Mixed polyanion (MP) glasses as cathode materials

Project ID: ES184

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DOE Annual Merit Review

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Overview

Timeline

- Start date: June 22nd, 2012
- End date: June 30th, 2016
- Percent complete: 78 %

Budget

- Total funding: $1.42M
  - DOE share: $1.42M
- Funding received in FY2014: $335K
- Funding received for FY2015: $335K

Barriers

- Higher energy densities (350 Wh/kg cell*)
  - Est. cathode energy densities up to >1000 Wh/kg
- Excellent cycle life (PHEV 3-5K deep discharges*)
  - Rigid covalent structure & no irreversible phase changes
- Cost (PHEV $300/kWh*)
  - Commercial, non-exotic processing methods

*VT Program Multi-Year Plan values

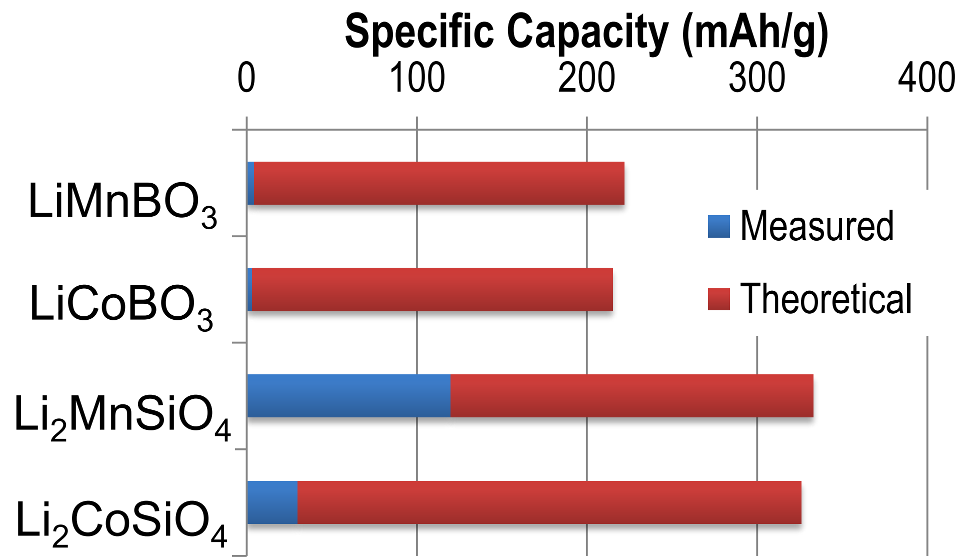
Partners

- Dr. Kyler Carroll (MIT): x-ray absorption spectroscopy of glass cathodes at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory

Crystalline polyanion cathodes have great theoretical promise.

Relevance

Why do these fail?



1. Legagneur V, et al., 2001. 2. Domiko R, et al., 2007.
3. Lyness C, et al., 2007.

Poor electrical conductivity

often ~10^{-12} S/cm.

Phase transformations not cycleable

Why glass?

Relevance

Mixed polyanion (MP) glasses can overcome key problems:

- proper polyanion content gives higher conductivity
- avoid irreversible phase transformations of crystalline materials

Material	Electrical conductivity
Lithium iron phosphate	~10^{-9}-10^{-10} S/cm
Iron phosphate glass	~10^{-10} S/cm
Iron phosphate glass – 30% vanadate substituted	~10^{-8} S/cm
Iron phosphate glass – 50% vanadate substituted	~10^{-6} S/cm

1. Mogus-Milankovic M, et al., 2004.
2. Tanaka K, et al.,1990.
3. Shapaan M, et al., 2009.
4. Santic B, et al., 2001.

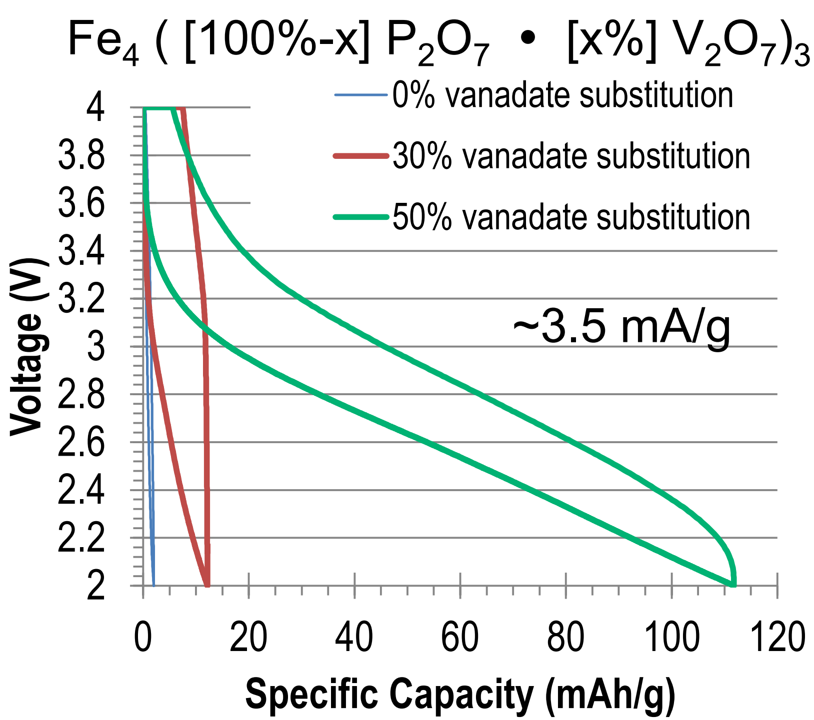
MP glass cathodes demonstrate high capacity.

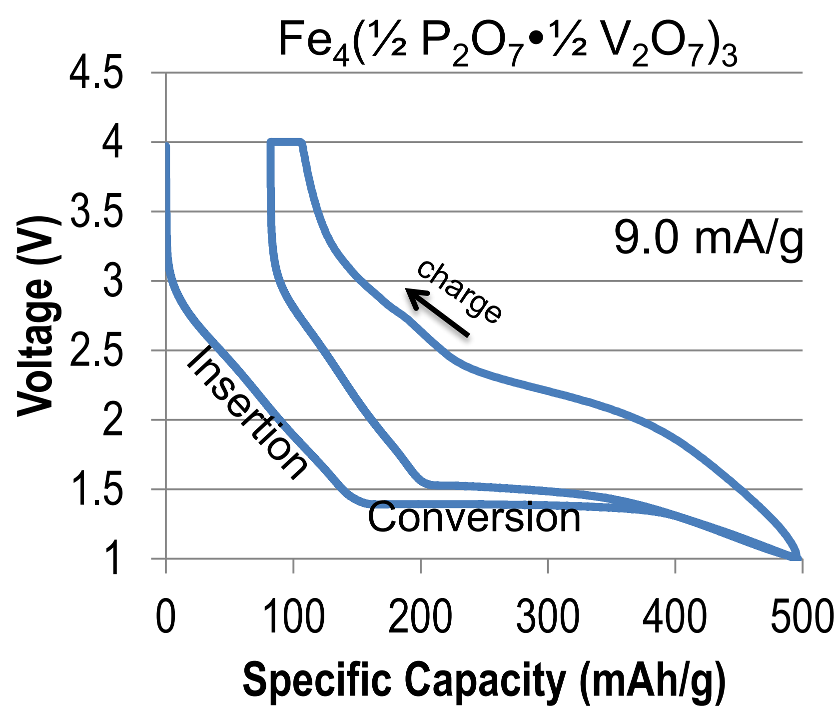
Relevance

Polyanion substitution dramatically improves the specific capacity and rate performance.

2 high capacity electrochemical reactions have been observed:

- Insertion (Intercalation)
- Conversion





FY14 Milestones

Approach

- Dec. 2013: Synthesize, characterize, and perform electrochemical testing on a mixed polyanion glass that is theoretically capable of a multi-valent transition. *Completed on schedule*
- Mar. 2014: Demonstrate the effect of submicron particle size on the electrochemical performance of mixed polyanion glass cathodes. *Completed on schedule*
- June 2014: Measure the electrical conductivities of a series of mixed polyanion glasses as a function of polyanionic substitution. *Completed on schedule*
- Sept. 2014: Synthesize, characterize, and perform electrical testing on at least 4 different glass cathode compositions with theoretical specific energies exceeding $LiFePO_4$. *Completed on schedule*

FY15 Milestones

Approach

- Dec. 2014: Perform electron microscopy on mixed polyanion glass cathodes at key states of charge. *Completed on schedule*
- Mar. 2015: Produce and electrochemically test MP glasses designed to have enhanced ionic diffusivity. *Completed on schedule*
- June 2015: Produce and electrochemically test an MP glass designed to have enhanced ionic diffusivity and theoretically capable of a multi-valent intercalation reaction. *In progress*
- Sept. 2015: Determine the polyanion substitution effect on a series of non-phosphate glasses. *On schedule*

Response to reviewer comments

Approach

Vehicle Technologies Annual Merit Review (June '14):

"The reviewer asked if the authors would synthesize the materials predicted by the simulations and try to analyze whether there is agreement between the model and actual materials."

- A series of MP glasses were made to test the agreement between the model and actual materials for conversion reactions. Unfortunately, the model did not agree well with observed voltage magnitudes or trends.

"… practical specific energies will not be attractive because of low capacities and voltages for the second reaction [glass-state conversion reaction]."

- MP glasses have demonstrated specific capacities of 250-500 mAh/g for the conversion reaction. Voltages up to 2.9V have been achieved, and new compositions are being developed to increase voltage. The real problem is cycleability.

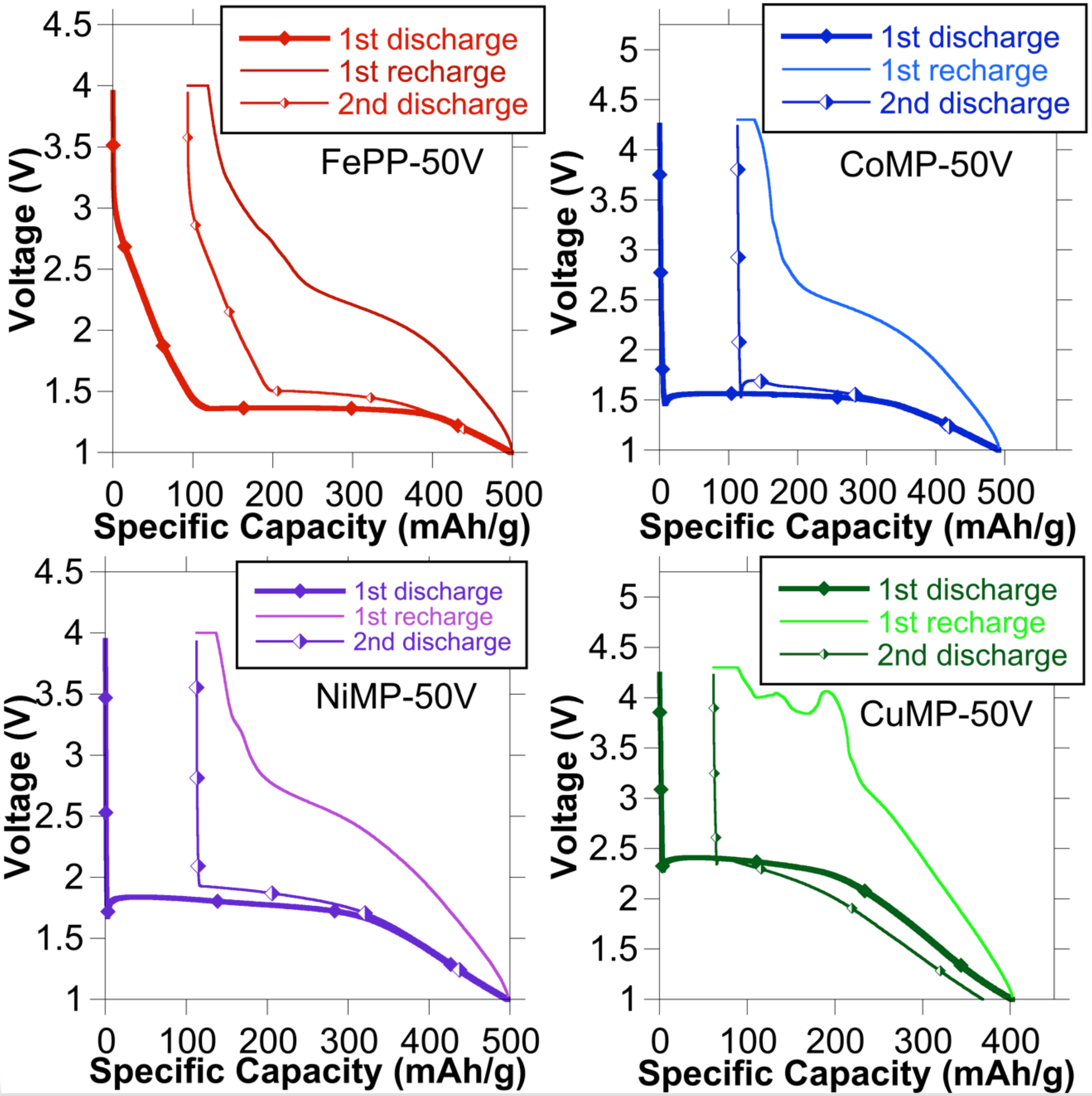
US DRIVE Merit Review Report (Sept '14):

"Focus on vanadium-based materials would seem to severely limit direct practical utility of project results for automotive or consumer applications due to environmental concerns."

- MP glasses with molybdate substitution were produced and demonstrated good electrochemical performance for conversion reactions.

Conversion reaction voltage depends on metal cation.

Technical Accomplishments



Glasses with various cations undergo conversion reactions.

The voltage depends on the transition metal (1.4 – 2.9V).

Proposed conversion reaction example:

$$M([1-n]\ PO_3 \bullet n\ VO_3)_y + y\ Li^+ + y\ e^- \rightarrow y\ Li([1-n]\ PO_3 \bullet n\ VO_3) + M$$

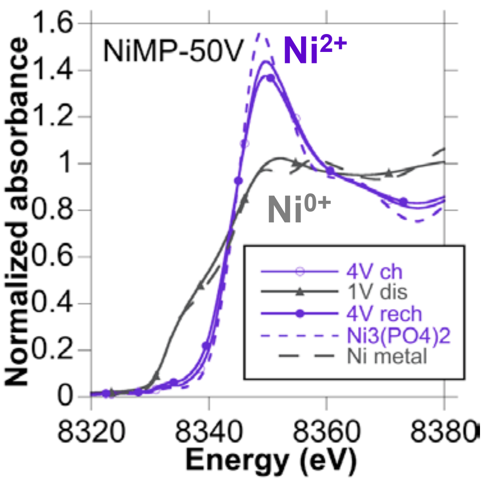
PP = pyrophosphate = $[P_2O_7]^{4-}$
MP = metaphosphate = $[PO_3]^{1-}$
-##V = % vanadate substitution

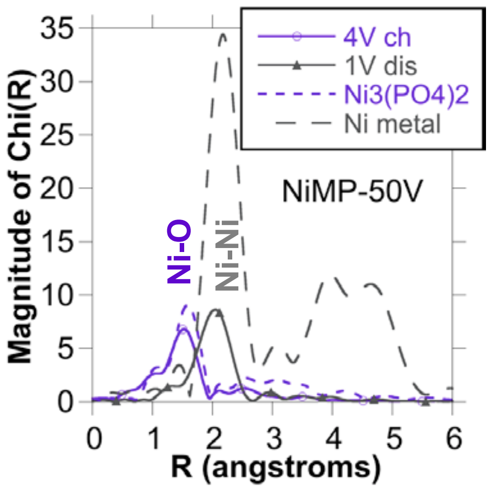
Ex: CoMP-50V is cobalt metaphosphate glass with 50% vanadate substitution.

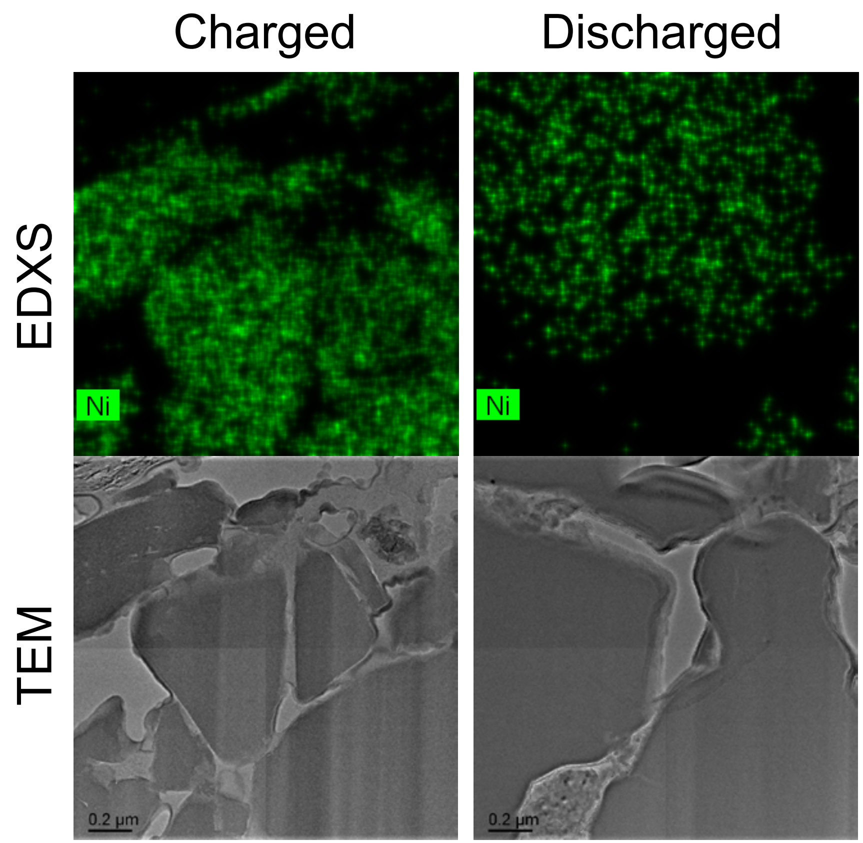
XAS and EDXS indicate metal nanoparticles form in glass.

Technical Accomplishments

Glass cathodes studied ex-situ to understand conversion reaction mechanism.





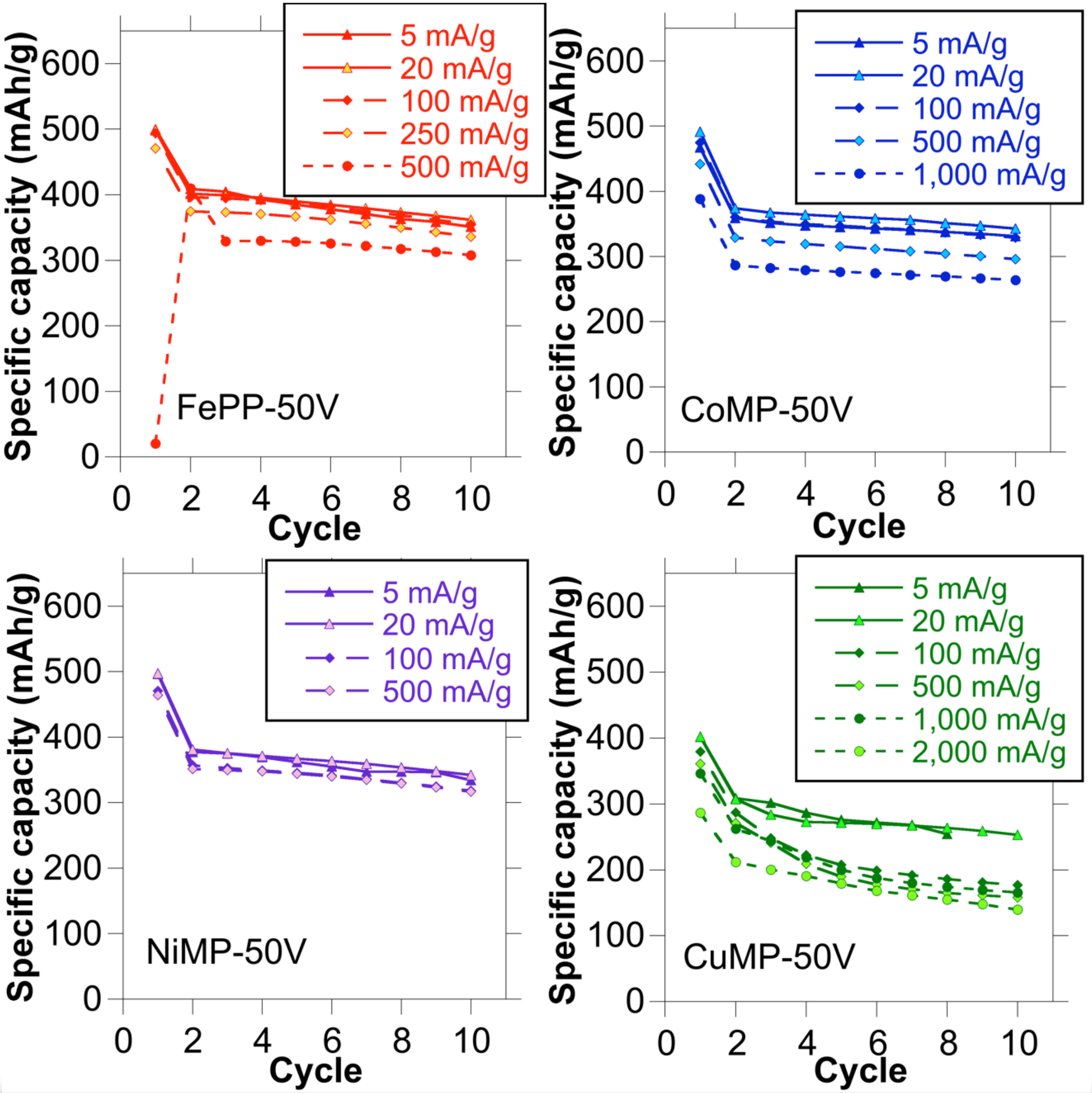


XAS showed valence state change and metal-metal bond formation.

Metal remained dispersed inside intact glass particles.

Glass showed good short-term cycling and rate performance.

Technical Accomplishments

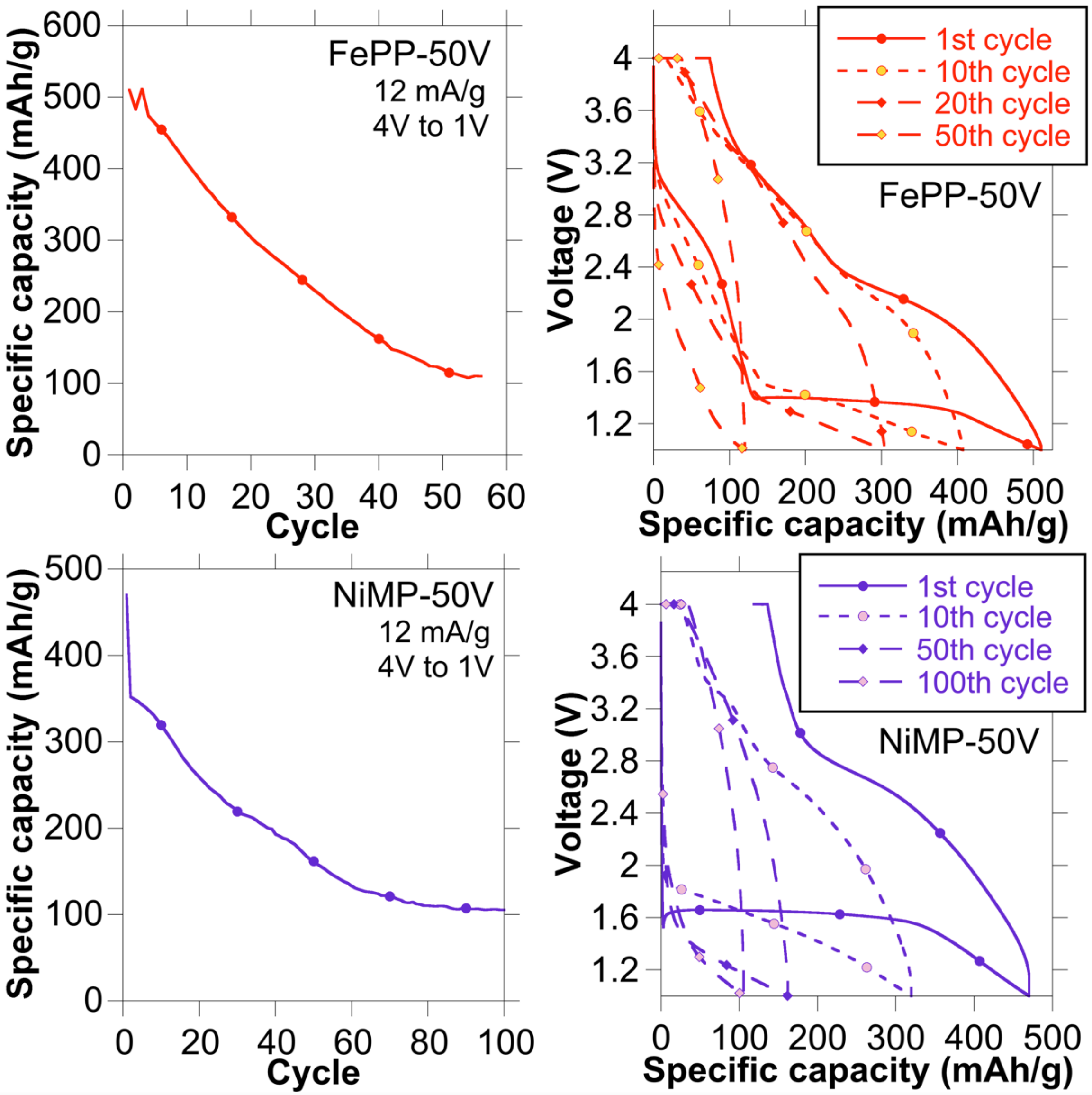


Conversion reaction cycling:

- irreversible capacity
- gradual capacity fade

Good capacity retention at high specific currents.

Glasses showed significant capacity fade in 100 cycles.



Glass conversion reactions exhibited typical capacity fade.

When discharged through conversion reaction, insertion reaction of FePP-50V demonstrated fade as well.

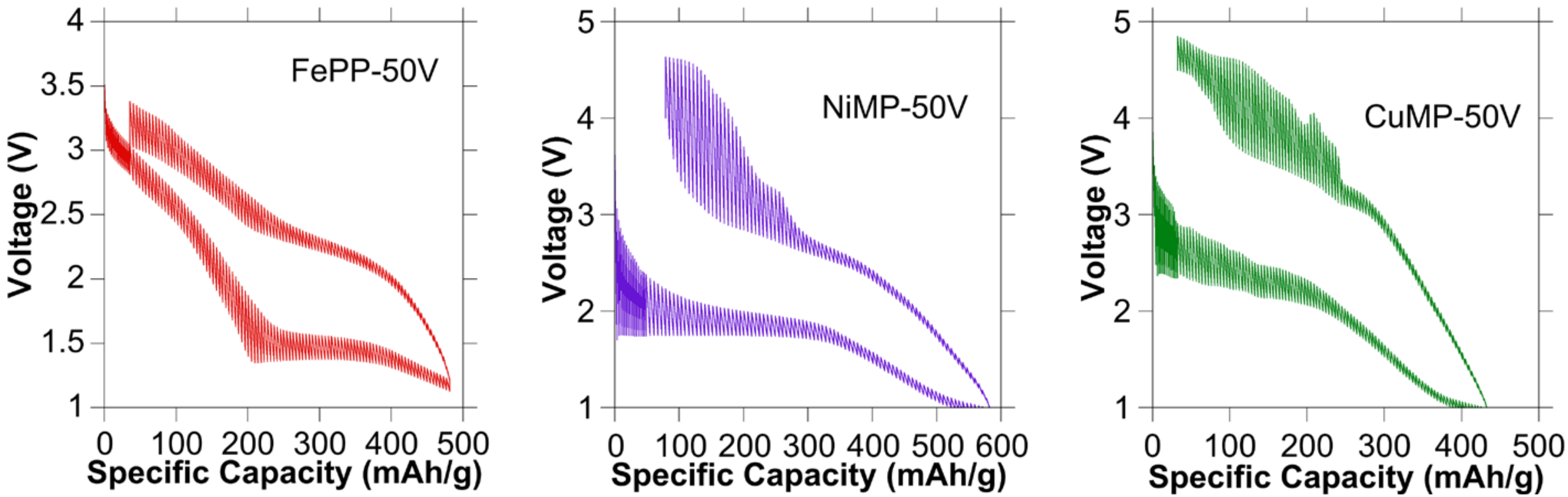
GITT testing demonstrated persistent hysteresis.

Technical Accomplishments

GITT testing showed reduced hysteresis, but substantial intrinsic hysteresis remains.

Apparently, equilibrium conversion reaction is kinetically very slow.

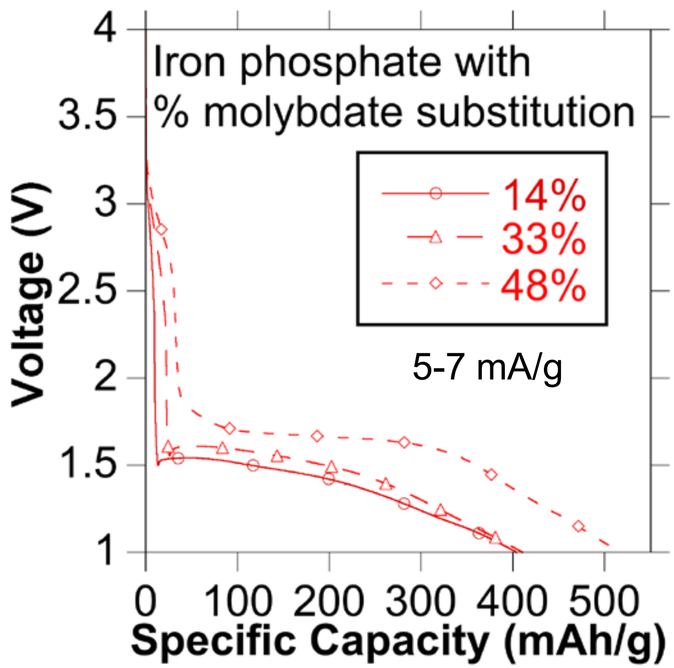
GITT test conditions:
10 hr dwells, 12.5 mAh steps

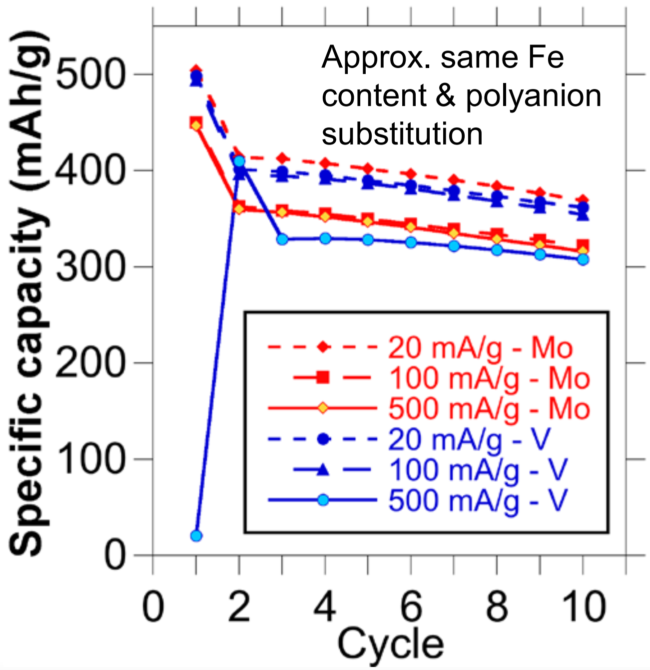


Molybdate is environmentally friendlier option.

Molybdate substitution:

- partial insertion
- complete conversion





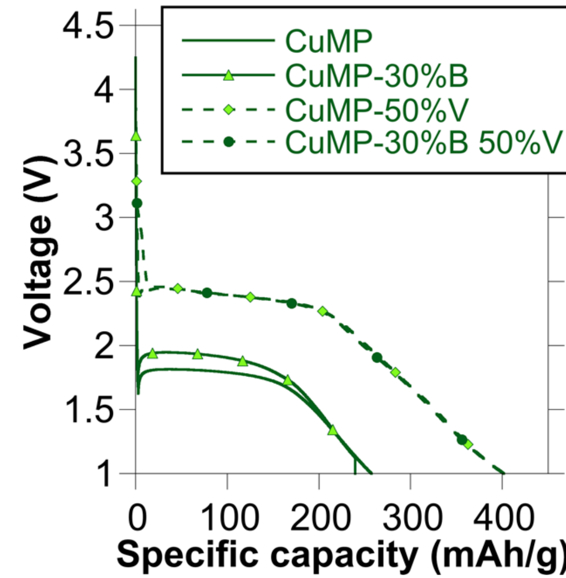
Phosphate glasses with vanadate or molybdate have similar total specific capacity and cycle performance.

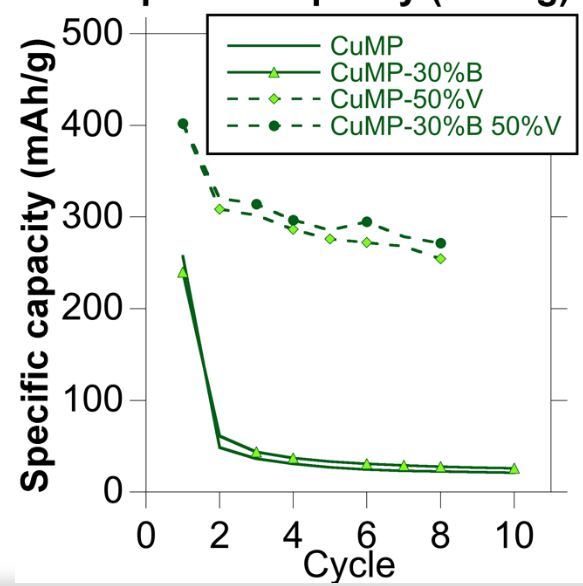
Polyanion substitution aimed at increased ionic diffusivity.

Borate is expected to increase free volume and ionic diffusivity.

Comparing different polyanion substitutions, borate showed only a weak effect.

	1st cycle Voltage	Cycleability
pure PO_3	1.82 V	poor
PO_3 / BO_2	1.95 V	poor
PO_3 / VO_3	2.45 V	moderate fade
PO_3 / BO_2 / VO_3	2.46 V	moderate fade



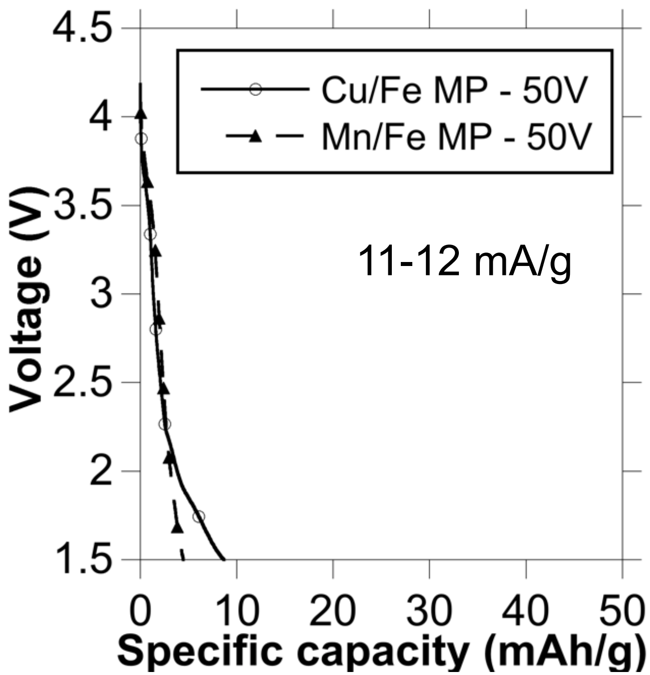


Mixed cation content explored to improve insertion reaction.

Technical Accomplishments

Mixed cation content in crystalline polyanion materials can improve electrochemical performance.

Li(Fe,Cu)PO_4,[1] Li(Fe,Ni)PO_4, Li(Fe,Co)PO_4, Li(Fe,Mg)PO_4,[2] Li(Mn,Fe)PO_4[3]



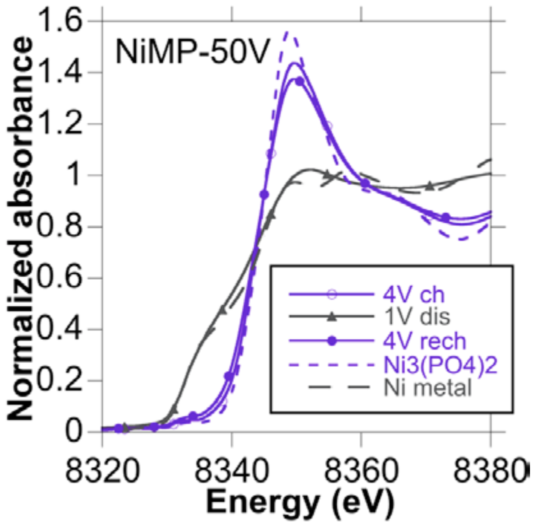
In glass, mixed cation content did not improve insertion reaction.

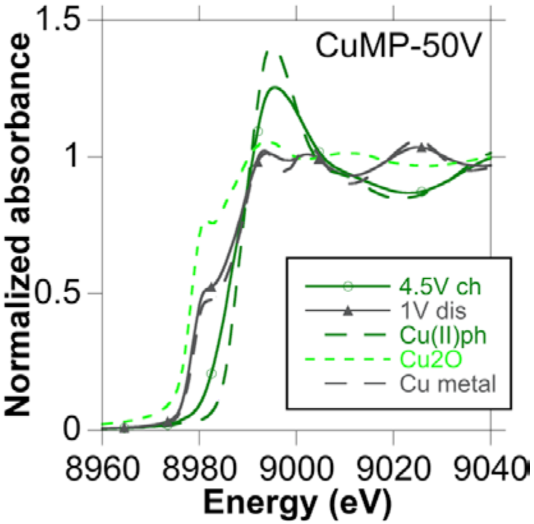
1. Lee SB, et al., Journal of Alloys & Compounds, vol. 488, 2009.
2. Novikova S, et al., Electrochemica Acta, vol. 122, 2014.
3. Yan SY, et al., Journal of Alloys & Compounds, vol. 628, 2015.

ORNL / MIT / BNL collaboration performed XAS on cathodes.

Collaboration with Dr. Kyler Carroll (MIT) and Dr. Syed Kahlid (BNL-NSLS):

XAS of ex-situ cathodes used to successfully identify valence changes & local bonding environments of conversion reactions





Remaining challenges & barriers

Future Work

- MP glass cathodes have key shortcomings that must be overcome to be commercially viable:
  1. <u>Multi-valent insertion:</u> Increased free volume & increased conductivity may enable.
  2. <u>Conversion:</u> Capacity fade is the primary issue. Higher voltage & reduced hysteresis are also needed.
- Only phosphate-based MP glasses have been tested as cathodes. The relationship between composition and cathode performance needs to be established for non-phosphate and non-traditional glasses.

Planned work for FY15 & FY16

Future Work

- Using glass compositional variation, electrochemical analysis, and ex situ characterization to focus on overcoming the key shortcomings of MP glass cathodes.
  - FY16 Q1: Ex-situ characterization of cycled cathodes exploring cycle fade mechanism.
- Produce cathode materials with intentional partial crystallization to develop composite structures for improved electrochemical performance.
  - FY16 Q2: Produce cathode materials with intentional partial crystallization.
- Produce glass cathodes using non-phosphate and non-traditional glass formers.
  - FY15 Q4: Determine the polyanion substitution effect on non-phosphate glasses.
  - FY16 Q3: Produce glass cathodes using non-traditional glass formers.

Summary

- MP glass are high-capacity cathode materials that can undergo two different electrochemical reactions:
    - Insertion
    - Conversion
- So far, insertion has only been observed in iron-based systems. Ongoing research seeks to develop glass compositions with higher conductivity and free volume to enable multi-valent insertion reactions.
    - Initial MP glass cathodes with borate have been electrochemically tested, which should have higher free volume and ionic diffusivity.
- High-capacity conversion reactions have been demonstrated for Ag, Co, Cu, Fe, and Ni bearing glasses.
    - Ex-situ electron microscopy and x-ray absorption spectroscopy of cathodes has provided key insights into the conversion reaction mechanism.
    - Good rate performance has been observed in MP glasses.
    - GITT testing suggested the equilibrium conversion reaction is very slow.
    - Ongoing research focuses on stabilizing the conversion reaction and reducing fade.
- MP glasses with molybdate have been demonstrated as an environmentally friendlier alternative to vanadate.