STABILIZED SPINEL AND NANO OLIVINE CATHODES

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February 27, 2008

This presentation does not contain any proprietary or confidential information

OUTLINE

- Purpose of work
- Addressing Previous Review Comments
- Barriers
- Approach
- Performance Measures and Accomplishments
- Technology Transfer
- Plans for Next Year Activities
- Summary
- Publications/Patents

PURPOSE OF WORK

- To develop high performance cathodes for lithium ion batteries
  - Low cost spinel manganese oxide cathodes that can offer acceptable capacity retention, high rate, and good storage properties at elevated temperatures
  - Low cost spinel + layered oxide composite cathodes that can offer a combination of high energy and high power
- To develop a firm understanding of the factors controlling the electrochemical performances

RESPONSE TO PREVIOUS REVIEW COMMENTS

2006 Merit Review Comments

- Need to include carbon anode
- Develop oxygen deficient spinels for higher capacity

Response to 2006 Merit Review

- Data have been collected with carbon anode now
- Our data show that not much oxygen deficiency could be accommodated in the spinel lattice
  - Substitution of F^- for O^{2-} is a better way to increase the capacity as we have shown

BARRIERS

- Cost
- Cycle life
- Safety
- Power density
- Energy density

APPROACH

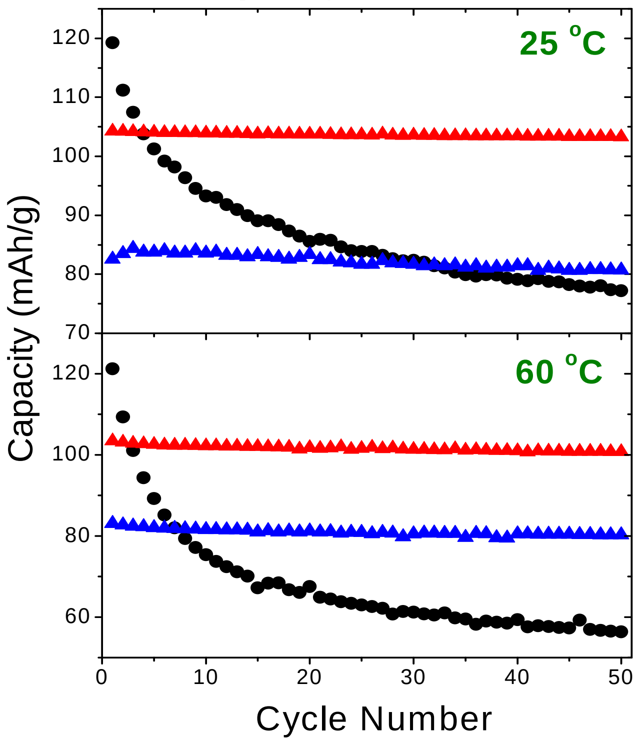
- Develop a firm understanding of the factors controlling the electrochemical performance of spinel cathodes and utilize the understanding to develop high performance cathodes

  - Cationic and anionic substitutions in 4 V and 5 V spinel cathodes
  - Surface modifications of 4 V and 5 V spinel cathodes
  - Stabilized spinel + layered composite cathodes to enhance performance

  - Solid state and solution-based synthesis approaches
  - Chemical and structural characterizations
  - Electrochemical evaluation with lithium and carbon anodes
  - Structure-property-performance relationships

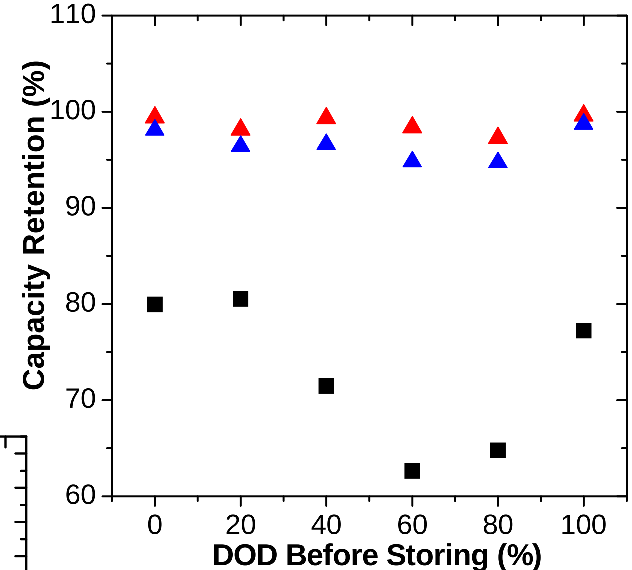
STABILIZED HIGH POWER SPINEL CATHODES

Capacity Retention

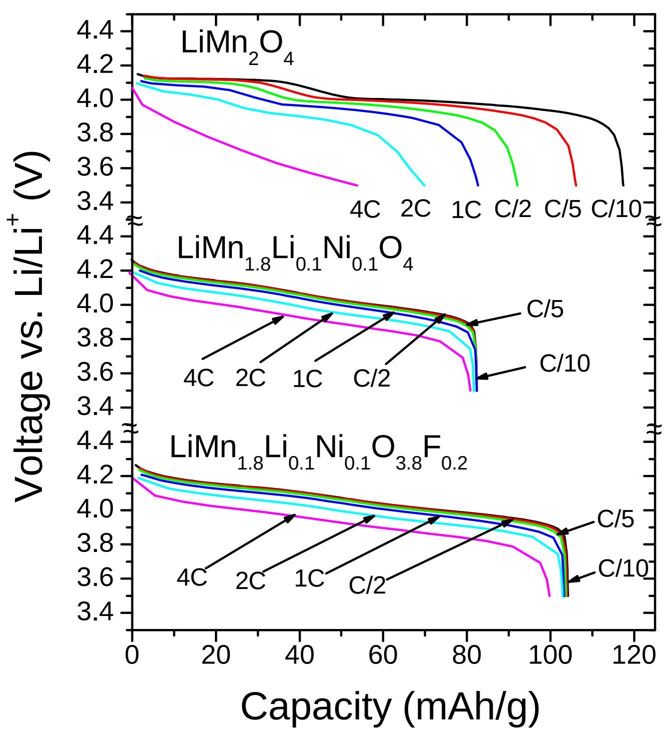


- ■ $LiMn_2O_4$
- ▲ $LiMn_{1.8}Li_{0.1}Ni_{0.1}O_4$
- ▲ $LiMn_{1.8}Li_{0.1}Ni_{0.1}O_{3.8}F_{0.2}$

After storage at 55 °C for 7 days



Power capability

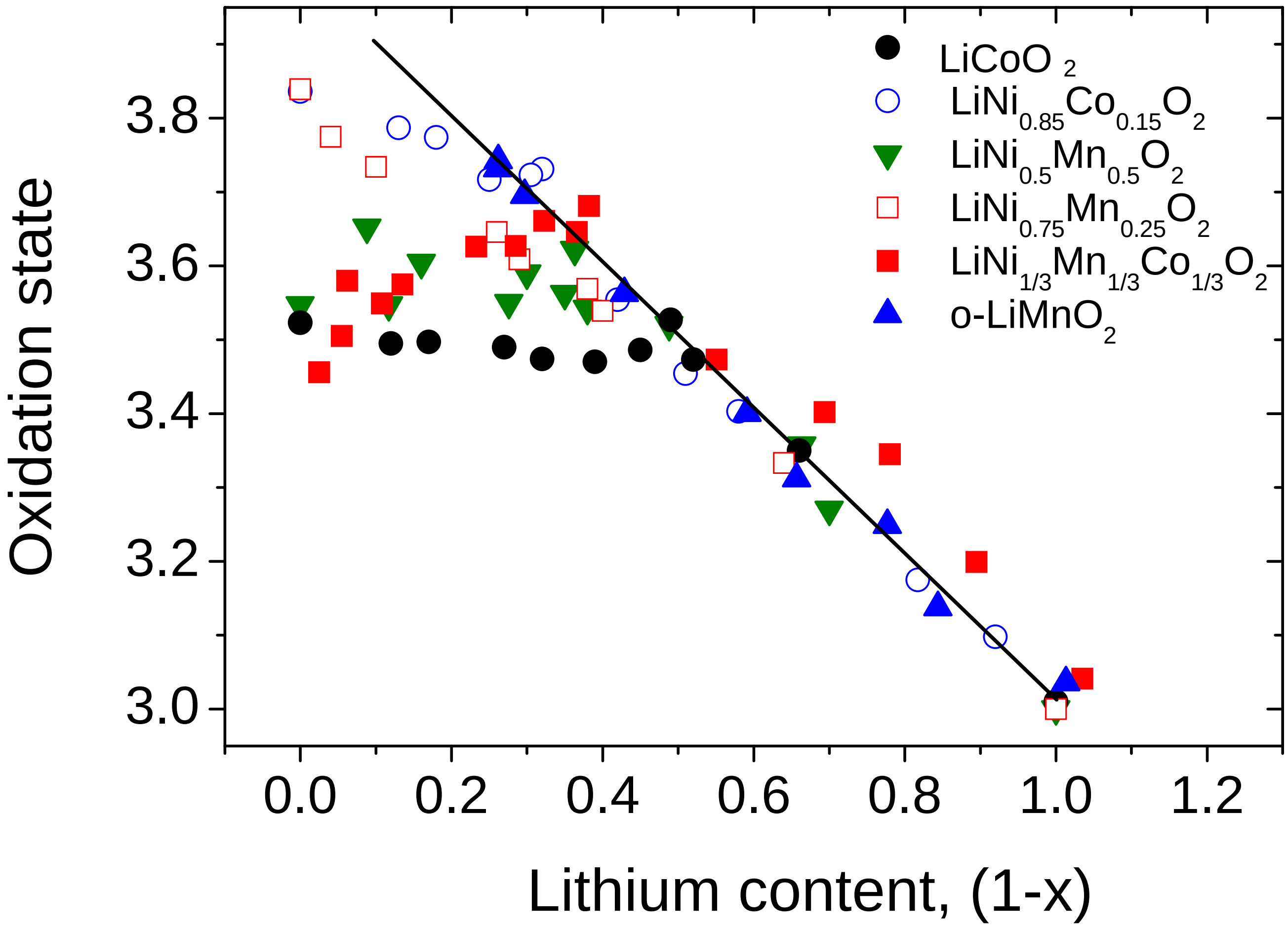


Charge efficiency

Sample	Irreversible capacity loss (mAh/g)
Li Mn_2O_4	12
$LiMn_{1.8}Li_{0.1}Ni_{0.1}O_4$	2.4
$LiMn_{1.8}Li_{0.1}Ni_{0.1}O_{3.8}F_{0.2}$	0.9

W. Choi and A. Manthiram, *Electrochem. Solid State Lett.* **9**, A245 (2006).

PROTON INSERTION INTO LAYERED OXIDES



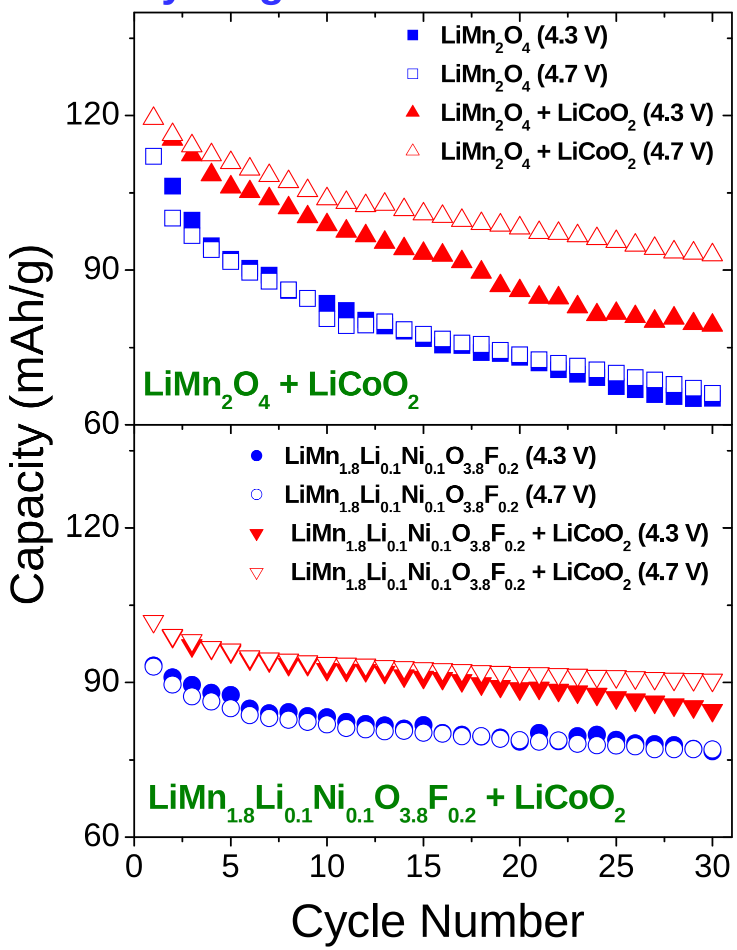
Oxidation state becomes constant due to proton insertion caused by chemical instability

$$LiMO_2 + x\,NO_2BF_4 \rightarrow Li_{1-x}MO_2 + x\,LiBF_4 + x\,NO_2$$

J. Choi, E. Alvarez, T. A. Arunkumar, & A. Manthiram, *Electrochem. Solid State Lett.* **9**, A241 (2006)

SPINEL + $LiCoO_2$ (70:30) CATHODE WITH CARBON ANODE

Cycling at 3.5 – 4.3 V at 60 °C



Composition	Dissolved Mn[a] (%)	Dissolved Mn[b] (%)	Dissolved Mn[c] (%)
Li Mn_2O_4	**0.93**	**0.83**	**0.88**
70% $LiMn_2O_4$ + 30% $LiCoO_2$	**0.88**	**0.59**	**0.41**
$LiMn_{1.8}Li_{0.1}Ni_{0.1}O_{3.8}F_{0.2}$	**0.30**	**0.27**	**0.27**
$LiMn_{1.8}Li_{0.1}Ni_{0.1}O_{3.8}F_{0.2}$ + $LiCoO_2$ (70:30)	**0.28**	**0.11**	**0.08**

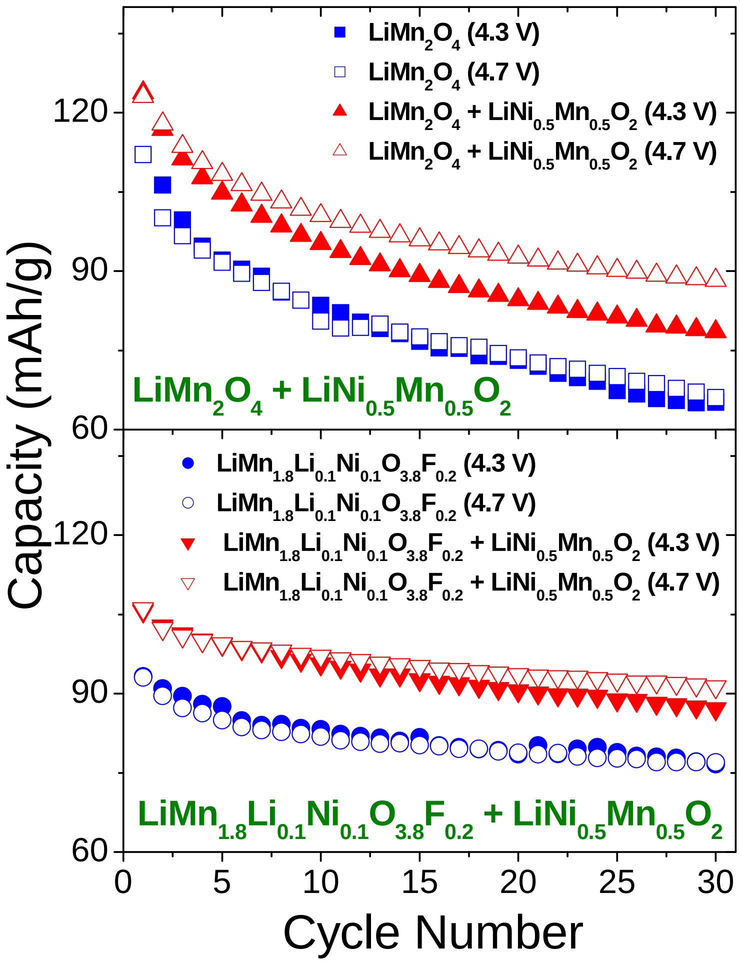
[a]After storing for 7 days without any charge-discharge
[b]After storing at 4.7 V for 7 days at the end of first charge
[c]After storing at 3.5 V for 7 days at the end of first discharge

A. Manthiram and W. Choi, *Electrochem. Solid State Lett.* **10**, A228 (2007).

- Charging the lithium ion cells at 60 °C to 4.7 V in the first cycle traps the protons within the layered oxide lattice and suppresses Mn dissolution

SPINEL + $LiNi_{0.5}Mn_{0.5}O_2$ (70:30) WITH CARBON ANODE

Cycling at 3.5 – 4.3 V at 60 °C

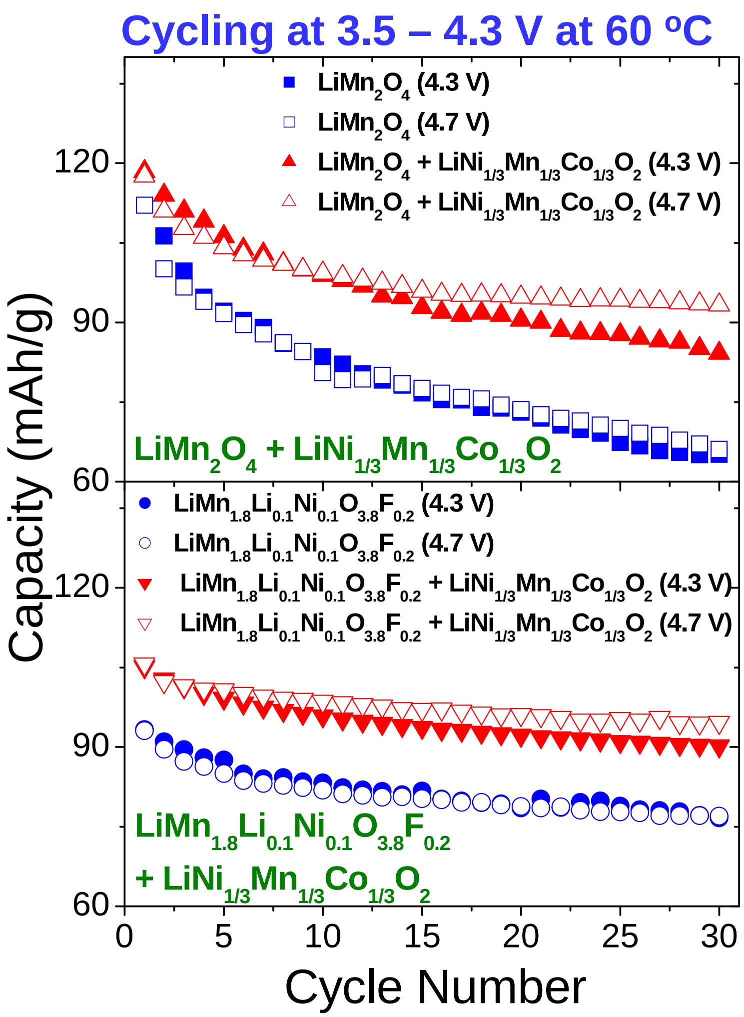


Composition	Dissolved Mn[a] (%)	Dissolved Mn[b] (%)	Dissolved Mn[c] (%)
Li Mn_2O_4	**0.93**	**0.83**	**0.88**
70% $LiMn_2O_4$ + 30% $LiNi_{0.5}Mn_{0.5}O_2$	**0.90**	**0.57**	**0.44**
$LiMn_{1.8}Li_{0.1}Ni_{0.1}O_{3.8}F_{0.2}$	**0.30**	**0.27**	**0.27**
$LiMn_{1.8}Li_{0.1}Ni_{0.1}O_{3.8}F_{0.2}$ + $LiNi_{0.5}Mn_{0.5}O_2$ (70:30)	**0.31**	**0.11**	**0.10**

[a] After storing for 7 days without any charge-discharge
[b] After storing at 4.7 V for 7 days at the end of first charge
[c] After storing at 3.5 V for 7 days at the end of first discharge

- Charging the lithium ion cells at 60 °C to 4.7 V in the first cycle traps the protons within the layered oxide lattice and suppresses Mn dissolution

SPINEL + $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (70:30) WITH CARBON ANODE

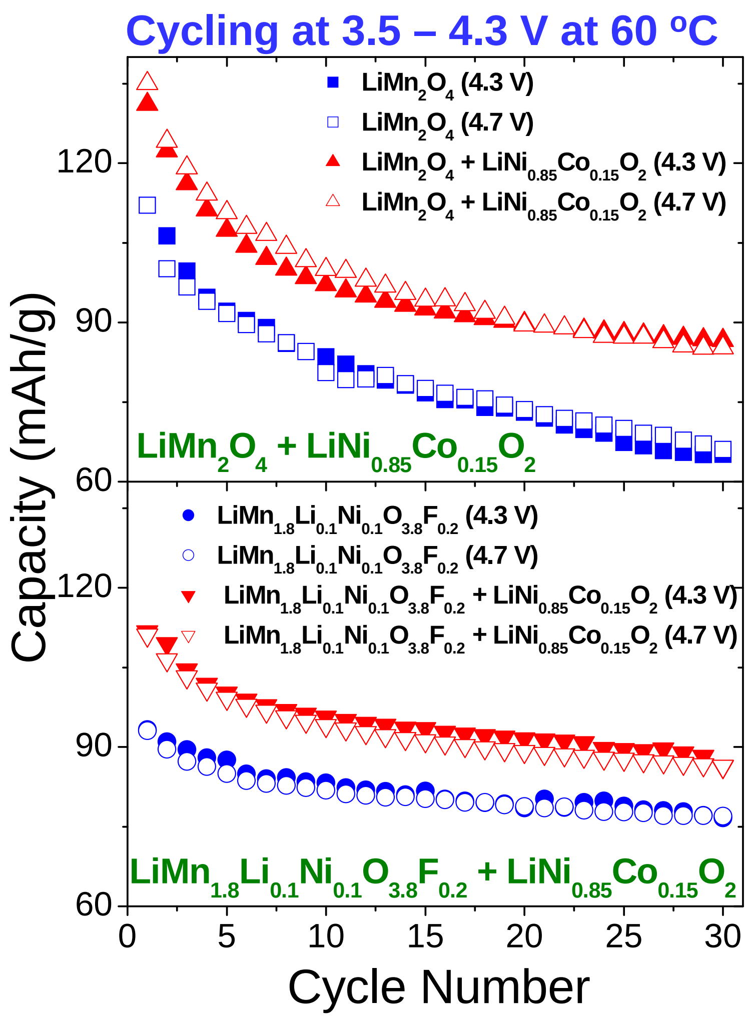


Composition	Dissolved Mn[a] (%)	Dissolved Mn[b] (%)	Dissolved Mn[c] (%)
Li Mn_2O_4	**0.93**	**0.83**	**0.88**
70% $LiMn_2O_4$ + 30% $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$	**0.90**	**0.52**	**0.39**
$LiMn_{1.8}Li_{0.1}Ni_{0.1}O_{3.8}F_{0.2}$	**0.30**	**0.27**	**0.27**
$LiMn_{1.8}Li_{0.1}Ni_{0.1}O_{3.8}F_{0.2}$ + $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (70:30)	**0.29**	**0.12**	**0.10**

[a] After storing for 7 days without any charge-discharge
[b] After storing at 4.7 V for 7 days at the end of first charge
[c] After storing at 3.5 V for 7 days at the end of first discharge

- Charging the lithium ion cells at 60 ºC to 4.7 V in the first cycle traps the protons within the layered oxide lattice and suppresses Mn dissolution

SPINEL + $LiNi_{0.85}Co_{0.15}O_2$ (70:30) WITH CARBON ANODE

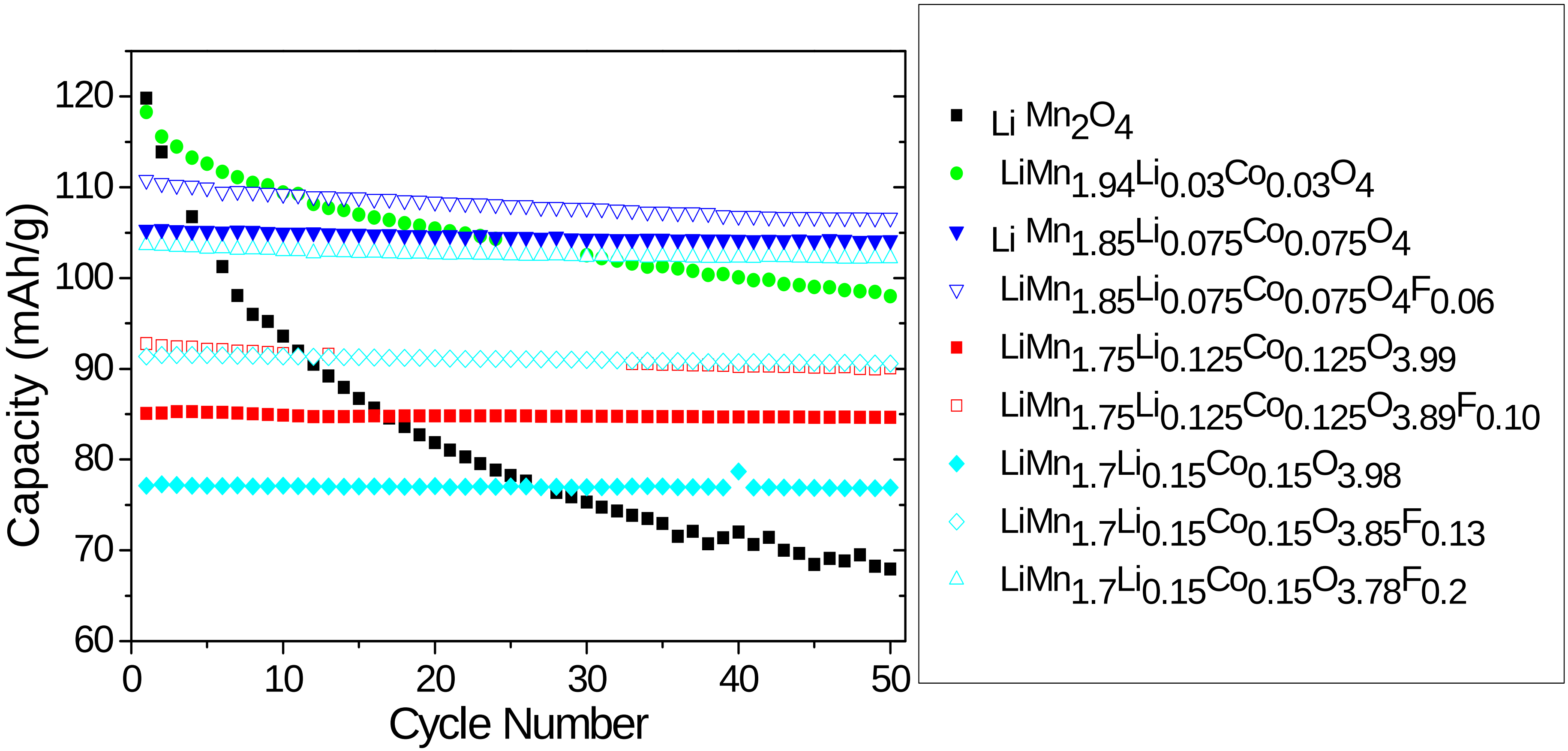


Composition	Dissolved Mn[a] (%)	Dissolved Mn[b] (%)	Dissolved Mn[c] (%)
Li Mn_2O_4	0.93	0.83	0.88
70% $LiMn_2O_4$ + 30% $LiNi_{0.85}Co_{0.15}O_2$	0.93	0.89	0.89
$LiMn_{1.8}Li_{0.1}Ni_{0.1}O_{3.8}F_{0.2}$	0.30	0.27	0.27
$LiMn_{1.8}Li_{0.1}Ni_{0.1}O_{3.8}F_{0.2}$ + $LiNi_{0.85}Co_{0.15}O_2$ (70:30)	0.31	0.31	0.29

[a] After storing for 7 days without any charge-discharge
[b] After storing at 4.7 V for 7 days at the end of first charge
[c] After storing at 3.5 V for 7 days at the end of first discharge

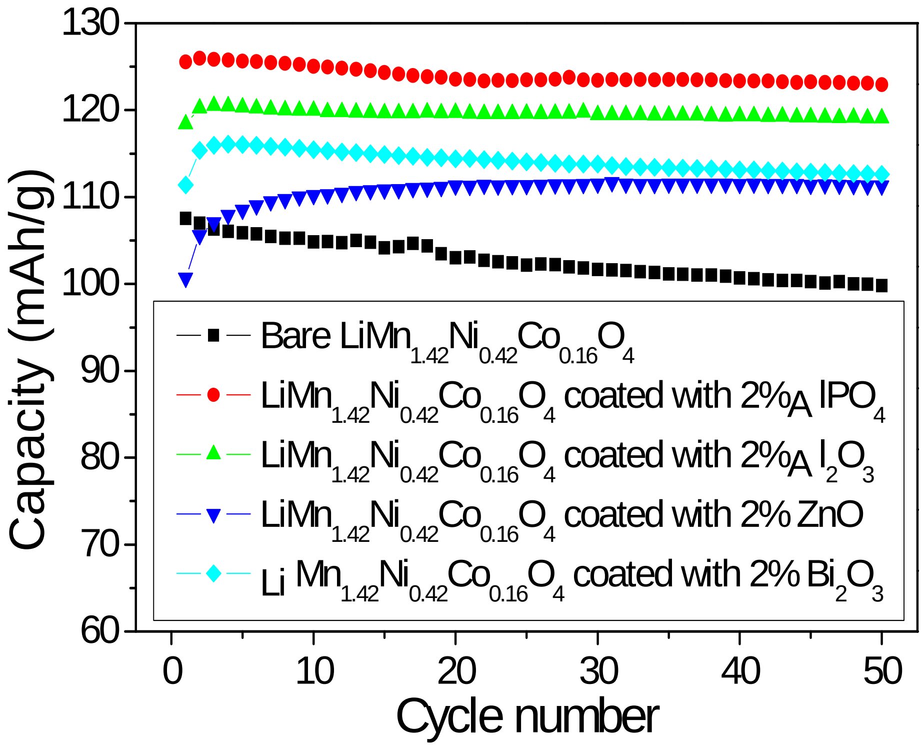
- Charging the lithium ion cells at 60 °C to 4.7 V in the first cycle ***does not trap*** the protons within the layered oxide lattice and suppresses Mn dissolution

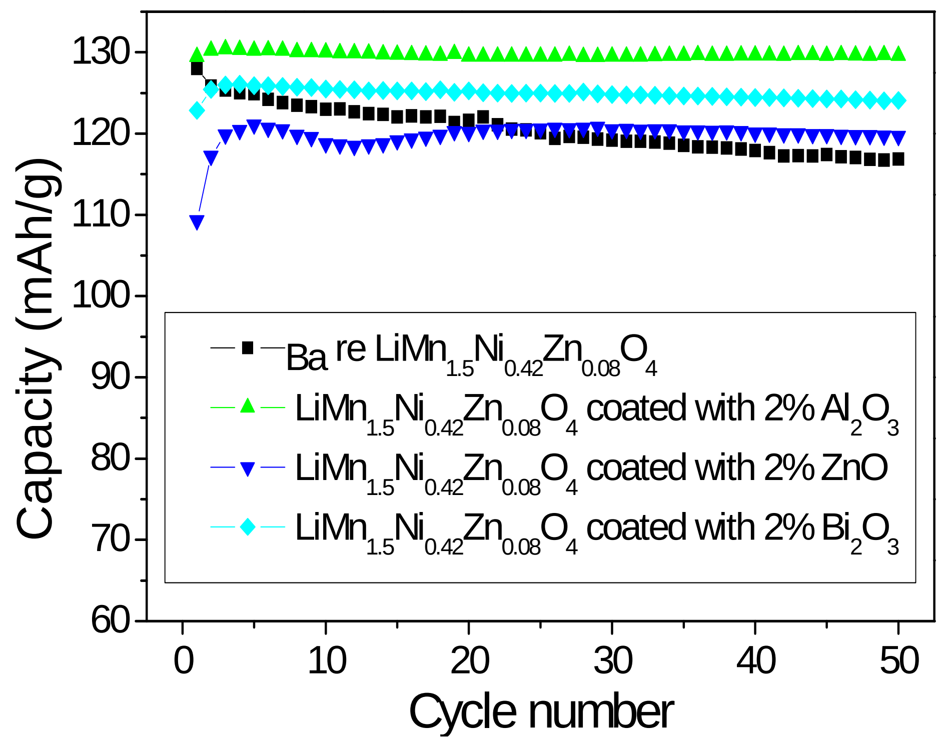
CYCLABILITY OF STABILIZED 4 V SPINEL CATHODES



- Extensive investigation with a variety of cationic and anionic substitutions reveals that the initial Mn valence needs to be above 3.6+ to reduce Mn dissolution and realize good capacity retention

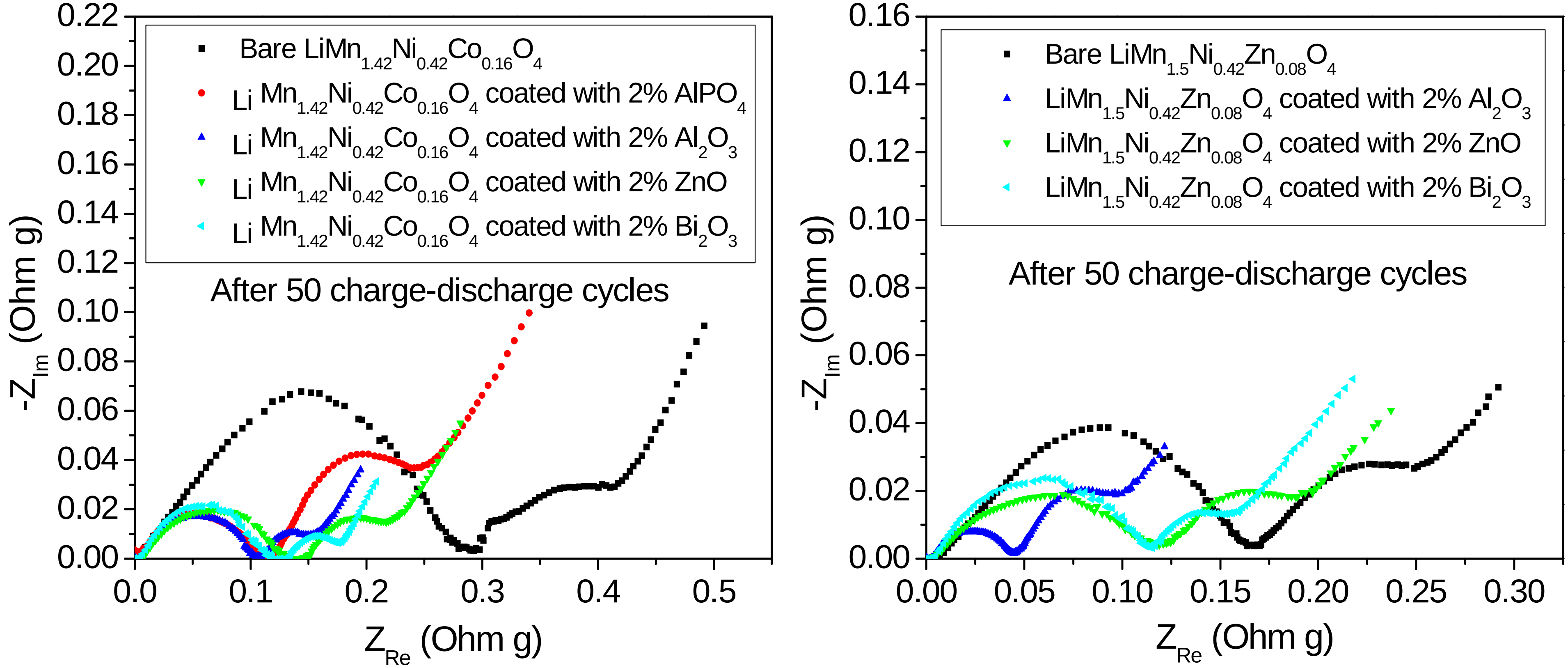
SURFACE MODIFIED, STABILIZED 5 V SPINEL CATHODES





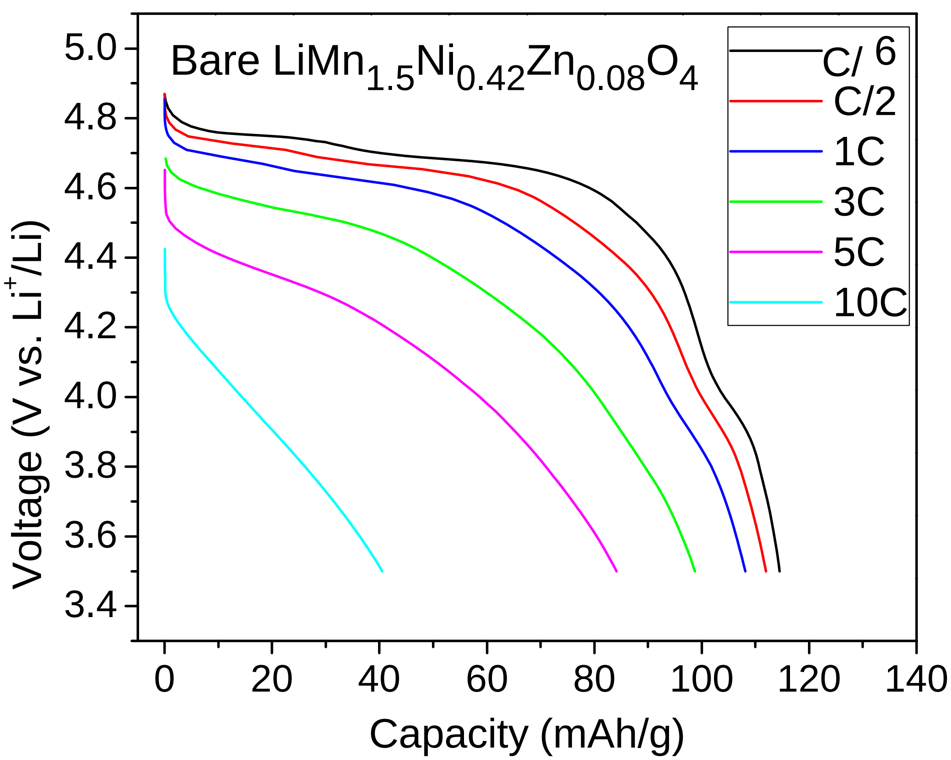
- Appropriate cationic substitutions reduce the lattice parameter difference among the three cubic phases and improve performance
- Surface modification with other oxides improve the cyclability further
- Some surface modifications also increase the capacity (~ 130 mAh/g)
- ~ 130 mAh/g at ~ 4.7 V offers attractive energy density at low cost

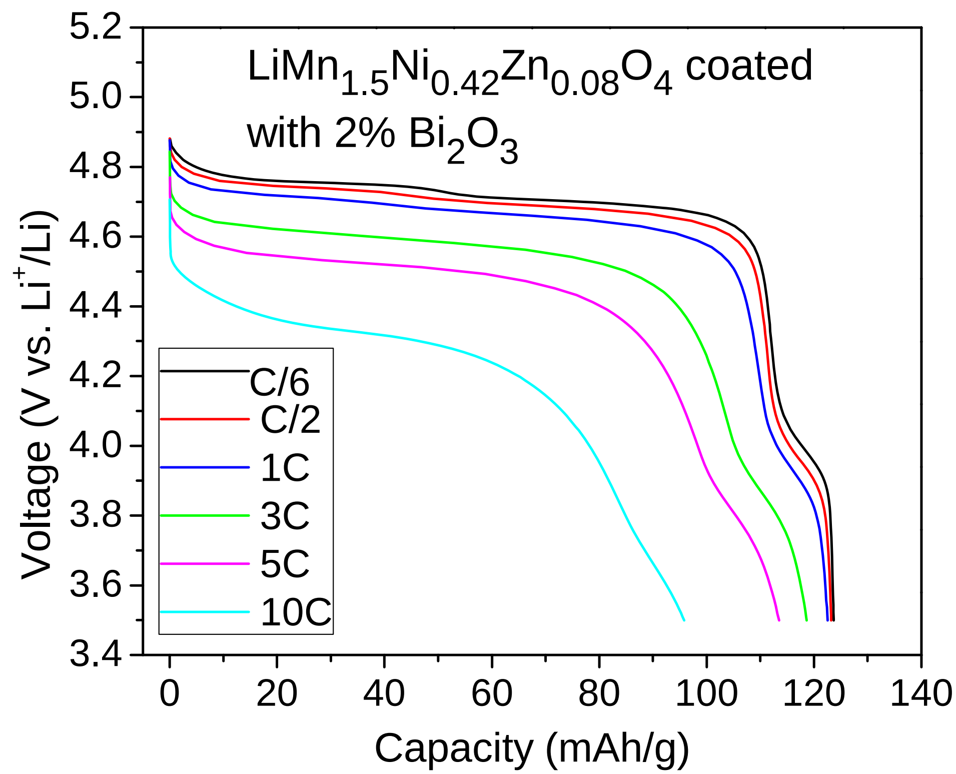
EIS OF STABILIZED 5 V SPINEL CATHODES



- Surface modification reduces both the electron transfer and SEI resistances due to the suppression of the reaction of cathode surface with the electrolyte and thereby improves the cyclability and capacity

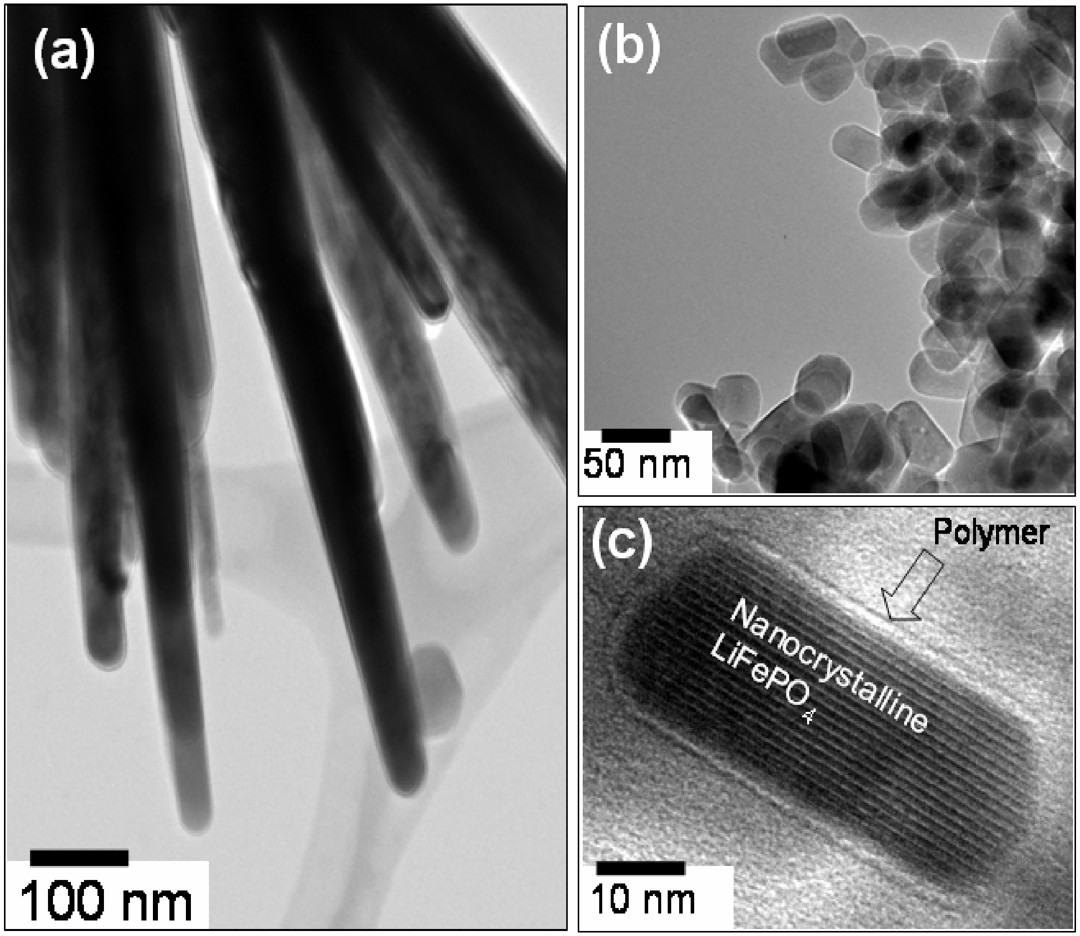
RATE CAPABILITY OF STABILIZED 5 V SPINEL CATHODES

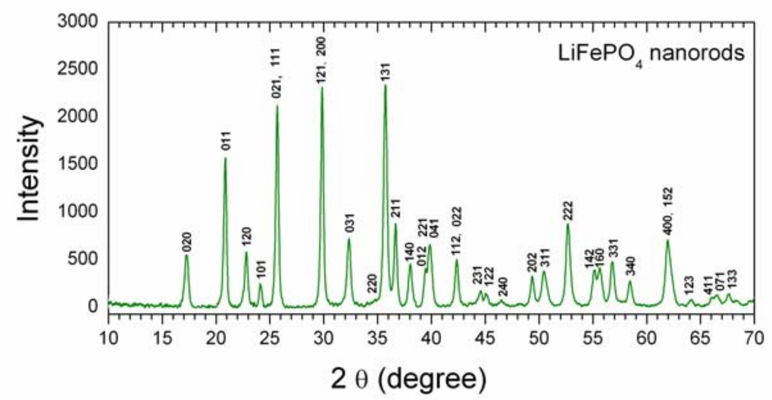


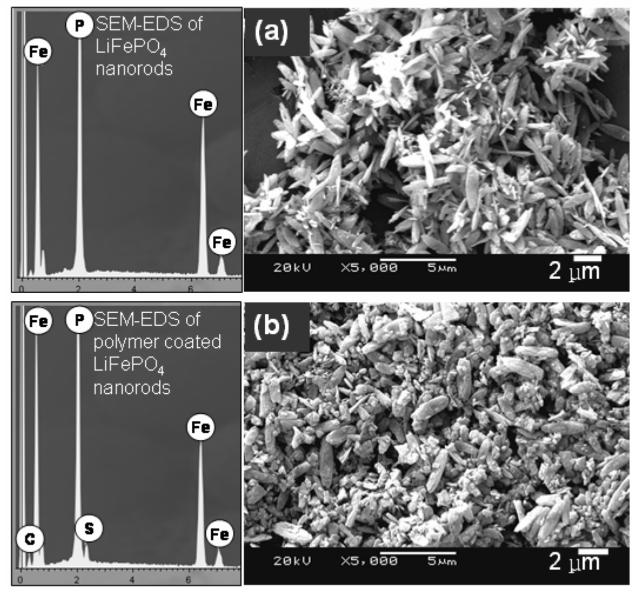


- Surface modification improves the rate capability significantly due to a reduction of electron transfer and ohmic resistances

RAPID SYNTHESIS OF $LiFePO_4$ NANORODS

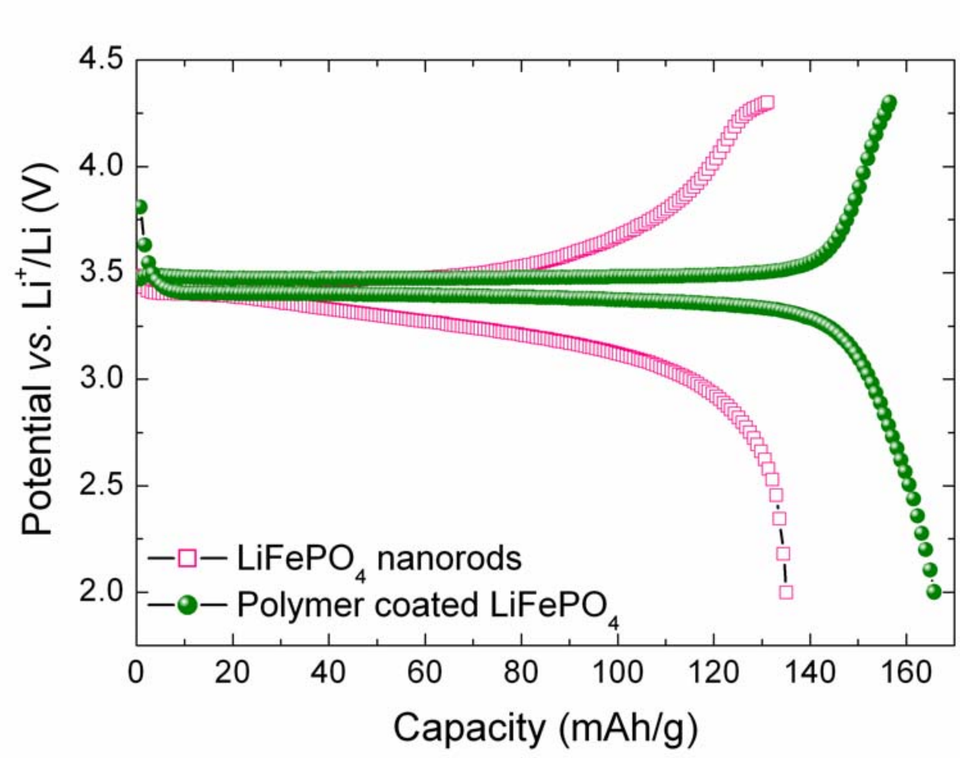


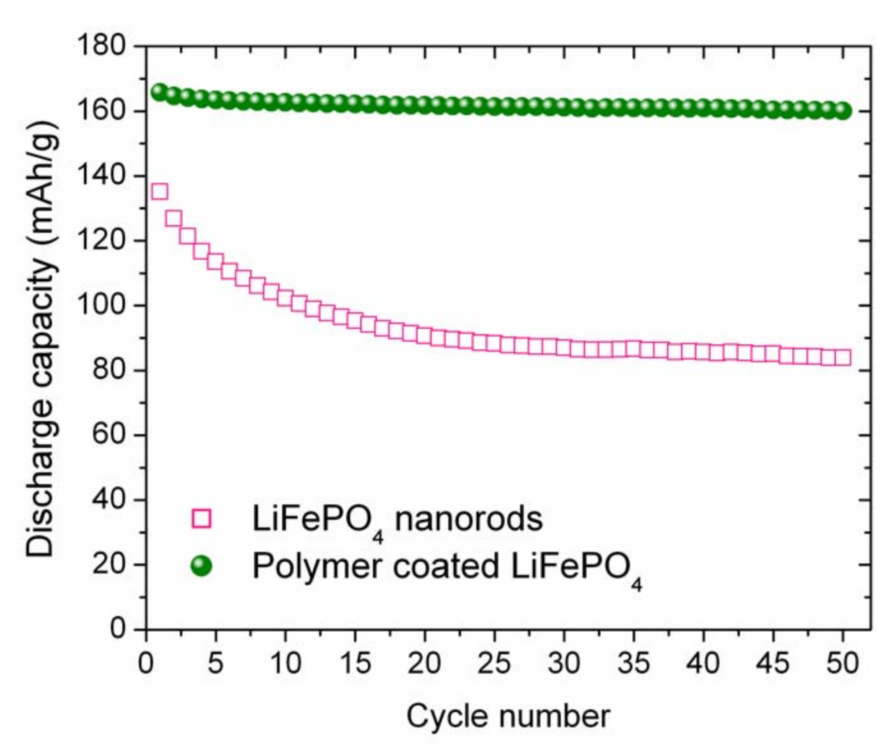




- Highly crystalline $LiFePO_4$ nanorods are synthesized in < 5 min at < 300 ^{o}C
- Nanorods (40 nm width, 1 mm length & 25 nm width, 100 nm length)

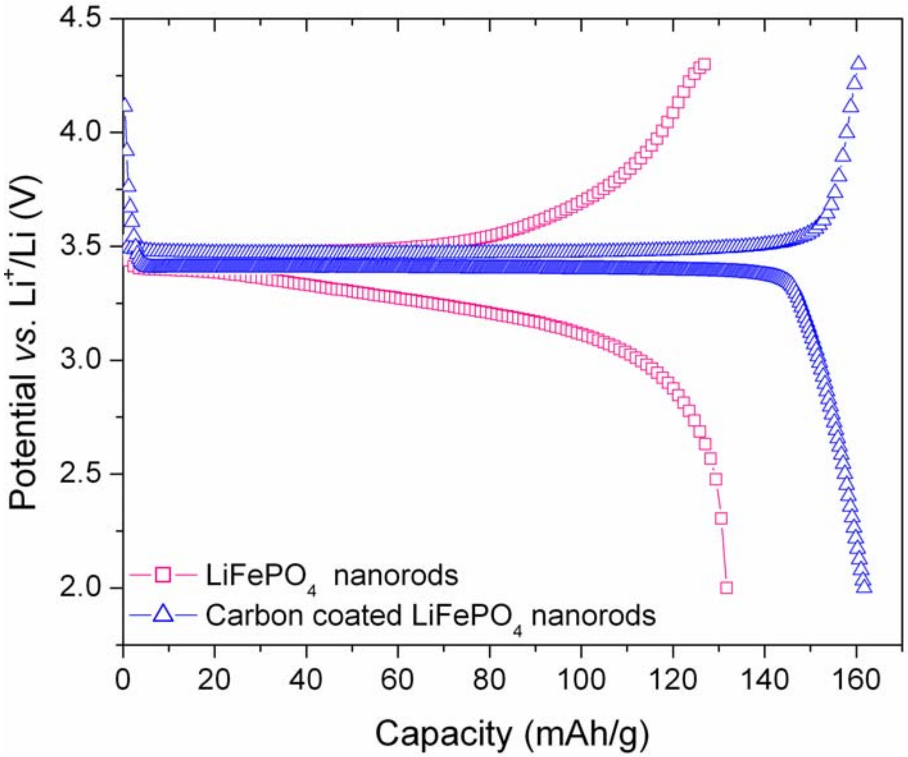
ELECTROCHEMICAL PERFORMANCE OF NANO $LiFePO_4$

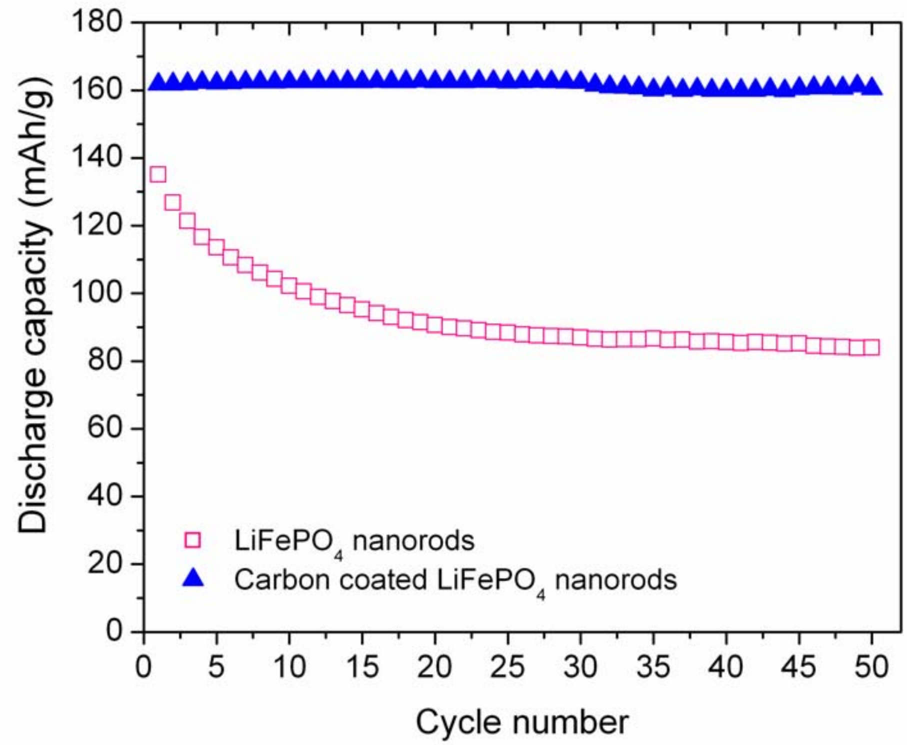




- $LiFePO_4$ nanorods coated with a mixed ionically and electronically conducting polymer exhibit > 160 mAh/g with excellent cyclability
- Synthesized at < 300 °C without requiring any reducing gas atmospheres, offering significant savings in manufacturing cost

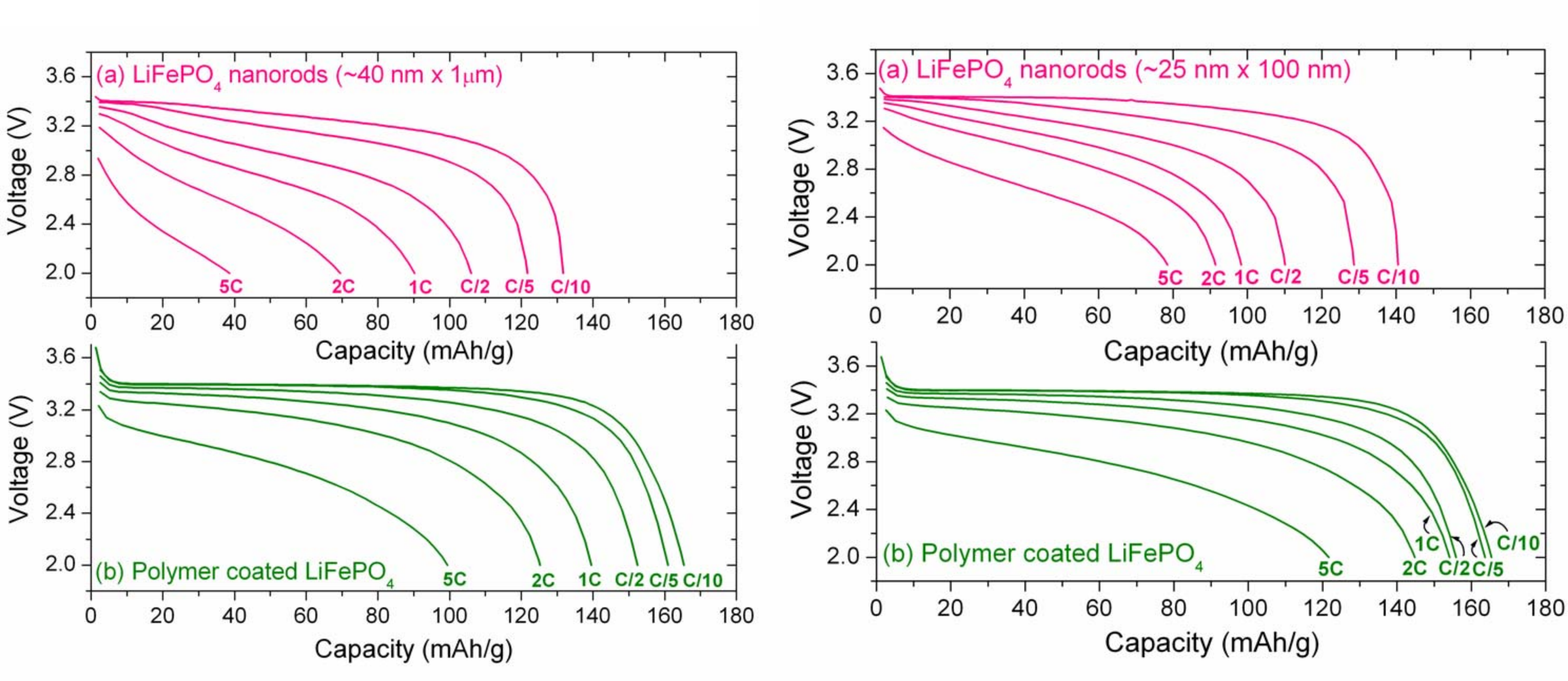
ELECTROCHEMICAL PERFORMANCE OF NANO $LiFePO_4$





- $LiFePO_4$ nanorods coated with carbon exhibit > 160 mAh/g with excellent cyclability

RATE CAPABILITY OF NANO $LiFePO_4$



- $LiFePO_4$ nanorods coated with a mixed ionically and electronically conducting polymer exhibit excellent rate capability
- Power capability increases with decreasing rod dimension

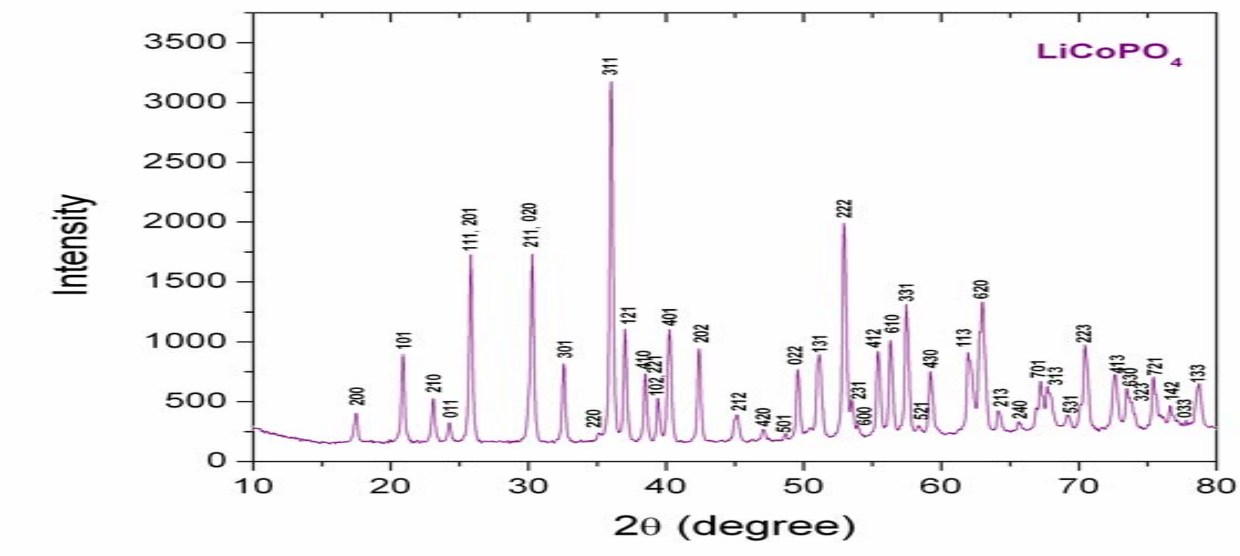
TECHNOLOGY TRANSFER

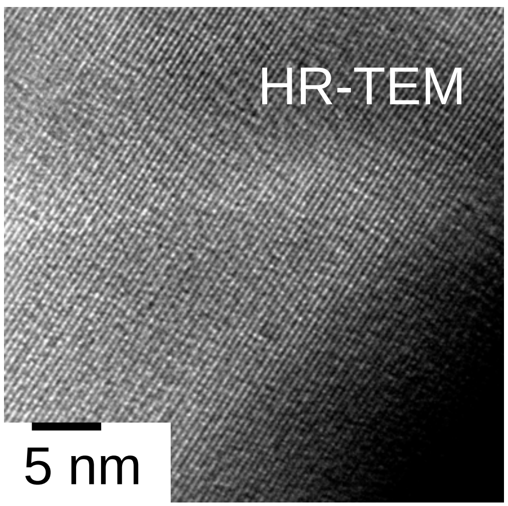
- Two patent applications filed have been licensed by ActaCell located in Austin to develop high power lithium ion cells
- Stabilized spinel + layered oxides for better capacity retention and a combination of high energy and power

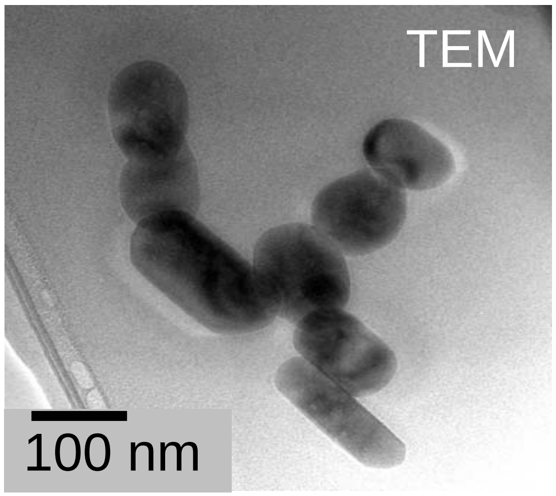
PLANS FOR NEXT YEAR

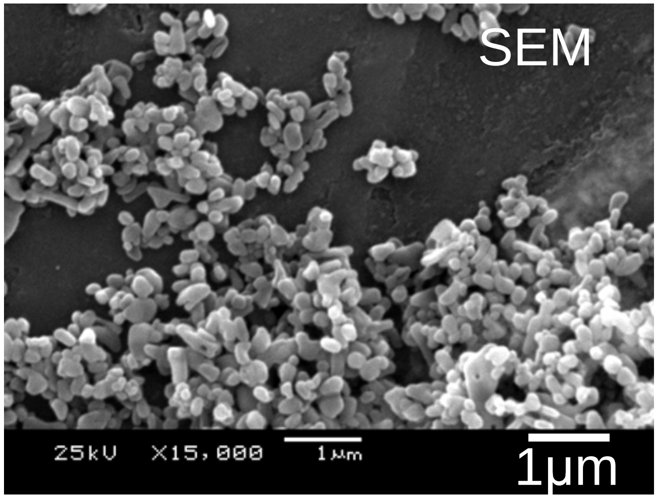
- Explore composite cathodes consisting of stabilized 4 V spinel (~ 100 mAh/g) and complex layered $Li[Li,Ni,Mn,Co]O_2$ (~250 mAh/g) to enhance energy density significantly while maintaining high power capability
- Study the performances of surface modified, stabilized 5 V spinel cathodes at elevated temperatures
- Explore the rapid synthesis approach to obtain high voltage phospho-olivines $LiMPO_4$ (M = Mn, Co, and Ni) in different nanomorphologies
- Barriers: Intimate mixing in the composites, realizing suitable interfaces in surface modified materials, and control of particle size and shape in olivines. We will address them by
  - appropriate synthesis and processing conditions
  - employing advanced characterization methodologies (high resolution TEM, XPS, and in-depth electrochemical measurements) to understand and optimize the interfaces

HIGH VOLTAGE NANO PHOSPHO-OLIVINES









- Highly crystalline nano $LiCoPO_4$ is synthesized in < 15 min at 300 ^{o}C

SUMMARY

- Stabilized 4 V and 5 V spinels offer low cost, high power cathodes with good safety for HEV and PHEV applications
  - Spinel oxyfluoride + layered oxide (*e. g.,* $LiMn_{1.8}Ni_{0.1}Li_{0.1}O_{3.8}F_{0.2}$ + $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$) composites exhibit excellent cyclability at elevated temperatures with carbon anode due to a trapping of protons within the layered oxide lattice and suppressed manganese dissolution
  - Surface modified 5 V spinels offer good cyclability with ~ 130 mAh/g
- Rapid synthesis of $LiFePO_4$ nanorods in < 5 minutes at < 300 ^oC and their coating with a mixed conducting polymer offers a low cost manufacturing approach without reducing gas atm for phospho-olivines
- Future work will focus on high energy, high power spinel + layered oxide composite cathodes, surface modified 5 V spinel cathodes, and rapid synthesis of high voltage phospho-olivines $LiMPO_4$ (M = Mn, Co, and Ni) and their advanced characterization

PUBLICATIONS AND PRESENTATIONS

Publications:

1. J. Choi and A. Manthiram, *Journal of Power Sources* **162**, 667-672 (2006).
2. Y. Wu and A. Manthiram, *Electrochemical and Solid State Letters* **10**, A151-A154 (2007).
3. W. Choi and A. Manthiram, *Journal of the Electrochemical Society* **154**, A614-A618 (2007).
4. W. Choi and A. Manthiram, *Journal of the Electrochemical Society* **154**, A792-A797 (2007).
5. A. Manthiram and W. Choi, *Electrochemical and Solid State Letters* **10**, A228-A231 (2007).
6. W. Choi and A. Manthiram, *Solid State Ionics* **178**, 1541-1545 (2007).

Three other manuscripts are currently in review or being submitted.

Presentations: 5 conference presentations