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2016 DOE Vehicle Technologies Office Review

"Solid electrolytes for solid-state and lithium-sulfur batteries"

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ES277

Overview

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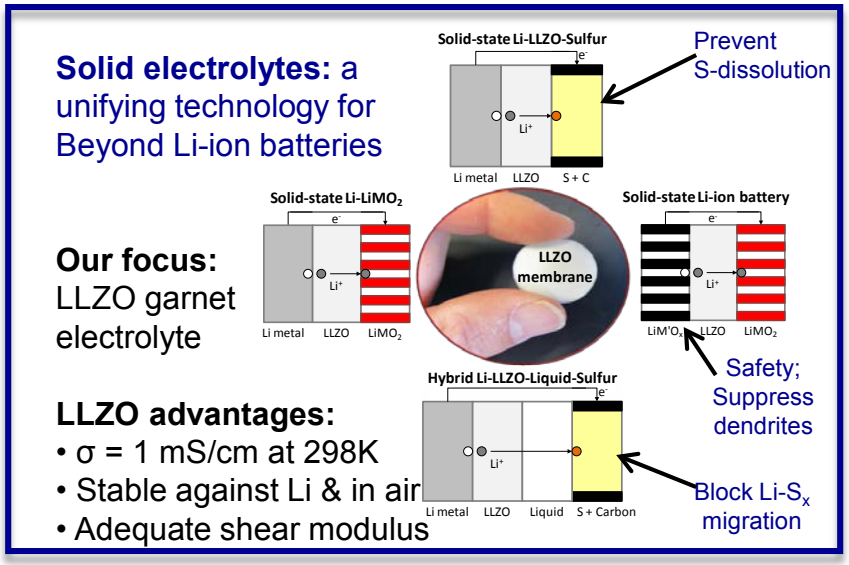
Timeline

- Project start date, Jan 1, 2015
- Project end date, Dec 31, 2017
- 42% complete

Budget

- $1,220K (total)
- Project end date, Dec 31, 2017
- 42% complete



Barriers

- Prevent Li dendrites to enable metallic Li anodes
- Integrated solid-electrolyte into advanced solid-state batteries
- Achieve high current densities approaching 1 mA/cm^2

Partners

- Oxford University, UK (C. Monroe)
- Army Research Lab (J. Wolfenstine and J. Allen)
- Oak Ridge National Lab (J. Nanda and N. Dudney)

Relevance

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Batteries enabling the transition to vehicle electrification

- Achieving > 50 Miles per gallon Corporate Avg. Fuel Economy (CAFE) standards by 2025 will likely require electric power trains.
- Increasing battery performance, improving safety, and reducing cost will facilitate vehicle electrification.
- Solid-state, non-flammable electrolytes could enable metallic Li anodes, thus achieving a step increase in safety and performance compared to state-of-the-art batteries (SOA).

Challenges

- Integrating solid-state electrolytes with metallic Li anodes and SOA and/or advanced high voltage cathodes
- Maintaining power density commensurate with EV powertrains

Milestones

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Project Plan, Tasks, and Milestones	YEAR 1			YEAR 2				YEAR 3				
Project Tasks	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 1: Li – LLZO stability												
1.1. Experimentally evaluate critical current density based on microstructural defects (UM, ORNL, ARL)	■	■	◆									
1.2. Complete critical current density vs porosity measurements (UM).		■	■	◆								
1.3. Correlate the critical current density based on the pore size and volume fraction of porosity (UM).		■	■	■	◆							
1.4. Experimentally evaluate critical current density based on microstructural defects (UM).				■	■	◆						
1.5. Correlate the critical current density based on microstructural defects (UM).				■	■	◆						
Go/No-Go Determine feasibility of controlling porosity and microstructural defects to achieve $\geq$ 1.0 mA/cm^2 at 298K						⊗						

◆ Symbol represents completed subtask milestone.

◆ Symbol represents completed subtask milestone.

⊗ Symbol represents a Go/No Go decision milestone.

Approach/Strategy

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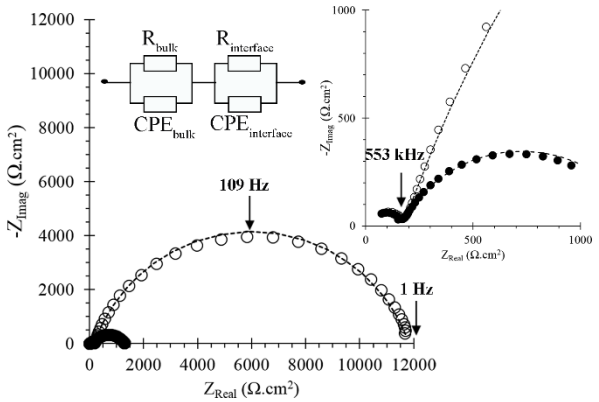
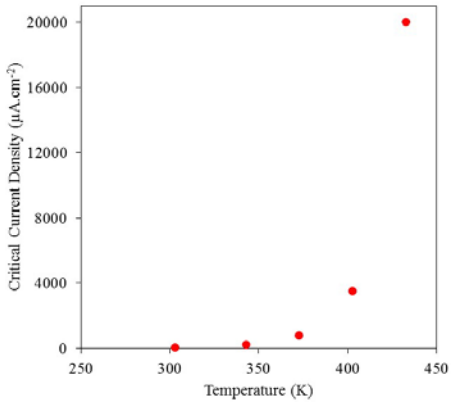
Develop solid-electrolyte technology

- Enabling metallic Li anodes could increase the energy density (>1000 Wh/l) at the battery cell and pack level.
- Because solid-electrolyte membrane technology is new, there is a need to understand the phenomena that govern performance in prototypical solid-state cells.
- This project seeks to understand how material processing affects the microstructure, which affects the highest tolerable current density or critical current density (CCD).
- To achieve relevance to EVs, our goal is to demonstrate a maximum tolerable current density of > 1 mA/cm^2 in prototypical half cells.
- This project involves close collaboration with ORNL (Dr. N. Dudney, EERE; “Mechanical Properties at the Protected Lithium Interface”).
- Go/No-Go Decision: Determine which microstructural defect has the most profound effect on the maximum tolerable current density (critical current density – CCD).

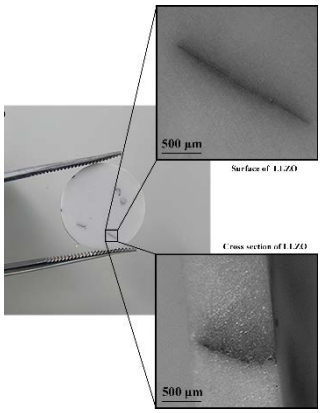
FY-2015 Accomplishments



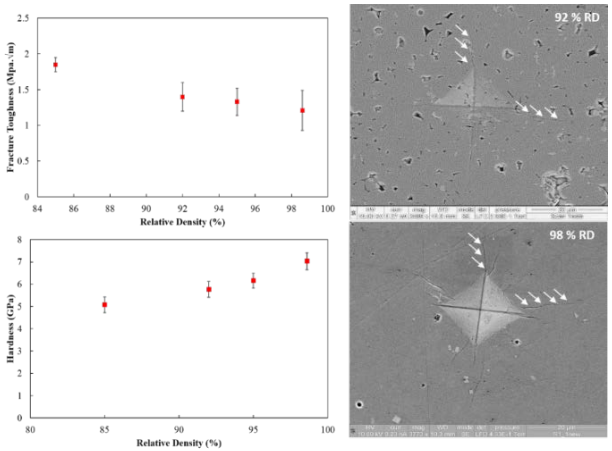
Demonstrated the ability to control, measure, and reduce Li-LLZO interfacial resistance



Developed a method to reduce the Li-LLZO interfacial resistance to increase the CCD.



Correlated the LLZO short-circuiting with Li dendrite penetration above the CCD.



Correlated relative density (RD) with ionic conductivity and mechanical properties. Vickers hardness increased with increasing RD while an inverse correlation between fracture toughness and RD was observed.

Table 1. Elastic Properties of Al- and Ta-Doped LLZO[a]

	C_{11}	C_{12}	C_{44}	B	E	G	ν
			Al-Doped LLZO				
DFT (0 K)	187.0	75.1	71.0	112.4	162.6	64.6	0.26
DFT extrapolated (298 K)					154.5	61.4	
impulse excitation (298 K)				100.2 ± 0.6	146.1 ± 0.8	58.1 ± 0.3	
dynamic nanoindentation (298 K)					150.3 ± 2.2	59.8 ± 0.9	
RUS (298 K) ref 22				102.8 ± 0.3	149.8 ± 0.4	59.6 ± 0.1	0.257 ± 0.002
			Ta-Doped LLZO				
DFT (0 K)	169.8	63.9	69.8	99.2	154.9	62.5	0.24
DFT extrapolated (298 K)					147.2	59.4	
impulse excitation (298 K)				96.0 ± 1.4	139.9 ± 2.1	55.7 ± 0.8	
dynamic nanoindentation (298 K)					153.8 ± 2.7	61.2 ± 1.1	

[a]The elastic constants and moduli are expressed in GPa.

Predicted and validated the elastic properties to determine if LLZO can suppress Li dendrite penetration, according to theory.

A. Sharafi, et al. J. Power Resources, 2016
S. Yu, et al. J. Chemistry of Materials, 2016

Responses to Preview Years Comments

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- None, new project.

Partners and Collaborators

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Prof. Don Siegel

- Lead the atomistic computational modeling component of the project

Dr. Jagjit Nanda

- Perform in-situ/in-operando spectroelectrochemical analysis

Drs. Jeff Wolfenstine and Jan Allen

- Atomic force microscopy in a state-of-the-art battery dry room to enable testing of cycling LLZO interfaces

Dr. Andy Drews

- Contribute in an advisory role through quarterly or bi-annual interaction

Prof. Chuck Monroe

- Lead the continuum-scale computational modeling

Remaining Challenges and Barriers

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Controlling the defects that control critical current density

- We believe atomic-scale phenomena could control the CCD.
- Li metal has been observed adjacent to atom-scale defects.
- New ceramic processing must be developed to eliminate these defects.
- Current materials characterization techniques are needed to help in elucidating the phenomenon; improved spatial resolution is needed.

Future work

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FY 2017

- Control microstructural feature(s) that govern the maximum current density.

- Correlate the critical current density with the size and distribution of the microstructural feature(s) that govern the CCD.

- Establish atomistic and continuum scale theory to explain the mechanism that correlates CCD with microstructural feature(s).

Summary

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Develop solid-electrolyte technology

- Enabling metallic Li anodes could increase energy density (>1000 Wh/l) at the battery cell and pack level.
- Because solid-electrolyte membrane technology is new, there is a need to understand the phenomena that govern performance in prototypes.
- Specifically, this project seeks to understand how material processing affects the microstructure, which affects highest tolerable current density (mA/cm^2). To achieve relevance to EVs, our goal is to achieve > 1 mA/cm^2.
- This project involves close collaboration with ORNL (Dr. N. Dudney, "Mechanical Properties at the Protected Lithium Interface").
- Go/No-Go Decision: Determine which aspect has the most profound effect on the maximum tolerable current density (critical current density – CCD).

Publications and Presentations

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Publications

- A. Sharafi, H. Mayer, J. Nanda, J. Wolfenstine, J. Sakamoto., Characterizing the Li-$Li_7La_3Zr_2O_{12}$ interface stability and kinetics as a function of temperature and current density. *J. Power Sources*, 2016
- S. Yu, R. Schmidt, R. Garcia-Mendez, E. Herbert, N. Dudney, J. Wolfenstine, J. Sakamoto, D. Siegel., "Elastic properties of the solid electrolyte $Li_7La_3Zr_2O_{12}$ (LLZO). *Chem. Mater.*, 2016

Oral Presentations

- J. Sakamoto, Mechanical Stability of Solid Electrolyte Interfaces in Solid-State Batteries, *The Electrochemical Society*, 2016.
- A. Sharafi, Chemical stability of garnet solid-state electrolyte, *The Electrochemical Society*, 2016.
- A. Sharafi, The stability of garnet based $Li_7La_3Zr_2O_{12}$ and Li anode interface as a function of current density *Material Research Society*, 2015.
- A. Sharafi., Recent progress with ceramic solid electrolytes for advanced battery concepts, *Plug Volt*, 2015.
- J. Sakamoto., Garnet Ceramic Electrolyte Enabling Li Metal Anodes and Solid-State Batteries. *Material Research Society*, 2015.
- J. Wolfenstine., Room and Elevated Temperature Mechanical Behavior of $Li_7La_3Zr_2O_{12}$. *Material Research Society*, 2015.
- J. Sakamoto., The Solid-State Revolution". Moderated a Session at The Battery Show in Novi, MI " Speakers from Toyota, Google, Samsung, and Intel participated.
- J. Sakamoto presented at the University of Michigan Energy Institute's Battery Lab Opening Ceremony on October 2, 2015 .

Poster Presentations

- A. Sharafi, Electrochemical performance of garnet-type solid state electrolyte $Li_7La_3Zr_2O_{12}$, *Material Research Society*, 2015 (Poster).