REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggesstions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any oenalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.
PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
05-10-2015	Final Report	1-Oct-2013 - 30-Sep-2014

4. TITLE AND SUBTITLE
Final Report: Ceramic Electrolyte Membrane Technology: Enabling Revolutionary Electrochemical Energy Storage

5a. CONTRACT NUMBER
W911NF-13-1-0475

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHORS
Jeff Sakamoto

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
Michigan State University
426 Auditorium Road, Room 2

East Lansing, MI 48824 -2601

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
64834-CH.4

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

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

15. SUBJECT TERMS
Ceramic electrolyte, Battery, solid-state

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
UU	UU	UU	UU		Jeff Sakamoto
					19b. TELEPHONE NUMBER 517-432-7393

Standard Form 298 (Rev 8/98)
Prescribed by ANSI Std. Z39.18

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)

Received		Paper
01/13/2014	1.00	Ezhiylmurugan Rangasamy, Jeff Wolfenstine, Jan Allen, Jeff Sakamoto. The effect of 24c-site (A) cation substitution on the tetragonalecubicphase transition in Li7 ┌xLa3 ┌xAxZr2O12 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)

Received	Paper

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):

Received Paper

TOTAL:

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

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

Received Paper

TOTAL:

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

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received	Book

TOTAL:

Received	Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
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 $\leq$ 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 < 200nm 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 $\leq$ 0.1mm 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 cm^2 LLZO membranes in the 92-98% theoretical density range with 1 to 2 mm thickness

  Demonstrated 5 cm^2LLZO 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 cm^2 LLZO membranes in the 92-98% theoretical density range with thickness $\leq$ 0.1mm and deliver to ARL for testing.

  Demonstrated 0.3mm thick 5 cm^2 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

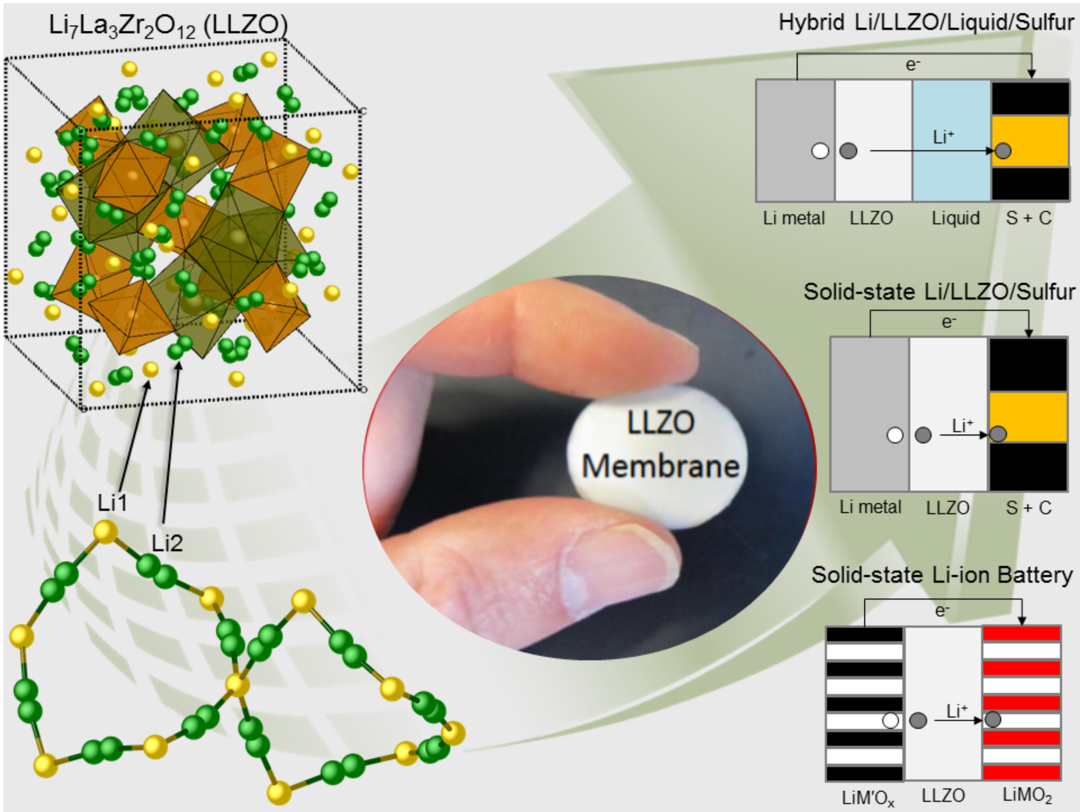
- I. N. David, T. R. Thompson, J. Wolfenstine, J. L. Allen, and J. Sakamoto, Microstructure and Li-ion conductivity of Hot-Pressed cubic $Li_7La_3Zr_2O_{12}$, *J. Amer. Ceram. Soc.*, Accepted December 2014.

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.



$Li_7La_3Zr_2O_{12}$ (LLZO)
Li1
Li2
LLZO
Membrane
Hybrid Li/LLZO/Liquid/Sulfur
e^-
Li^+
Li metal
LLZO
Liquid
S + C
Solid-state Li/LLZO/Sulfur
e^-
Li^+
Li metal
LLZO
S + C
Solid-state Li-ion Battery
e^-
Li^+
$LiM'O_x$
LLZO
$LiMO_2$