DESIGN OF HIGH ENERGY, HIGH PERFORMANCE CATHODE MATERIALS

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ES 052

Overview

Timeline

- Project start date-10/1/2011
- Project end date- 9/30/2015
- 40% complete

Budget

- Total project funding
  - DOE share $475k/yr ($1900k total)
- Funding received in FY12 $475k
- Funding for FY13
- $475k

Barriers

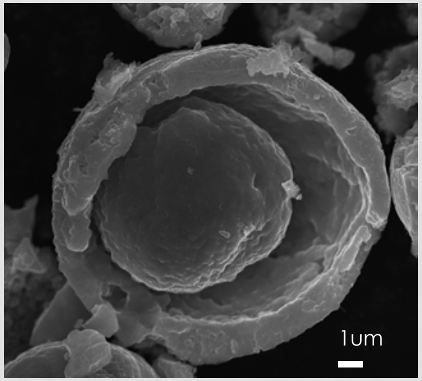
- Barriers addressed
  - Energy Density
  - Cost
  - Cycle Life

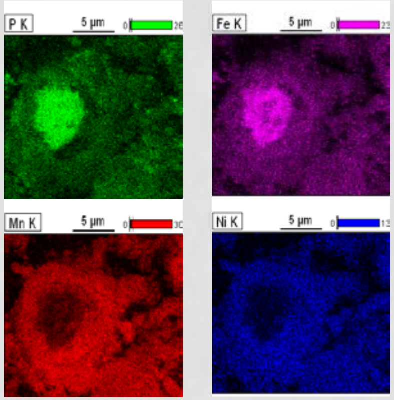
Partners

- Interactions/ collaborations
  - LBNL, SSRL, UCB
- Project lead=LBNL

RELEVANCE/OBJECTIVES

- Develop high energy, high performance cathode materials that cost less
  - Partial Ti-substitution of NMCs to reduce first cycle inefficiencies and obtain higher practical discharge capacities
  - Spray pyrolysis and related techniques to produce coated and composite materials containing high voltage electrode materials
    - Example: $LiFePO_4@LiNi_{0.5}Mn_{1.5}O_4$

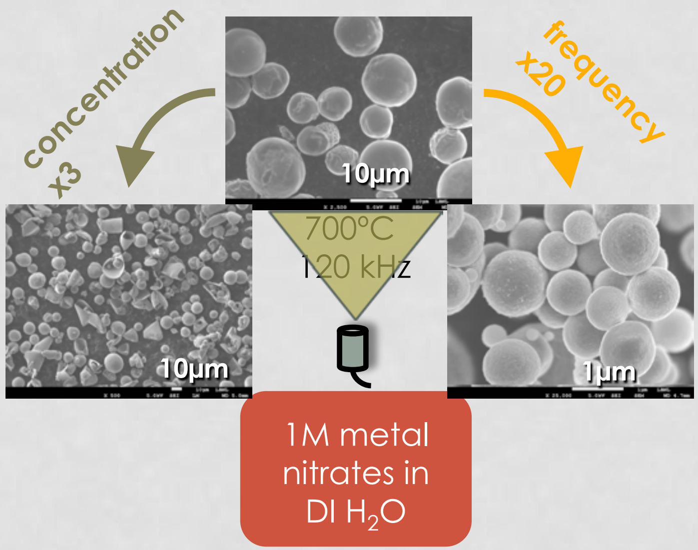




MILESTONES

Milestone	Due date	Status/Comments
Composites consisting of spray-pyrolyzed LNMS hollow particles containing and coated with $LiFePO_4$ or a manganese oxide spinel will be synthesized and electrochemically characterized.	9/13	On track. Will consider $LiMnPO_4$ as an alternative, less reactive, coating.
Thin film electrodes of a high energy Ti-substituted NMC suitable for synchrotron studies will be produced and electrochemically characterized.	9/13	Particulate electrodes with no binder/carbon may be suitable for synchrotron studies. Replace milestone.

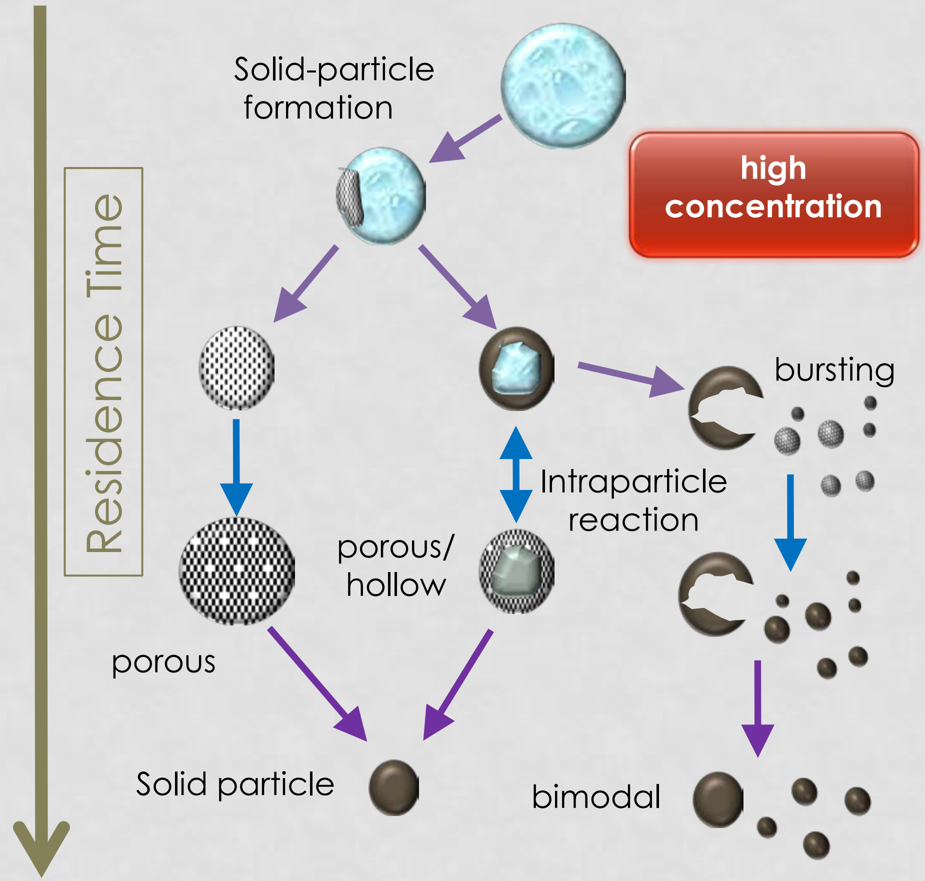
TECHNICAL APPROACH
SPRAY PYROLYSIS



$$d_h = 0.73 \sqrt[3]{\frac{T}{\rho f_a^{2}}}$$

T = *surface tension*
ρ = *density of solution*
f_a = *frequency*

Control of particle size



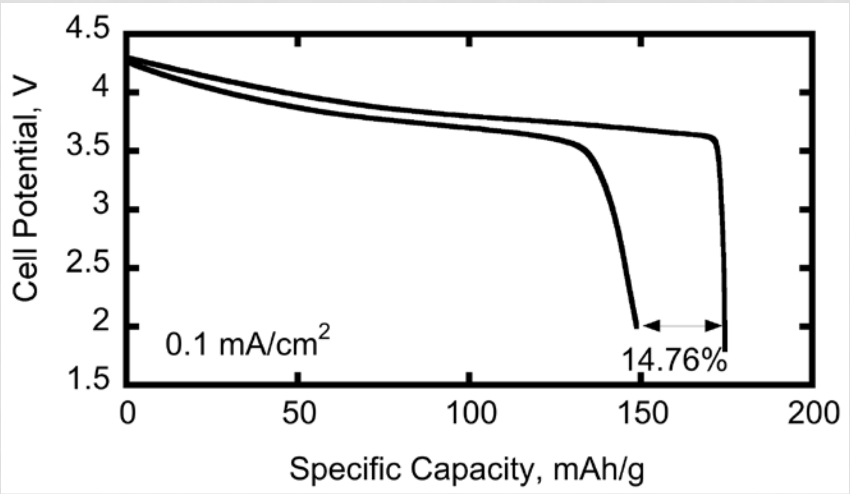
Morphology control

Coat/fill particles via
choice of precursors (one step) and postprocessing (two steps)

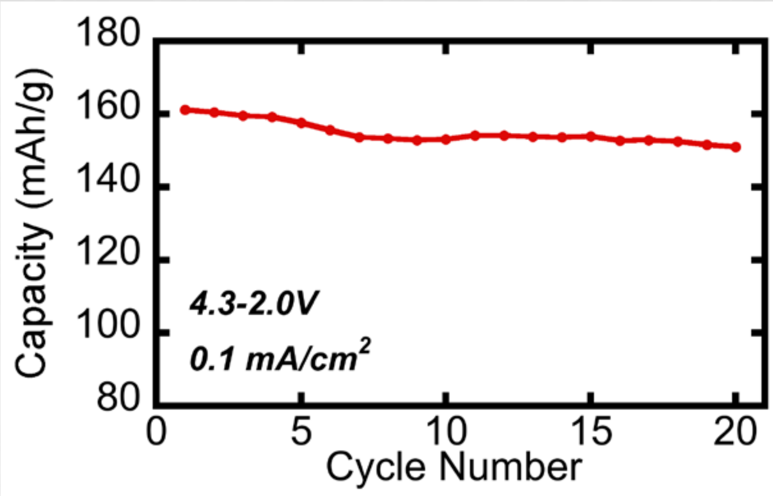
TECHNICAL APPROACH
HIGH CAPACITY NMCS

- Synthesize substituted NMCs
  - Coprecipitation
  - Combustion synthesis
  - Spray pyrolysis (planned, not yet carried out)
- Characterize
  - Electrochemical (half cells)
  - Conventional physical methods
  - Synchrotron methods
- Goal is higher capacity without sacrificing stability, safety

TECHNICAL ACCOMPLISHMENTS/TYPICAL VOLTAGE CHARACTERISTICS OF NMCS



Li/NMC-333 cell

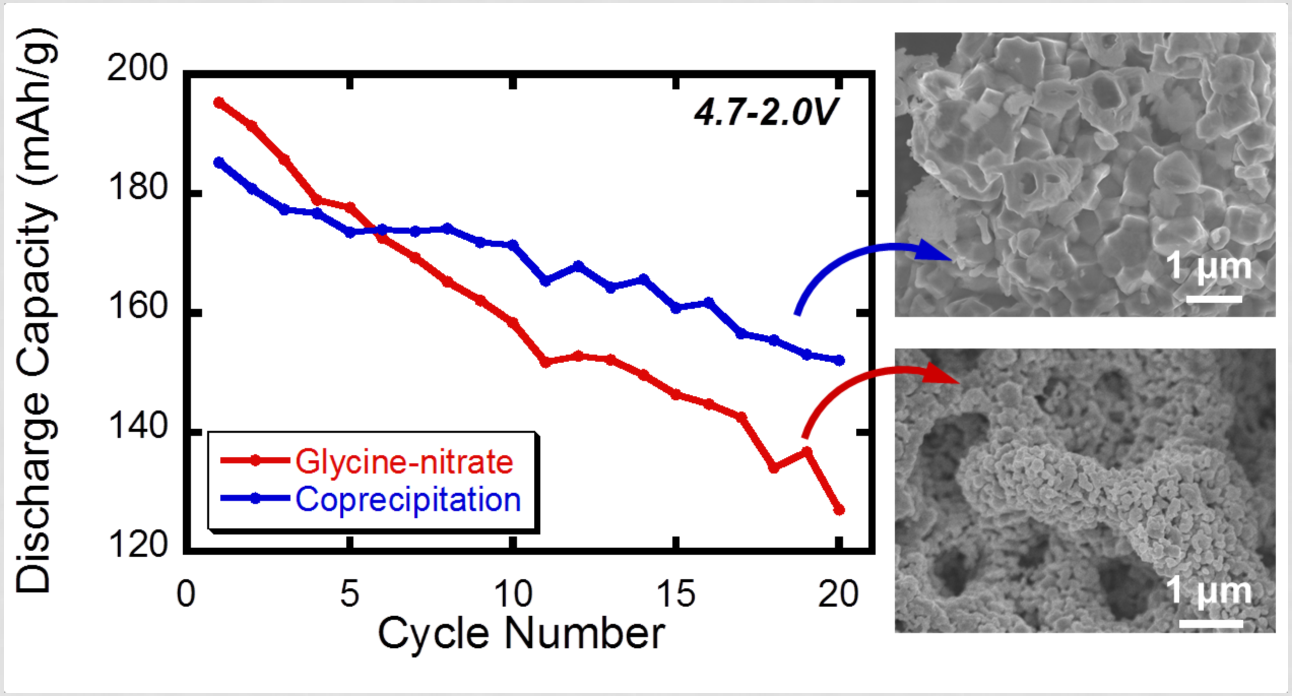


Li/NMC-442 cell

- 1st cycle inefficiency observed ***even with low charge voltage limits***
- Half cell cycling with 4.3V charge limit is stable
- Typical capacity is ~160 mAh/g

NMC-333=$Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$; NMC-442=$Li[Ni_{0.4}Mn_{0.4}Co_{0.2}]O_2$

TECHNICAL ACCOMPLISHMENTS/CYCLING OF NMCS TO HIGHER POTENTIALS



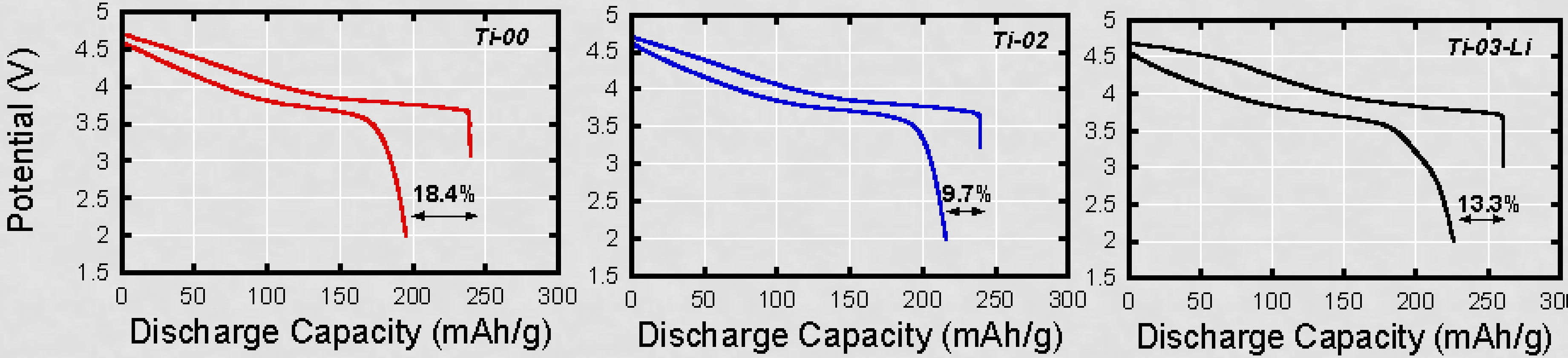
Li/NMC-333 cells

- Higher capacity in half cells can be obtained by cycling to higher voltage limits
- This results in a rapid capacity fade
- Nanoparticulate electrode materials perform worse than conventional ones

From "Electrode Materials for Lithium Ion Batteries" Kinson C. Kam and Marca M. Doeff, **Materials Matters**, Aldrich Materials Science, 7(4), 56 (2012).

TECHNICAL ACCOMPLISHMENTS/TI-SUBSTITUTED NMCS

Li/NMC-333 series cells



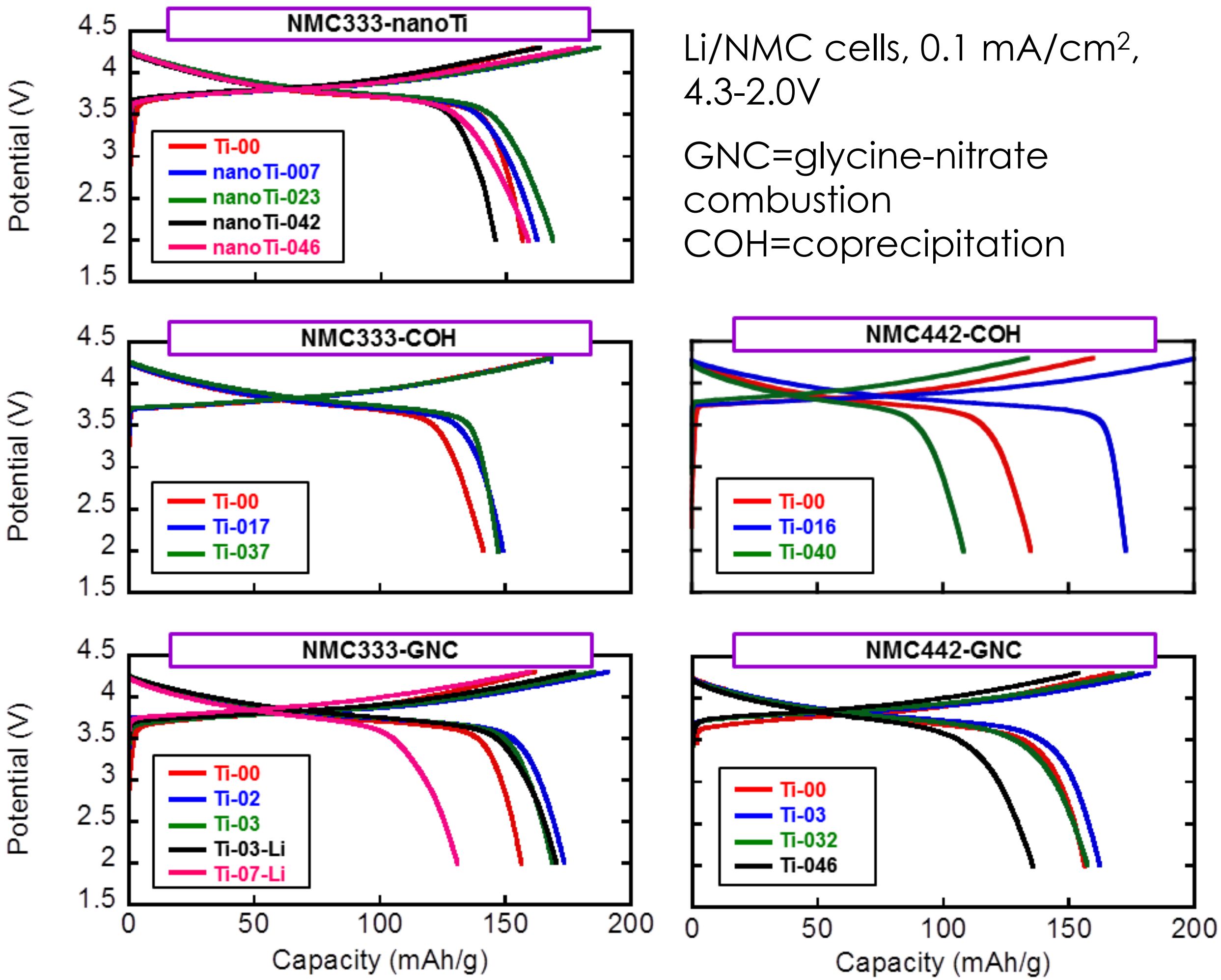
- Partial Ti-substitution for Co in NMCs increases practical capacity
- Limit of substitution is ~4% Ti for Co
- Both Li-excess and Li-stoichiometric compounds can be prepared
- Capacities as high as 225 mAh/g seen
- Improvement is due to better first cycle efficiencies

From "Aliovalent Titanium Substitution in Layered Mixed Li Ni-Mn-Co Oxides for Lithium Battery Applications" Kinson Kam and Marca M. Doeff, J. Mater. Chem., 21, 9991 (2011).

TECHNICAL ACCOMPLISHMENTS/NMC AND TI-SUBSTITUTED NMC VOLTAGE PROFILES-4.3-2.0V

Li/NMC cells, 0.1 mA/cm^2, 4.3-2.0V

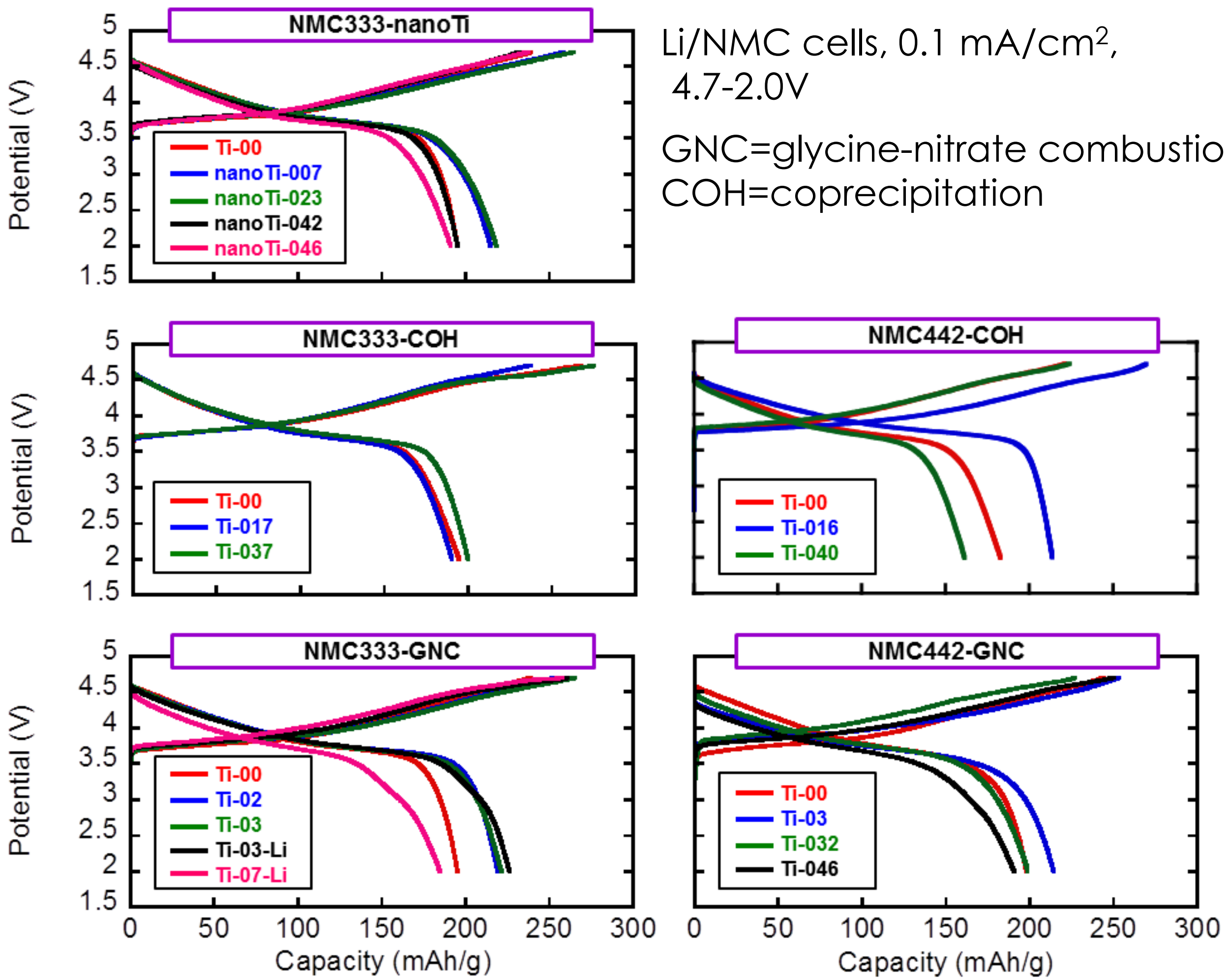
GNC=glycine-nitrate combustion
COH=coprecipitation



- •Ti contents below ~4% improve discharge capacities
- •Best results 170 mAh/g (baseline materials=150-160 mAh/g)
- •Ti contents above ~4% have neutral or negative effect
- •Better first cycle efficiencies when Ti<~4% but not when Ti>4%

From "Electrochemical and Physical Properties of Ti-substituted Layered Nickel Manganese Cobalt Oxide (NMC) Cathode Materials" Kinson C. Kam, Apurva Mehta, John T. Heron, and Marca M. Doeff, **J. Electrochem. Soc.** 159, A1383 (2012).

TECHNICAL ACCOMPLISHMENTS/NMC AND TI-SUBSTITUTED NMC VOLTAGE PROFILES-4.7-2.0V

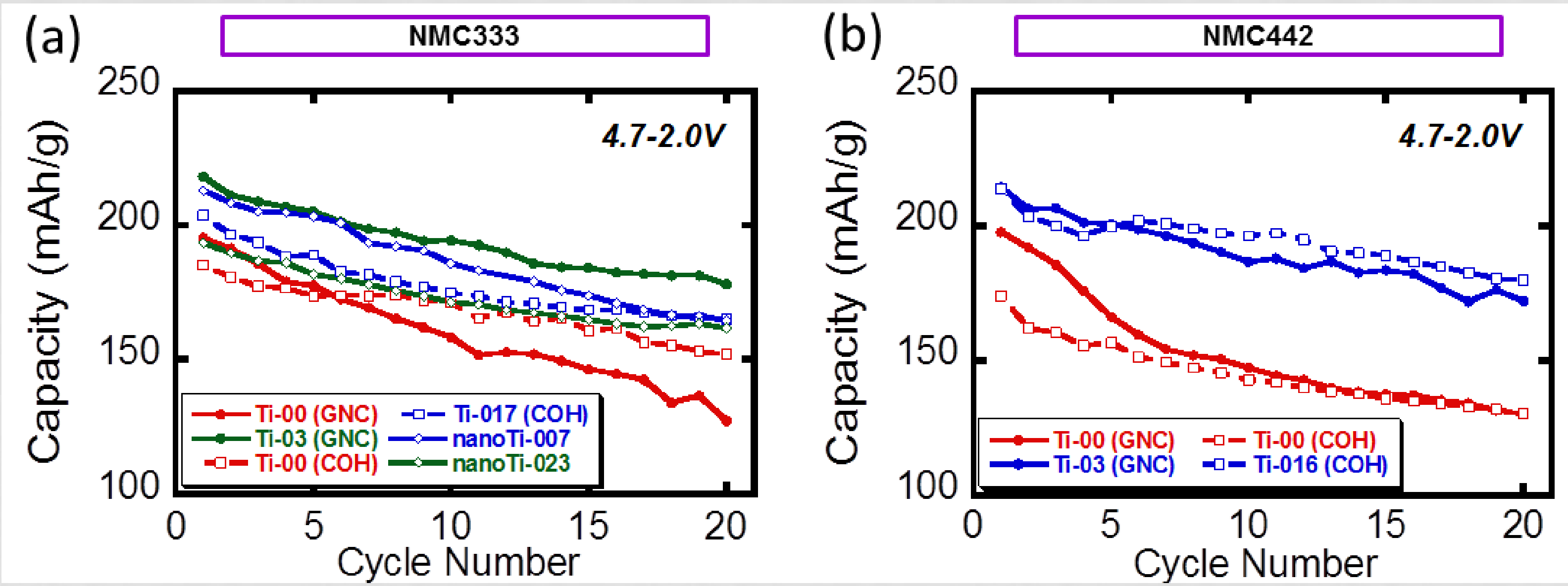


Li/NMC cells, 0.1 mA/cm^2, 4.7-2.0V

GNC=glycine-nitrate combustion
COH=coprecipitation

- Ti contents below ~4% improve discharge capacities
- Best results ~225 mAh/g (baseline materials≈190-200 mAh/g)
- Improved first cycle efficiencies for low Ti substitution

TECHNICAL ACCOMPLISHMENTS/CYCLING OF SELECTED SAMPLES 4.7-2.0V

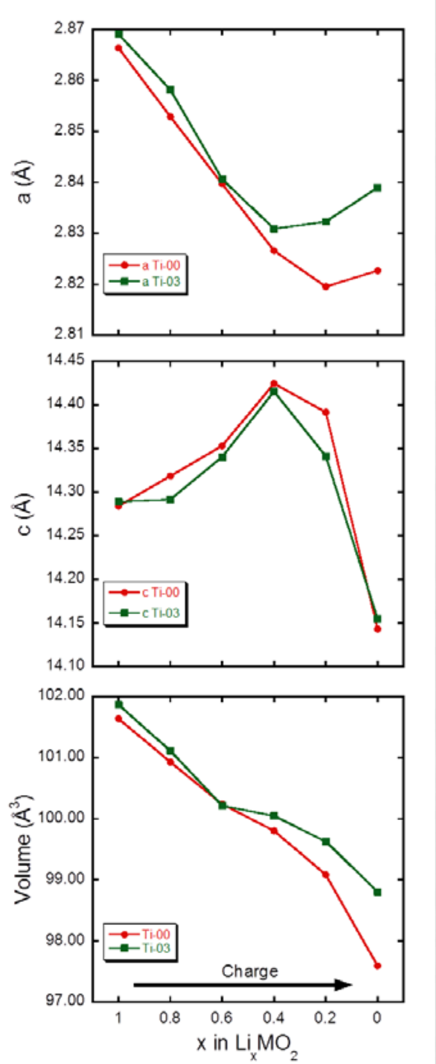


Red=baseline, Blue and Green =Ti substituted

- Ti-substituted electrodes ***cycle with better capacity retention***
- More dramatic results with NMC-442 than with NMC-333
- **NOTE:** No difference between COH and GNC made samples for Ti-substituted NMC-442

Best results with Ti-substituted 442-NMC (lower Co content)

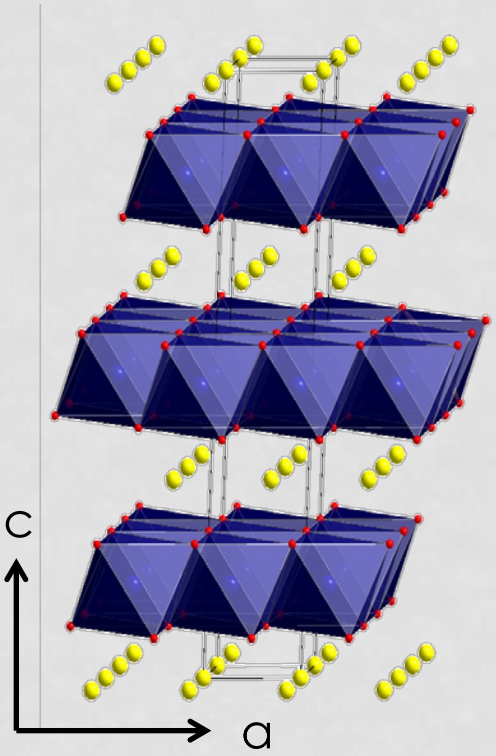
TECHNICAL ACCOMPLISHMENTS/SYNCHROTRON XRD STUDIES OF ELECTRODES



- *a* lattice parameter first decreases as delithiation proceeds, then increases

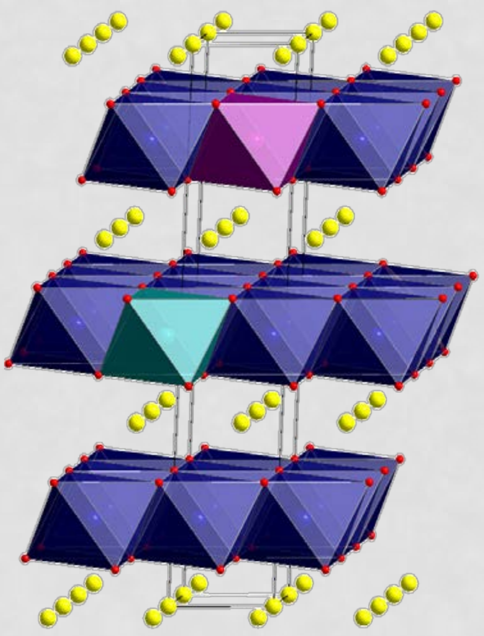
- c parameter first increases then decreases, past about x=0.4

- Total cell volume change is -4% for NMC333-Ti-0 and -3% for NMC333-Ti-03
- Ti substitution limits changes in T.M. layer



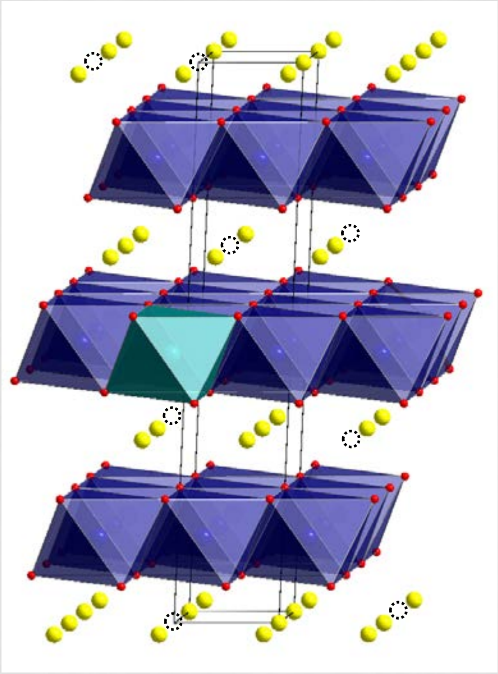
TECHNICAL ACCOMPLISHMENTS/MECHANISM OF ALIOVALENT TI-SUBSTITUTION

Generation of Mn^{3+}



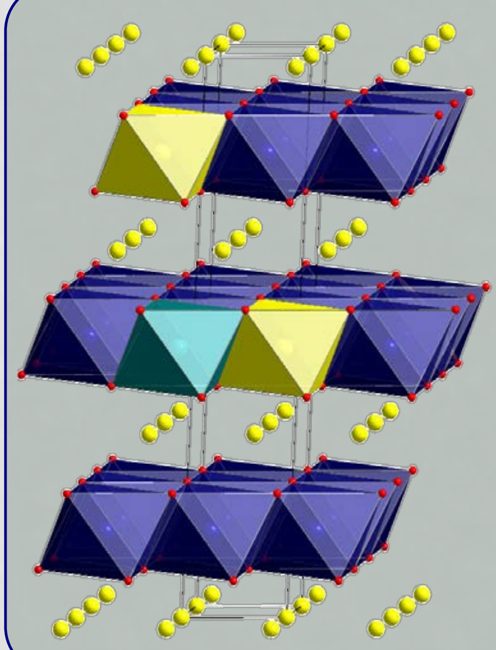
- Stoich-iometric samples

Li deficiency on *3a* site



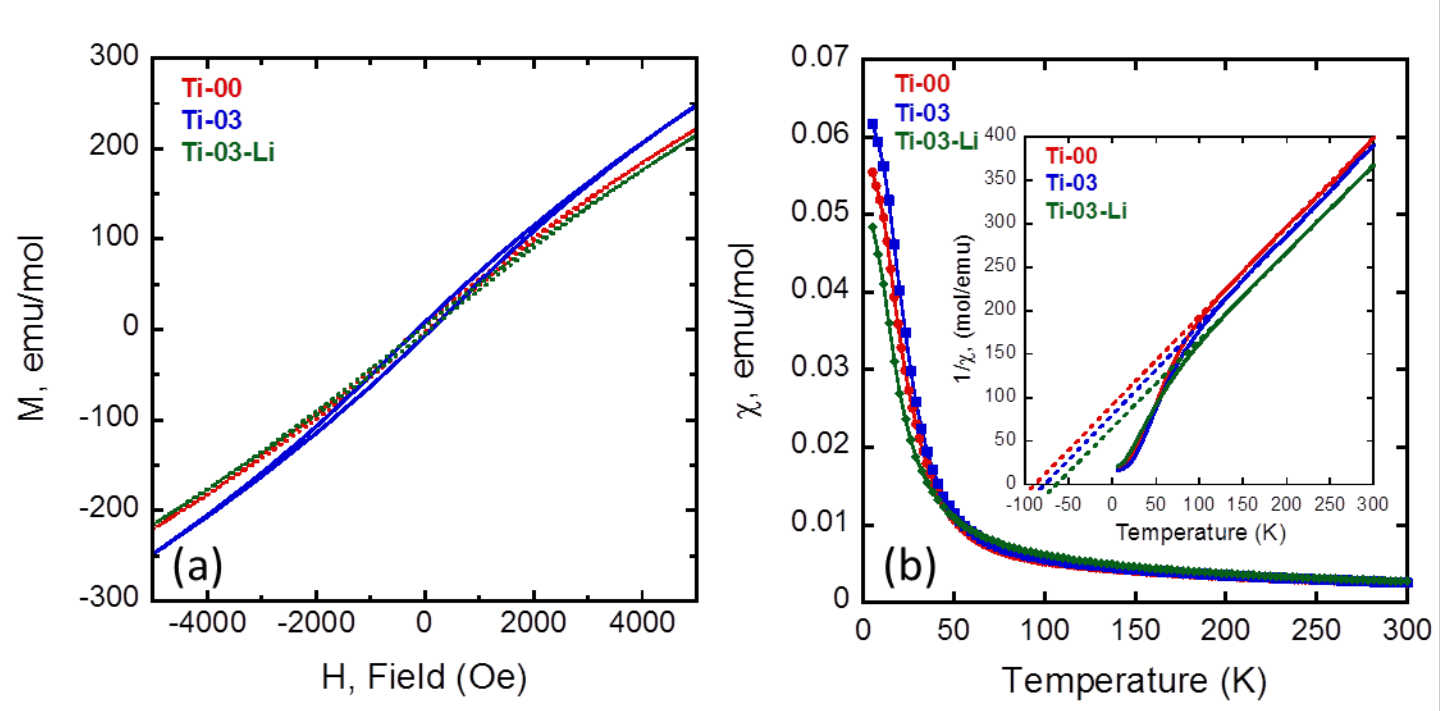
- Possible

Li/Ti on *3b* site



- Li-excess samples

TECHNICAL ACCOMPLISHMENTS/MAGNETIC MEASUREMENTS



Magnetic curves (a) and temperature dependent magnetic susceptibility (b) of NMC333-Ti-00, NMC333-Ti-03, and NMC333-Ti-03-Li compounds collected in a magnetic field of 1000 Oe. The inset shows the reciprocal susceptibilities as a function of temperature along with the fits to the Curie-Weiss equation (dashed lines).

TECHNICAL ACCOMPLISHMENTS/MAGNETIC PARAMETERS

Table 3. Magnetic Parameters of the GNC333 compounds.

Compound	*C, emu-K/mol*	*θ, K*	μ_{exp}, μ_B
NMC333-Ti-0	0.991	-93.4	2.83
NMC333-Ti-03	0.962	-78.6	2.79
NMC333-Ti-03-Li	0.971	-66.9	2.80

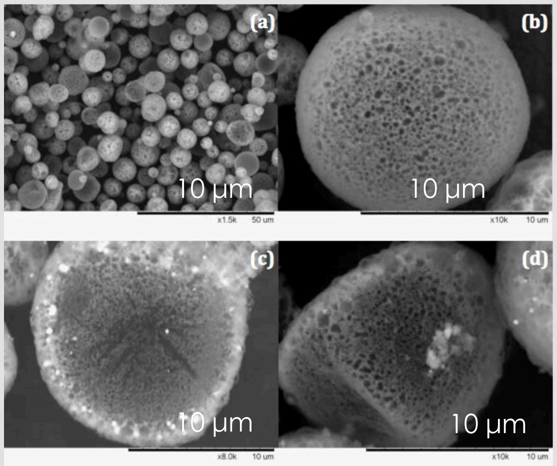
Ion	S
Ni^{2+}	1
Co^{3+} (L.S.)	0
Mn^{4+}	3/2
Mn^{3+}	2
Ti^{4+}	0

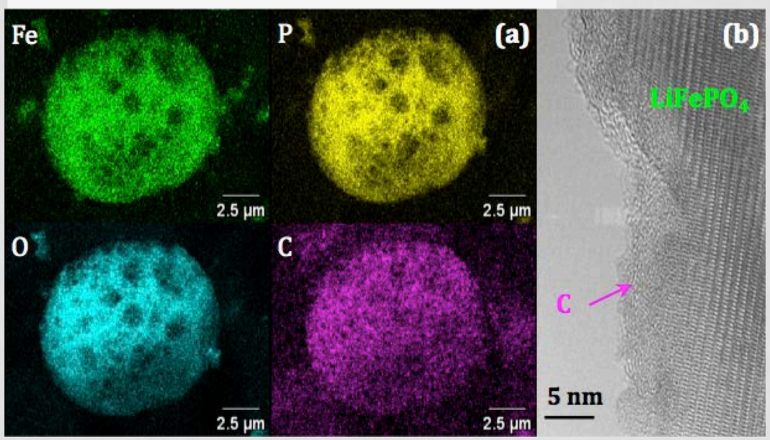
$\mu = g\sqrt{S(S+1)}$: g=2.0023

Curie-Weiss equation: $\chi = C/(T-\theta)$
C=Curie constant, θ=Curie-Weiss temperature
$C = N_a \mu^2 / k_b$
N_a=Avogadro's number, k_b=Boltzmann constant

Composition	Predicted μ_{exp}
No Mn^{3+}	2.77
3% Mn^{3+}	2.81

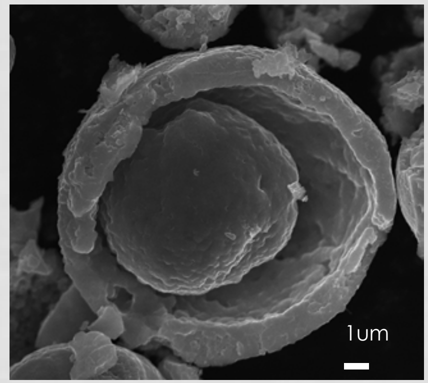
TECHNICAL ACCOMPLISHMENTS/HIGH PERFORMANCE CATHODE MATERIALS MADE BY SPRAY PYROLYSIS



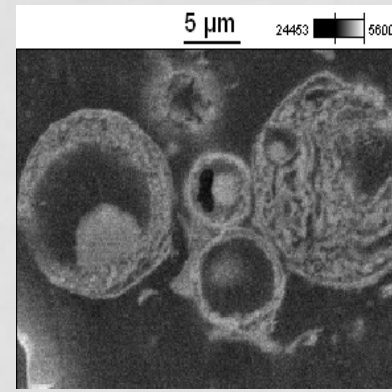


Porous solid carbon-coated $LiFePO_4$ made in one step by spray pyrolysis

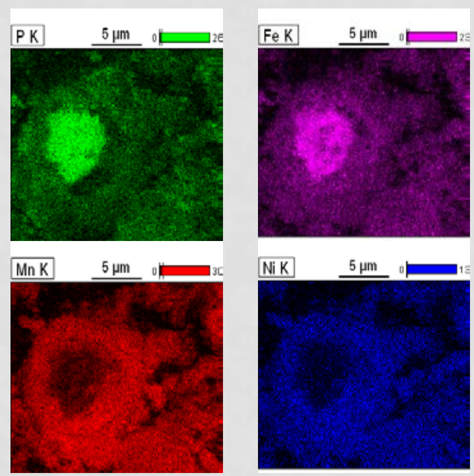
See Doeff et al, **J. Mater. Chem.** 21, 9984 (2011).

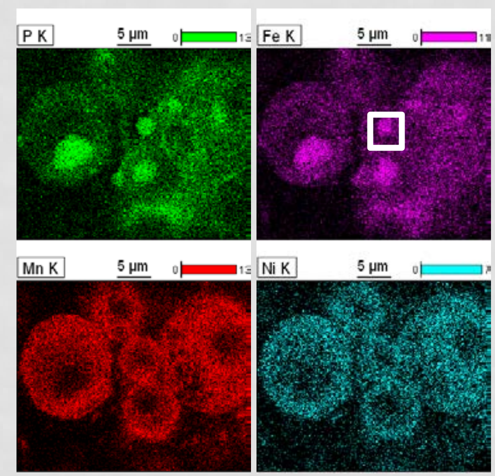


A single particle, broken open



Cross-sectioned particles





Hollow $LiNi_{0.5}Mn_{1.5}O_4$ spheres, filled and coated with $LiFePO_4$, using spray pyrolysis followed by infiltration

COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

- Jordi Cabana, Guoying Chen, Tom Richardson, LBNL-BATT synchrotron experiments at SSRL, high voltage spinel work
- Apurva Mehta, Stanford Synchrotron Radiation Lab (not in VT program), interpretation of synchrotron data and synchrotron experimental set-ups
- Alpesh Shukla, LBNL-BATT TEM studies
- Phil Ross (LBNL-BATT) and LBNL Advanced Light Source personnel (not in VT program)-synchrotron XPS experiments (planned work)
- Professor Mark Asta, Materials Sciences and Engineering Department, UCB (not in VT program) Computational studies on NMCs-Isaac Markus shared graduate student
- John Heron (graduate student, Prof. R. Ramesh, Materials Sciences and Engineering Department, UCB) not in VT program-magnetic measurements on NMCs
- Vince Battaglia, LBNL-BATT, cell development, testing of NMCs (planned work)

PROPOSED FUTURE WORK-FY13/14

- Work on Ti-substituted NMCs will be emphasized
  - Full evaluation of best Ti-substituted 442-NMC in full and half cells (different charge voltage limits, rates, cycling) with V. Battaglia (LBNL)
  - Thermal and structural characterization of charged Ti-substituted NMCs (safety and oxygen release) with G. Chen (LBNL)
  - Experiments and computational effort directed towards understanding origin of improved 1st cycle efficiency/enhanced capacity –surface or bulk effect?
    - Surface characterization of pristine and partially charged materials with spectroscopic methods (FTIR, Raman)
    - Surface characterization using synchrotron XPS and other synchrotron techniques (with P. Ross and J. Cabana of BATT/LBNL and ALS personnel (LBNL)
    - Computational work (Prof. M. Asta in MSE/UCB with Isaac Markus)
  - Lower Co compositions
  - Milestones will be rewritten to reflect new emphasis and plans for this task
- Spray pyrolysis work will continue at a lower level
  - Address reactivity issue between $LiFePO_4$ and $LiNi_{0.5}Mn_{1.5}O_4$ in $LiFePO_4$ @ $LiNi_{0.5}Mn_{1.5}O_4$ system (buffer layer, change heating régime)
  - Try $LiMnPO_4$ as filler/coating for hollow $LiNi_{0.5}Mn_{1.5}O_4$ spheres if this doesn't work
  - Attempt NMC and Ti-NMC spray pyrolysis with and without protective coatings

SUMMARY

- Aliovalent Ti-substitution in NMCs enhances practical capacities and improves capacity retention upon cycling to high voltage limits
  - Discharge capacities up to 225 mAh/g have been demonstrated
  - Capacity improvement is due to better first cycle efficiencies (possible surface effect)
  - Cycling improvement may be due, in part, to decreased changes in the *a* lattice parameter upon delithiation (bulk effect)
- This is a possible route to higher energy density if thermal stability and cycle life can be maintained
- Experiments are underway to evaluate this approach
- Spray pyrolysis can be used to synthesize hierarchically structured cathode materials including coated powders and composites, with good control of particle sizes and morphologies