Next Generation Lithium Sulfur Batteries for Mission Enabling Energy Storage Systems - NASA Iowa EPSCoR Grant NNX13AD36A

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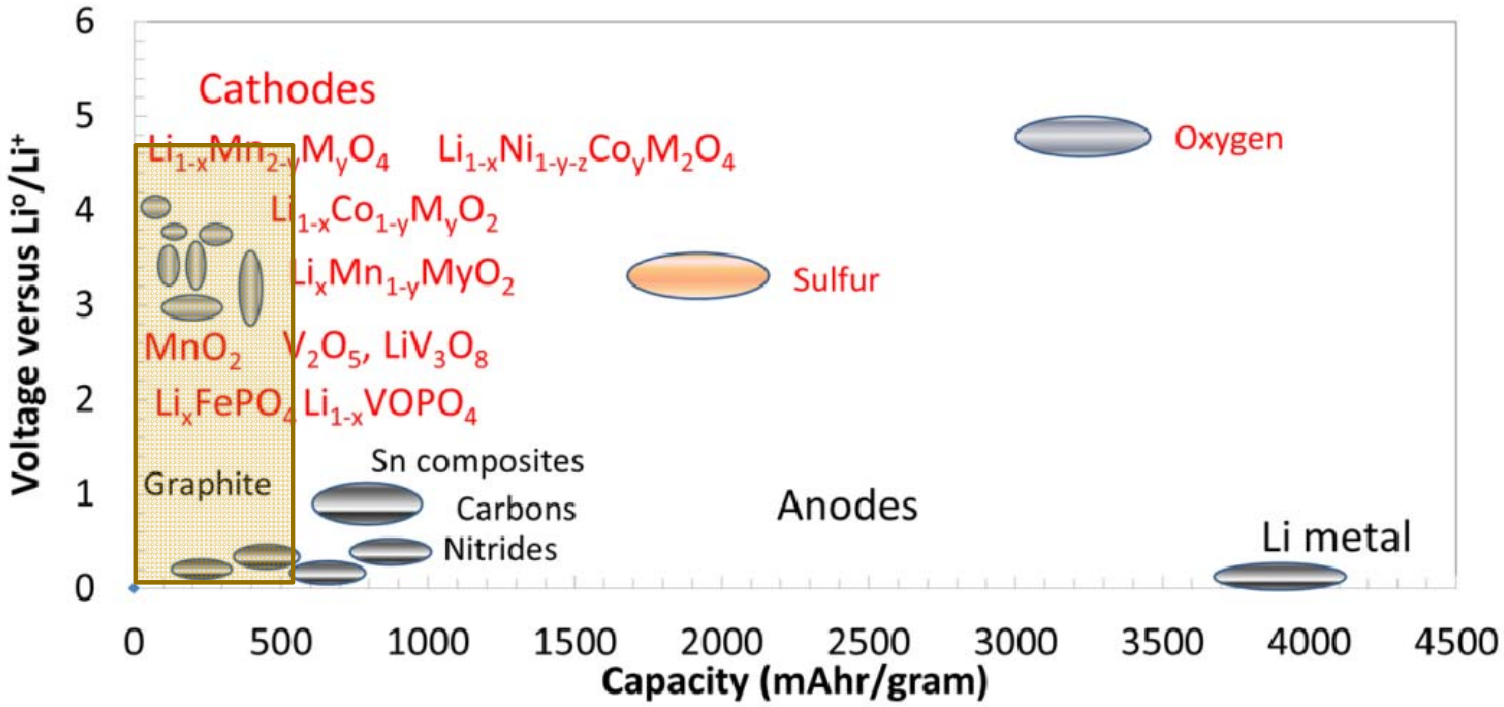
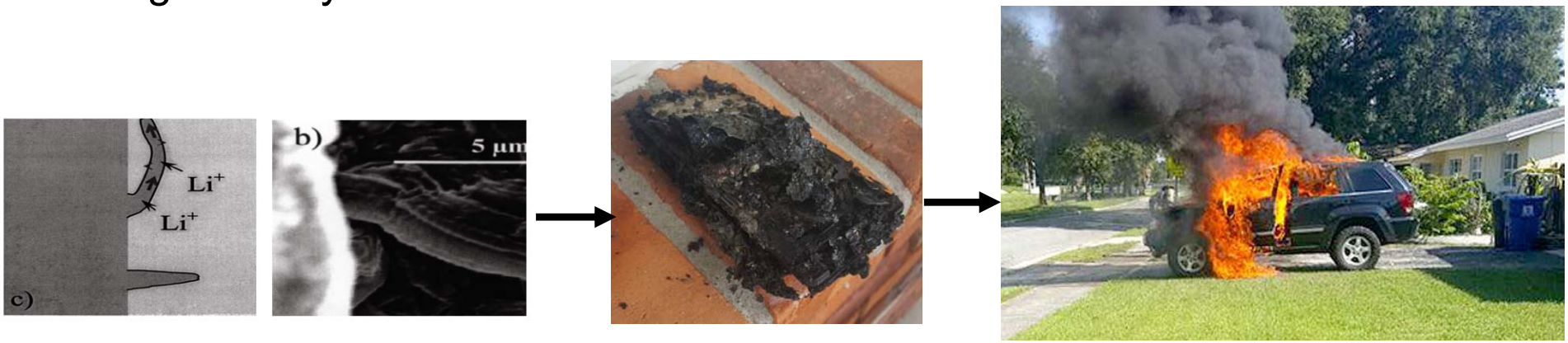
Next Generation Lithium Sulfur Batteries for Mission Enabling Energy Storage Systems

- Overall goal of the project
- Develop safer, more energy dense, lower cost, and higher performance all-solid state Lithium – Sulfur Batteries



Next Generation Lithium Sulfur Batteries for Mission Enabling Energy Storage Systems

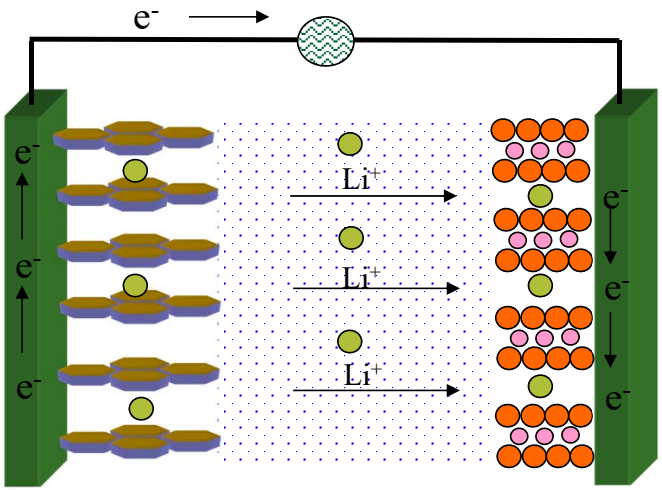
- All – Solid – State Lithium – Sulfur Batteries
  - 7x increase in energy density over traditional Lithium – ion batteries
  - No flammable liquid electrolytes
  - Based upon very low cost abundant (waste product) sulfur
  - Solid cell prismatic formats stack more efficiently
  - Wider temperature range for safe operation -40^{o}C to 160 ^{o}C
  - Significantly more abuse tolerant



Next Generation Lithium Sulfur Batteries for Mission Enabling Energy Storage Systems

- Iowa State's Project – Developing new solid electrolytes for new Li-S batteries

Lithium Ion



Li_xC_6 | Li^+ conducting Liquid electrolyte | $Li_{1-x}CoO_2$

Anode: $Li_xC_6 \rightarrow xLi^+ + xe^- + C_6$

Cathode: $Li_{1-x}CoO_2 + xLi^+ + xe^- \rightarrow LiCoO_2$

Lithium Sulfur

Anode: $2Li \rightarrow 2Li^+ + 2e^-$

Cathode: $S + 2Li^+ + 2e^- \rightarrow Li_2S$

New Solid Electrolytes for Li-S Batteries

Project Objective:

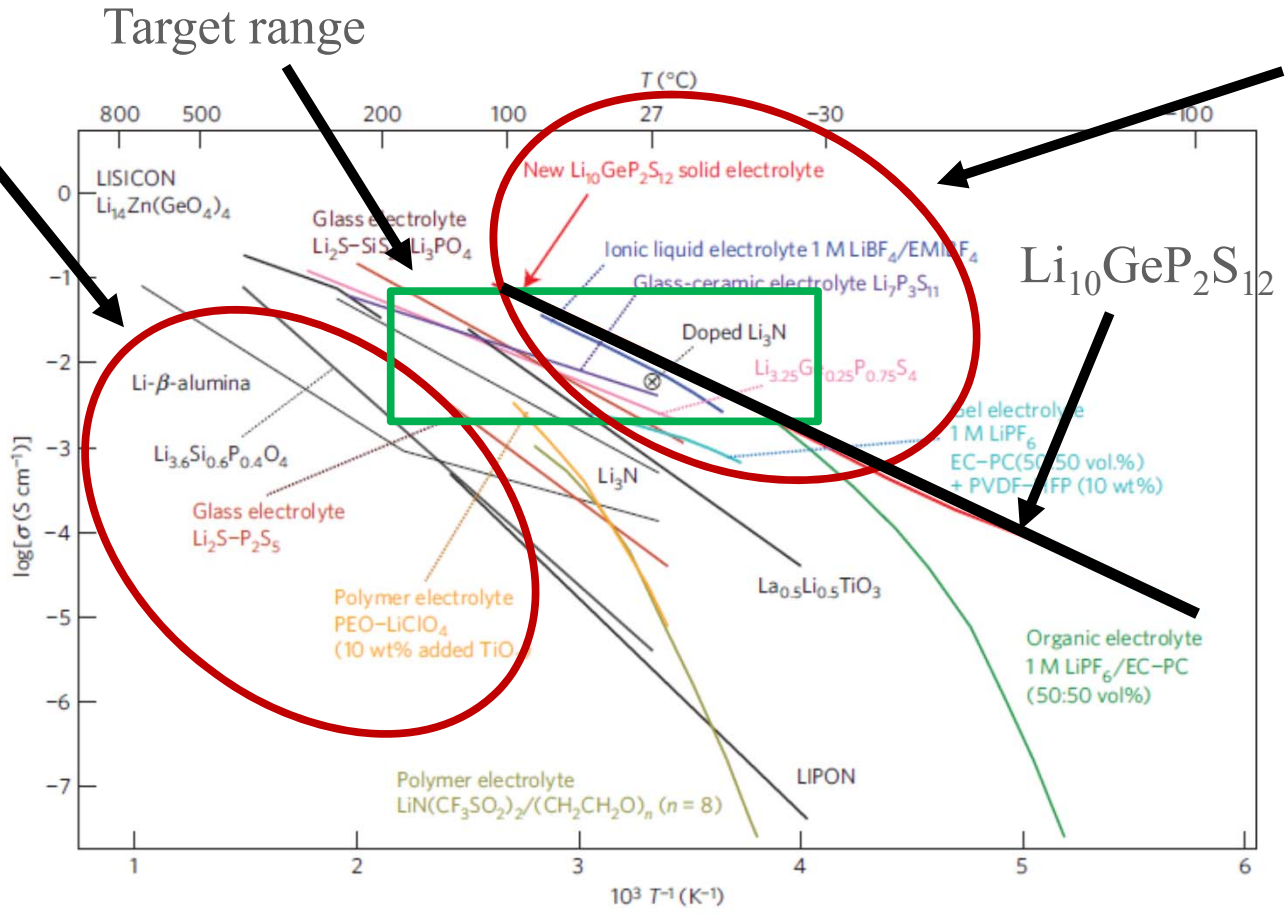
- ISU's focus is on the solid electrolyte separator
- Most critical aspect
- Least amount of research so far conducted
- Greatest opportunity for significant advancements

Project Goals:

- Extremely High Li^+ conductivity – Target > 10^{-3} $(\Omega cm)^{-1}$ at 25 ^oC
- Extremely Low Electronic conductivity – Target < 10^{-9} $(\Omega cm)^{-1}$ at 25 ^oC
- Low cost – Target < $1/kg
- Easily manufactured – Target <100 μm and >10 m^2/hour
- Low toxicity, reactivity, and chemically stable – Target < ± 0.1% wt/hr weight change in air at 25 ^oC

Lithium ion conductivities of solid electrolytes

- **Oxide materials**
- Cheap
- Easy to make
- Durable like sand
- But Poorly conducting…



- **Sulfide materials**
- Expensive
- Difficult to make
- Very Reactive
- But Highly conducting…

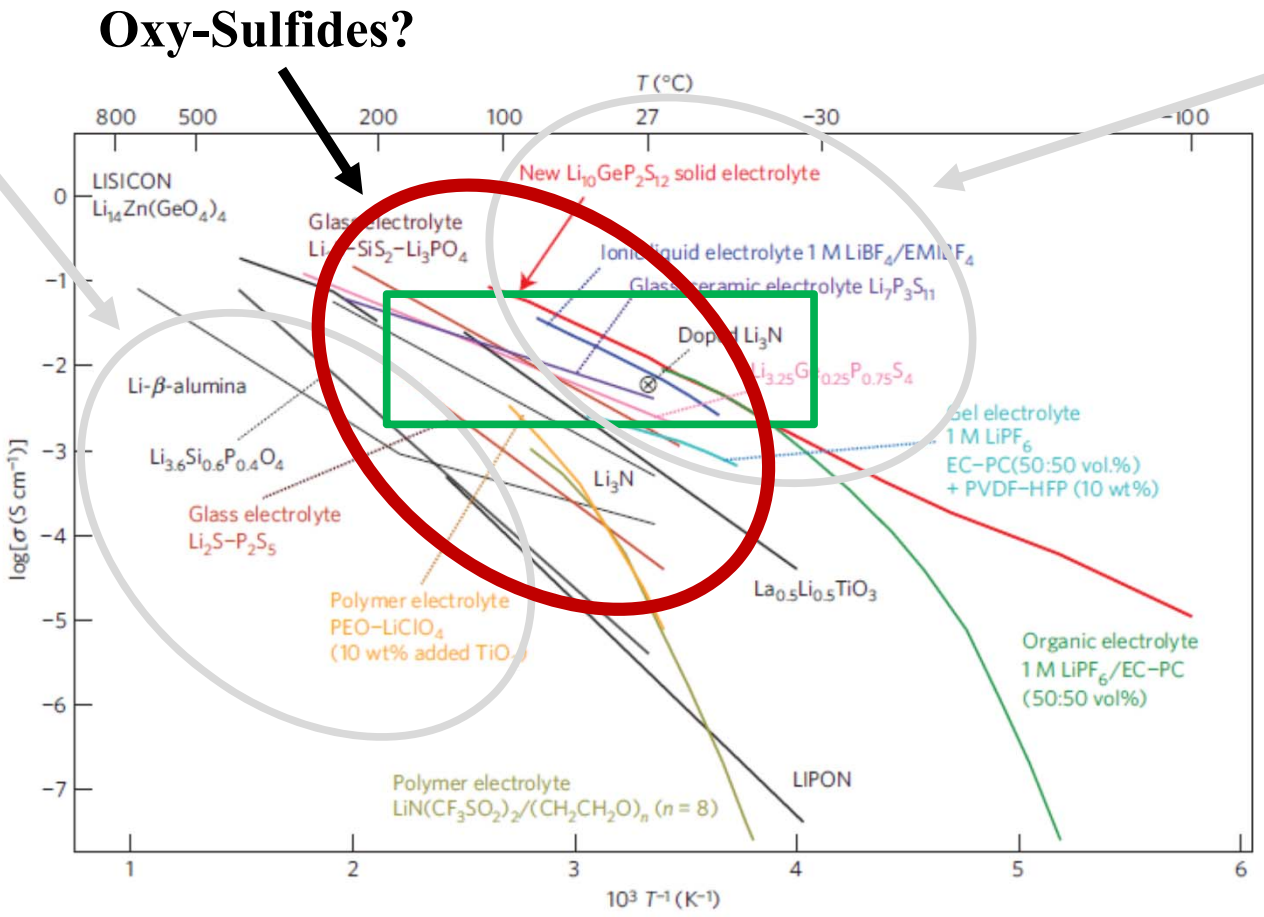
New Oxy-Sulfide Li^+ Ion Conducting Solid Electrolyte

- **Idea:**
- Can we make new mixed Oxy-Sulfide Solid Electrolytes?
- Do they blend the best properties of each family?
- Can they be made to have the good Li^+ ion conductivities of the Sulfides?
- Can they be made to have the good chemical durability's of the oxides?
- Are they easier and cheaper to make than the sulfide materials?

- **Selection of the sulfide starting material….**
- The best possible Li^+ ion conductor…$Li_{10}GeP_2S_{12}$
- Expensive, reactive, hard to make…
- But a great solid electrolyte…
- Can we make Oxygen doped versions that are easier to make and cheaper and yet have good conductivities?

New Lithium Ion Conducting Solid Electrolytes – **Oxy-Sulfides**

- **Oxide materials**
- Cheap
- Easy to make
- Durable like sand
- But Poorly conducting…



- **Sulfide materials**
- Expensive
- Difficult to make
- Very Reactive
- But Highly conducting…

High cost of LGPS material

- Ge is expensive, so Sn and Si has been used to replace Ge to lower the synthesis cost.
- Conductivity of $Li_{10}SnP_2S_{12}$ (LSnPS) and $Li_{10}SiP_2S_{12}$ (LSiPS) are 4 x 10^{-3} and 2.3x10^{-3} S/cm respectively [5-7].
- The smaller conductivities….

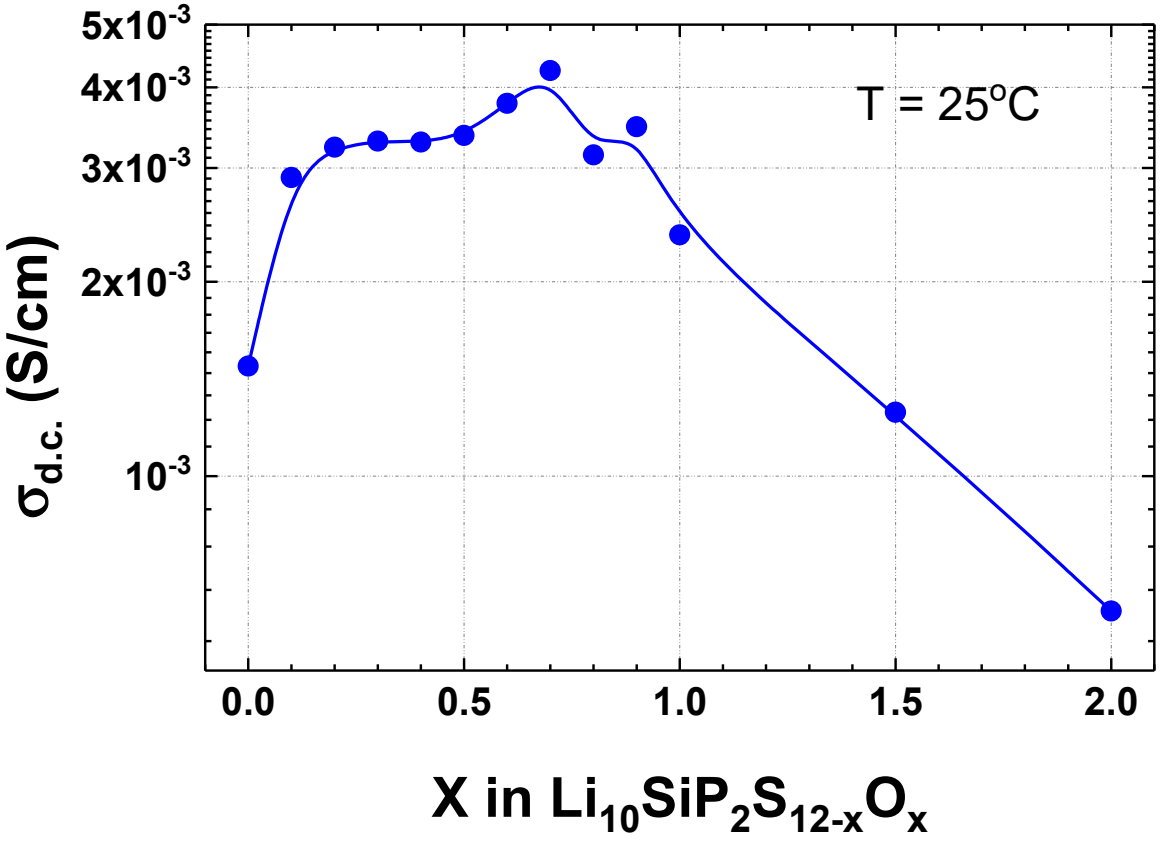
- Si is smaller than Sn so the cell volume for conduction is smaller…
- LSiPS is not a pure phase, but a solid mixture of different phases

- All Sulfide conductors are also unstable in air and must be handled carefully….
- **Concept:** *Can we prepare and characterize more easily made, more chemically stable, lower cost, yet sufficiently conductive LSiPSO – oxysulfide solid electrolytes?*

Experimental Methods

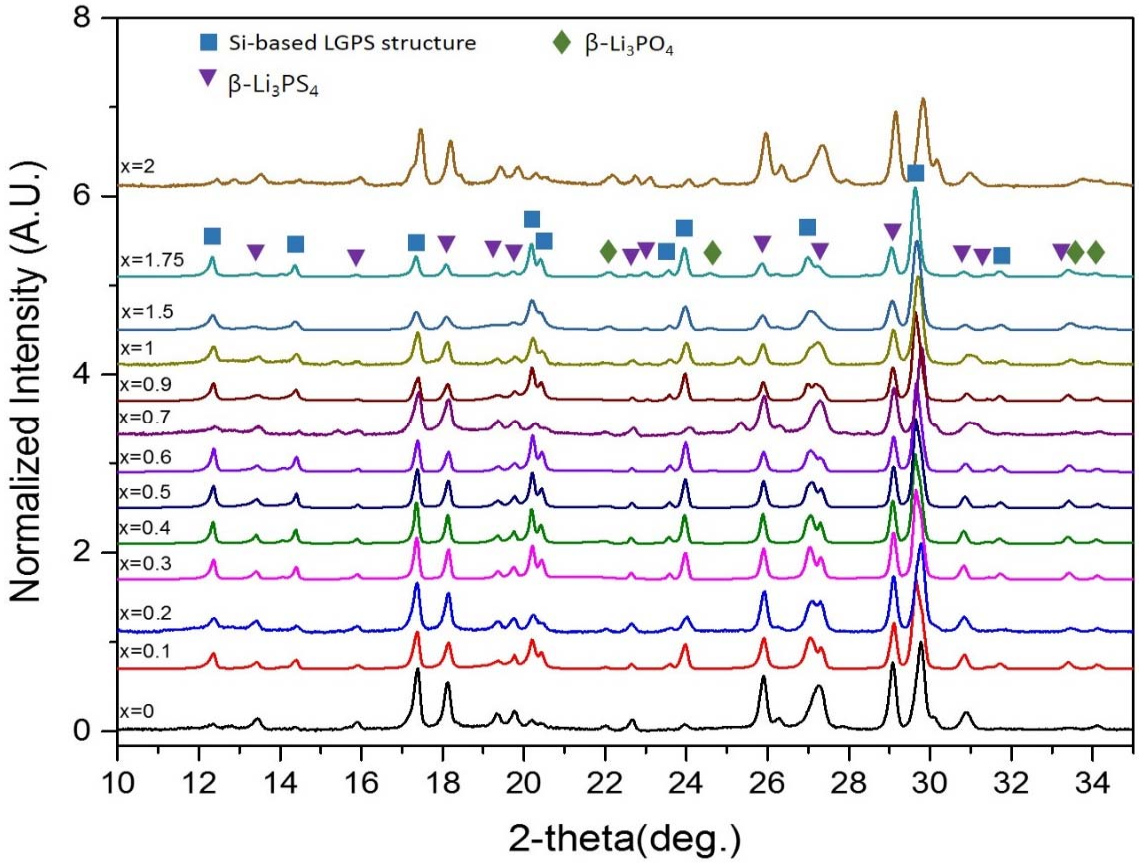
- Chemicals, Li_2S, P_2S_5, SiS_2, SiO_2 and P_2O_5 were used for synthesis in appropriate amounts
- Compound of $Li_{10}SiP_2S_{12}$ and modified series of $Li_{10}SiP_2S_{12-x}O_x$ were made by mechanical milling and then pressed into bar shaped pellets under Ar atmosphere glovebox.
- O substitution (so far) is from 0.1 to 2
- Products are examined to determine their crystalline phases, structures, ionic conductivity, and electrochemical properties.

Ionic Conductivities of $Li_{10}SiP_2S_{12-x}O_x$ Oxy-Sulfide Solid Electrolytes

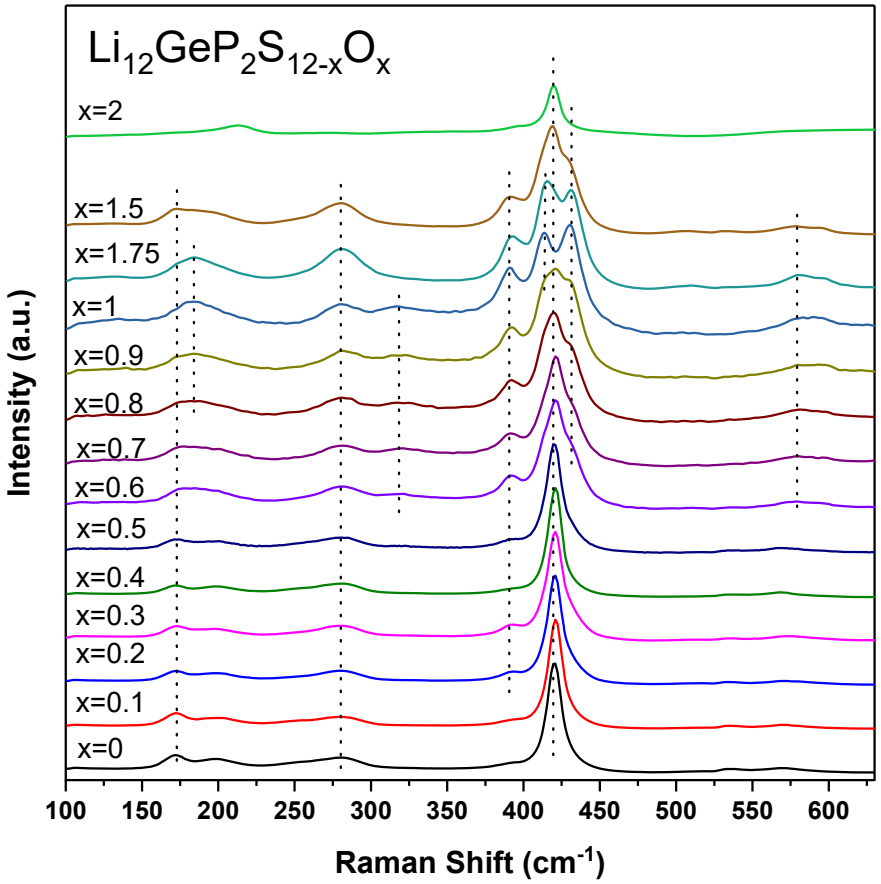


XRD of $Li_{10}SiP_2S_{12-x}O_x$ Oxy-Sulfide Solid Electrolytes

- $Li_{10}SiP_2S_{12}$ has second β–Li_3PS_4 phase
- The β–Li_3PS_4 phase is replaced by β–Li_3PO_4



Raman Spectra of $Li_{10}SiP_2S_{12-x}O_x$



- SiS_4^{-4} and PS_4^{3-} Tetrahedral groups at 420 cm^{-1}
- Oxygen substitution on SiS_4 and PS_4 tetrahedral units
- Create high frequency shoulders due to $SiS_{4-x}O_x$ and $PS_{4-x}O_x$ units

Summary and Future Research

- O substitution on base $Li_{10}SiP_2S_{12}$ from 0.1 to 1 creates a new phase as LSiPSO.
- A phase change from β–Li_3PS_4 to β–Li_3PO_4 is confirmed from XRD.
- This phase change trend is also seen in Raman spectra.
- Further investigation using ^{29}Si and ^{31}P MAS NMR will be used to confirm these structural changes.
- Battery tests will be used to investigate the efficacy of these new Oxy-Sulfide Solid Electrolytes in new Li-S Batteries

EPSCoR Research Capacity Building Activities

- **2013 Research Building Activities…**
- New proposals - NSF MRSEC pre-proposal, NASA JPL, and DARPA all have very strong battery research components to them.
- Developed new courses related to battery materials, components, and systems
- Collaborated with other research groups at ISU to develop further battery research capacity
- Acquired new XPS spectrometer that will provide important battery research capability
- Collaborated with NASA JPL, GRC, and ORNL to develop proposals for new solid state lithium batteries
- Strengthen our use of ISU mechanical, glass-blowing and electrical shops to strengthened the overall research enterprise.
- Given seminars on battery related research to groups on and off campus describing the new battery research programs at ISU.
- Hired post-graduate and undergraduate research assistants

EPSCoR Research Capacity Building Activities

- **2013 Research Funding Building…**
- Established a faculty hiring plan for 200+ new faculty
- Established a faculty hiring plan for 20+ new research faculty to the College of Engineering,
- Established a faculty hiring plan that will bring two new teaching and research faculty into MSE
- MSE has hired a new Laboratory technical support staff person
- MSE has hired a new informational technical support staff person
- MSE and the COE have begun a new $2,000,000 laboratory reinvestment program
- ISU has funded four new three-year research capacity building projects
- ISU built a new $75M research laboratory
- ISU has made very large increases in funding and support of the ISU Research Park

EPSCoR Research Capacity Building Activities

- **2013 Research Funding Building…**
- NASA EPSCoR, Kennedy Space Center, “Towards Next Generation Lithium Sulfur Batteries for Mission Enabling Energy Storage Systems,” $750,000 with additional $375,000 cost share from ISU, 2/1/2013 – 1/31/2016, (PI) (Co-PI S. Beckman)
- National Science Foundation, Division of Materials Research, Ceramics Program, AGEP Graduate Research Assistant Supplement to “Diametric Extremes in Ionic Conductivity of Mixed Glass Former Solid Electrolytes,” $59,975, 8/1/2013 – 7/31/2014, (PI).
- National Science Foundation, Division of Materials Research, Ceramics Program, “Diametric Extremes in Ionic Conductivity of Mixed Glass Former Solid Electrolytes,” $510,000, 8/1/2013 – 7/31/2017 (PI).
- National Science Foundation, Division of Materials Research, AGEP Graduate Research Assistant Supplement to “Materials World Network: An International Education and Research Program in the Use of the Mixed Glass Former Effect to Study Ion Conductivity in Solid Electrolytes,” $75,091, September 1, 2012 – August 31, 2013, (PI)
- **Total $1,770,066**

EPSCoR Research Capacity Building Activities

- **2014 Research Building Activities…**
- We have been funded by and completed a $60,000 project for the NASA JPL
- Course and lecture development related to battery materials, components, and systems
- Collaborated with other research groups at ISU on battery research
- Traveled internationally to report on the results of this research
- Collaborated with researchers in Japan at Osaka Prefecture University to exchange students
- Collaborated with the HBCU Prairie View A&M University to discuss our battery research program.
- Collaborated with the HBCU Tuskegee University to discuss our battery research program with them.
- Collaborated with a battery research group in South Korea at Gyeongsang National University
- Developed strong collaborations with the NASA Glenn Research Center to foster a sustainable research program in high capacity

EPSCoR Research Capacity Building Activities

- **2014 Research Funding Building…**
- ISU and COE have completed the $20,000,000 total renovation of our flagship engineering building, Marston Hall, Iowa State University
- ISU has completed a major capital campaign to build a new 190,000 ft^2 (net assignable) “Student Innovation Center” that will provide state of the art student learning, research, teamwork, and design space
- The State of Iowa has provided significant new funding to Iowa State University to fully fund faculty and staff salaries,
- Iowa State University has made very large increases in funding and support of the ISU Research Park on the ISU campus.

EPSCoR Research Capacity Building Activities

- **2014 Research Funding…**
- PI-Martin, Steve National Science Foundation, Division of Materials Research, Ceramics Program, AGEP Graduate Research Assistant Supplement to "Diametric Extremes in Ionic Conductivity of Mixed Glass Former Solid Electrolytes," $59,901, 8/1/2014 – 7/31/2015.
- PI C. Austen Angell, Co-PI Martin, Steve. Arizona State University, subcontract from Sandia National Laboratory, Department of Energy, Office of Electricity Energy Storage Systems Program, "Strategies for Liquid Anode Alkali Batteries of High Energy Density operating at 0 to 100ºC," $170,000, ISU share $87,500, March 20, 2014 – March 21, 2015
- PI-Martin, Steve The Charles Stark Draper Laboratory (Cambridge, MA), "Solid State Alkali Atom Source (SSAAS), $125,000, March 1, 2014 – February 28, 2015.
- PI-Martin, Steve National Science Foundation, Division of Chemical, Bioengineering, Environmental, and Transport Systems, Energy for Sustainability Program, "SusChEM: Ultra-High Li+ Ion Conductivity Chemically Stable Mechanically Strong Mixed Oxy-Sulfide Solid Electrolytes, "$300,000, September 1, 2014 – August 31, 2017.
- PI-Martin, Steve Iowa State University, Foreign Travel Grant, Conference and Research Participation, Germany and South Korea, $1,433, March 14, 2014 – September 30, 2014.

EPSCoR Research Capacity Building Activities

- **2014 Research Funding…**
- PI-Martin, Steve NASA Jet Propulsion Laboratory, “Preparation and Assembly of Solid State Lithium Batteries,” $55,110, February 13, 2014 – August 1, 2014.
- PI John Ballato, co-PI Martin, Steve U. S. Department of Energy, Idaho Operations Office, “Novel High Temperature and Radiation Resistant Infrared Glasses and Optical Fibers for Sensing in Advanced Small Modular Reactors,” $800,000, ISU Share as subconstract from Clemson University, January 13, 2014 – December 12, 2017, $300,000, (co-PI)
- PI Jonathan Bernstein, Co-PI Steve W. Martin, Defense Advanced Research Projects Agency (DARPA), “Solid State Alkali Atom Source (SSAAS),” in Response to BAA 12-64 of 30 August 2012, Amendment # 02, $125,000, August 1, 2014 – July 31, 2015
- **Total $1,553,944**

EPSCoR Research Capacity Building Activities

- **2015 Research Building Activities…**
- New proposals, Honda Research of America, DOE ARPA-E, and NSF AGEP
- Honda - $170,000 per year for 5 years
- Department of Energy Advanced Research Projects Agency-Energy, ARPA-E, $2,950,000 for three years, to develop a new kind of all-solid-state Sodium battery for grid scale energy storage.
- New course and lecture development related to battery materials, components, and systems
- Acquired a new DSC that will be use to characterize the thermal properties
- Acquired a new $750,000 Dynamic Nuclear Polarization NMR spectrometer that will be used to characterize the structural properties of the battery materials being developed on this project.
- Hired a new faculty member in the area of solid state NMR spectroscopy who will collaborate with our research team
- MSE has hired two new faculty positions, one in ceramic materials, and one in polymeric materials.
- New collaboration with the small battery company, PolyPlus Battery, Inc.,
- Hired a new PhD graduate student and undergraduate research assistants

EPSCoR Research Capacity Building Activities

- **2015 Research Funding…**
- In Year 3, this Iowa EPSCoR research program received total of $3,183,723 in new non-EPSCoR funding. All of these research funds are directed towards battery research projects.
- Department of Energy, Advanced Research Project Agency – Energy (ARPA-E) "OPEN 2015", "Low-Cost, Low-Temperature, Safe, High-Energy-Density Solid-State Na Batteries Made from Renewable Materials," $2,950,000 with $327,745 cost-sharing, February 1, 2016 – January 31, 2019, (PI)
- Honda Research Institute of America, "Development of New Lithium Ion Conducting Glassy Solid Electrolytes, $170,000, January 1, 2015 – June 30, 2016 (PI).
- National Science Foundation, Division of Materials Research, Ceramics Program, AGEP Graduate Research Assistant Supplement to "Diametric Extremes in Ionic Conductivity of Mixed Glass Former Solid Electrolytes," $63,723, 1/1/2016 – 12/31/2016, (PI).
- **Total $3,183,723**

EPSCoR Research Capacity Building Activities

- **2016 Research Building Activities…**
- Hired new research and teaching faculty member in the area of battery and energy storage materials.
- Sc-I Martin and Professor Xu have collaborated to purchase more than $500,000 equipment.
- Sc-I Martin and Professor Xu have been assigned a new 1,000 ft^2 battery research laboratory
- Sc-I Martin and Professor Xu have been awarded Department of Energy Advanced Research Projects Agency-Energy, ARPA-E, $2,880,184 for three years, to develop a new kind of all-solid-state lithium battery for portable energy storage.
- Acquired a new XRD to characterize the structural properties of the battery materials
- Acquired a new SEM to characterize the micro-structural properties of the battery materials
- Collaborated Professor Gary DeBoer to conduct battery research for the summer
- Collaborated with LeTourneau University and ISU to hire a PhD graduate student
- Collaborated with California State University at Los Angeles to hire an under represented PhD graduate student.

EPSCoR Research Capacity Building Activities

- **2016 Research Funding Building…**
- In Year 4, this Iowa EPSCoR research program received total of $2,973,907 in new non-EPSCoR funding with all of these $2,973,907 funds coming to Iowa. All of these research funds are directed towards battery research projects.
- Department of Energy, Advanced Research Project Agency – Energy (ARPA-E) "IONICS," "Development and Testing of New, Strong, High Li+ Ion Conductivity, Li-Impermeable Thin-Ribbon Glassy Solid Electrolytes for High-Energy-Density Li Batteries," $2,880,184 with $380,184 ISU cost-sharing, February 1, 2017 – January 31, 20120, (PI)
- Honda Research Institute of America, "Development of New Lithium Ion Conducting Glassy Solid Electrolytes, $30,000, June 30, 2016 – February 28, 2017 (PI).
- National Science Foundation, Division of Materials Research, Ceramics Program, AGEP Graduate Research Assistant Supplement to "Diametric Extremes in Ionic Conductivity of Mixed Glass Former Solid Electrolytes," $63,723, 1/1/2016 – 12/31/2016, (PI).
- **Total $2,973,907**

EPSCoR Research Capacity Building Activities

- **Total new research funding since start of the ISU NASA EPSCoR**

- **2016 $2,973,907**
- **2015 $3,183,723**
- **2014 $1,553,944**
- **2013 $1,770,066**

- **Total $9,481,640**