Contract No:

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Direct LiT Electrolysis in a Metallic Lithium Fusion Blanket

A process that simplifies the extraction of tritium from molten lithium based breeding blankets was developed. The process is based on the direct electrolysis of lithium tritide using a ceramic Li ion conductor that replaces the molten salt extraction step. Extraction of tritium in the form of lithium tritide in the blankets/targets of fission/fusion reactors is critical in order to maintained low concentrations. This is needed to decrease the potential tritium permeation to the surroundings and large releases from unforeseen accident scenarios. Because of the high affinity of tritium for the blanket, extraction is complicated at the required low levels. This work identified, developed and tested the use of ceramic lithium ion conductors capable of recovering the hydrogen and deuterium thru an electrolysis step at high temperatures.

Awards and Recognition

U.S. Provisional application (SRS-14-014) entitled: "Recovery of Tritium from Molten Lithium Blanket" was awarded for the proposed process developed in the LDRD.

Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publically published in its current form.

SRNL Legal Signature

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Signature **Date**

LDRD-2014-00029
LDRD Report

Direct LiT Electrolysis in a Metallic Lithium Fusion Blanket

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Thrust Area: SI4-2

Project Type: Strategic

Project Start Date: October 1, 2013
Project End Date: September 30, 2015

A process that simplifies the extraction of tritium from molten lithium based breeding blankets was developed. The process is based on the direct electrolysis of LiT using a ceramic Li ion conductor that replaces the molten salt extraction step. Extraction of T_2 from LiT in the blankets/targets of fission/fusion reactors is critical in order to maintained low concentrations. This is needed to decrease the potential T permeation to the surroundings and large releases from unforeseen accident scenarios. Because of the high affinity of T to the blanket, extraction is complicated at the required low levels. This work identified, developed and tested the use of ceramic lithium ion conductors capable of sustaining LiT electrolysis at high temperatures. An electrochemical cell was designed, fabricated, and used to test the proposed process. At the LiH concentrations tested, successful electrolysis of LiH was confirmed with residual gas analyzer and electrochemical measurements.

FY2015 Objectives

- Conductivity tests in high temperature cell and electrolyte optimizations
- Analytical demonstration of LiH decomposition in metallic Li electrode
- High temperature electrochemical characterization

Introduction

Liquid tritium breeder materials, such as lithium and Pb-Li eutectic, are attractive as their breeding potential is very high and separate neutron multipliers are not necessarily required. Because of it being a liquid, the tritium recovery system can be designed outside the neutron environment and will not suffer from radiation damage. In the designs where the breeding material is also used as a coolant, the nuclear heating is directly deposited inside the breeding material simplifying blankets designs. However, there are a number of engineering design difficulties such as magneto-hydrodynamic pressure drops, corrosiveness of liquid metal, efficient tritium recovery and containment from the liquid metal breeder.[1,2]

In most applications, the tritium inventory in the blanket has to be kept low (~1 appm) for a reliable and safe operation. The extraction of tritium can be problematic since the tritium in the blanket exists bound to lithium in the form of LiT. Extraction from liquid Li is considered more challenging due to the high solubility of LiT in the melt. On the other hand, the solubility of LiT in Pb-Li eutectic is several orders of magnitude lower, making extraction somewhat less challenging. Nevertheless the state of the art extraction approaches are essentially similar. Among the considered extraction technologies are molten salt extraction followed by electrolysis (Maroni Process), “gettering”, permeation followed by molten liquid extraction, fractional distillation, cold trapping and a combination of all. However, all of the proposed extraction technologies require a series of complicated mechanical steps (expensive mechanical parts with limited lifetimes) in order to carry out the separation and prevent the buildup of impurities in the extraction process [1]. This work simplifies and eliminates many of the problems associated with the current extraction technologies.

Approach

In the typical Maroni process, molten Li is mixed with a molten salt in order to extract the LiT. Afterwards, the LiT is electrolyzed and the hydrogen extracted. Our approach simplifies the process by incorporating a solid Li ion conductor to eliminate many of the mechanical steps in the extraction section. Figure 1 (left) shows the Maroni process. The shaded area indicates the section where the SRNL approach can be incorporated. Figure 1 (right) shows the electrochemical cell designed during FY14 to perform the Li/LiH electrolysis

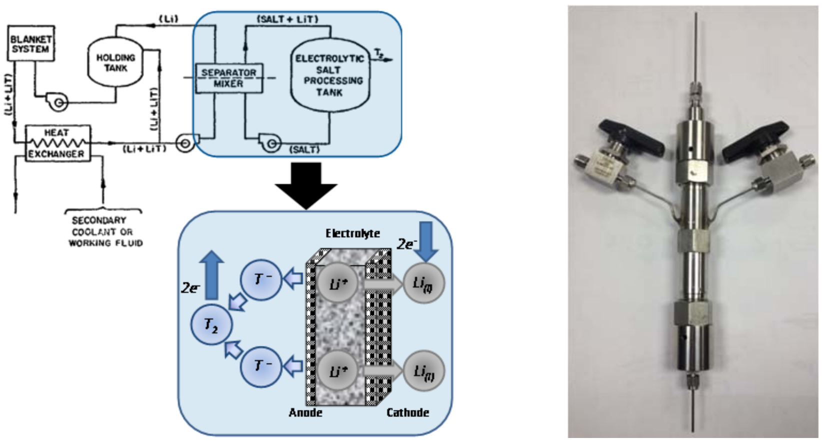

Figure 1. (left) Simplified Maroni process [3]. Shaded area depicts where the SRNL process approach can be incorporated. (right) Electrochemical cell design for LiH electrolysis

Results/Discussion

Two main versions of the electrochemical cell were designed, made and used to test the materials. Typically the electrolyte consisted of $Li_7La_3Zr_2O_{12}$ (LLZO) that has been pressed and sintered into a pellet. Once prepared, the pellet was characterized using X-ray Diffraction (XRD) to confirm cubic phase formation. Heat treatments and mixing conditions were explored to determine the optimal synthesis methodology for the cubic phase formation and development of mechanically stable pellet. Figure 2 shows the XRD confirmation of the cubic and tetragonal phases during synthesis optimization. Ionic conductivity was evaluated as well to confirm high conductivity phase formation.

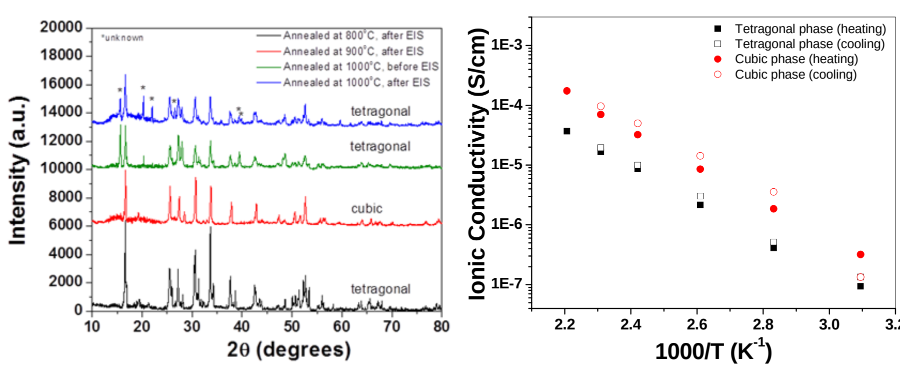

Figure 2. XRD (left) and ionic conductivity (right) examination of the LLZO solid electrolyte.

The electrolysis cell consisted of a Li/LiH electrode, the LLZO electrolyte and a gold contact counter electrode. The evolution of H_2 was monitored in-situ with a residual gas analyzer (RGA) during cell operation. Figure 3 (left) shows the validation run of the proposed process at 350 °C as well as a picture of the prepared electrode. The results show a direct correlation between the point when the potential is applied and the point when H_2 is released from the Li/LiH electrode. The H_2 signal slowly decays as the LiH closest to the electrolyte is consumed. Figure 3 (right) shows the Tafel polarization for the LiH electrolysis at 350 °C. An exchange current density of 3.06 mA/cm^2 and limited current density of 20.4 mA/cm^2 was observed. Improvements such as operation at higher temperatures and fluidization of the working electrode should result in higher current densities.

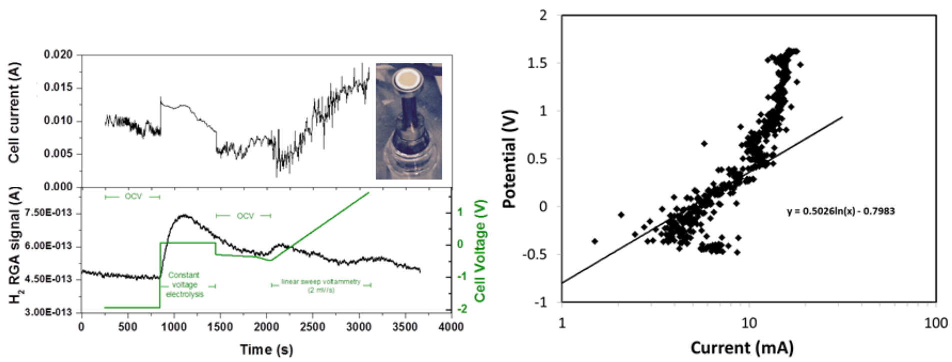

Figure 3. (left) Electrolysis at 350 °C using LLZO electrolyte, gold counter electrode and Li/LiH as a working electrode. Inset shows LLZO pellet. (right) Tafel polarization for the electrolysis of LiH.

FY2015 Accomplishments

- Successfully synthesized and evaluated Li-ion conducting materials
- Filed U.S. provisional application
- Developed an electrochemical cell based on Li-ion conducting electrolytes that can be immersed directly into the metallic cooling blanket
- Evaluated the feasibility of cell operation for LiH decomposition
- Characterized the decomposition of LiH in Li metal

Future Directions

- Improve electrolyte and cell geometry in order to perform experiments under truly molten conditions and avoid shorting
- Test under low concentration of hydrogen isotopes
- Engage with researchers at national laboratories to discuss how to incorporate the modified extraction process in projects requiring hydrogen extraction

FY 2015 Publications/Presentations

None

References

1. H. Moriyama, S. Tanaka, D.K. Sze, J. Reimann, A. Terlain. Fusion Engineering and Design, 28 (1995) 226-239
2. S. Malang, R. Mattas. Fusion Engineering and Design, 27 (1995) 399-406

3. V. Maroni, R. Wolson, G. Staahl. Nuclear Technology, 25 (1975) 83-91.List any references used in the report.

Acronyms

LiH	lithium hydride
LiT	tritium tritide
LLZO	lithium lanthanum zirconium oxide
T	tritium
XRD	X-ray diffraction

Intellectual Property

U.S. Provisional Application SRS-14-014- Recovery of Tritium from Molten Lithium Blanket

Total Number of Post-Doctoral Researchers

1 postdoctoral student half time