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14. ABSTRACT The goal of this work is to enable the development of safe, high energy density batteries by advancing ceramic electrolyte technology for use in solid-state Li-ion batteries. Solid-state Li-ion batteries could significantly improve safety and eliminate the need for complex, massive thermal management systems often required for vehicle electrification. Li-S and Li-air cells could offer a two to five-fold increase in specific energy, thus improving electric vehicle range. In collaboration with the Army Research Laboratory, the MSU-Sakamoto group is one of the first groups to investigate a new ceramic electrolyte based on cubic garnet structured lithium lanthanum					
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Report Title

Final Report: Ceramic Electrolyte Membrane Technology: Enabling Revolutionary Electrochemical Energy Storage

ABSTRACT

The goal of this work is to enable the development of safe, high energy density batteries by advancing ceramic electrolyte technology for use in solid-state Li-ion batteries. Solid-state Li-ion batteries could significantly improve safety and eliminate the need for complex, massive thermal management systems often required for vehicle electrification. Li-S and Li-air cells could offer a two to five-fold increase in specific energy, thus improving electric vehicle range. In collaboration with the Army Research Laboratory, the MSU-Sakamoto group is one of the first groups to investigate a new ceramic electrolyte based on cubic garnet-structured lithium lanthanum zirconium oxide (LLZO) exhibiting the unprecedented combination of fast ion conductivity, stability against Li, air and moisture. While the initial stages of research involved relatively small prototypes, an accurate performance assessment in the proposed advanced batteries requires new materials processing technology to fabricate larger LLZO ceramic membranes. The goal of this work is to develop ceramic processing technology to fabricate LLZO membranes that have tens of square centimeters of area and are < 0.1 millimeter thick. The ability to fabricate these electrolyte membranes will allow for high fidelity testing to accurately access LLZO's potential for use in advanced energy storage, specifically for vehicle electrification.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
01/13/2014	1.00 Ezhiylmurugan Rangasamy, Jeff Wolfenstine, Jan Allen, Jeff Sakamoto. The effect of 24c-site (A) cation substitution on the tetragonalcubicphase transition in $\text{Li}_{7-x}\text{La}_3\text{F}_x\text{Zr}_2\text{O}_{12}$ garnet-based ceramicelectrolyte, Journal of Power Sources, (12 2012): 261. doi:
01/22/2014	2.00 Jeff Sakamoto, Ezhiylmurugan Rangasamy, Hyunjoung Kim, Yunsung Kim, Jeff Wolfenstine. Synthesis of nano-scale fast ion conducting cubic Li, Nanotechnology, (10 2013): 0. doi: 10.1088/0957-4484/24/42/424005
TOTAL:	2

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
TOTAL:	

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

<u>NAME</u>	<u>PERCENT_SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT_SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Names of Under Graduate students supported

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):.....

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:.....

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:.....

Names of Personnel receiving masters degrees

NAME

Isabel David 100%

Total Number:

1

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

5 Additives to enable liquid phase sintering of the solid electrolyte Li₇La₃Zr₂O₁₂

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: Isabel David-Boona

5f-1a: Same as Jeff Sakamoto

5f-c:

5a: Jeff Sakamoto

5f-1a: MSU

5f-c: 2527 Engineering

East Lansing

MI

48824

Scientific Progress

Technology Transfer

Project Summary - Grant W911NF-13-1-0475
(Reporting Period: January 1, 2014 – December 31, 2014)

**CERAMIC ELECTROLYTE MEMBRANE TECHNOLOGY:
ENABLING REVOLUTIONARY ELECTROCHEMICAL ENERGY STORAGE**

Jeff Sakamoto (PI)
Chemical Engineering and Materials Science
Michigan State University, East Lansing, MI, 48824

TARDEC: Yi Ding
Warren, MI 48088

Objective

The goal of this work is to enable the development of safe, high energy density batteries by advancing ceramic electrolyte technology for use in solid-state Li-ion batteries and high specific energy Li-S and Li-air batteries. Solid-state Li-ion batteries could significantly improve safety and eliminate the need for complex, massive thermal management systems often required for vehicle electrification. Li-S and Li-air cells could offer a two to five-fold increase in specific energy, thus improving electric vehicle range. In collaboration with the Army Research Laboratory, the MSU-Sakamoto group is one of the first groups to investigate a new ceramic electrolyte based on cubic garnet-structured lithium lanthanum zirconium oxide (LLZO) exhibiting the unprecedented combination of fast ion conductivity, stability against Li, air and moisture. While the initial stages of research involved relatively small prototypes, an accurate performance assessment in the proposed advanced batteries requires new materials processing technology to fabricate larger LLZO ceramic membranes. The goal of this work is to develop ceramic processing technology to fabricate LLZO membranes that have tens of square centimeters of area and are ≤ 0.1 millimeter thick. The ability to fabricate electrolyte membranes of this scale will allow for high fidelity testing to accurately access LLZO's potential for use in advanced energy storage, specifically for vehicle electrification.

Approach

The Sakamoto group has the capability to make high purity LLZO powders using conventional solid state reactions and sol-gel methods. The former produces 1-3 micron particles while the latter produces $< 200\text{nm}$ particles. Smaller particles facilitate sintering compared to large particles, thus the proposed work will focus on sol-gel processing to produce LLZO particles with optimal size (Roughly 0.1 to 1 μm) (MSU-Sakamoto group).

- 6 months: demonstrate the ability to control porosity of 4 to 25 cm^2 LLZO membranes in the 92-98% theoretical density range with 1 to 2 mm thickness
- 9 months: demonstrate the ability to fabricate 4 to 25 cm^2 LLZO membranes in the 92-98% theoretical density range with thickness $\leq 0.1\text{mm}$ and deliver to ARL for testing.
- 12 months: in collaboration with ARL (Jeff Wolfenstine and Jeff Read), demonstrate LLZO membrane technology feasibility in solid-state Li-ion, Li-air and Li-S cells.

Relevance to Army

Solid-state batteries could significantly improve the Army's efforts to electrify vehicles and advance silent watch technology. Also, to achieve the EV Everywhere *Grand Challenge* targets, significant breakthroughs in energy storage technology are needed. While recent efforts have focused on improving electrode performance, this work pursues the development of new electrolytes to revolutionize battery

technology. Owing to its fast Li-ion conductivity at room temperature, LLZO can replace conventional liquid electrolytes to allow for all solid-state batteries. The advantages over SOA Li-Ion include: higher volumetric energy density, non-flammability, and improved durability. The goal of this work is to establish manufacturing techniques, which are not available today, but are required to fabricate the next generation of batteries. At present, no company has commercialized solid-state batteries for electric vehicles. If successful, this work will develop scale-able tools to manufacture solid-state batteries, thus laying the foundation for a new and substantial industry based in the United States. Because the industry does not exist, this is an opportunity to re-establish the Nation's battery manufacturing industry at significant scale. Successful development of the solid-state battery described in this proposal could represent a cost savings of 28 – 36% at the cell level and 20 – 33% at the pack level if the manufacturing techniques are scalable.

Accomplishments for Reporting Period

Below are the bullets from the approach section above. Each bullet is followed by the accomplishment in *italics*.

- 6 months: demonstrate the ability to control porosity of 4 to 25 cm² LLZO membranes in the 92-98% theoretical density range with 1 to 2 mm thickness

Demonstrated 5 cm² LLZO membranes at 96% theoretical density. This is the largest LLZO membrane at this density reported.

- 9 months: demonstrate the ability to fabricate 4 to 25 cm² LLZO membranes in the 92-98% theoretical density range with thickness ≤ 0.1 mm and deliver to ARL for testing.

Demonstrated 0.3mm thick 5 cm² area LLZO membranes.

- 12 months: in collaboration with ARL (Jeff Wolfenstine and Jeff Read), demonstrate LLZO membrane technology feasibility in solid-state Li-ion, Li-air and Li-S cells.

LLZO membranes currently under testing at ARL.

Collaborations and Technology Transfer

- Invention disclosure: TEC2014-0127 submitted June 1, 2014
- Interacted regularly with Drs. Jeff Wolfenstine and Jan Allen at the Army Research Lab, Adelphi, MD.
- Interacted with Ford Motor Company regarding solid-state battery development
- Interacted with the Oak Ridge National Lab Neutron Diffraction Spallation Source

Resulting Journal Publications During Reporting Period

- I. N. David, T. R. Thompson, J. Wolfenstine, J. L. Allen, and J. Sakamoto, Microstructure and Li-ion conductivity of Hot-Pressed cubic Li₇La₃Zr₂O₁₂, *J. Amer. Ceram. Soc.*, Accepted December 2014.

Graduate Students Involved During Reporting Period

- Mrs. Isabel N. David received her M.S. degree on June 6, 2014. She was fully supported by this project.

Awards, Honors and Appointments

- Jeff Sakamoto: National Academies of Science, Session chair, US-Indo Kavli Frontiers of Science, Medan, Indonesia July 2014.
- Jeff Sakamoto: National Academy of Engineering, Session chair on “Battery Anxiety”, Beckman Center, Irvine, CA September 2014.

