STABILIZED SPINELS AND NANO OLIVINES

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Materials Science and Engineering Program
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Project ID #: es_23_manthiram

OVERVIEW

Timeline

- Project start date: April 2004
- Project end date: May 2010
- 75 % complete

Budget

- Total project funding
  - DOE: $871K
- Funding for FY08
  - $165K
- Funding for FY09
  - $260K

Barriers

- Barriers
  - Cost
  - Cycle life
  - Energy and power densities

- Targets
  - Acceptable cycle life for spinel cathodes
  - Low manufacturing cost for olivine cathodes
  - Increased energy and power densities with spinel cathodes

OBJECTIVES

- To develop high performance cathodes for lithium ion batteries and a fundamental understanding of their structure-composition-performance relationships

  - To develop low cost spinel manganese oxide compositions exhibiting improved capacity retention at elevated temperatures

  - To develop spinel-layered oxide composite cathodes offering a combination of high power and energy

  - To develop low cost manufacturing processes for olivine cathodes with controlled size and nanomorphologies

MILESTONES

Month/Year	Milestone
March 2008	Optimization of the 4 V spinel to layered oxide ratios and microstructures in the spinel-layered oxide composite cathodes
September 2008	Optimization and surface modification of the 5 V spinel cathodes based on $LiMn_{1.5}Ni_{0.5}O_4$
March 2009	Rapid synthesis and characterization of various phospho-olivines with controlled size and nanomorphologies
June 2009	Optimization of stabilized spinel-layered oxide composite cathodes
September 2009	New cathode materials based on polyanions

APPROACH

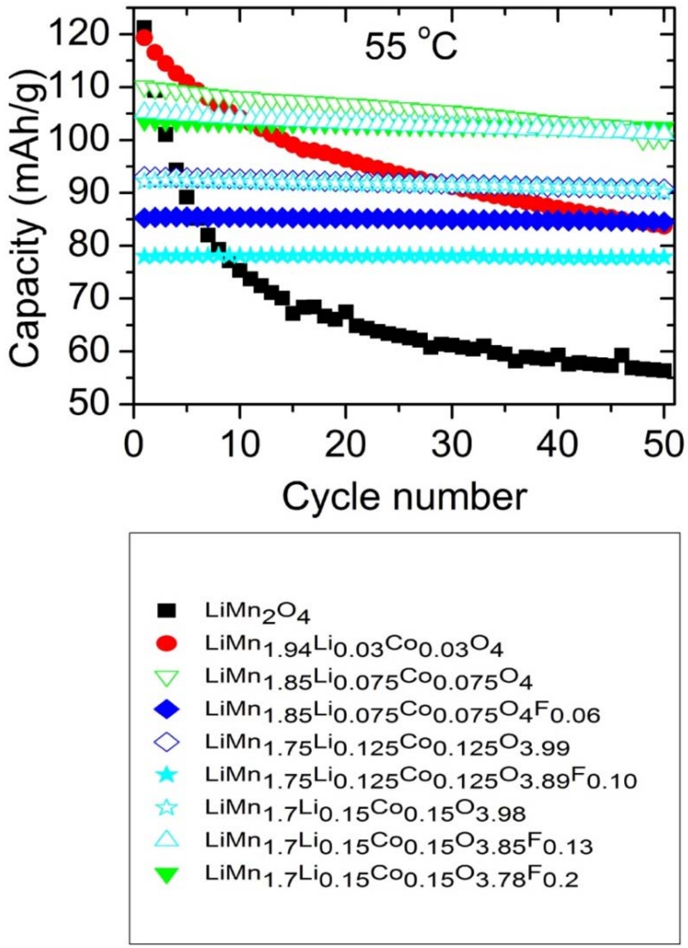
- Develop a firm understanding of the factors controlling the electrochemical performances of cathode materials and utilize the understanding to develop high performance cathodes

  - Cationic and anionic substitutions in 4 V spinel cathodes
  - Cationic substitutions in 5 V spinel cathodes
  - Surface modifications of 5 V spinel cathodes
  - Composites consisting of high power spinel & high energy layered oxides
  - Olivine cathodes with controlled particle size & unique nanomorphologies

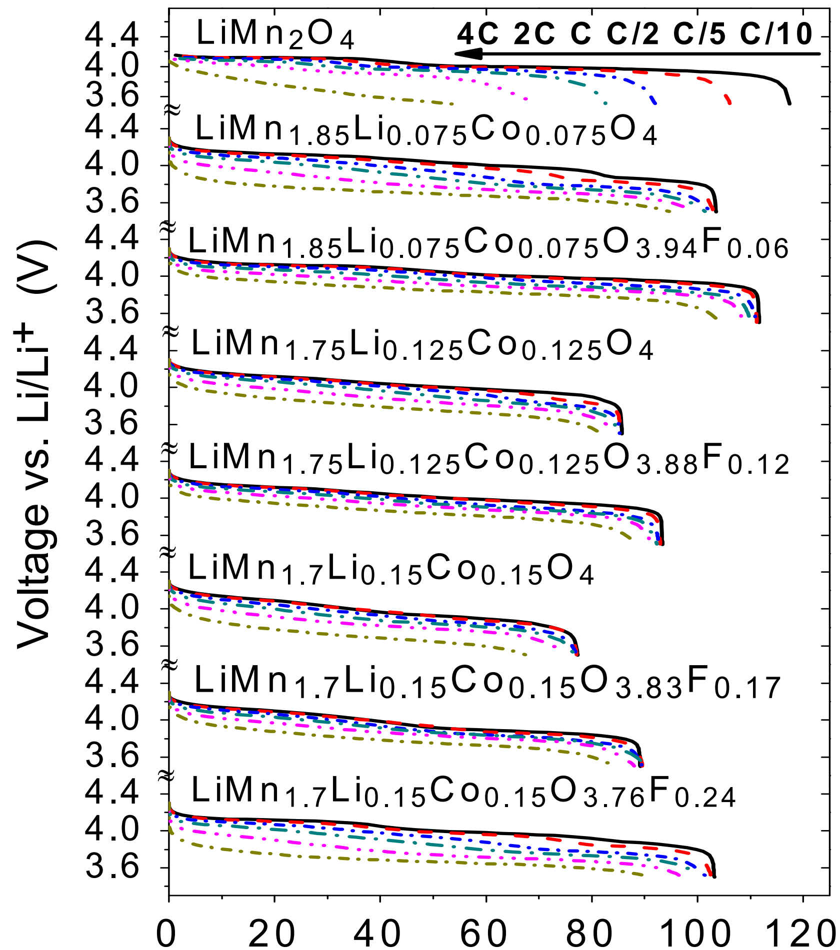
  - Solid state and solution-based synthesis approaches
  - Advanced chemical and structural characterizations
  - In-depth electrochemical evaluation including impedance analysis
  - Understanding of the structure-property-performance relationships

STABILIZED HIGH POWER 4 V SPINEL CATHODES

High temperature cyclability

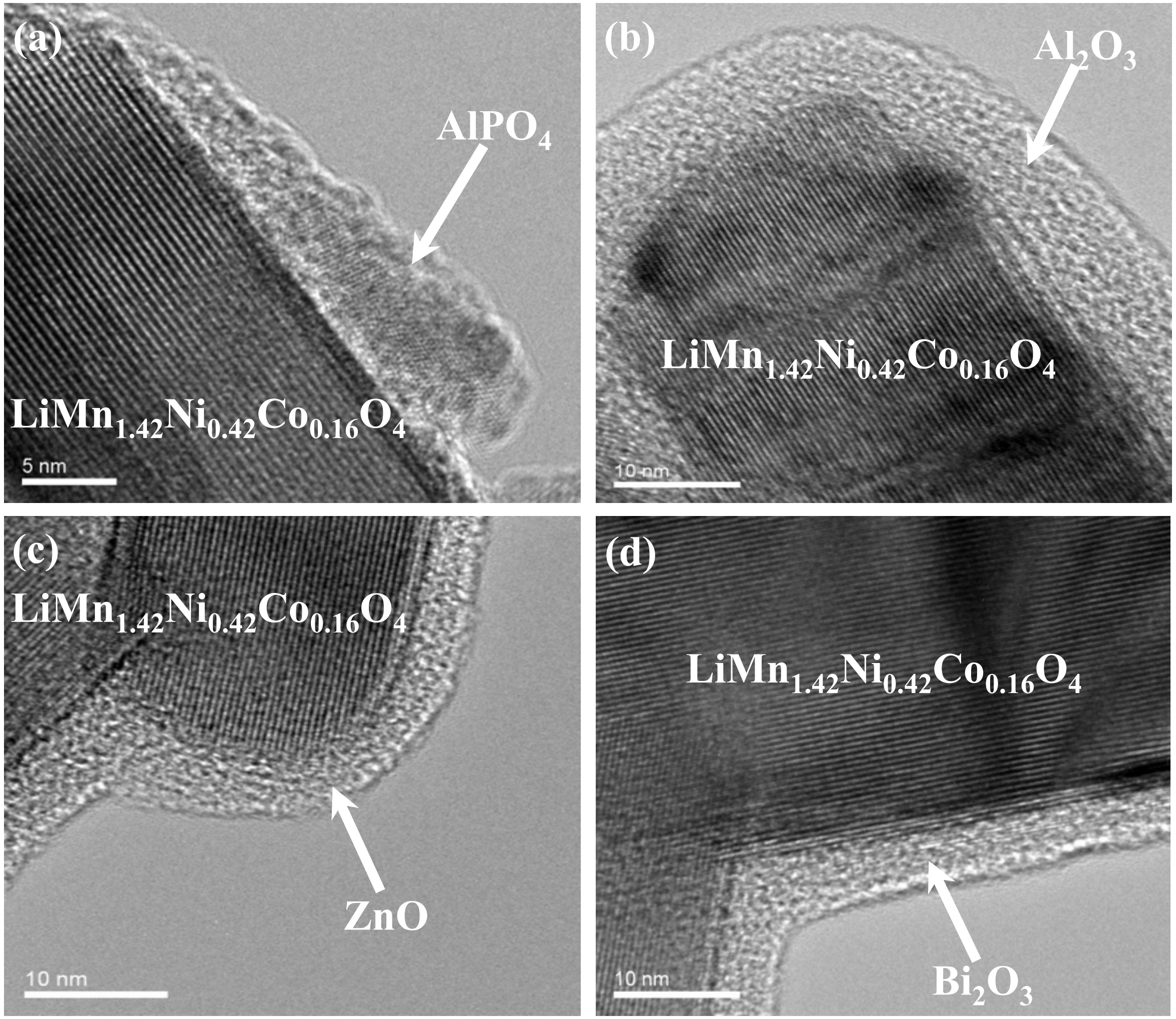


Rate capability



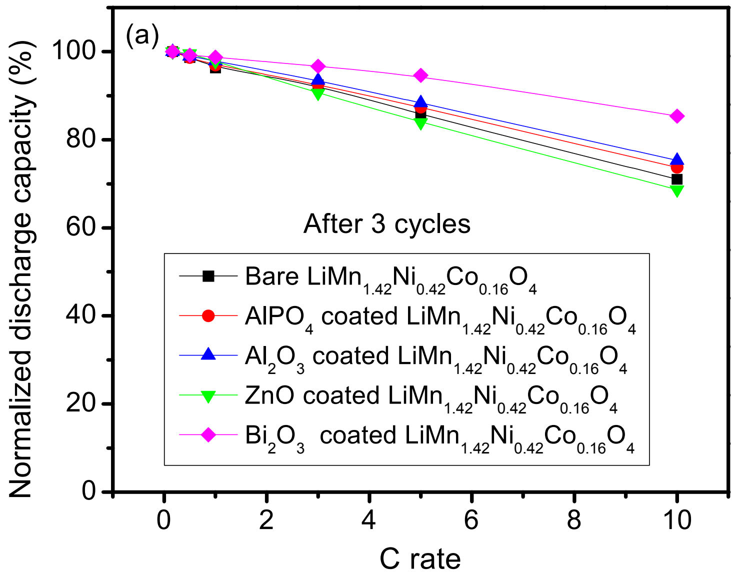
- Stabilized spinels with optimized cationic and anionic substitutions offer superior capacity retention at elevated temperatures with high rate capability

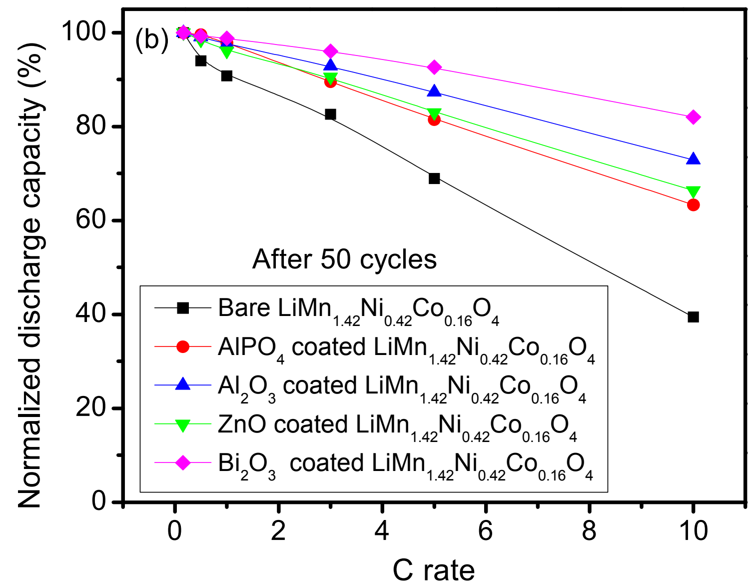
SURFACE MODIFIED, STABILIZED 5 V SPINEL CATHODES

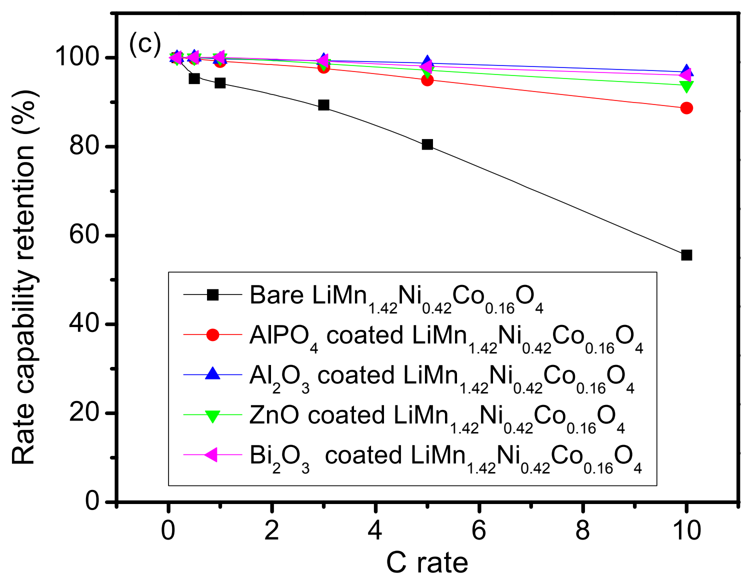


- Surface modifying Al_2O_3, ZnO, and Bi_2O_3 layers are continuous on the layered oxide
- Surface modifying $AlPO_4$ layer is crystalline, but not continuous

RATE CAPABILITY RETENTION OF 5 V SPINEL CATHODES



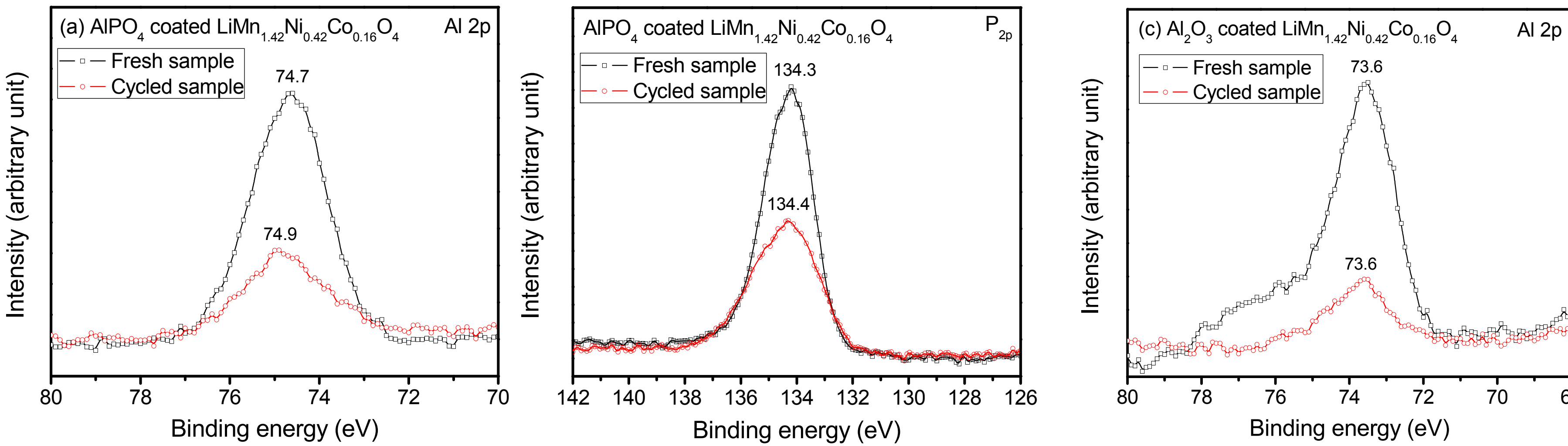


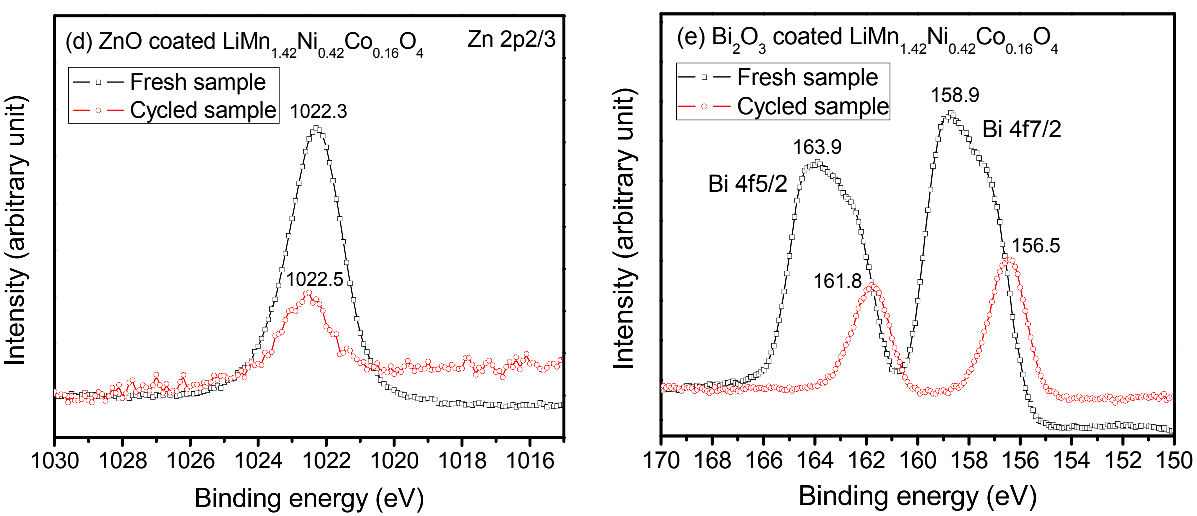


- Surface modification improves the rate capability and rate capability retention due to the suppression of thick SEI layer formation

- Bi_2O_3 coating gives the best rate capability
- Al_2O_3 coating gives the best rate capability retention

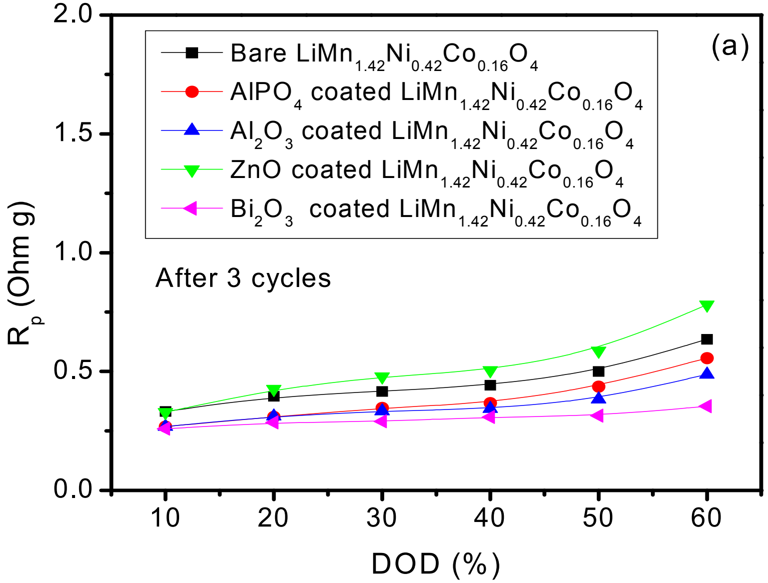
SURFACE (XPS) CHARACTERIZATION OF 5 V SPINELS

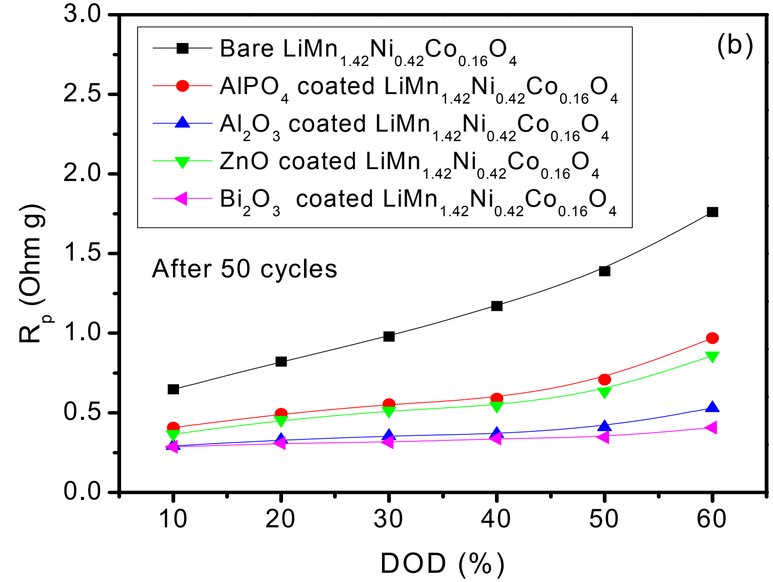


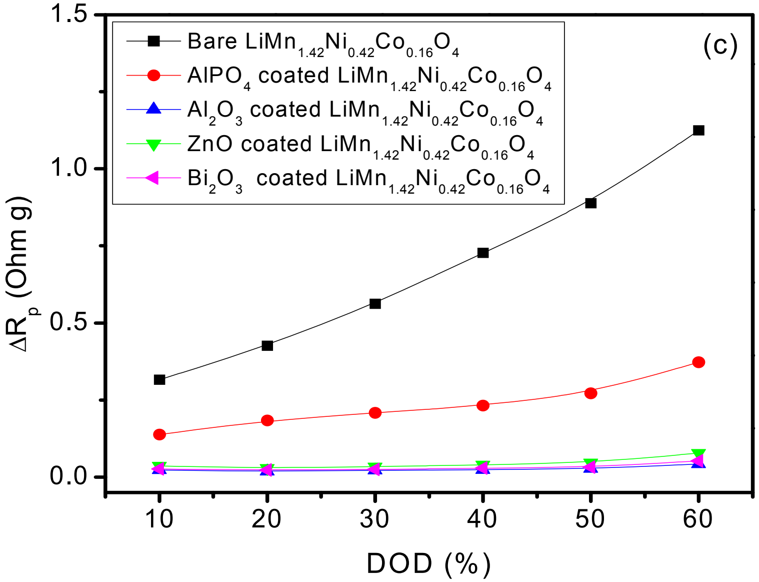


- $LiAlO_2$ formed on Al_2O_3 coated sample surface during sintering
- Bi formed on Bi_2O_3 coated sample surface during cycling
- Formation of Li^+-conducting $LiAlO_2$ and metallic Bi improves rate capability

COMPARISON OF THE POLARIZATION RESISTANCE, R_P





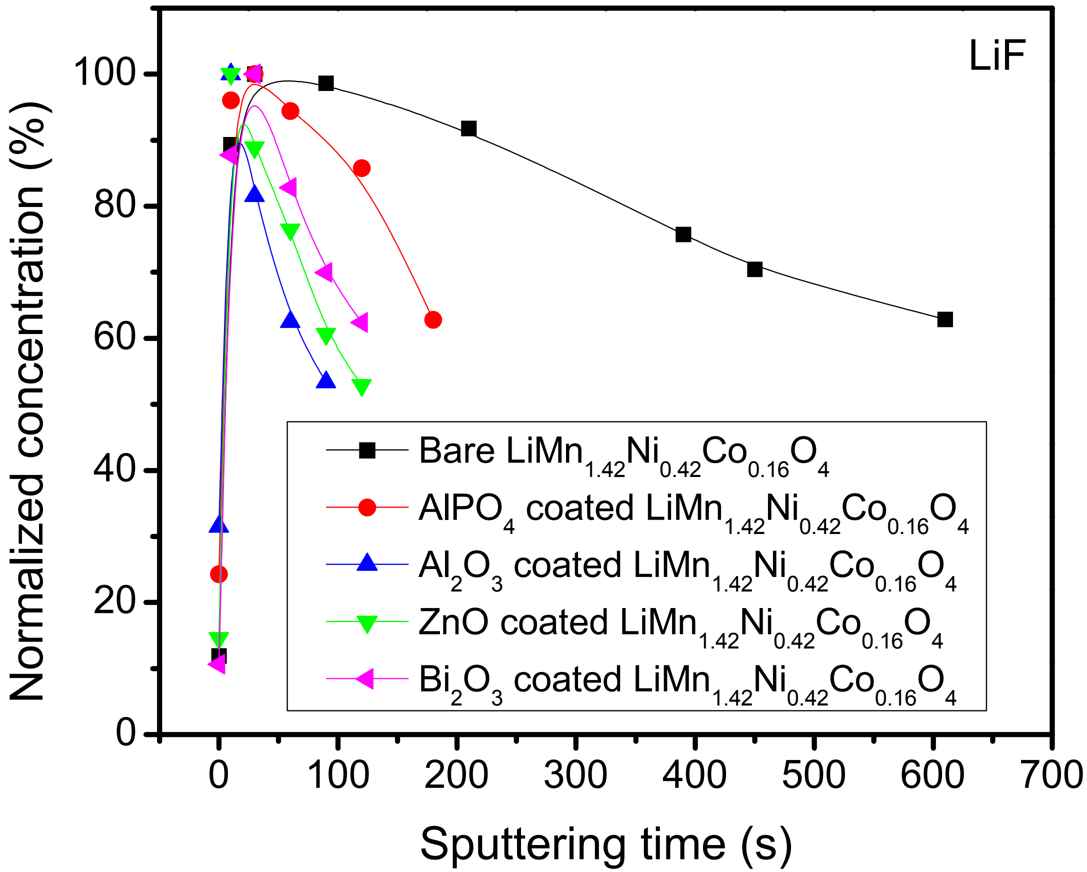


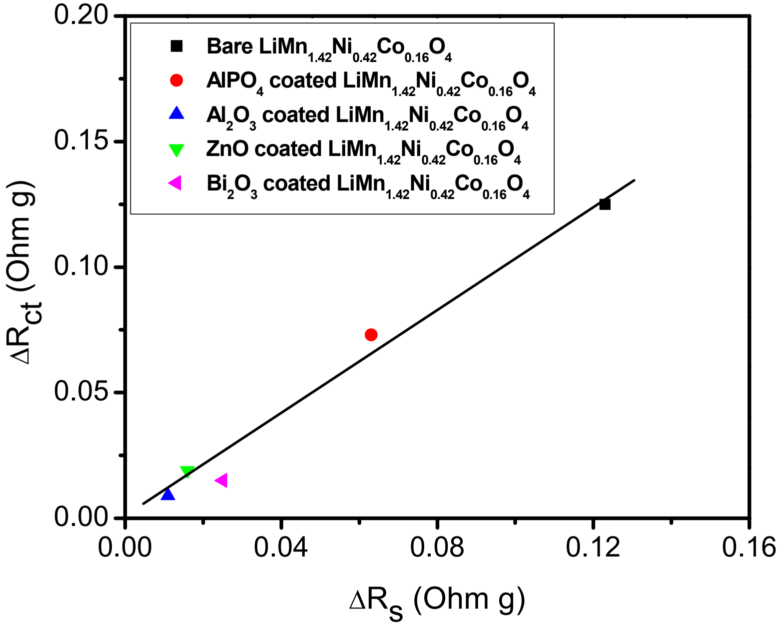
- R_p values are obtained from the slope of the voltage vs current curves after 3 and 50 cycles

$$R_P = R_{ohm} + R_{ct} + R_{diff}$$

- Bi_2O_3 coating shows the smallest R_p, resulting in the best rate capability
- Al_2O_3 coating shows the smallest ΔR_p, resulting in the best rate capability retention

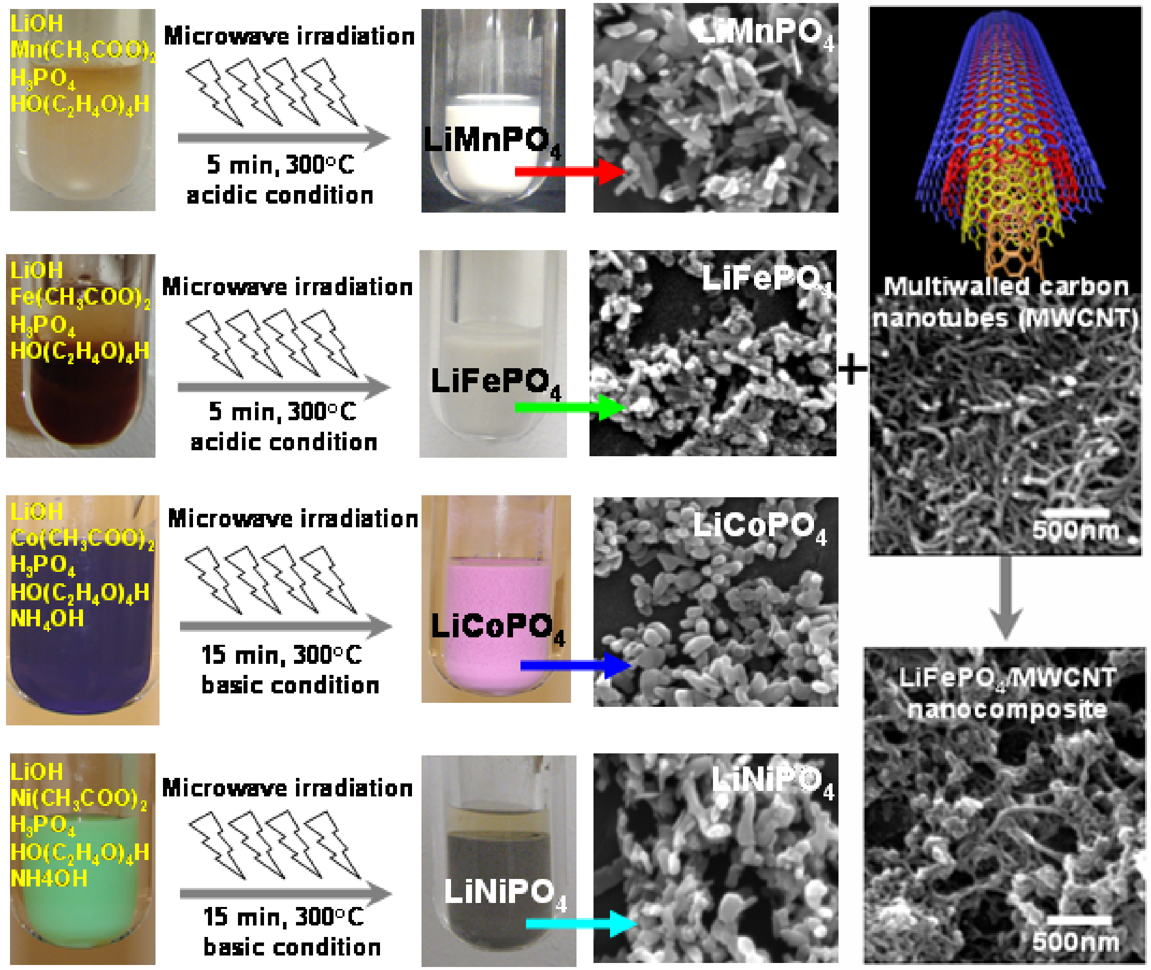
DEPTH PROFILE ANALYSIS OF SEI LAYER ON 5 V SPINEL





- Al_2O_3 is the most effective and $AlPO_4$ is the least effective in preventing the growth of SEI layer as revealed by the XPS analysis of LiF concentration at various depths
- XPS data are consistent with the ΔR_s values
- The differences in R_p and ΔR_p are due to the differences in R_{ct} and ΔR_{ct}, and ΔR_{ct} originates from ΔR_s

RAPID SYNTHESIS OF OLIVINE $LiMPO_4$ (M = Mn, Fe, Co, Ni)



- Microwave-assisted solvothermal (MW-ST) process to produce $LiMPO_4$ (M = Mn, Fe, Co, Ni) within a short reaction time of 5 – 15 minutes at < 300 °C, followed by ambient-temperature networking with multi-walled carbon nanotubes (MWCNT)

XRD PATTERNS OF OLIVINE $LiMPO_4$ (M = Mn, Fe, Co, Ni)

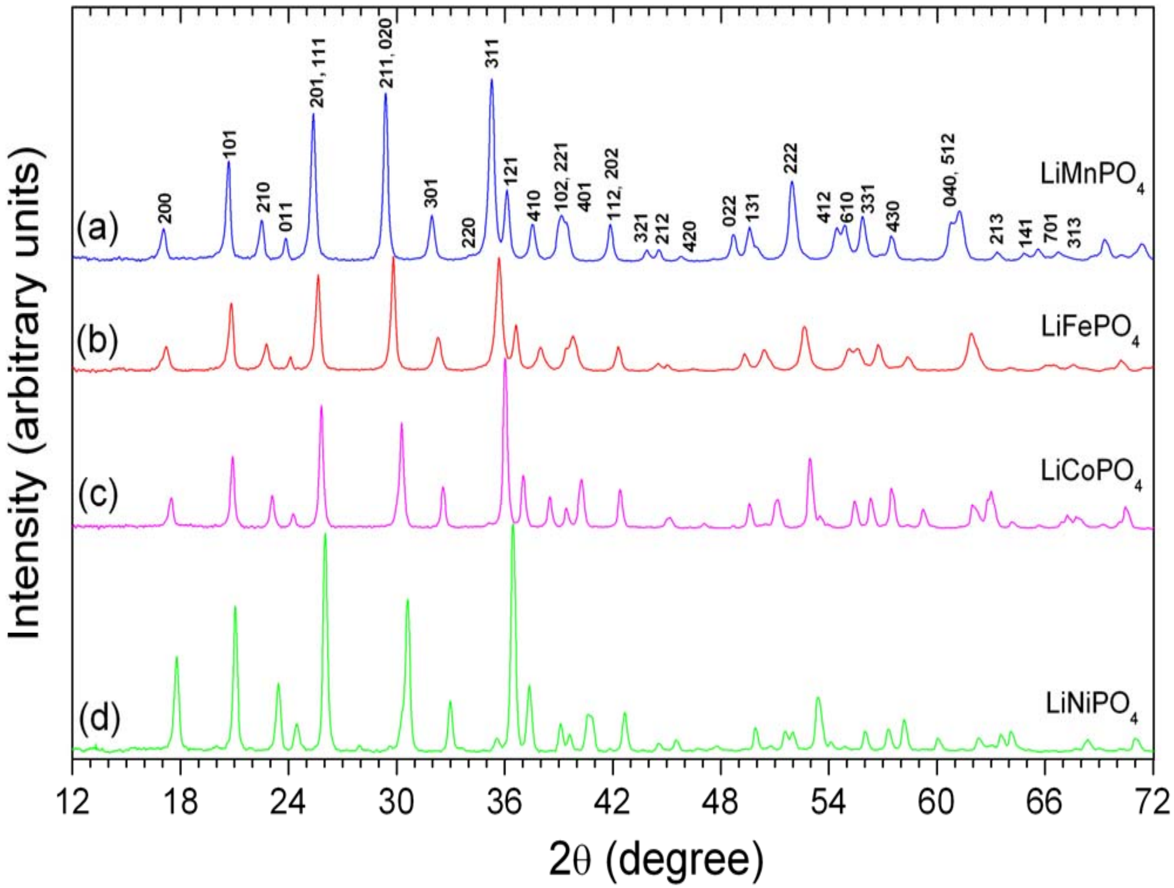
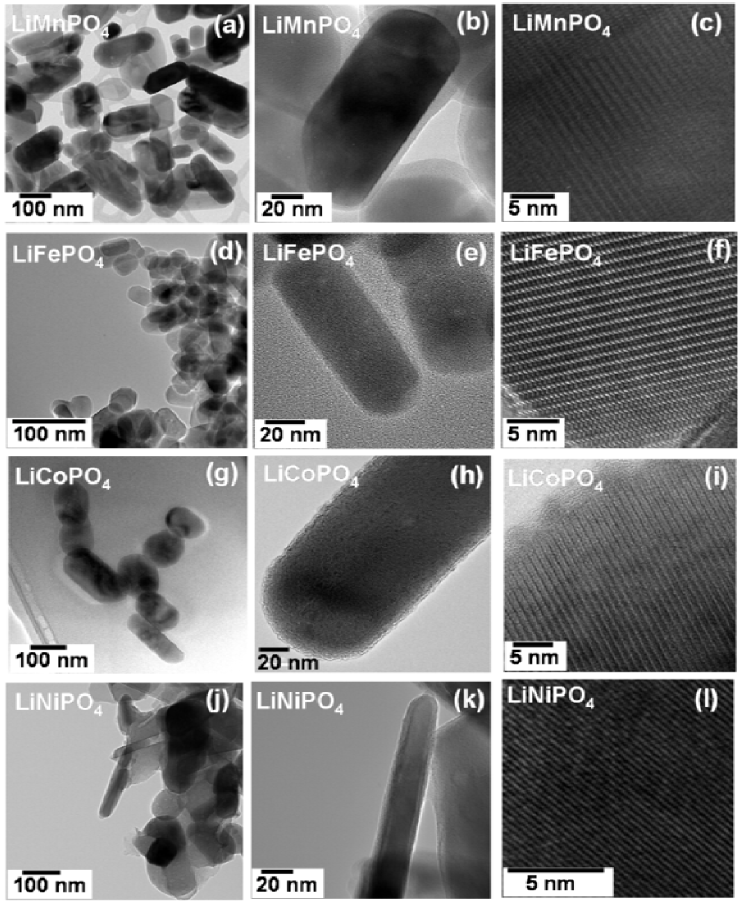


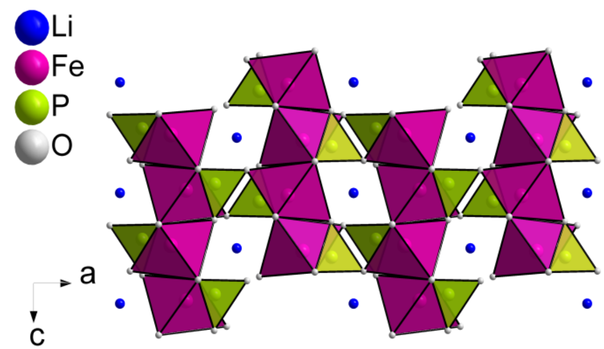
Table : Crystallographic Unit cell Parameters of $LiMPO_4$

Compound	a (Å)	b (Å)	c (Å)	V, (Å)
$LiMnPO_4$	10.446	6.106	4.746	302.71
$LiFePO_4$	10.321	6.000	4.695	290.74
$LiCoPO_4$	10.216	5.923	4.704	284.64
$LiNiPO_4$	10.047	5.862	4.681	275.69

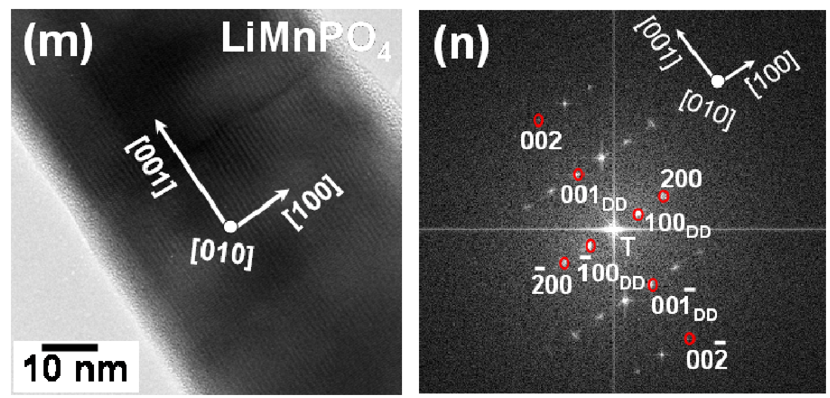
- Highly crystalline, phase pure $LiMPO_4$ (M = Mn, Fe, Co, Ni) are formed by the MW-ST method without requiring any post heat treatment in reducing gas atmospheres
- The lattice parameters and unit cell volume decrease as we go from M = Mn to Ni in $LiMPO_4$ due to the decreasing ionic radius of the M^{2+} ions

TEM IMAGES OF $LiMPO_4$ (M = Mn, Fe, Co, Ni)



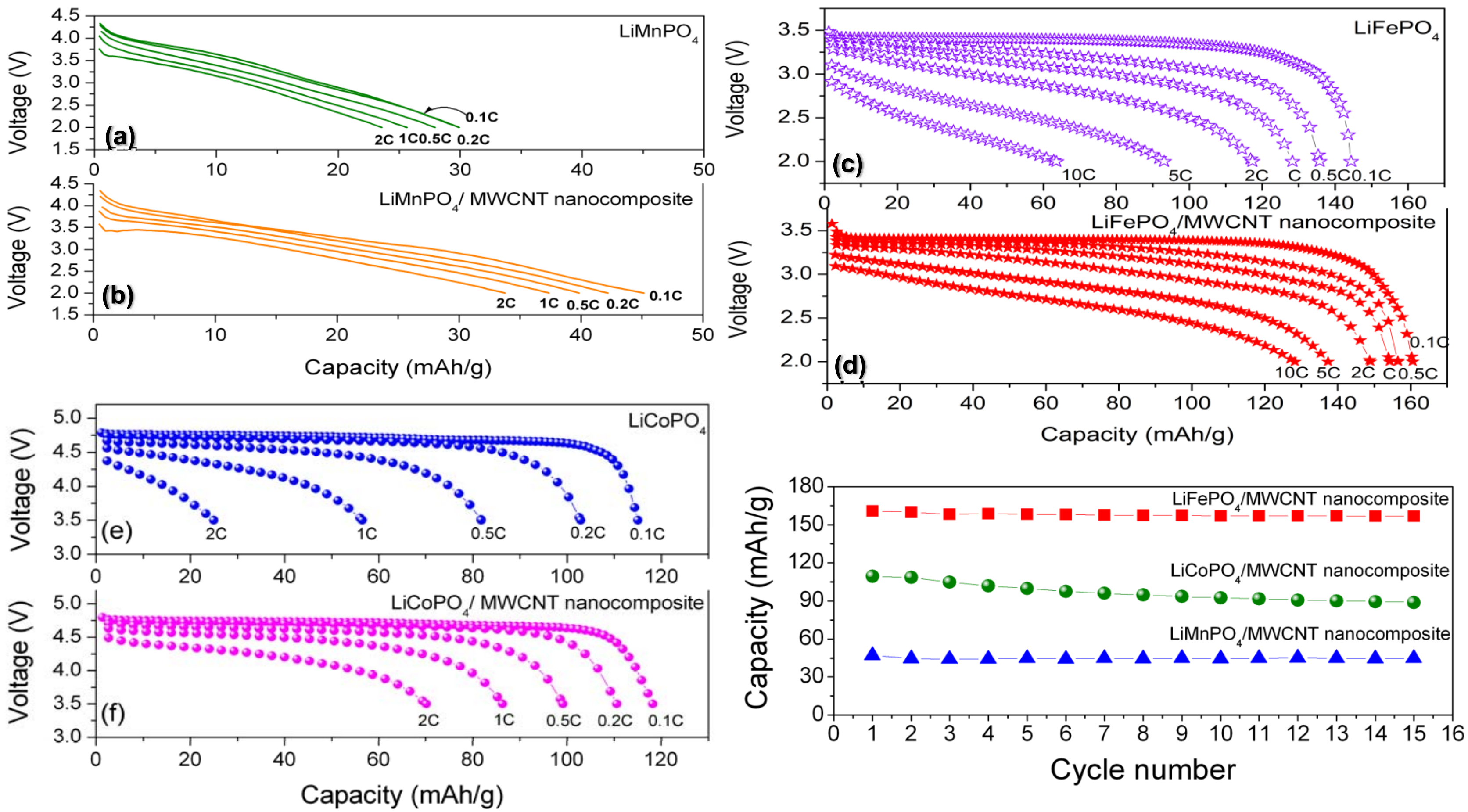


The orthorhombic olivine structure of $LiFePO_4$ projected onto the (010) plane



- Single crystalline $LiMPO_4$ (M = Mn, Fe, Co, Ni) with nanothumb-like shapes are formed by the microwave-solvothermal method
- The $LiMPO_4$ nanocrystals exhibit a preferential growth along the [001] direction with the easy lithium diffusion direction (*b* axis) perpendicular to the long axis

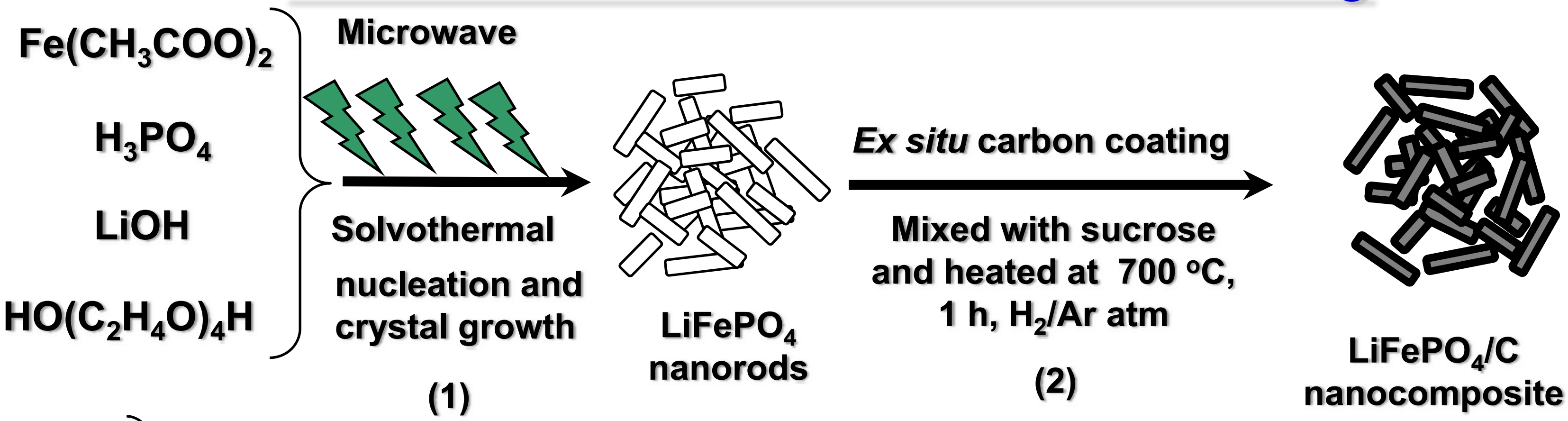
ELECTROCHEMICAL PERFORMANCES OF $LiMPO_4$-MWCNT



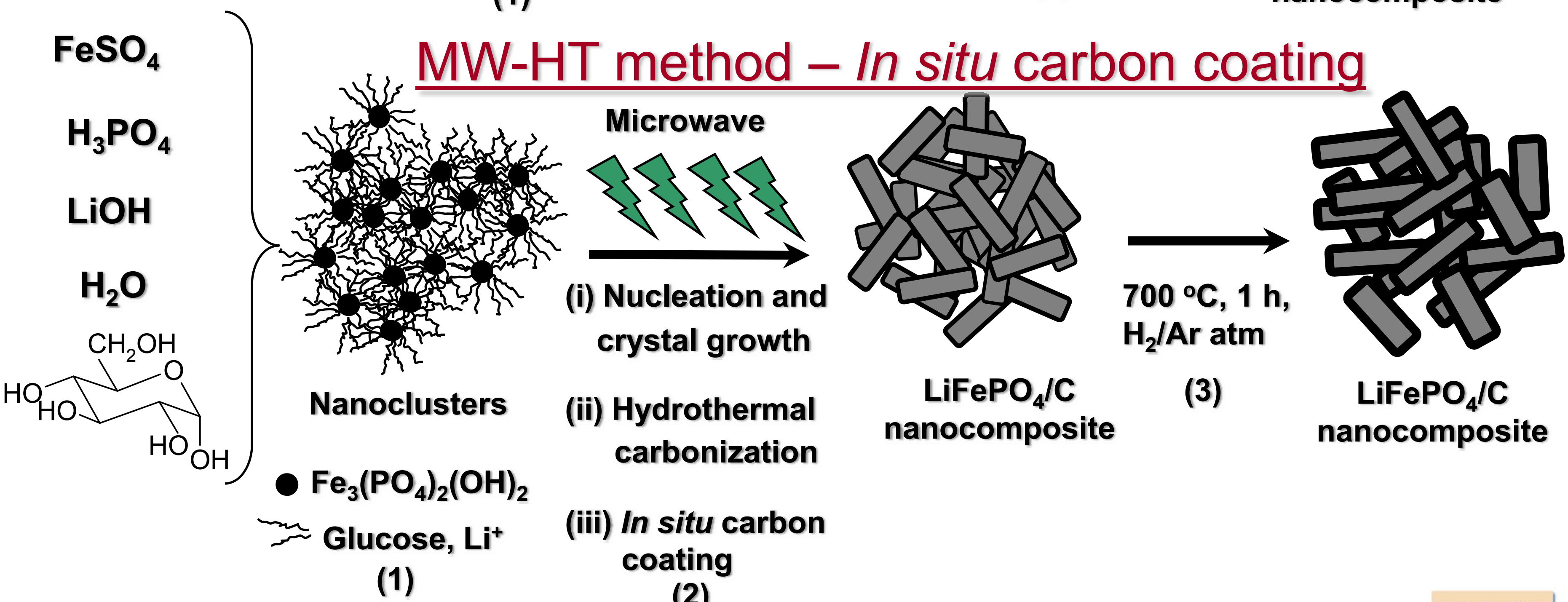
- Nano networking with MWCNT increases the rate capability due to the enhancement in electronic conductivity
- Performances of $LiMnPO_4$ and $LiCoPO_4$ are inferior compared to that of $LiFePO_4$

RAPID SYNTHESIS OF $LiFePO_4$/C NANOCOMPOSITES

MW-ST method – *Ex situ* carbon coating

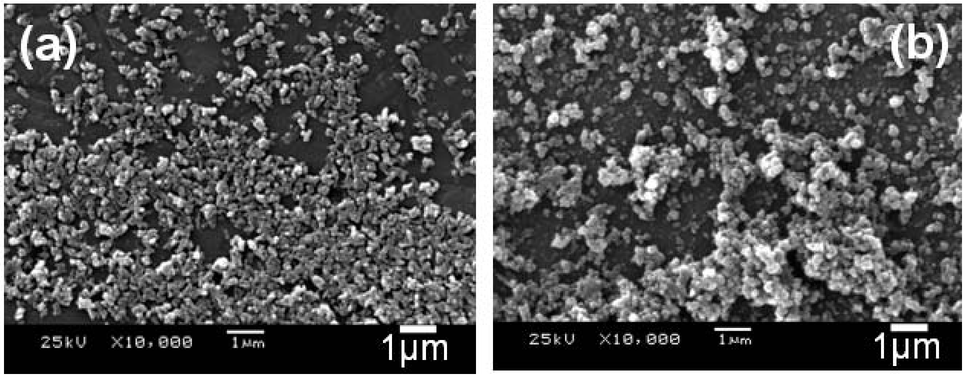


MW-HT method – *In situ* carbon coating

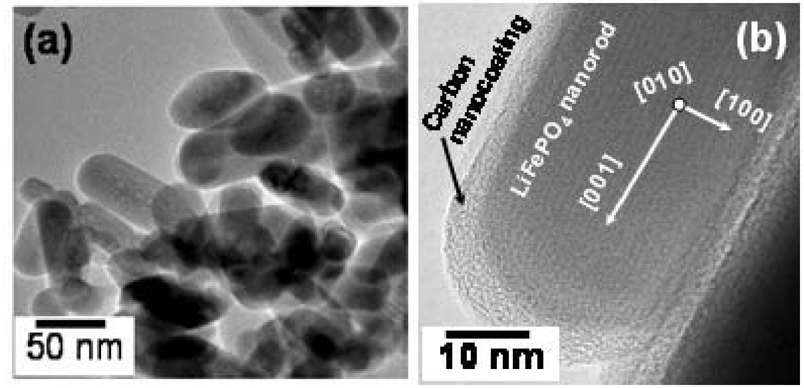


SEM AND TEM IMAGES OF $LiFePO_4$/C NANOCOMPOSITES

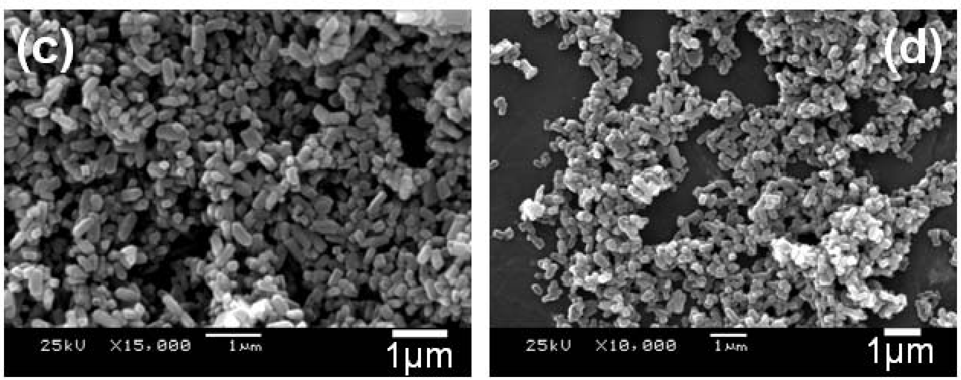
MW-ST



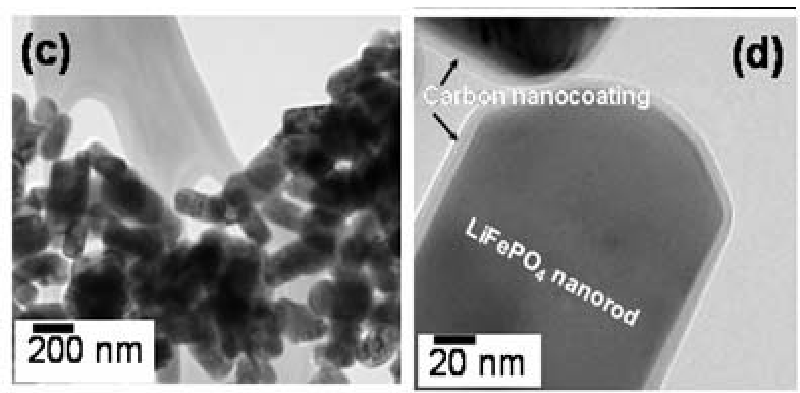
MW-ST



MW-HT



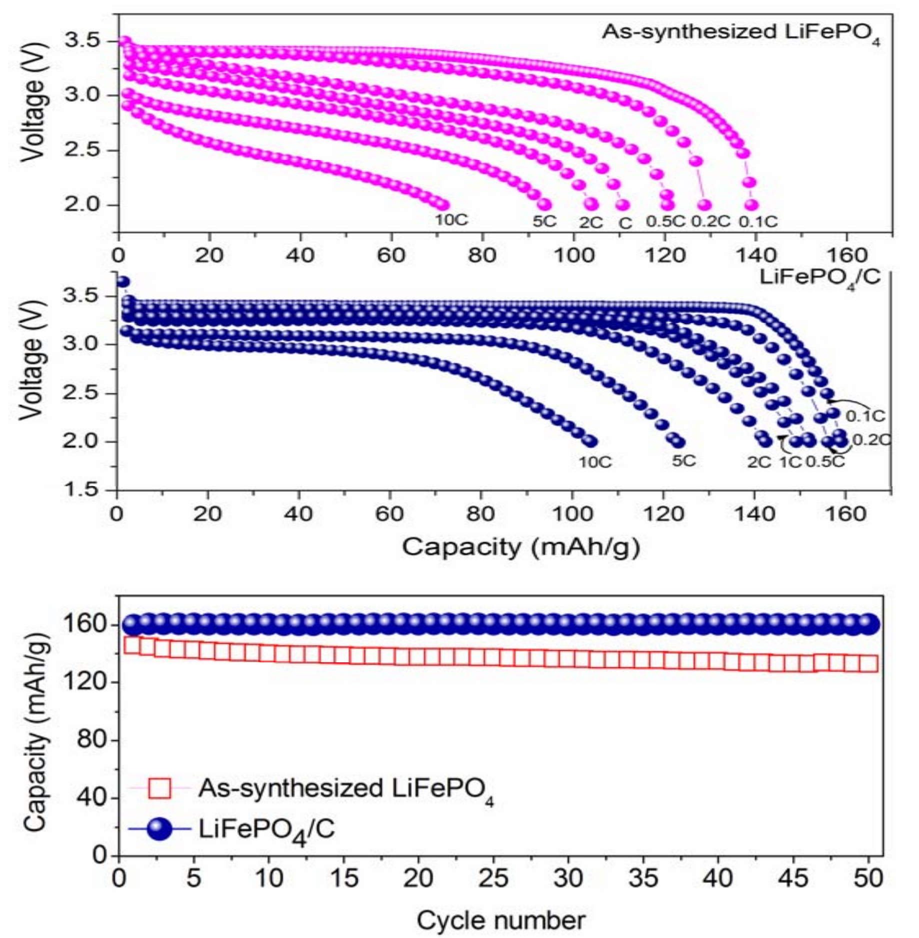
MW-HT



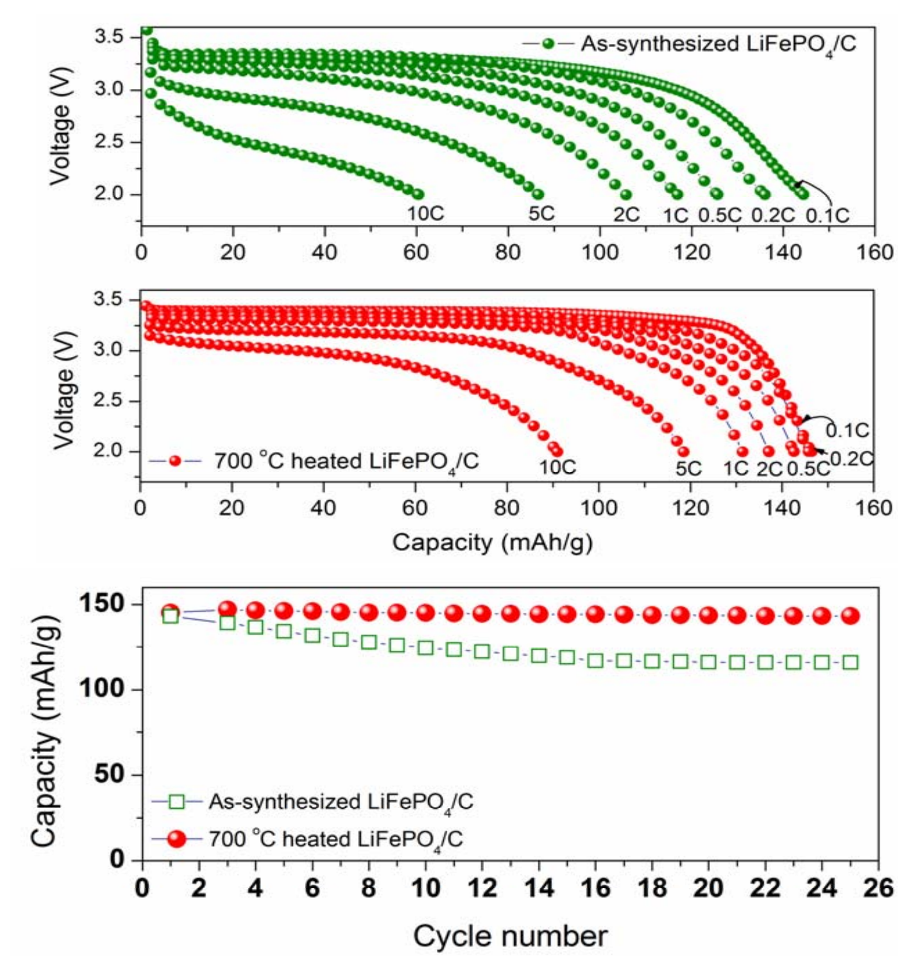
- MW-HT method gives larger particle size than the MW-ST method
- The easy lithium diffusion direction (*b* axis) is perpendicular to the long axis, providing an advantage to enhance lithium diffusion and rate capability

ELECTROCHEMICAL PERFORMANCES OF $LiFePO_4/C$

MW-ST (ex-situ carbon coating)



MW-HT (in-situ carbon coating)



- Carbon coating improves rate capability due to enhanced electronic conductivity
- MW-ST sample shows higher rate capability due to smaller particle size

FUTURE WORK

- Continue on the optimization of 4 V and 5 V spinel cathodes by cationic and anionic substitutions and surface modifications
- Investigate the electrochemical performances of composites consisting of a high power stabilized spinel and a high energy layered oxide
- Understand the role and effectiveness of various surface coatings in controlling the growth of undesired SEI layer on high voltage (> 4.5 V) cathodes by employing various characterization techniques (XPS, FTIR, Raman, & impedance analysis)
- Understand the influence of crystallite size/shape and defect chemistry on the charge-discharge mechanisms of olivine $LiMPO_4$ by making use of the novel microwave-solvothermal (MW-ST) and microwave-hydrothermal (MW-HT) methods
- Synthesize solid solutions between various olivine $LiMPO_4$ (M = Mn, Fe, Co, and Ni) by MW-ST and MW-HT approaches and understand their structure-composition-performance relationships
- Synthesize and characterize new cathode compositions containing polyanions, employing the microwave-assisted processes

SUMMARY

- Stabilized spinel compositions with appropriate cationic and anionic substitutions exhibit superior cyclability compared to the conventional spinel cathode

- Surface modified 5 V spinel cathodes exhibit better cyclability, rate capability, and rate capability retention due to the suppression of SEI layer growth during cycling and lower polarization and charge transfer resistances

- Microwave-assisted solvothermal and hydrothermal approaches give olivine cathodes in 5 – 15 minutes at < 300 ^{o}C without requiring any reducing gas atmospheres, offering the potential to lower the manufacturing cost

- Building on the fundamental understanding gained, the future work will continue focusing on developing high performance cathode compositions

- IP developed through the BATT program has led to the founding of a startup (ActaCell) in Austin, TX