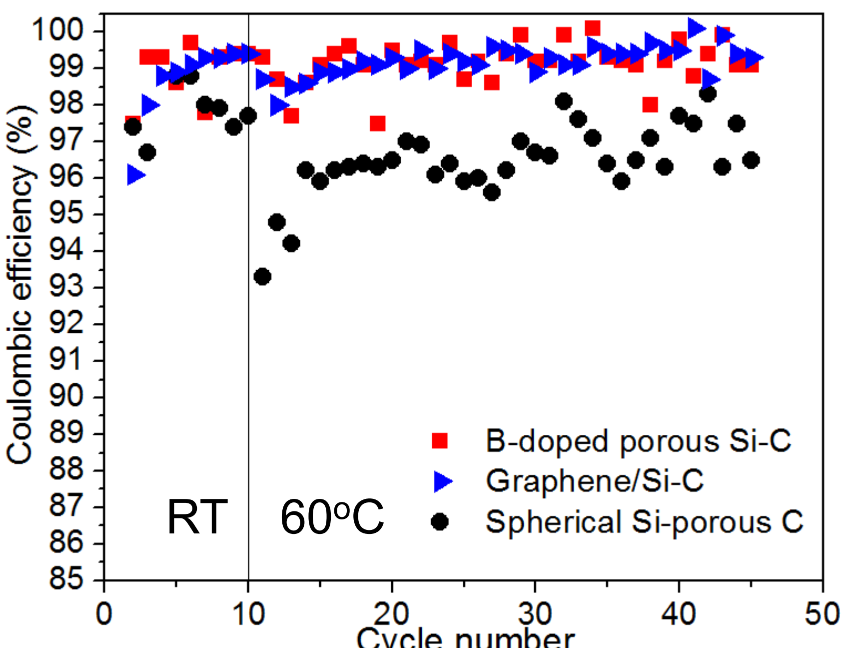


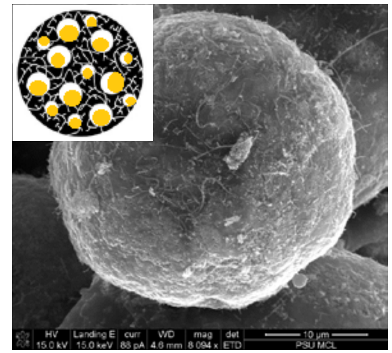


- Industrial slurry coating approaches
- Good cyclability
- Uncompromised high efficiency even at high mass loading

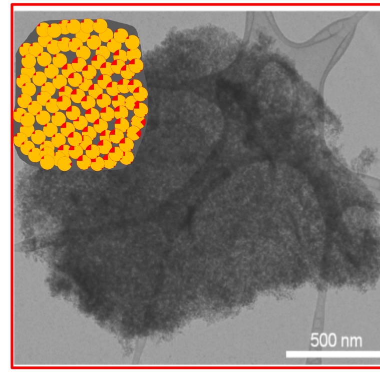
V. High Temperature Performance and Screening



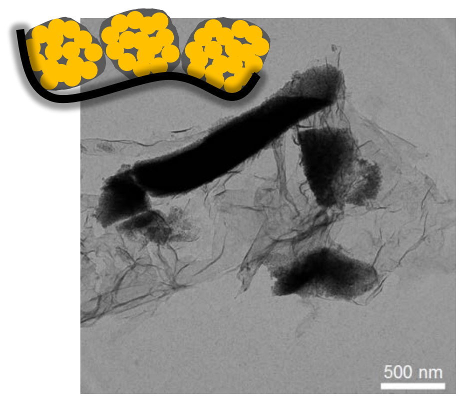




- High capacity
- Fast fading
- Low CE



- Medium capacity
- Stable cycling
- High CE



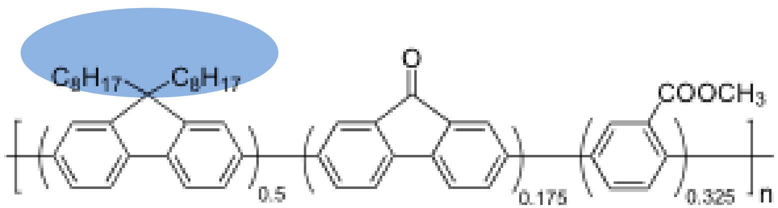
- Low capacity
- Stable cycling
- High CE

Room temperature for 10 cycles then 60 °C
400 mA/g EC/DEC/FEC $LiPF_6$

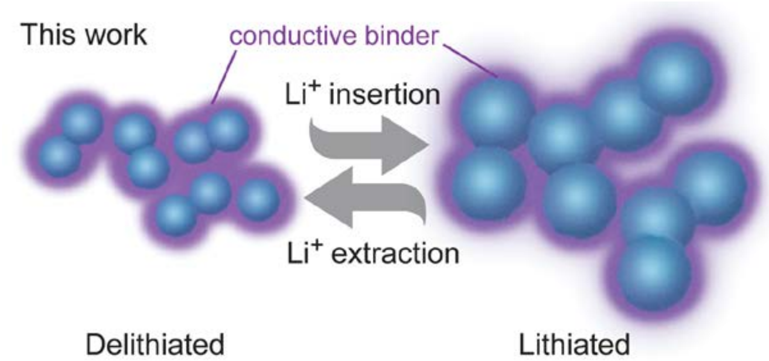
VI. Conductive Binder for Si Anodes

1st generation of binder PFM

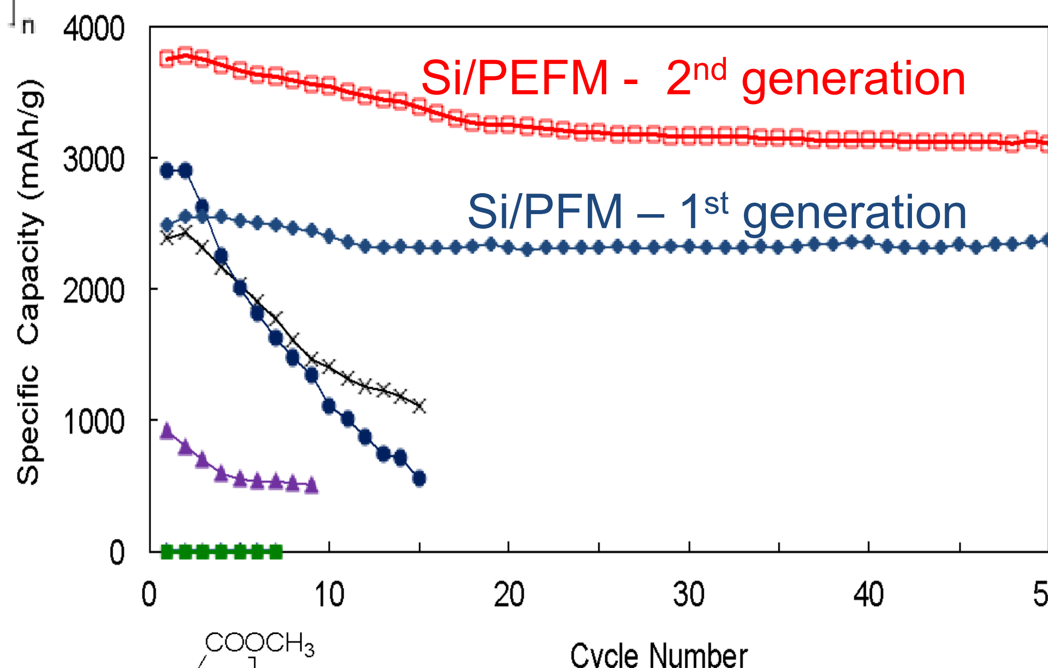
Non-polar



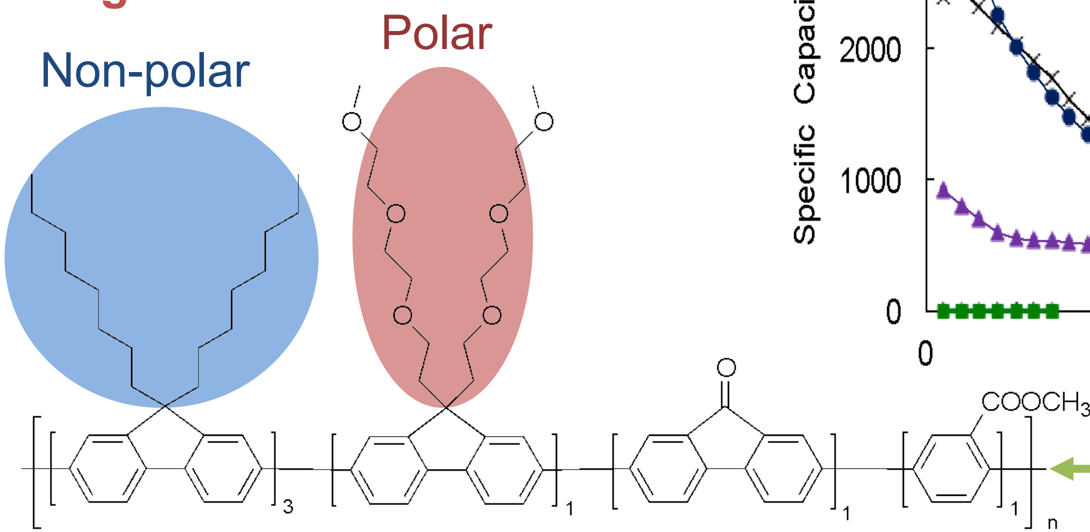
PFM



← Electric conduction



2nd generation of binder PEFM

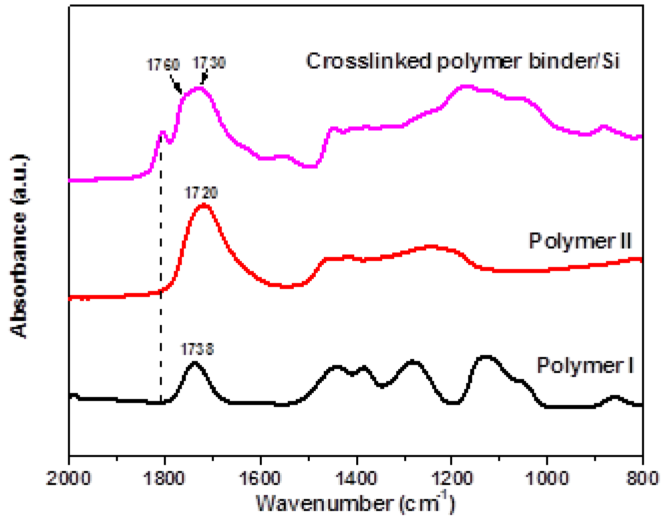


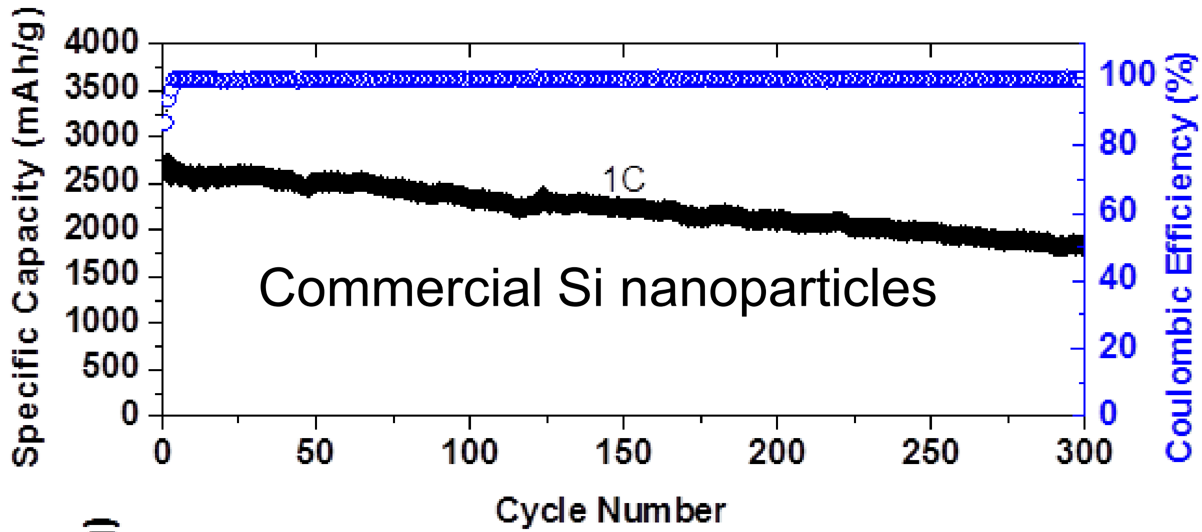
← Electric conduction

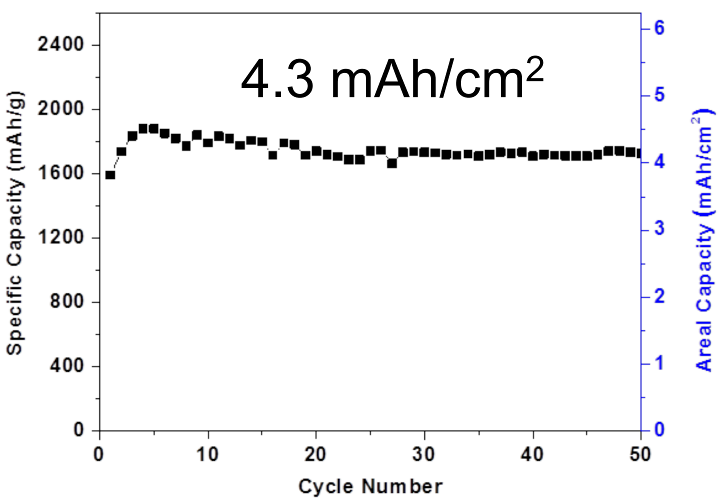
PEFM

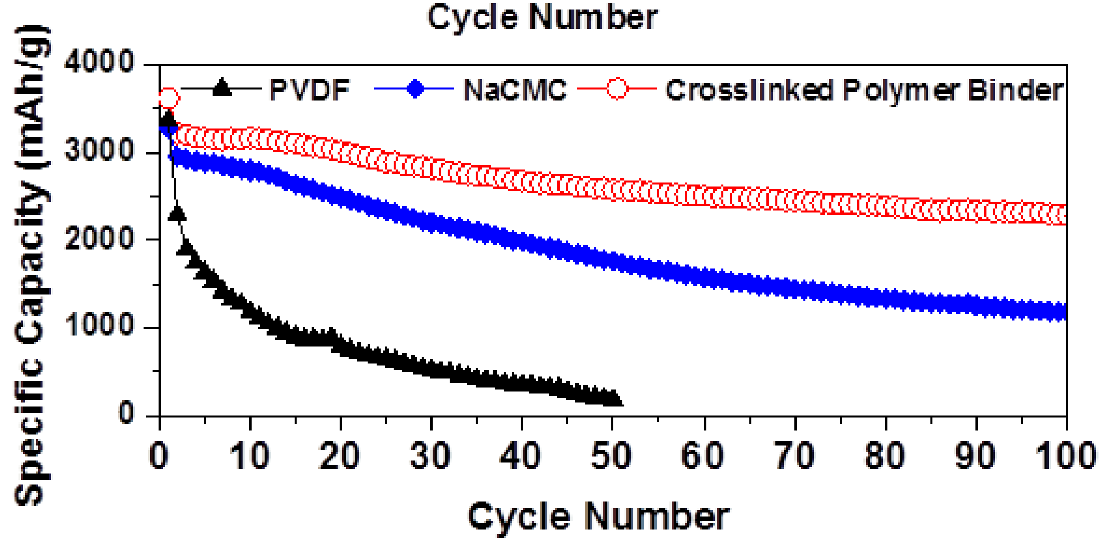
- Electrically conductive network for improved cycling stability
- High specific capacity using commercial Si nanoparticles

VII. Crosslinked Binder for Si Anodes



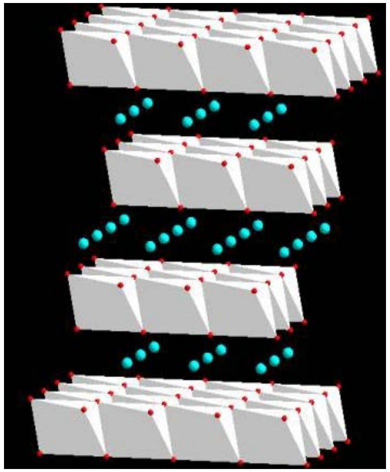






- Interpenetrated polymer network for much improved cycling stability
- High areal capacity using commercial Si nanoparticles

VIII. Layered Oxide Cathodes

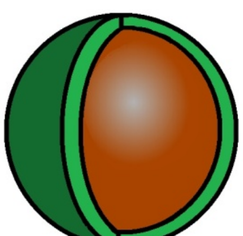


$LiCoO_2$	Ni-rich
• Low capacity • High cost • Good cyclability	• High capacity • Lower cost • Poor cyclability

Surface control? Or …

Theoretical capacity: 280 mAh/g

Sample	Core	Shell	Discharge capacity
$Li[Ni_{0.8}Co_{0.2}]_{0.7}[Ni_{0.2}Mn_{0.8}]_{0.3}O_2$	**$Ni_{0.8}Co_{0.2}$**	**$Ni_{0.2}Mn_{0.8}$**	**209 mA h g^{-1}**
$Li[Ni_{0.8}Co_{0.2}]_{0.7}[Ni_{0.5}Mn_{0.5}]_{0.3}O_2$	$Ni_{0.8}Co_{0.2}$	$Ni_{0.5}Mn_{0.5}$	187 mA h g^{-1}
$Li[Ni_{0.8}Co_{0.2}]_{0.7}[Ni_{0.8}Mn_{0.2}]_{0.3}O_2$	$Ni_{0.8}Co_{0.2}$	$Ni_{0.8}Mn_{0.2}$	176 mA h g^{-1}

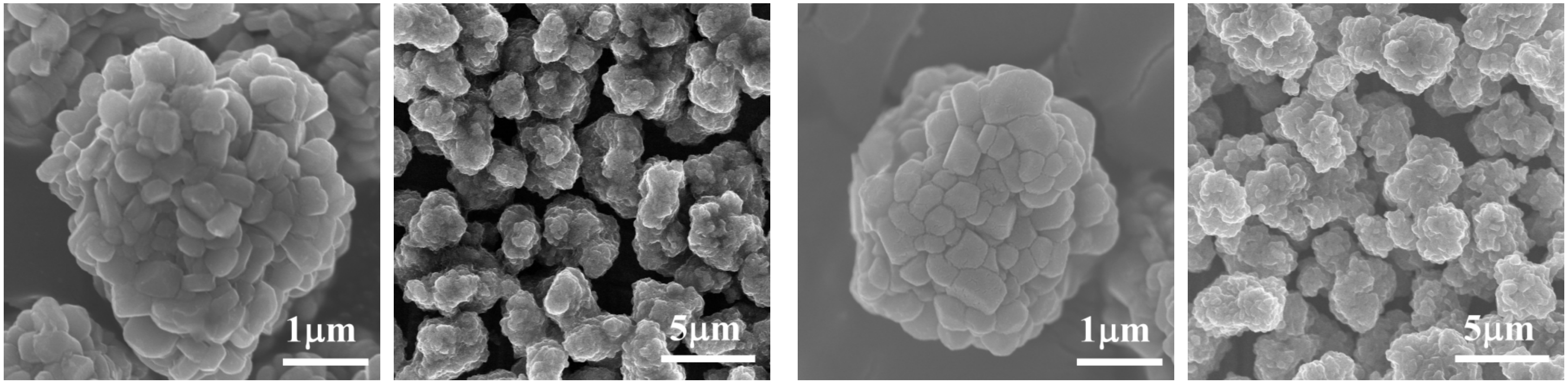


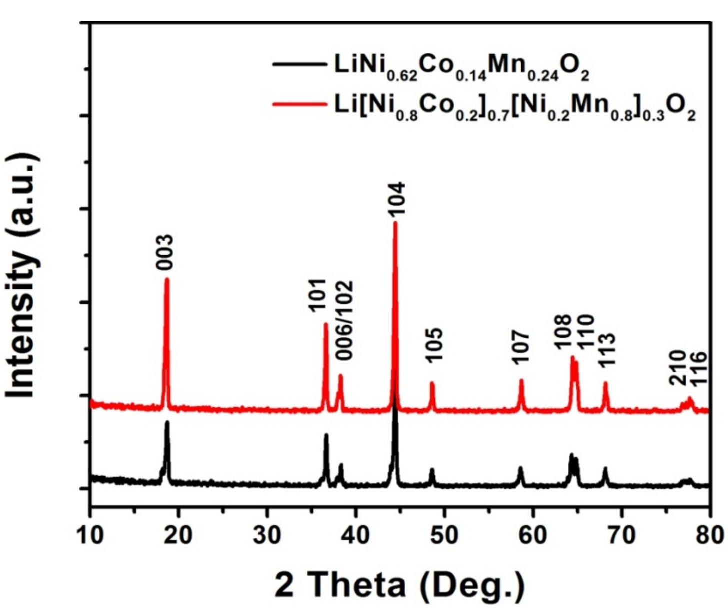
$Li[Ni_{0.8}Co_{0.2}]_{0.7}[Ni_{0.2}Mn_{0.8}]_{0.3}O_2$ with Ni-poor, Mn-rich surface exhibits the highest capacity

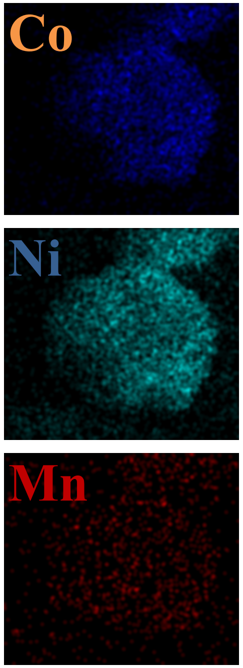
VIII. Layered Oxide Cathodes – Characterization

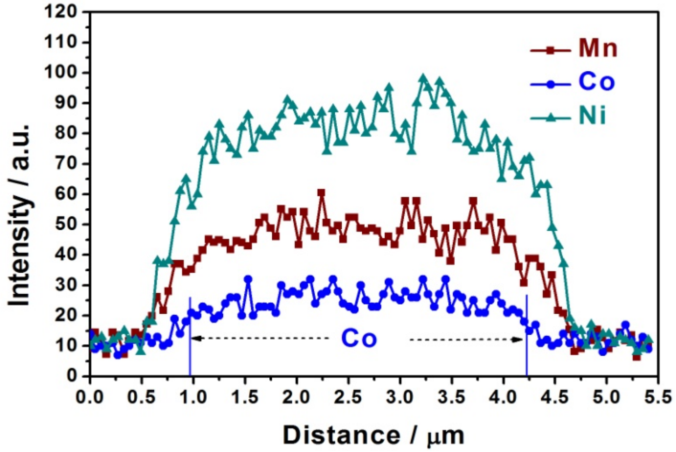
$LiNi_{0.62}Co_{0.14}Mn_{0.24}O_2$ with uniform Ni distribution

$Li[Ni_{0.8}Co_{0.2}]_{0.7}[Ni_{0.2}Mn_{0.8}]_{0.3}O_2$ With Concentration-gradient





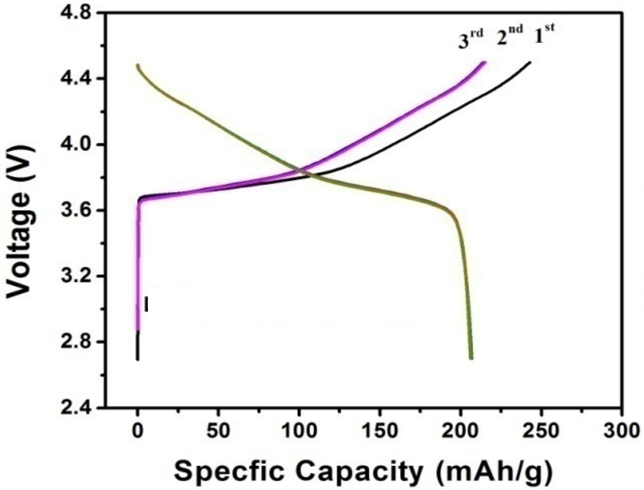


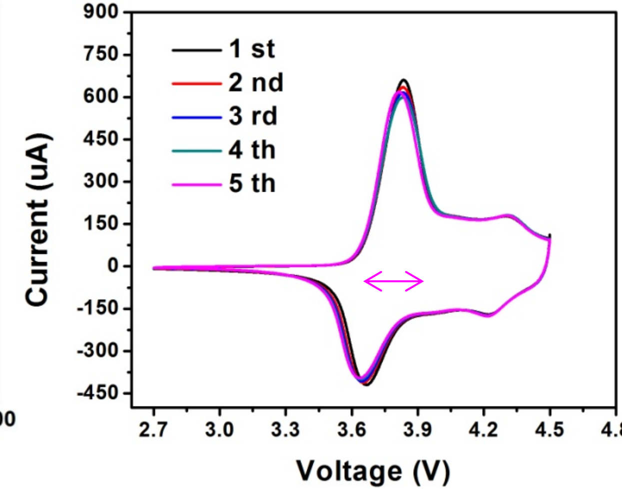


- 3 - 4 μm particle with concentration-gradient structure

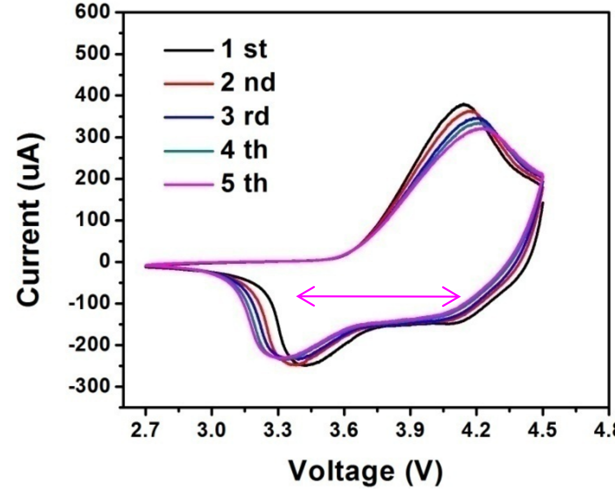
VIII. Layered Oxide Cathodes - Electrochemical Performance (I)

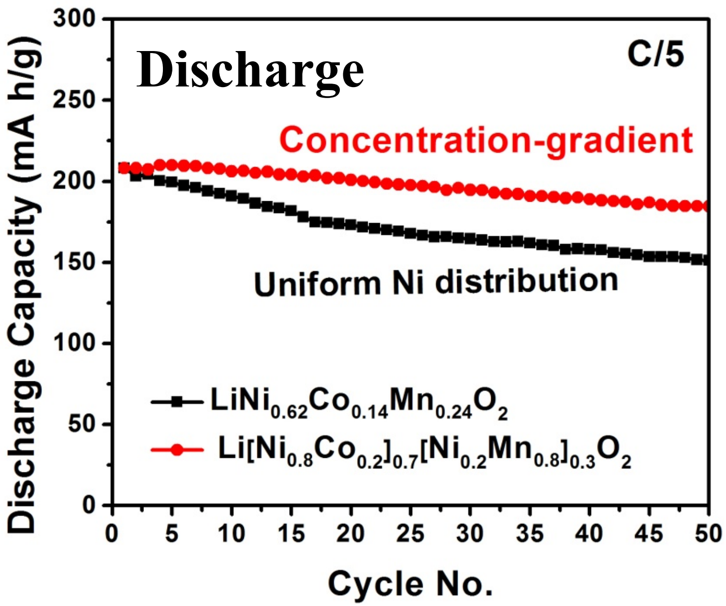
"Concentration-gradient" $Li[Ni_{0.8}Co_{0.2}]_{0.7}[Ni_{0.2}Mn_{0.8}]_{0.3}O_2$





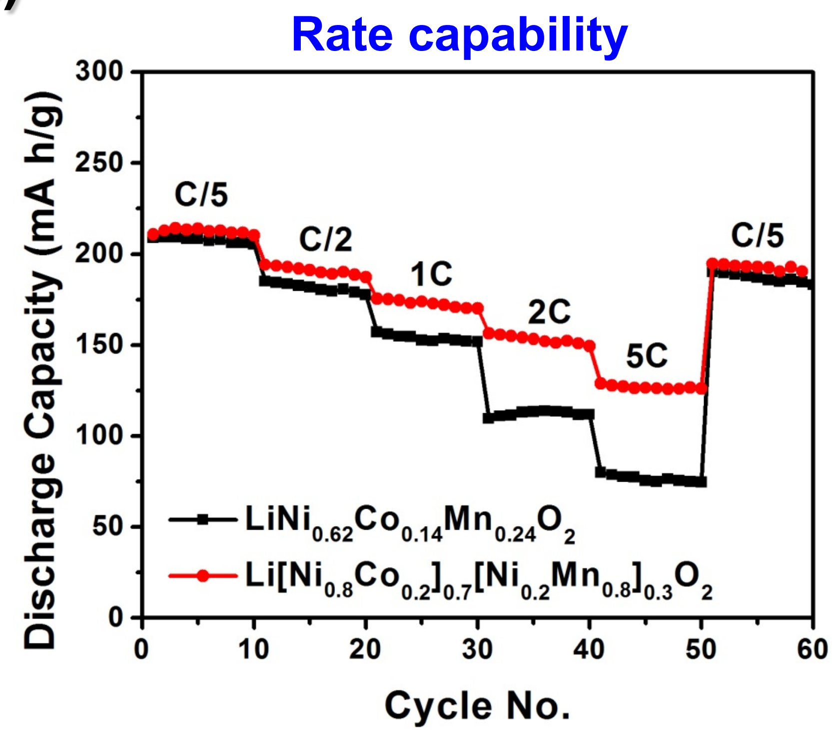
$LiNi_{0.62}Co_{0.14}Mn_{0.24}O_2$ with uniform Ni distribution

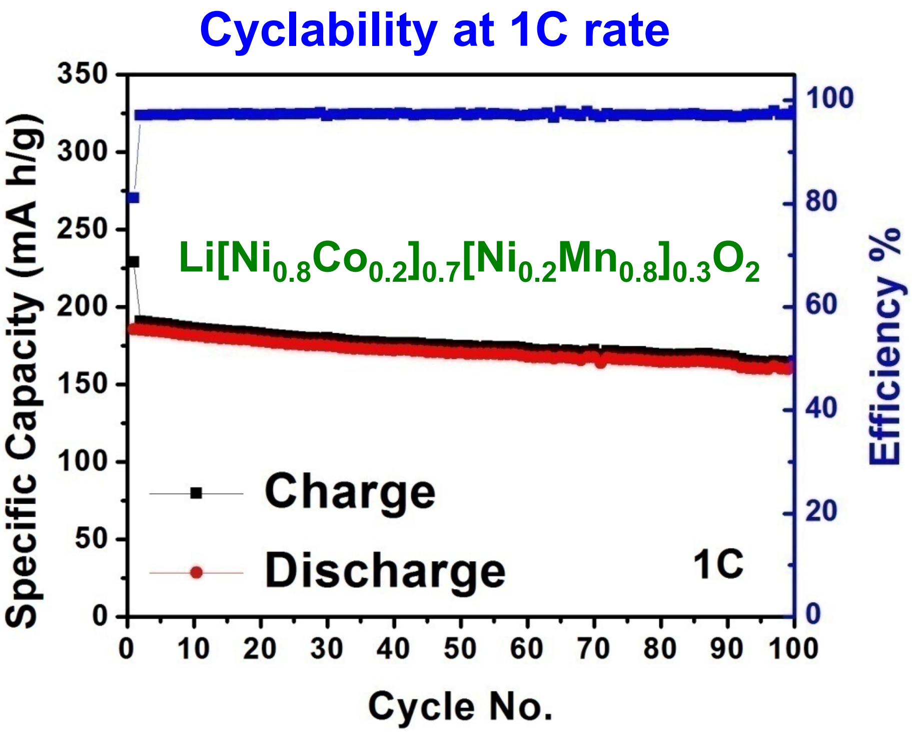


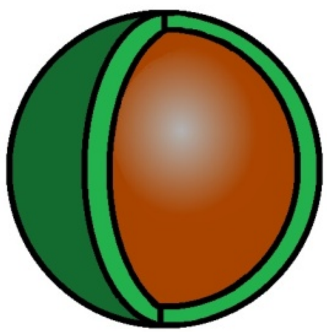


- The "concentration-gradient" sample with Ni-poor, Mn-rich surface shows better cyclability with a high capacity of ~ 210 mA h g^{-1}

VIII. Layered Oxide Cathodes - Electrochemical Performance (II)



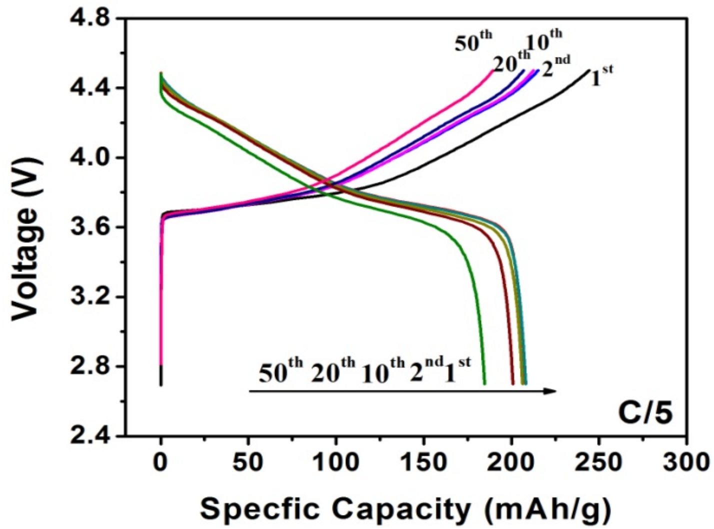




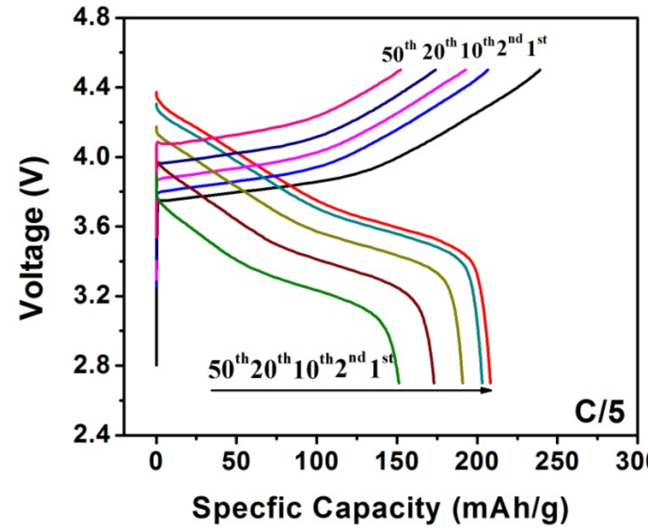
- The higher rate capability of the “concentration-gradient” sample is due to the Ni-poor, Mn-rich surface and high electronic conductivity in the core

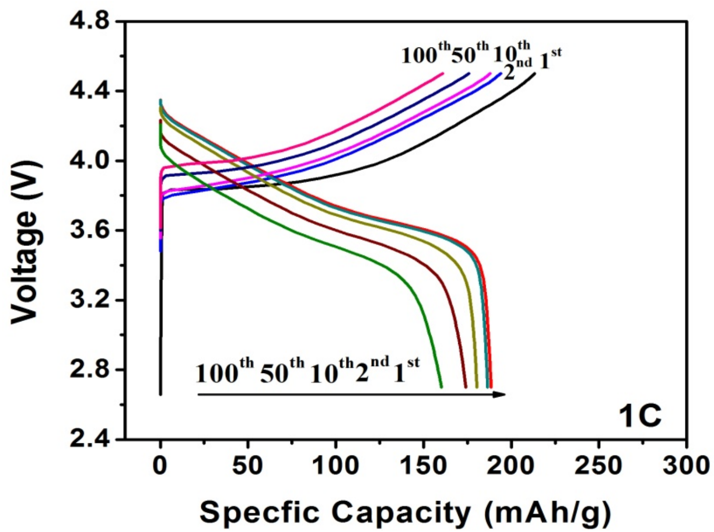
VIII. Layered Oxide Cathodes - Voltage stability

"Concentration-gradient" $Li[Ni_{0.8}Co_{0.2}]_{0.7}[Ni_{0.2}Mn_{0.8}]_{0.3}O_2$



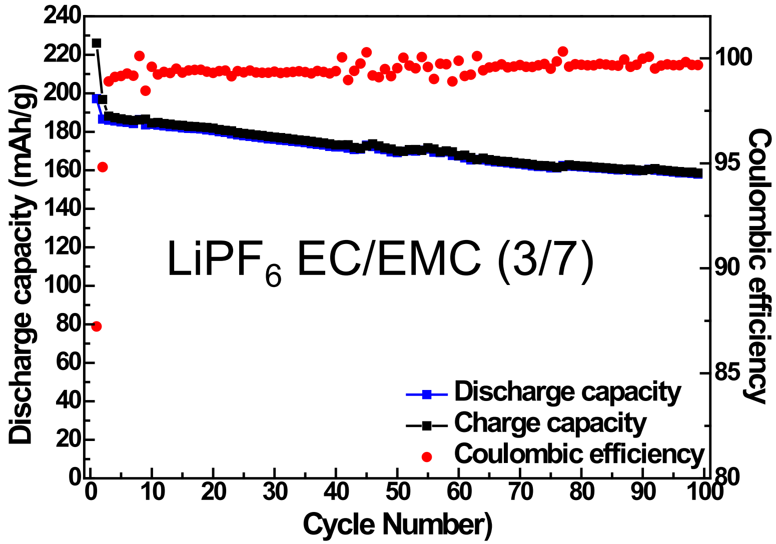
$LiNi_{0.62}Co_{0.14}Mn_{0.24}O_2$ with uniform Ni distribution

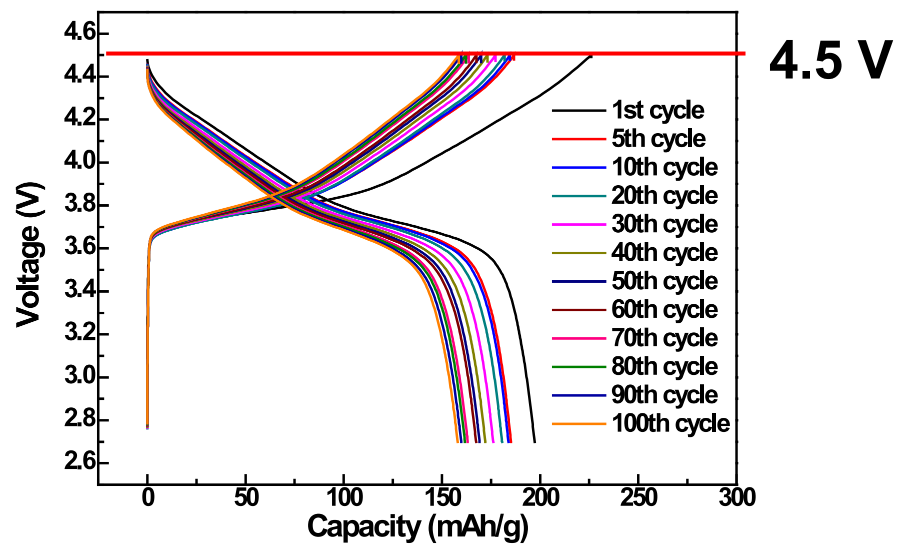


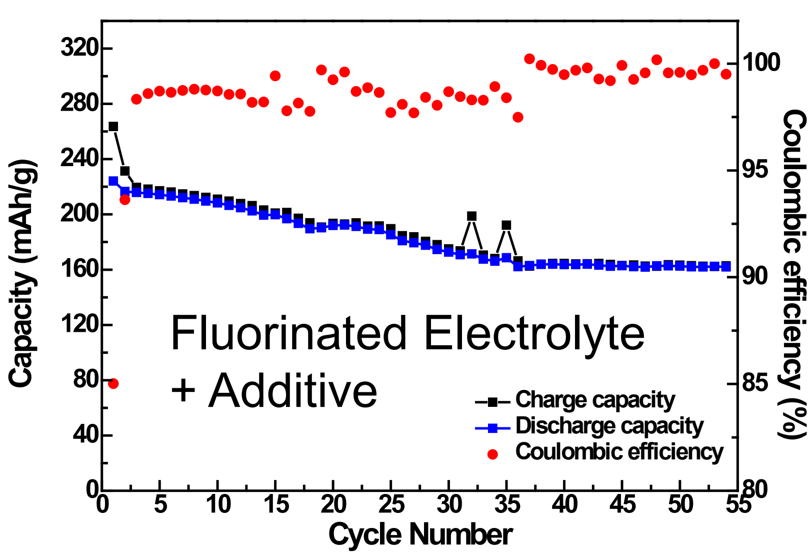


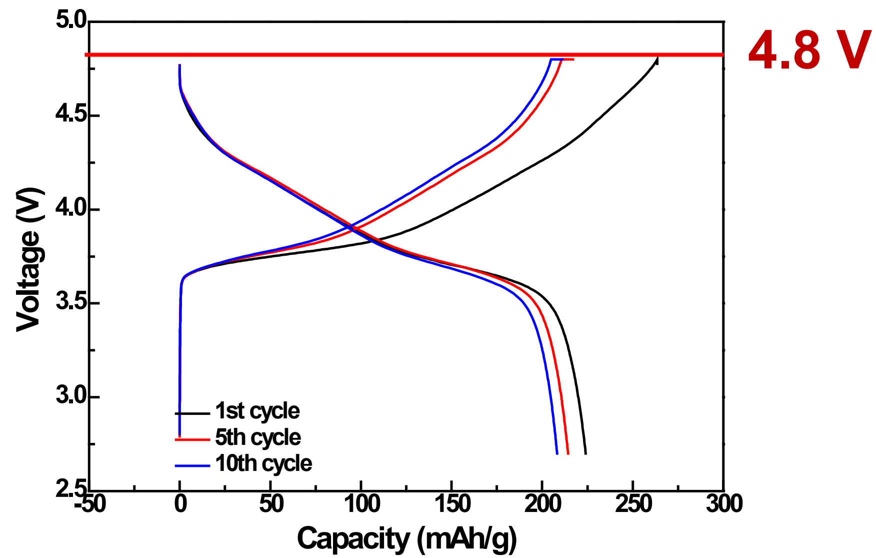
- The "concentration-gradient" sample shows superior voltage stability during cycling due to reduced surface reaction with the electrolyte

IX. High-Voltage Electrolytes - Oxidation Stability









TFP-PC-E-1:
1.2 M $LiPF_6$ in TFP-PC-E/EMC (3/7, w/w);
Voltage window: 4.8–2.7 V

- Fluorinated electrolyte/additive enables higher capacity at 4.8 V

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 pouch cells is being conducted by Idaho National Lab.

Remaining Challenges and Barriers

- Key challenges in anode are improving the 1st cycle efficiency of Si/Si alloy - carbon anodes and subsequent efficiency.
- New processes need to be developed and optimized to incorporate new binders to improved electrode performance
- 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 with good anode compatibility for an extended cycle life

Proposed Future Work

- Optimize the composition and structure of electrodes to maximize cycling stability and energy density.
- Develop a prelithiation approach to improve 1st cycle efficiency of Si/Si alloy-carbon anodes.
- Investigate the compatibility of new binder with Si/Si alloy-carbon micro-size particles.
- Develop an understanding of the factors influencing the electrochemical performances of Ni-rich layered oxide cathodes, *e.g.*, determine bulk and surface compositions/atomic arrangements with TEM, XPS, and TOF-SIMS.
- Modify the surface of Ni-rich oxides with $FePO_4$ or Al_2O_3 to provide better chemical stability with the electrolyte at higher voltages.
- Develop fluorinated electrolyte solvents and additives for Si alloy-carbon composite anodes and Ni-rich layered oxide cathodes.

Summary

- Three types of micro-sized Si-based anode materials exhibit good cycling life and high efficiency.

- High areal capacity (>3.2 mAh/cm^2) and good high temperature (60 ^{o}C) performance with high efficiency (99.5%) have been achieved by Si-based electrodes prepared by the industrial viable slurry coating approach.

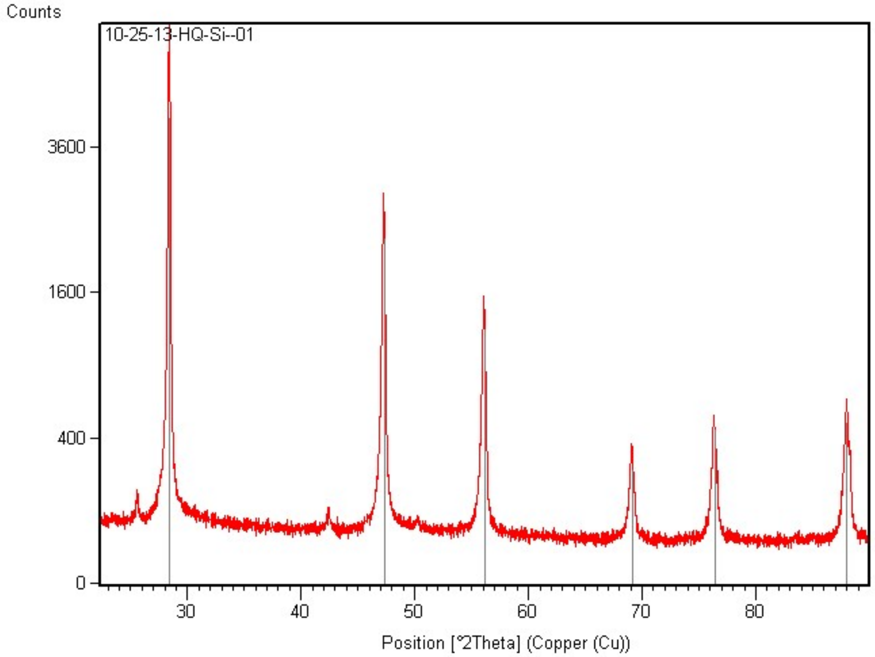
- Conductive polymer binders show much improved capacity and cycling stability and cross-linked binders show improved cycling performance over NaCMC for Si anode materials.

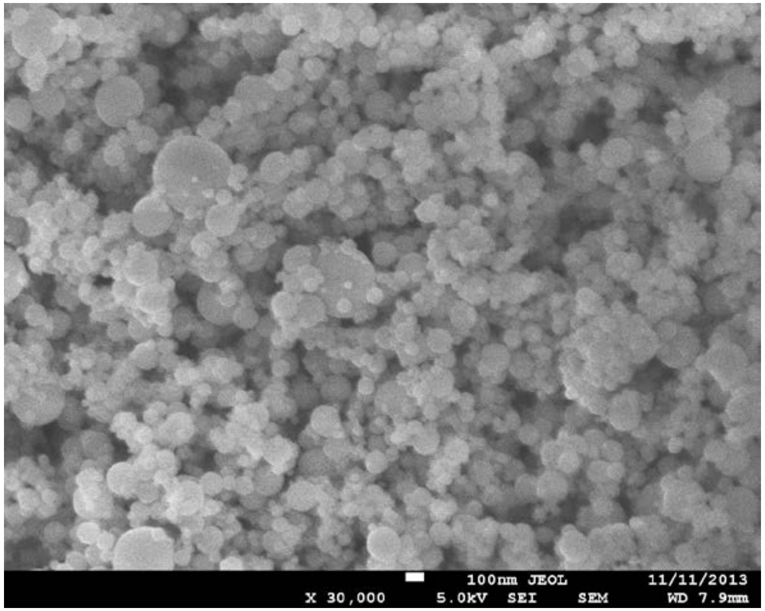
- Ni-rich layered oxide cathodes with a Ni-poor, Mn-rich surface and Ni-rich core (or a concentration-gradient structure) exhibit high capacities of > 200 mA h g^{-1} with good cyclability and rate capability due to better surface stabilization.

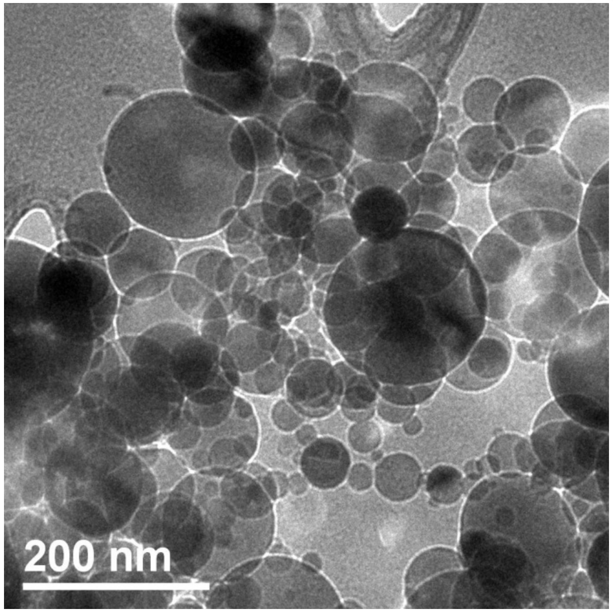
- Fluorinated electrolyte/additive for layered oxides cathodes enables the delivery of higher capacity at 4.8 V.

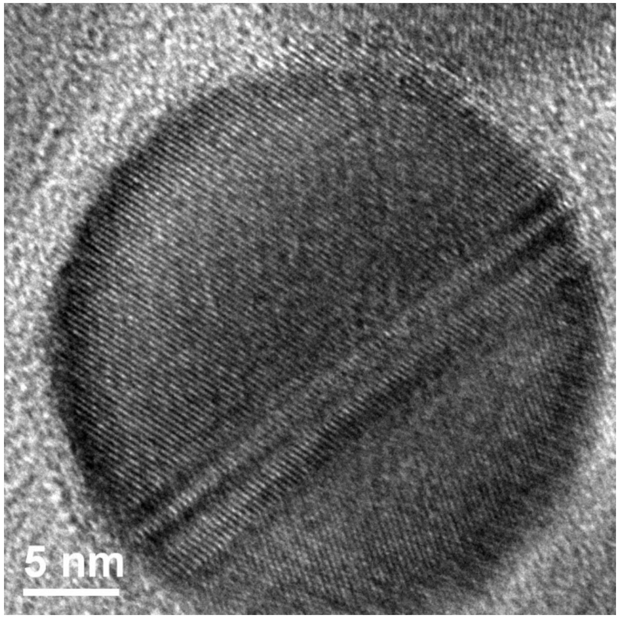
Technical Back-Up Slides

Commercial Baseline Si Anode Materials



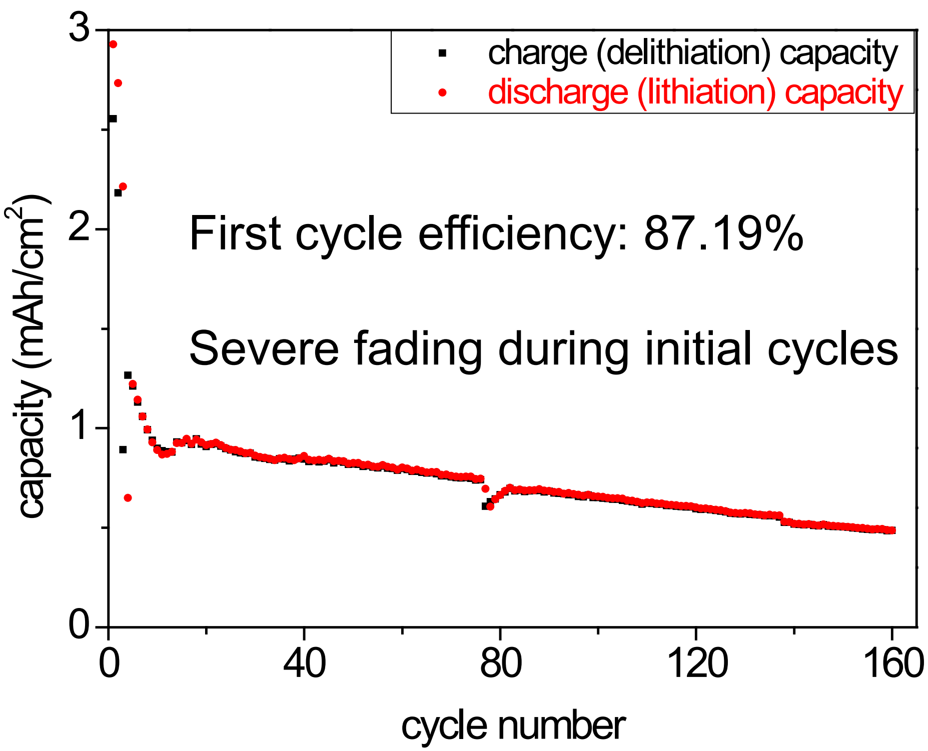


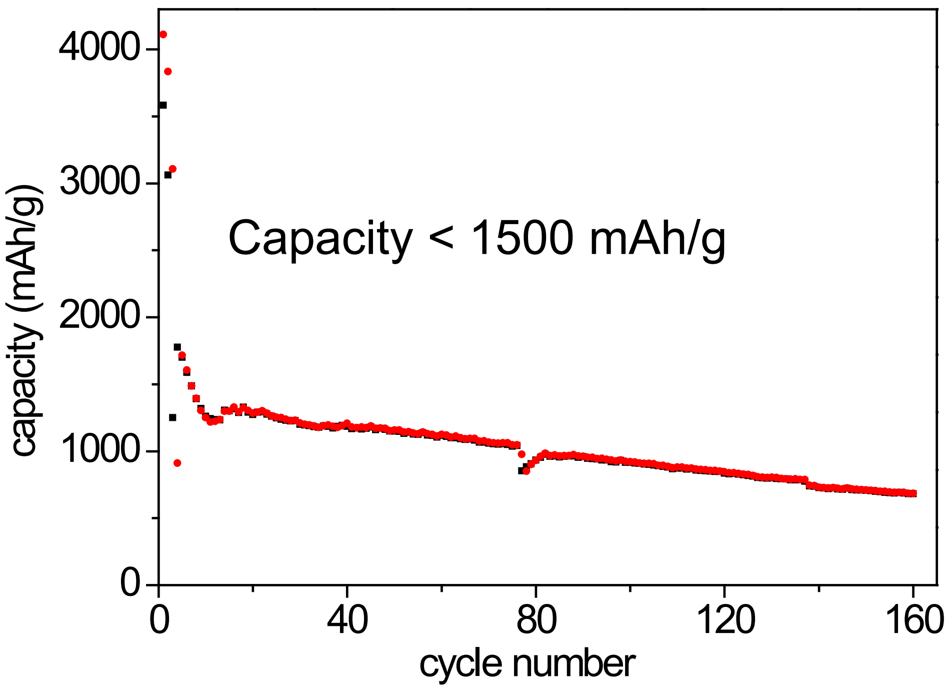




- Spherical particles
- Particle size 50-150 nm
- High crystallinity

Performance of Commercial Si Anode Materials

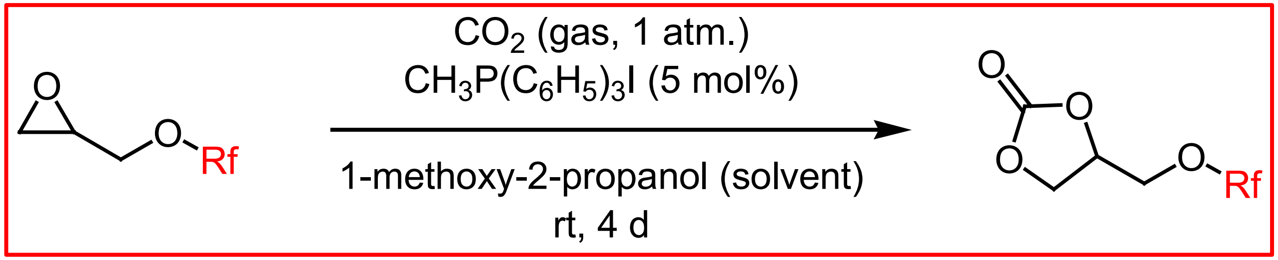




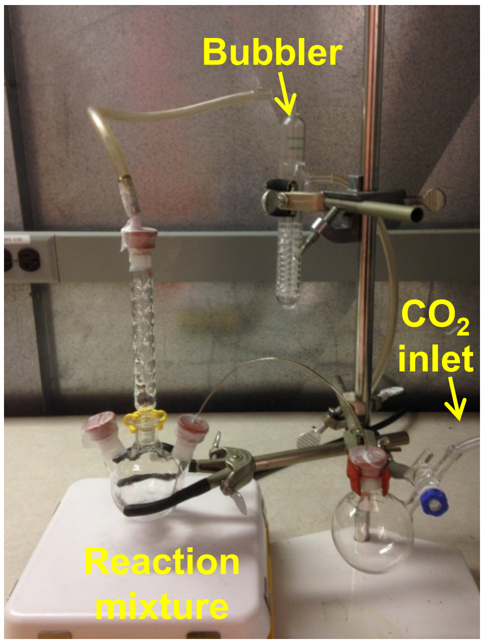
Thickness: 31 um
Porosity: 80.8%
loading: 0.71 mg/cm2

- C/25 for 3 cycles, C/3 lithiation and C/2 delithiation
- Electrolyte: EC/DEC=1, 10 wt% FEC, 1 M LiPF6
- Cut-off voltage: 0.01 V~1V
- 25% AB, 50% silicon, 20% CMC and 5% PVA

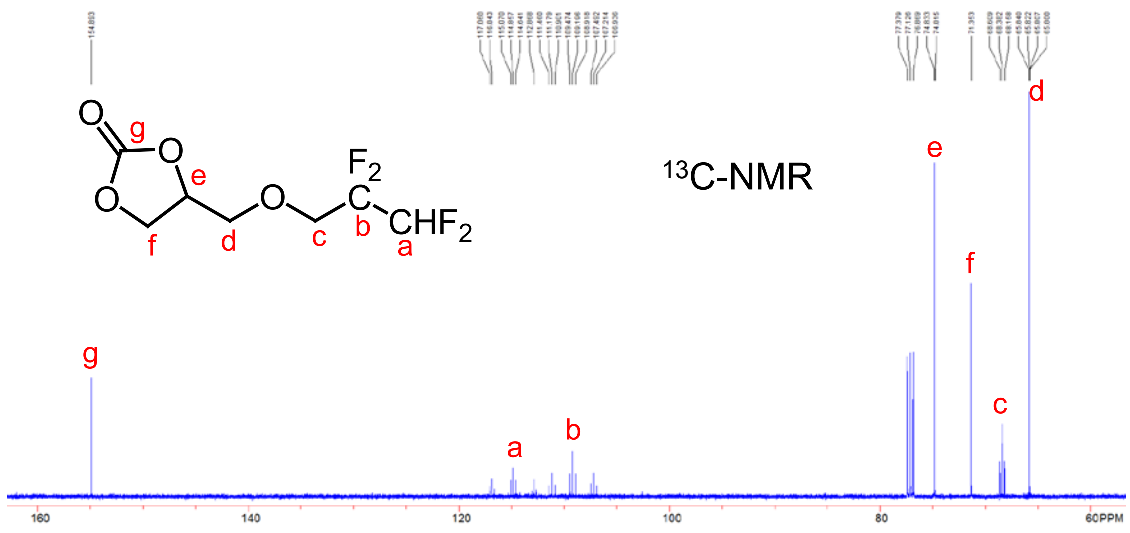
High-Voltage Electrolytes - Solvent/Additive Synthesis



TFP-PC-E-1



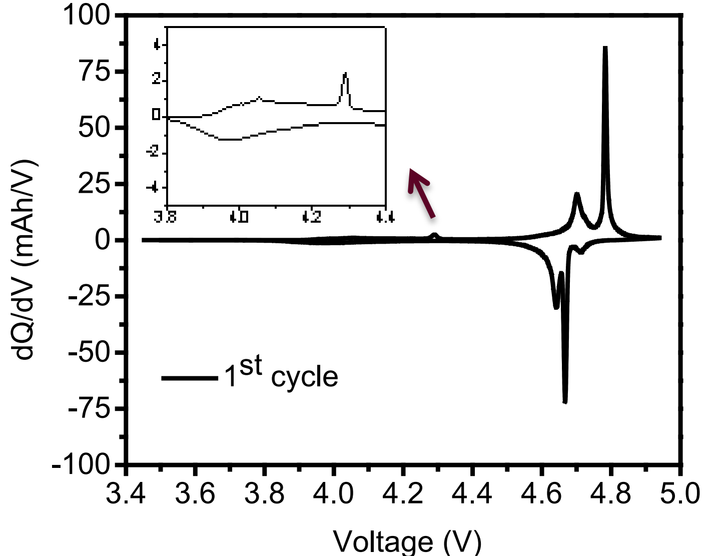
Organic synthesis setup



1) Epoxide conversion goes to maximum in 4 days (>97%) monitored by GC-MS without internal standard calibration.
2) Pure fluorinated cyclic carbonate was obtained by two vacuum distillation (90 C/0.3 mmHg) processes affording pure product with >99.8% purity (by GC-MS); yield is ~45%;
3) Vacuum-distilled fluorinated cyclic carbonate was further characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and FT-IR and K-F titration.

High-Voltage Electrolytes - Voltage Stability (LNMO/Li)

TFP-PC-E-1:
1.2 M $LiPF_6$ in TFP-PC-E/EMC (3/7, w/w);
Voltage window: 4.95–3.5 V



Voltage window: 4.95–3.5 V