

Contract No:

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Direct LiT Electrolysis in a Metallic 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 fusion/fission reactors is critical in order to maintain low concentrations. This is needed to decrease the potential tritium permeation to the surroundings and large releases from unforeseen accident scenarios. Extraction is complicated due to required low tritium concentration limits and because of the high affinity of tritium for the blanket. This work identified, developed and tested the use of ceramic lithium ion conductors capable of recovering hydrogen and deuterium through an electrolysis step at high temperatures.

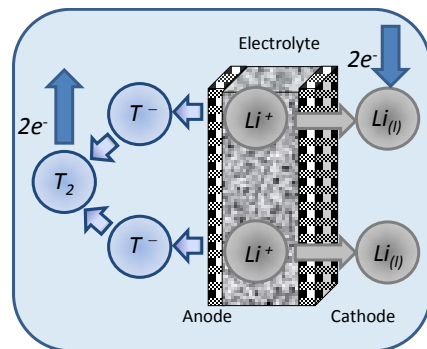


Figure 1. (left) Simplified depiction of the SRNL process approach for LiH electrolysis.

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

Signature

Date

Direct LiT Electrolysis in a Metallic Fusion Blanket

Project Team: Luke Olson, Brenda Garcia-Diaz, Hector Colon-Mercado, Joe Teprovich, Dave Babineau

Subcontractor: Greenway Energy, LLC

Thrust Area: SI4-2

Project Type: Strategic

Project Start Date: October 1, 2013

Project End Date: September 30, 2016

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 T₂ from LiT in the blankets/targets of fusion/fission reactors is critical in order to maintain low concentrations. This is needed to decrease the potential T permeation to the surroundings and large releases from unforeseen accident scenarios. Extraction is complicated due to the low concentrations required and because of the high affinity of T to the blanket. This work identified, developed and tested the use of ceramic lithium ion conductors capable of sustaining LiT

electrolysis at high temperatures. Multiple electrochemical cells were designed, fabricated, and used to test the proposed process. Successful electrolysis of LiH was confirmed with a residual gas analyzer and electrochemical measurements at the LiH concentrations tested. Additional work scope was added in FY16 to test the electrolytes in a Li immersion cell to better simulate expected operating conditions in reactor, and positive results indicating the stability of the electrolyte in molten Li at 300 °C were obtained.

FY2016 Objectives

- Design immersion cell and experiments for cell characterization
- Fabricate immersion cell, solid electrolyte contactor and balance of experimental setup
- Demonstrate LiT electrolysis in bench-scale test with molten Li immersed solid electrolyte
- Analysis of reaction products and reaction characterization (Quantify selectivity toward LiT decomposition)
- Optimize solid electrolyte for improved performance during lithium immersion

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 it is a liquid, the tritium recovery system can be designed outside the neutron environment and will not incur radiation damage. Blanket designs are simplified when the breeding material is also used as a coolant because nuclear heating also occurs in the breeding material. However, there are a number of engineering design difficulties such as magneto-hydrodynamic pressure drops, corrosion due to 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 reliable and safe operation. The extraction of tritium can be problematic from the blanket since the tritium 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 complex 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 or 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 undergoes electrolysis and the hydrogen is 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.

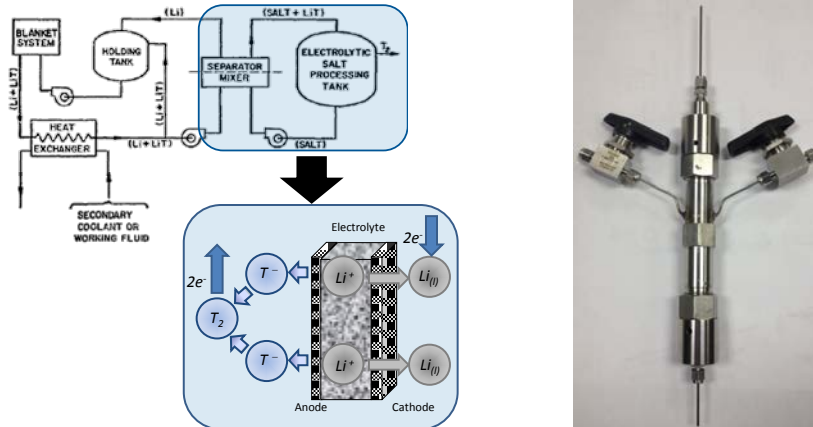


Figure 1. (left) Simplified Maroni process [3]. Shaded area depicts where the SRNL process approach can be incorporated. (right) Electrochemical cell design for LiH electrolysis

In FY16 a Li immersion cell was designed to more effectively simulate conditions expected to be encountered in plant operation, Figure 2. This new cell allowed for the solid electrolyte to be submerged in molten Li at 300 °C, and for stirring of the molten Li/LiH mixture. This cell allowed for better simulation of conditions expected for use in a plant, and to explore and begin to address challenges that would be encountered during such operations.

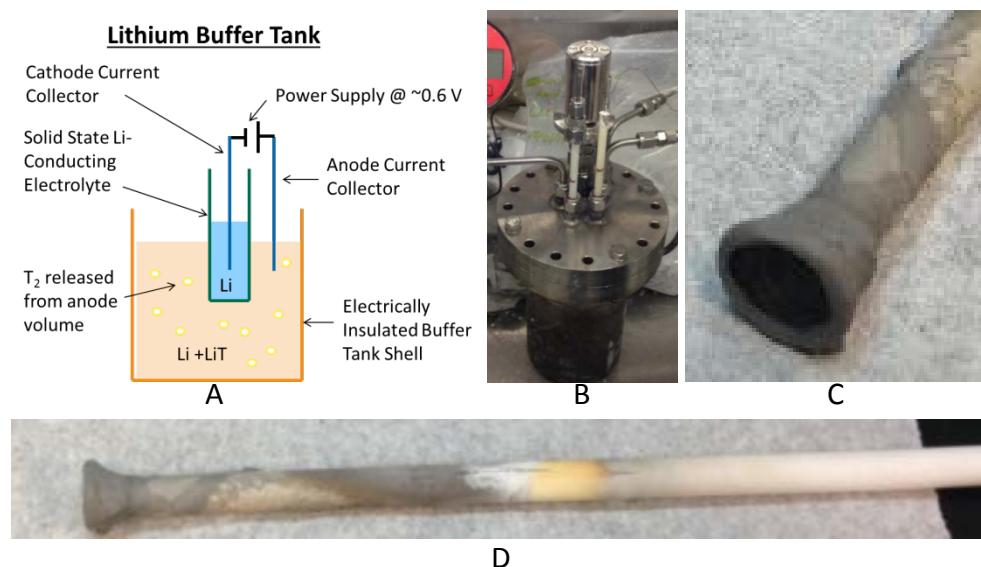


Figure 2. A) Immersion Cell Concept, B) immersion reactor vessel showing gas and cooling ports, electrodes, and stirring mechanism, c) solid electrolyte immersion electrode, note black circular region is the electrolyte that is attached to an alumina tube using boron nitride paint, inside the electrode is a tungsten wire contacting a small pool of molten Li, D) the electrode is sealed from atmosphere, but can exchange gas within the vessel through a slit in the side so that the vessel can be evacuated without breaking the electrolyte electrode.

Results/Discussion

Two main versions of the electrochemical cell from Figure 1 were designed, fabricated and used to test the initial electrolyte materials. Typically the electrolyte consisted of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) that has been pressed and sintered into a pellet. LLZO has been shown to have among the highest conductivities at the temperatures of interest. Once prepared, the pellet was characterized using X-ray Diffraction (XRD) to confirm cubic phase formation. The cubic phase in LLZO has the highest conductivity of the potential phases present. Heat treatments and mixing conditions were explored to determine the optimal synthesis methodology for the cubic phase formation and development of mechanically stable pellet.

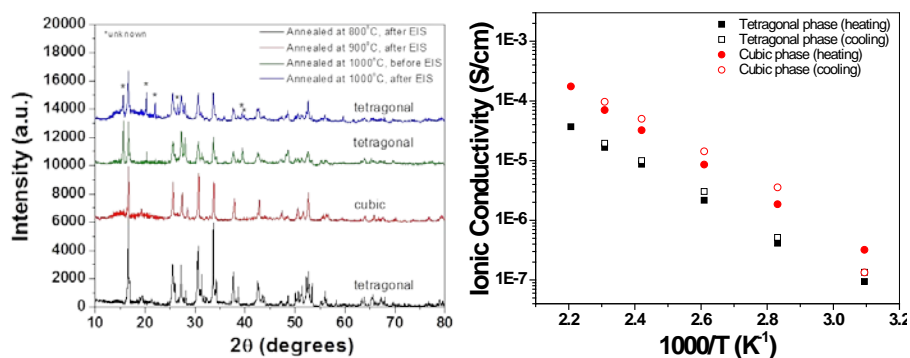


Figure 3. XRD (left) and ionic conductivity (right) examination of the LLZO solid electrolyte.

Figure 3 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.

The electrolysis cell in Figure 1 consisted of a Li/LiH electrode, the LLZO electrolyte and a gold contact counter electrode. The evolution of H₂ 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 H₂ is released from the Li/LiH electrode. The H₂ signal slowly decays as the LiH closest to the electrolyte is consumed. Figure 4 (right) shows the Tafel polarization for the LiH electrolysis at 350 °C. An exchange current density of 3.06 mA/cm² and limited current density of 20.4 mA/cm² was observed. Improvements such as operation at higher temperatures and fluidization of the working electrode should result in higher current densities.

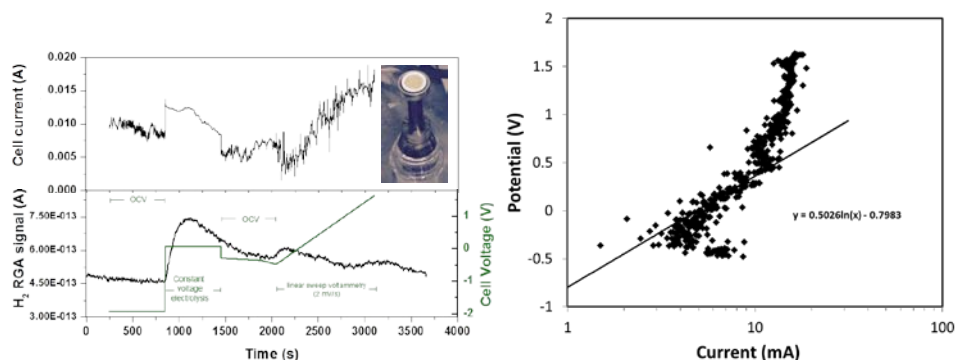


Figure 4. (left) Electrolysis at 350 °C using LLZO electrolyte, gold counter electrode and Li/LiH as a working electrode. Inset shows LLZO pellet. (right) Tafel polarization for the electrolysis of LiH.

The electrolysis cell in Figure 2 Consisted of a tungsten wire current collector that contacted a Li droplet that sat on the top of the LLZO electrolyte, with the electrolyte, attached to an insulating alumina rod with BN and/or alumina, which was submerged into molten Li-LiH mixture at 300 °C. An RGA was used to monitor H₂ evolution during electrolysis tests. A total of 11 trials were made using the immersion cell in FY16, during which electrolyte fabrication methods were improved to give an electrolyte without the carburization observed post testing shown in C of Figure 2, and improved functionality and survivability of the electrolyte/Li contactor.

FY2016 Accomplishments

- Designed, fabricated, demonstrated, and characterized an electrochemical reactor that immersed a Li conducting electrolyte in molten Li to electrolyze LiH into Li and H
- Characterized the LiH electrolysis reaction in molten Li and analyzed reaction products
- Successfully synthesized and evaluated Li-ion conducting materials for molten Li immersion and improved processing techniques partially reducing carburization at solid electrolyte surface.

Future Directions

- Improve electrode/electrolyte cell design geometry to delay shorting and allow for longer experiment durations
- Perform experiments using 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
- Improve hydrogen gas collection system in Li immersion cell to improve RGA signal collection from electrolysis

LDRD Report

- Further improve processing techniques to make a higher conductivity, thinner walled electrolyte microstructure for improved electrolytic efficiency
- Investigation of electrolyte fabrication using slip casting to more easily enable closed end tubes that could be bundled

FY 2016 Publications/Presentations

1. **“Electrolytic Tritium Extraction in Molten Li-LiT,”** L.C. Olson, B.L. Garcia-Diaz, H. Colon-Mercado, J. Teprovich, D. Babineau, SRNL-STI-2015-00605, Fall 2015 Tritium Focus Group Meeting, November 3-5, 2015, Los Alamos National Laboratory.

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.

Acronyms

appm	atomic parts per million
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