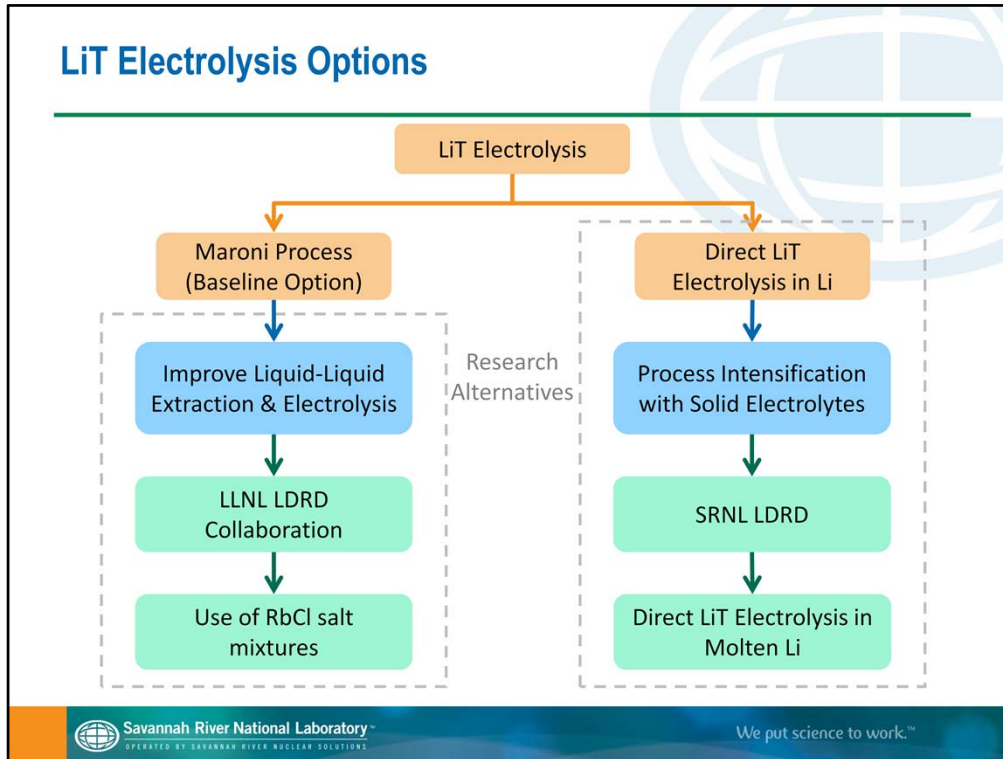


LiT Electrolysis Research at SRNL

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Tritium Focus Group
4/29/2015



- Maroni is the Baseline for LiT Electrolysis
- LLNL LDRD tries to improve molten salt liquid-liquid extraction and SRNL is contributing by investigating RbCl containing salts
- SRNL LDRD tries process intensification to eliminate molten salt liquid-liquid extraction using advanced solid state electrolytes



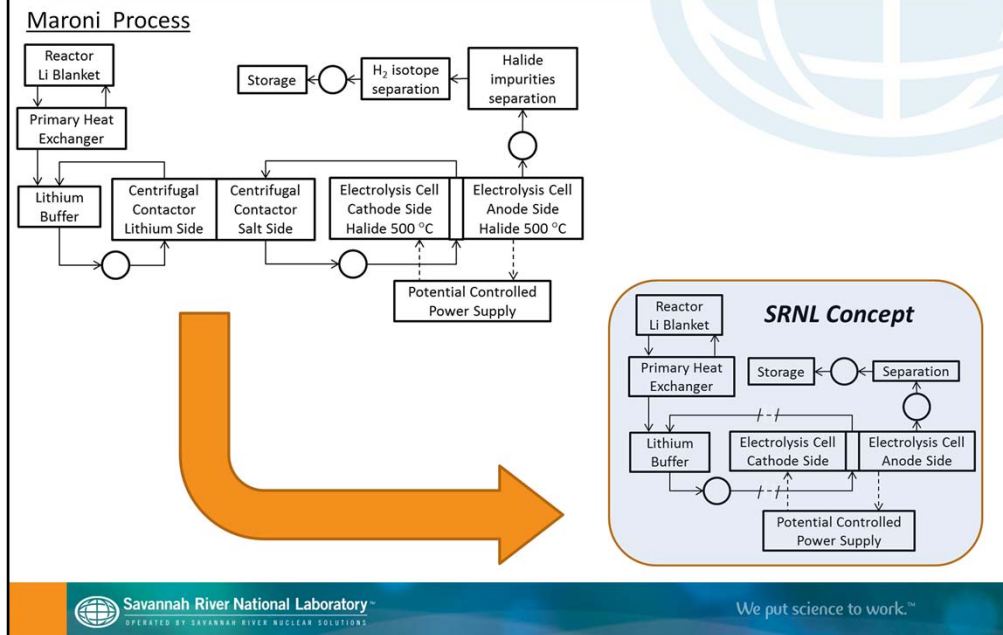
Direct LiT Electrolysis in a Metallic Lithium Fusion Blanket



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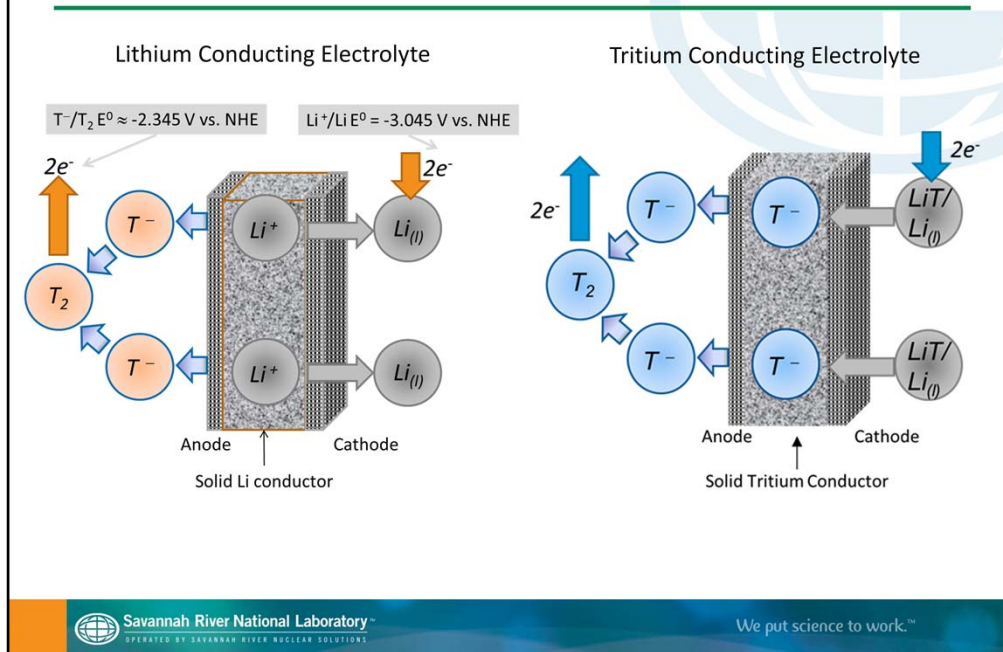
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Tech: Approach: SRNL Direct LiT Electrolysis Concept



- Upper Process shows generalized process flow diagram for Maroni Process
- Lower right shows the simplification in the process flow diagram through the elimination of the liquid-liquid extraction step and elimination of the halide salt

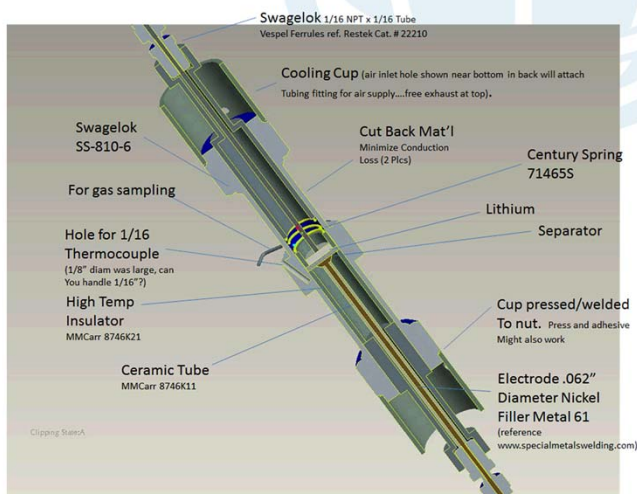
Tech. Approach: SRNL Solid State Conduction Process



- SRNL filed a provisional patent for this process
- The patent covers variations of the electrolysis cell that include both Li-conducting and T-Conducting solid electrolytes
- Most of SRNLs research to date has been conducted on the Li-conducting electrolytes

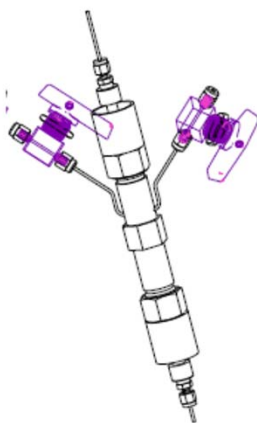
Results: High Temperature Cell Design

- Cell designed for molten Li electrolysis
- Cell allows conductivity tests at relevant operating conditions above 200°C
- Gas sampling ports included for testing LiT electrolysis in the electrode
- Will provide guidance on cell designs for use in the molten Li blanket



- Developed high temperature cell designs to test electrolysis process using materials such as Ni, alumina and stainless steel

Results: High Temperature Cell Photographs



- Cell was designed and constructed based on common Swagelok fittings
- Cell fabrication was completed with assistance from the SRS machine shop
- The design should allow for multiple Li conductors to be tested in the same cell
- Testing will also provide information on compatibility of cell materials for Li electrolysis cell construction

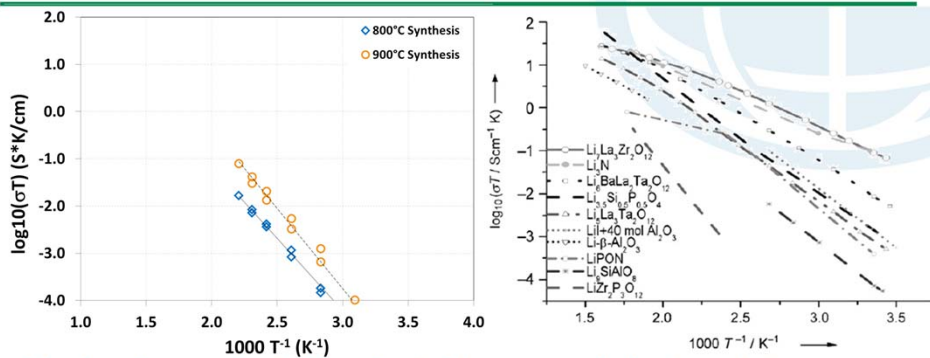


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- Final cell design and construction that allows for flowing gases through the sample for RGA analysis
- Cells could be operated either inside a glovebox or outside the glove box

Results Comparison of LLZO Lithium Ion Conductivities



- Pellets have been synthesized by adapting literature methods using a Li_2CO_3 precursor for lithium in the solids
- An important step in the synthesis of lithium lanthanum zirconate is the sintering of the pellet
- Initial attempts with sintering temperatures of 800°C and 900°C have been attempted and resulted in lower than expected conductivity
- Higher sintering temperatures will likely result in increased conductivity



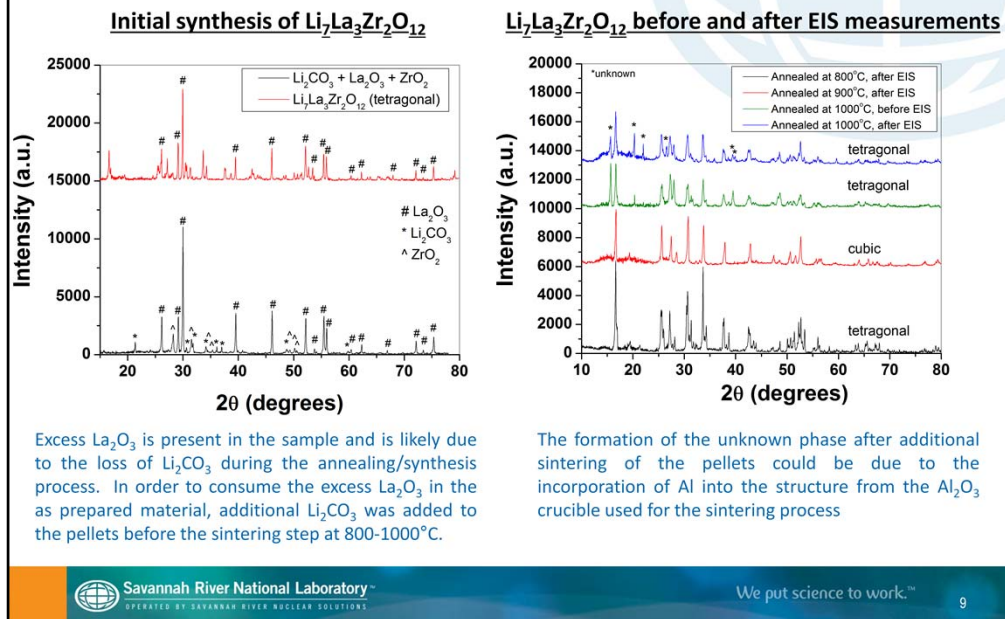
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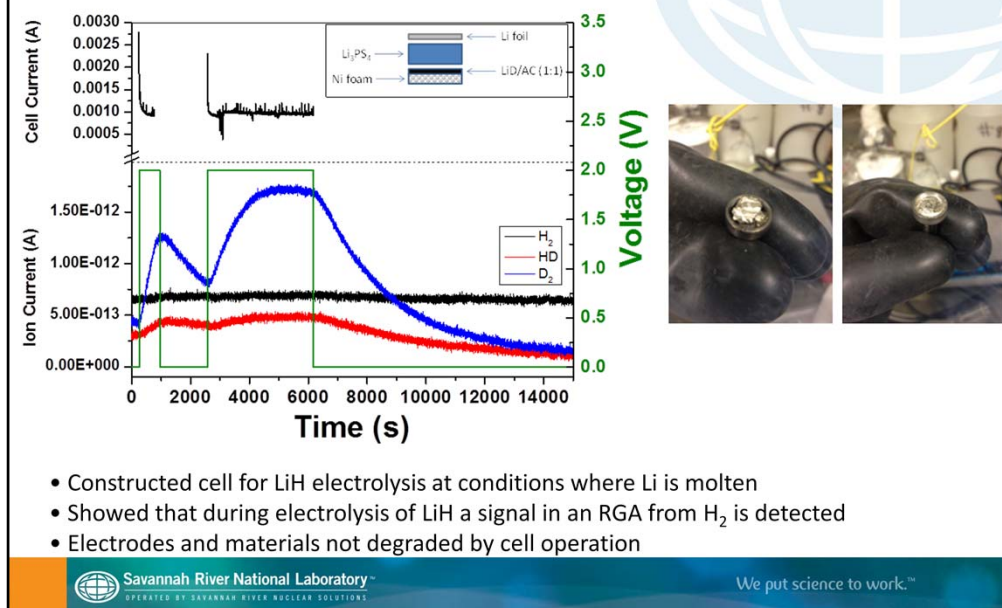
- SRNL synthesized Lithium Lanthanum Zirconate Garnet (LLZO) electrolyte in-house
- LLZO electrolytes are stable in molten Li
- LLZO electrolytes and variations are pre-commercial, but have been studied in the literature for a variety of variations
- There is room for improvement in the Li-conductivity that can be achieved

Technical Progress: XRD study of the electrolyte



- Through varying synthesis parameters, we have been able to optimize the structure of the electrolyte
- Heat treatment at 900°C gave the cubic phase that has the highest conductivity
- Conductivity of the electrolyte is measured with temperature using techniques such as electrochemical impedance spectroscopy

Phase 1 Results: Achieving TRL 3



- To prove that LiT electrolysis is feasible, SRNL decomposed LiD in Molten Li as a surrogate
- This figure overlays the electrochemical current at the top with the RGA signal for hydrogen isotopes
- The RGA shows an increase in D2 and HD evolution when the electrolysis is occurring
- Results demonstrate process feasibility

Project Summary



➤ *Relevance*

- Eliminating the need for solvent extraction of LiH from metallic cooling blankets for electrolysis
- Reduce tritium release from fusion processes by controlling LiH inventory in the cooling blanket

➤ *Technical Approach*

- Develop an electrochemical cell based on solid Li-ion conducting electrolytes that can be immersed directly into the metallic cooling blanket
- Evaluate the feasibility of cell operation for LiH decomposition
- Develop high temperature Li-ion conductors for electrolytes that can be immersed in molten Li and that have high conductivity
- Characterize the degradation of LiH in molten Li

➤ *Technical Accomplishments*

- Designed a cell for LiH decomposition in molten Li
- Successfully synthesized and evaluated Li-ion conducting materials
- Constructed the cell for LiH decomposition
- Demonstrated Electrolysis of LiH



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Novel Salts for LiT Extraction and Electrolysis

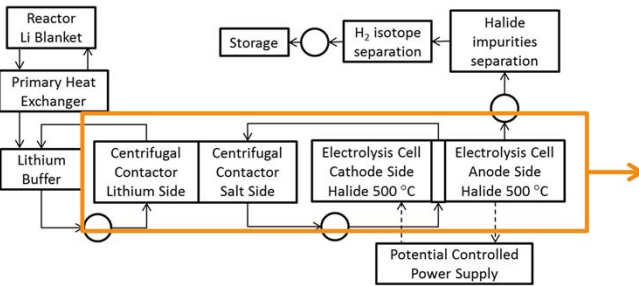


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LLNL LDRD to Improve Molten Salt Extraction Project

Maroni Process

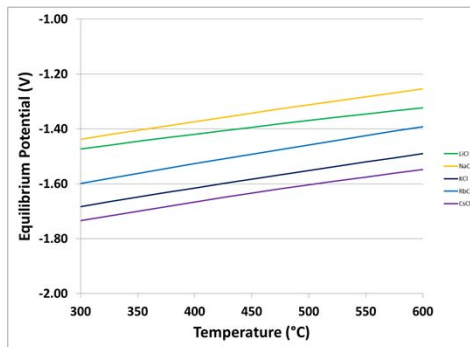


- SRNL and LLNL searching for alternatives to current molten salts
- LLNL investigating ionic liquid: LiTFSI
- SRNL investigating RbCl-containing molten salts for reducing risk of neutronics impact
- SRNL quantifying LiH extraction in molten salt

- LLNL has an LDRD led by Susana Reyes that is also investigating improvements in LiT electrolysis through selection of the molten salt electrolyte for LiT extraction
- SRNL also has expertise in molten salts through LDRDs in novel molten salt reprocessing method development and through the SunShot program
- SRNL has proposed studying Rb containing salts that may have lower neutronics impact than other alternatives should the salt be entrained in the Li blanket and enter the reactor

Salt Selection: Electrochemistry

- Extraction of LiT requires use of a salt with a lower equilibrium potential than Li to prevent contamination of molten Li
- Salt components should have low neutronic impact in case they get in reactor
- Need melting point below $\sim 450^{\circ}\text{C}$ to operate at 500°C



- Alkali Earth Metals Sr and Ba could fit the temperature and electrochemical requirements, but not the neutronic requirements
- Alkali metals K, Rb, and Cs fit the temperature and electrochemical profile
- K and Cs do not fit the neutronics requirements
- Rb was the only possible salt to pair with Li



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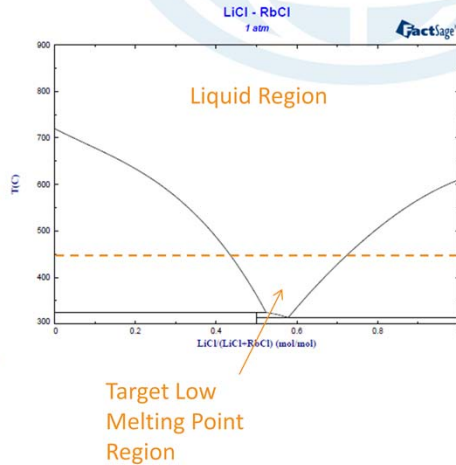
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There were 3 main requirements that Susana indicated they wanted to try and meet:

- 1) that the salt needs to be stable and not contaminate the Li blanket,
 - 2) that salt components should have a low neutronics impact if they get in the reactor, and
 - 3) a melting point below 450°C is needed.
- Main cations considered were alkali metal and alkali earth metals and we settled on chlorides as an anion that would have acceptable neutronics while being stable.
 - Quickly ruled out all the alkali earth metals except for Sr and Ba due to their high equilibrium potentials relative to Li. Susana indicated that the neutronics impact of Ba and Sr were not good and they should be avoided too.
 - This left us with the alkali earth metals. Potassium, Rubidium, and Caesium all had the necessary thermodynamic stability, but only Rb had acceptable neutronics according to Susana's analysis.

Salt Selection: Two Phase LiCl-RbCl Melting Point

- Phase diagrams were calculated in FactSage
- Diagram at left is the two phase diagram for only LiCl-RbCl with x-axis showing increasing LiCl mole fraction
- Target is a melting point below 450°C
- Target melting point can be achieved between 30 – 55 mol % RbCl (45 – 70 mol% Li)
- LiCl-RbCl has a melting point below 350°C for the eutectic mixture (~58% LiCl – 42% RbCl)
- For simplicity, our initial testing will use the eutectic mixture that gives the lowest melting point near 325°C, which gives the most operational flexibility



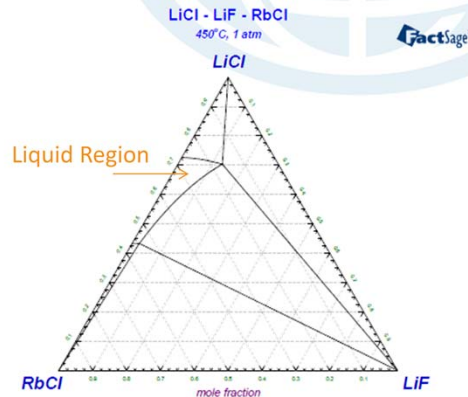
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- We focused most of our simulation efforts on 450°C because is what Susana indicated is about the maximum practical melting point for engineering a system.
- Orange line on the diagram at 450°C illustrates the two-phase salt composition region considered.
- The RbCl content in this region is between 30-55 mol% and 45-70 mol% LiCl.
- The eutectic melting point at around 58% LiCl is below 350°C and is close to 325°C.
- SRNL is using the eutectic composition of the salt for initial tests since that would provide the greatest operational window for an engineered system.

Salt Selection: Three Phase LiCl-RbCl-LiF Melting Point

- Ran simulations to see if RbCl content could be reduced by adding LiF as a third component
- Individual three phase diagrams require targeting a specific temperature
- Main simulation focused on the 450°C temperature and the boundary compositions for the liquid region
- Most of liquid region is between 20-40 mol% RbCl and 50-70% LiCl
- LiF was generally between 3-10 mol% for the liquid
- Judged that adding LiF could slightly lower RbCl content, but that it is not likely worth the added complication for initial tests



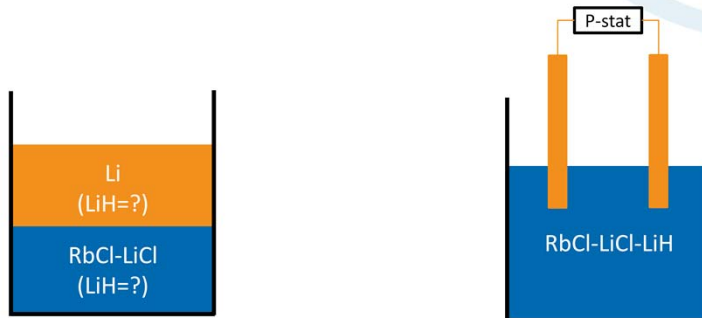
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- We simulated adding LiF to see if it would significantly lower the amount of RbCl needed in the salt mixture to achieve a melting point of 450°C. The basic thought for considering this is that there may be advantages in terms of neutronics of having as large a fraction of lithium ions as possible in the mixture.
- The liquid region is similar to a long skinny triangle at the left of the diagram.
- Most of the liquid region is between 20-40 mol% RbCl with the LiF between 3-10 mol%.
- This showed that the LiF would allow the RbCl to be slightly decreased, but not significantly. Therefore, we decided to use the two phase chloride system for the initial testing to make it as simple as possible.

Research Overview & Objectives

- Characterize the partition coefficient for extraction of LiH from LiCl-RbCl
- Characterize the thermodynamics and kinetics of LiH Electrolysis from LiCl-RbCl



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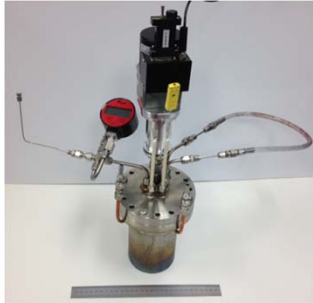
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The research of SRNL has two main parts:

- 1) Perform extraction of LiH from molten Li using LiCl-RbCl and quantify the amount of LiH extracted in the salt
 - 2) Perform electrolysis of LiH in RbCl-LiCl to prove the LiH can be sufficiently decomposed
- SRNL has been setting up for both of these tests and is now starting to run these tests.

Cell Design Overview

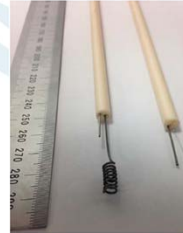
Assembled Cell
with Rotator and Electrodes



Cell Lid with
Electrodes & Stirrer



Electrodes



600 g Eutectic RbCl-LiCl



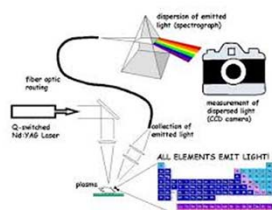
- SRNL designed a cell based roughly on concepts from electrochemical testing in the SunShot program
- Cell with rotator fabricated and ready to start electrolysis and extraction testing
- Cell made smaller to fit in a glovebox to facilitate loading with air sensitive LiH containing salt
- Cell operation will be outside the glove box with a flowing atmosphere of high purity Ar

GC and LIBS Techniques for LiH determination

These two methods are the most promising for determining the LiH concentration in a LiCl/Rb mixture with Li metal. These methods target H_2 concentration without water quenching.

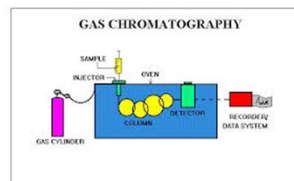
LIBS

- Can measure the spectra lines for H_2 with low detection limits (100ppm).
- No solvent needed.



GC

- Can measure trace amounts of hydrogen with an appropriate calibration curve.
- Needs specially designed cell into desorb hydrogen and contain Li.



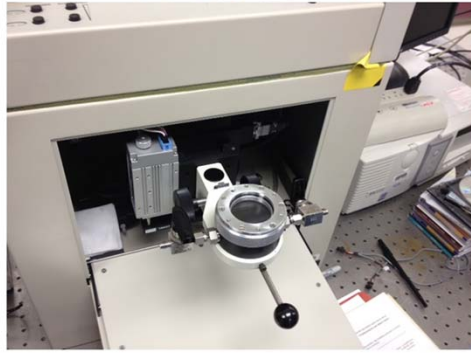
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- Cells made smaller to fit in a glovebox to facilitate loading with air sensitive LiH containing salt
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LIBS Instrument

A laser ablation system was modified to act as a laser induced breakdown spectrometer.



- The system is up and operational and LIBS spectra on standards such as brass, TiO_2 , and Cu have been acquired.
- A residual gas analyzer (RGA) has also been attached in tandem to look for gas species that are given off by the ablation process.
- The instrumental conditions are currently being optimized for light elements. (Li, H)



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LIBS Hydrogen Quantification Practicality

- Literature shows detection of H and D in Zircaloy-4 down to <1000 ppm using LIBS
- Detection of D in Zircaloy-4 was allowed quantification to less than 200 ppm of D
- These examples demonstrate that detection of low concentrations of LiH and LiD in RbCl-LiCl are likely possible using LIBS

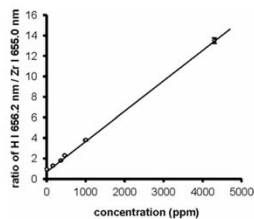


Figure 19. Calibration curve obtained from zircaloy-4 samples with error bars indicating deviations around 1.3%. Reprinted with permission from Kurniawan et al. (89). Copyright (2007) American Chemical Society.

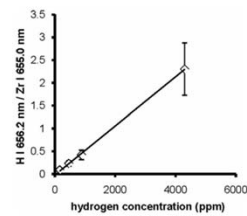
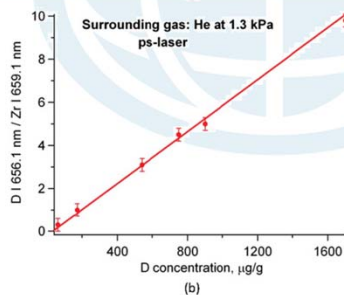


Figure 42. Calibration curve from zircaloy-4 samples of 0, 161, 461, 1,000, and 4,300 ppm hydrogen concentrations with the data obtained from the averaged results over 100 shots under +10 nm defocused condition. The gate delay and gate width of the OMA system were set at 5 and 50 µs, respectively. Reprinted from Ramli et al. (97).



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Extra Slides



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