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LiT Electrolysis Research at SRNL

Brenda L. García-Díaz
Hector Colon-Mercado
Joe Teprovich
Dave Babineau
Savannah River National Laboratory

Tritium Focus Group
4/29/2015

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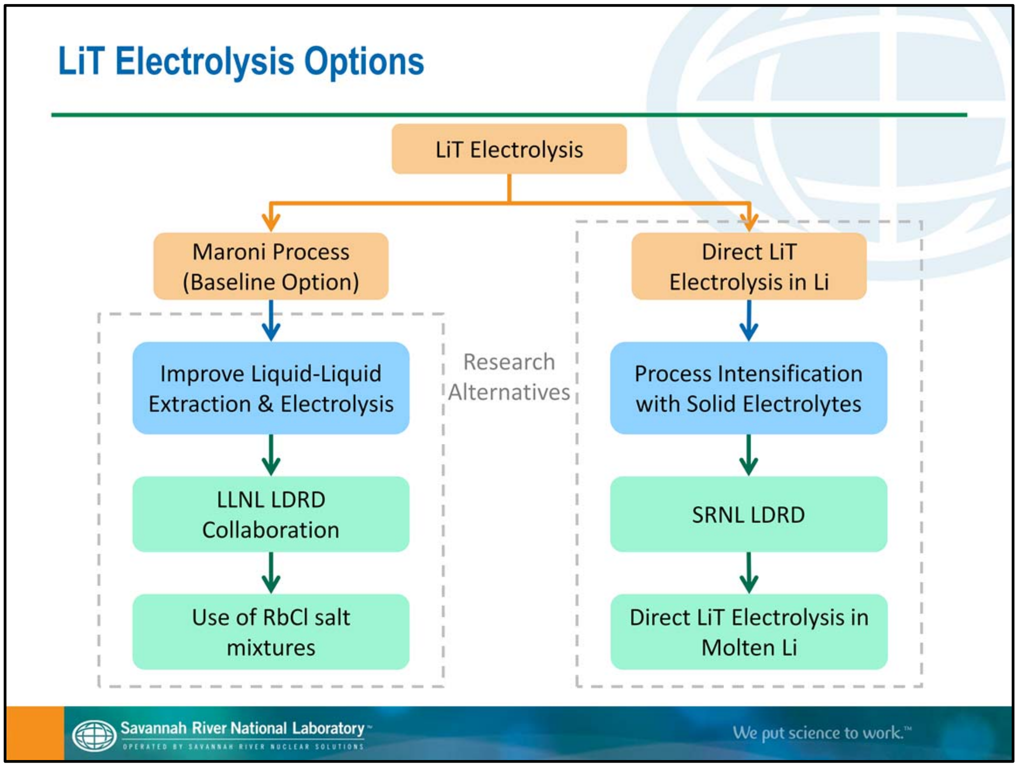
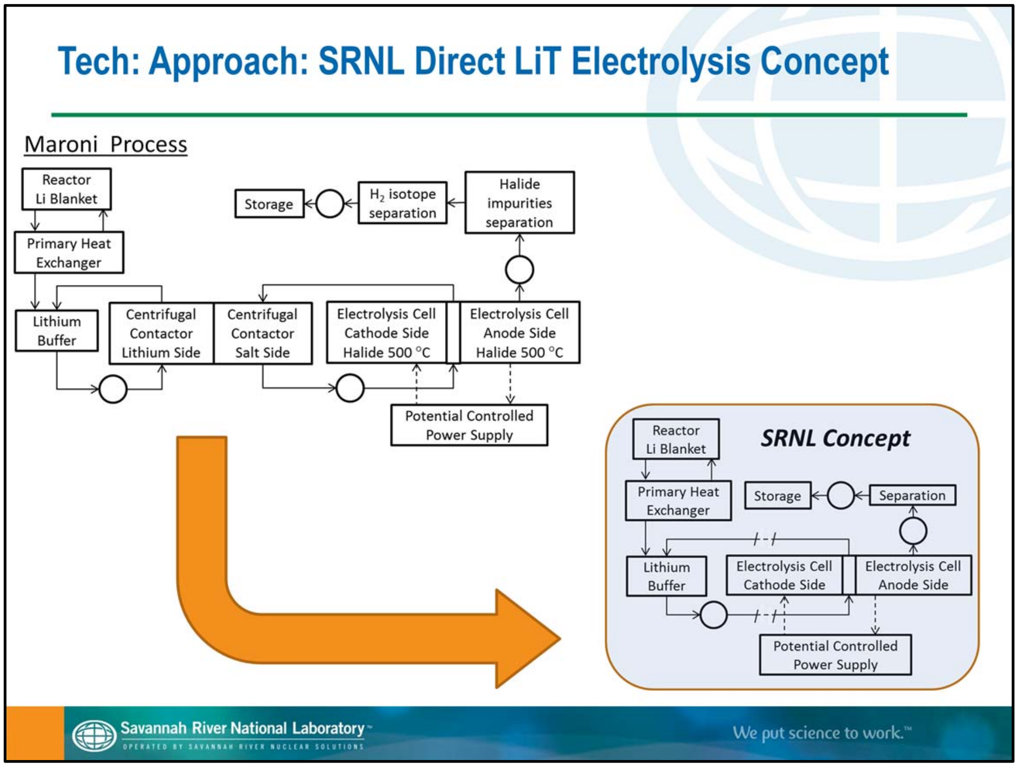
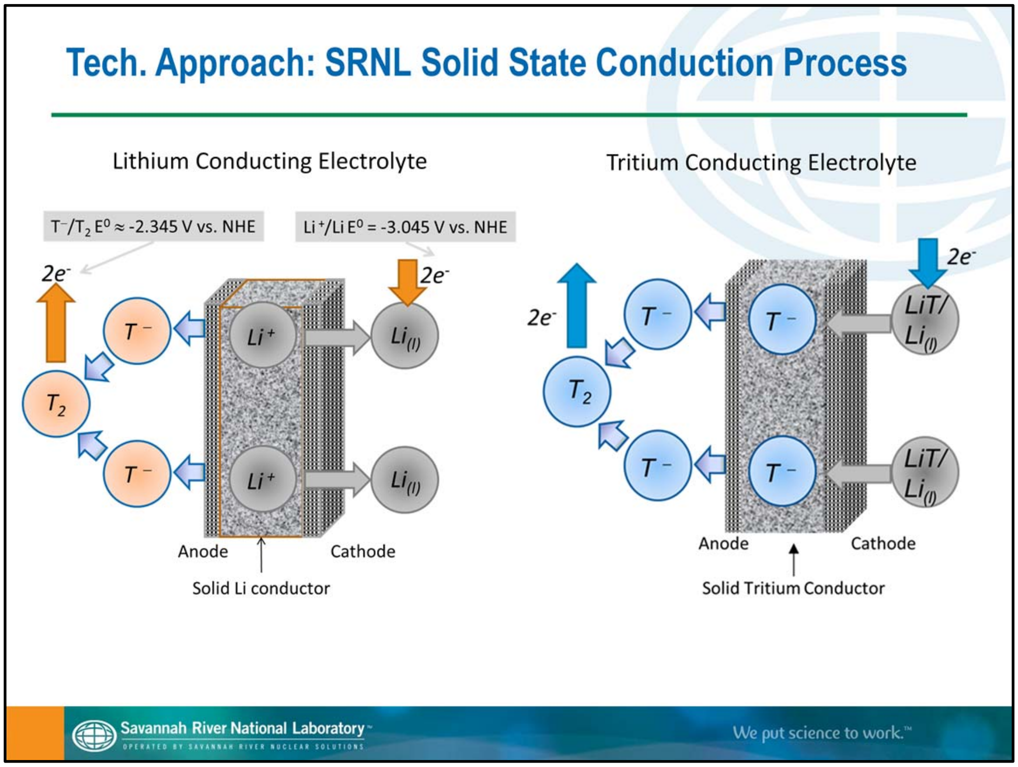


- Maroni is the Baseline for LiT Electrolysis
- LLNL LDRD tries to improve molten salt liquid-liquid extraction and SRNL is contributing by investigating RbCl containing salts
- SRNL LDRD tries process intensification to eliminate molten salt liquid-liquid extraction using advanced solid state electrolytes

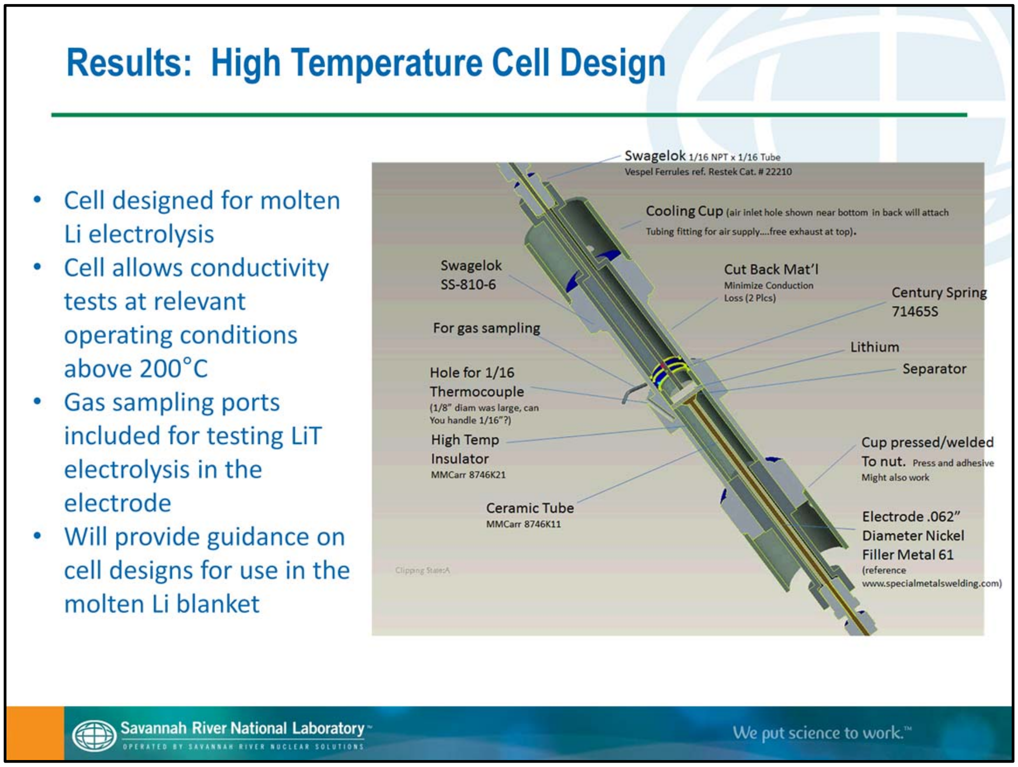
Direct LiT Electrolysis in a Metallic Lithium Fusion Blanket



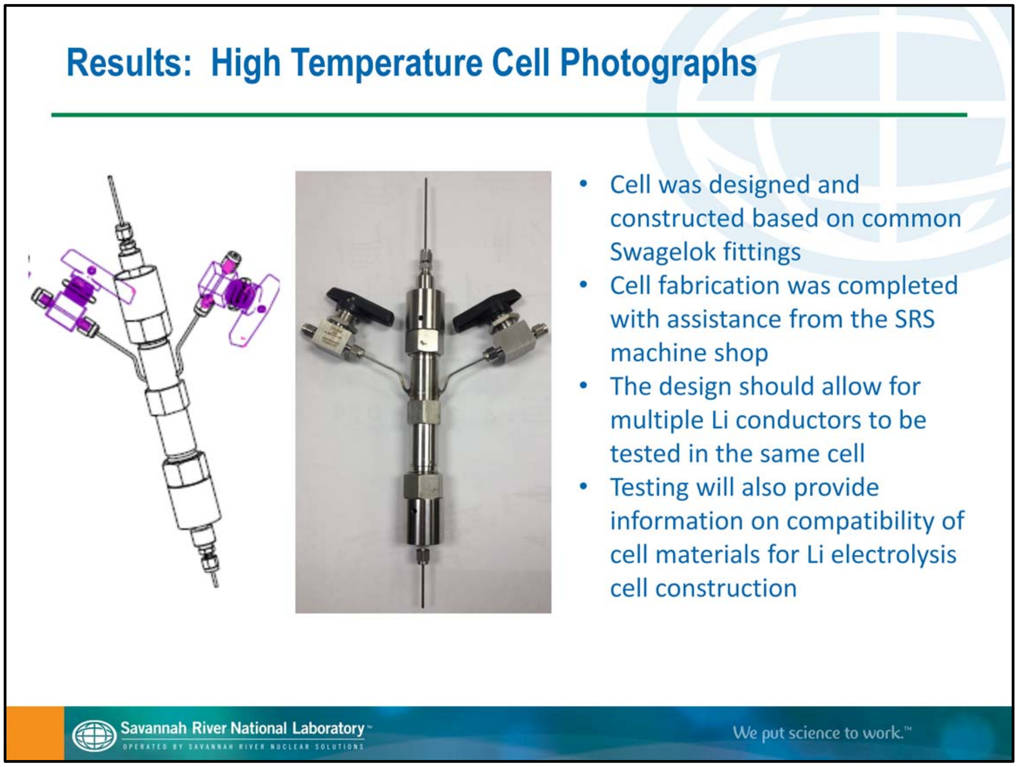
- Upper Process shows generalized process flow diagram for Maroni Process
- Lower right shows the simplification in the process flow diagram through the elimination of the liquid-liquid extraction step and elimination of the halide salt



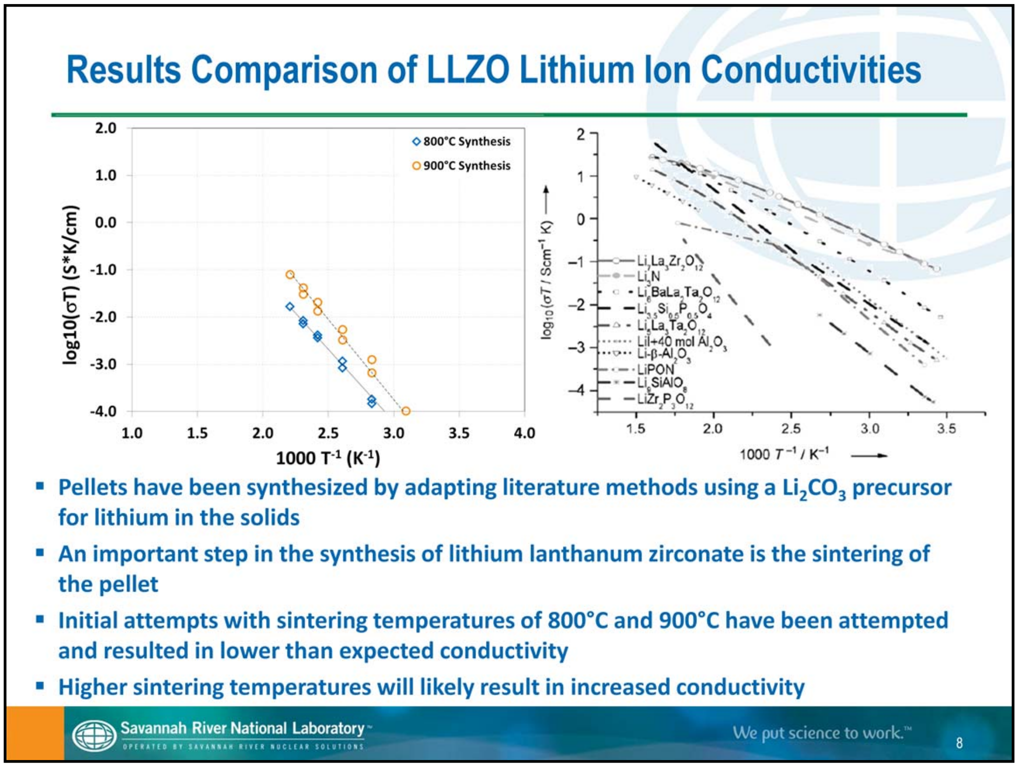
- SRNL filed a provisional patent for this process
- The patent covers variations of the electrolysis cell that include both Li-conducting and T-Conducting solid electrolytes
- Most of SRNLs research to date has been conducted on the Li-conducting electrolytes



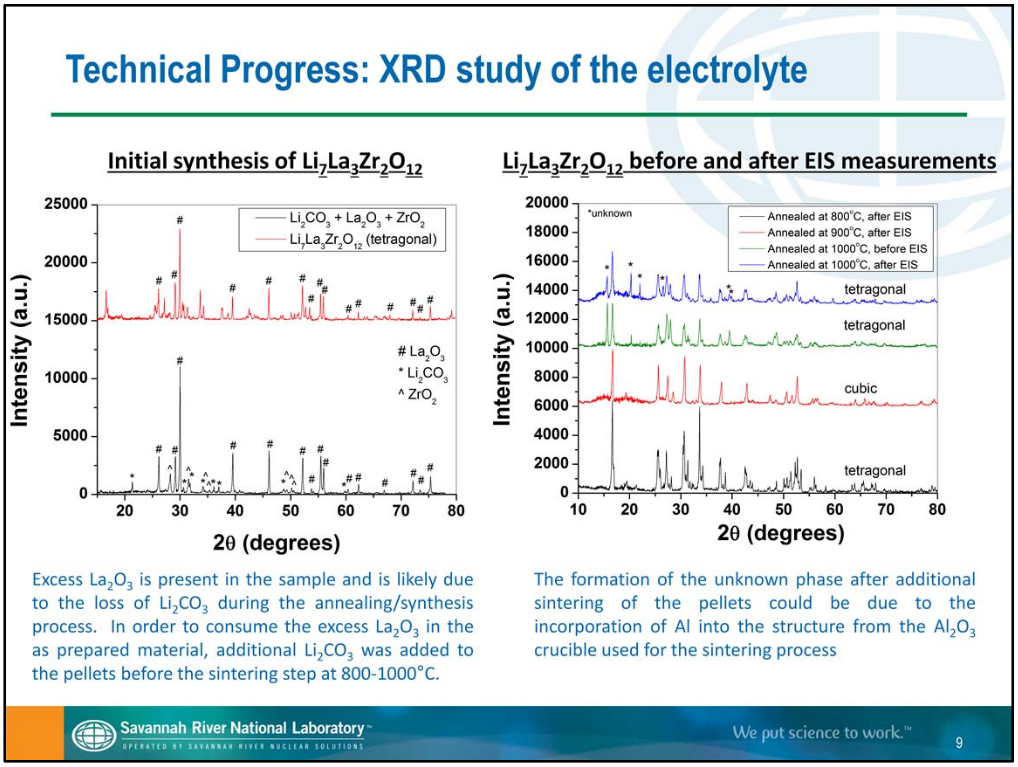
• Developed high temperature cell designs to test electrolysis process using materials such as Ni, alumina and stainless steel



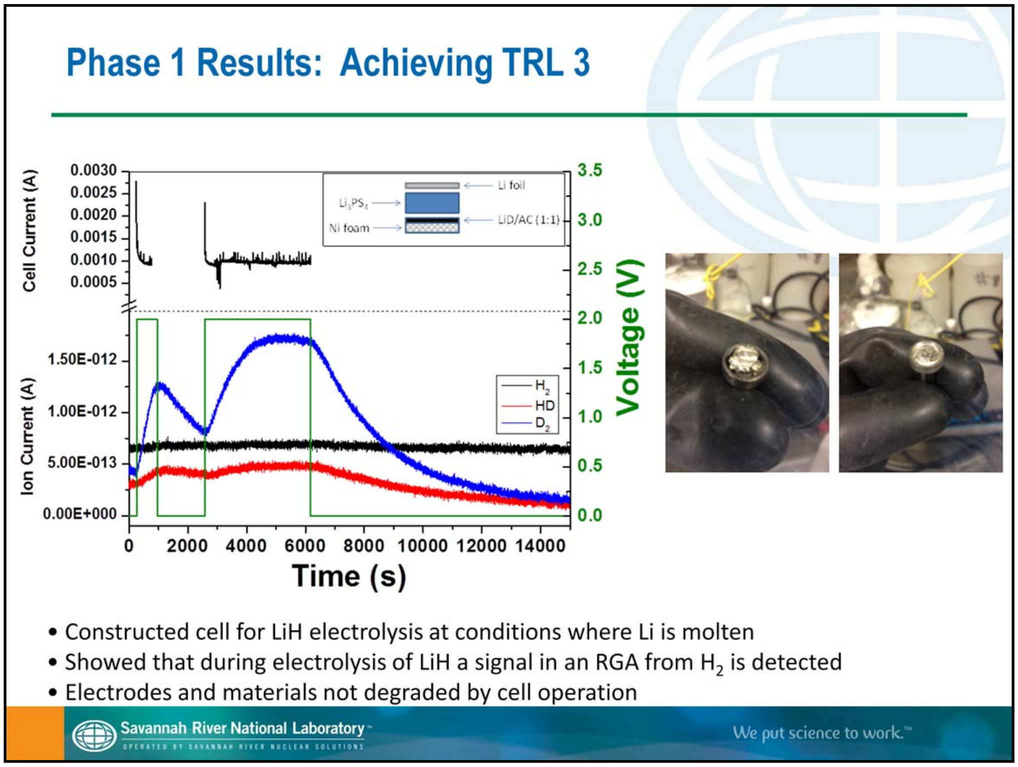
- Final cell design and construction that allows for flowing gases through the sample for RGA analysis
- Cells could be operated either inside a glovebox or outside the glove box



- 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



- 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



- 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

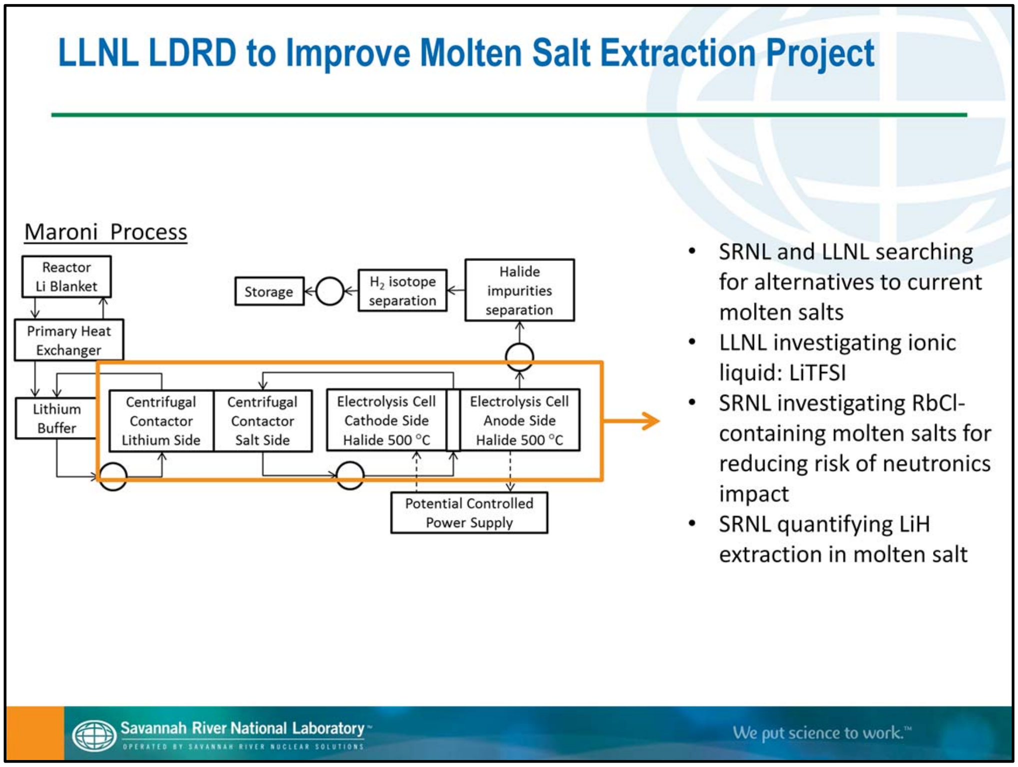
➢ *Technical Approach*

- 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

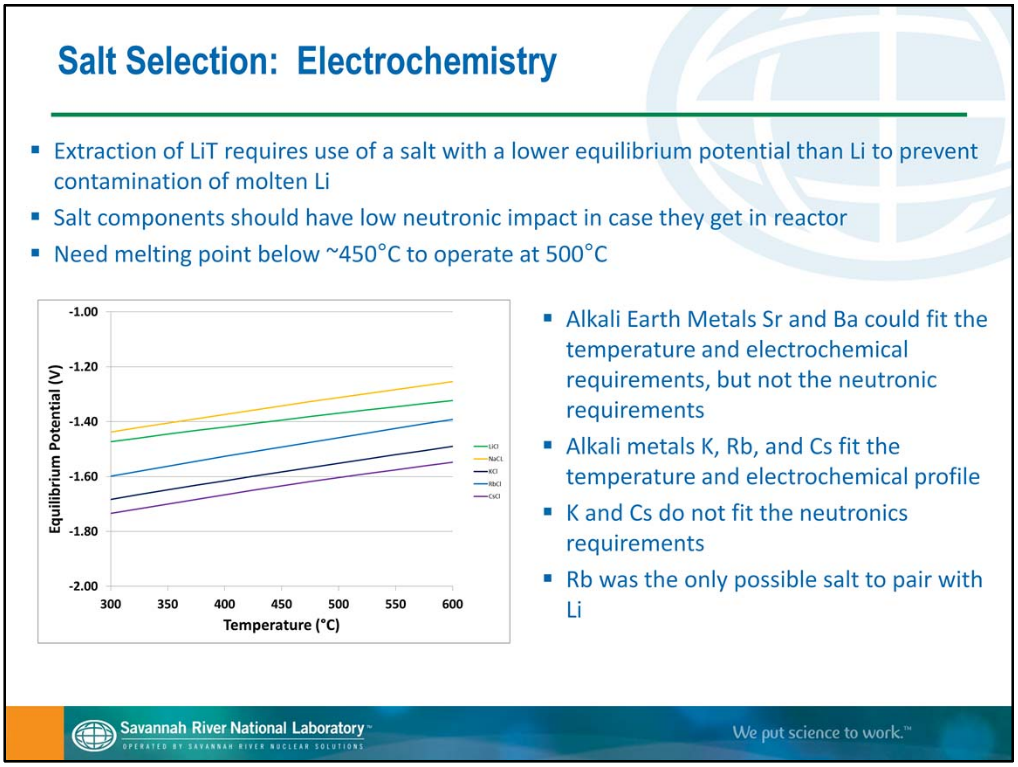
➢ *Technical Accomplishments*

- 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

Novel Salts for LiT Extraction and Electrolysis



- 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

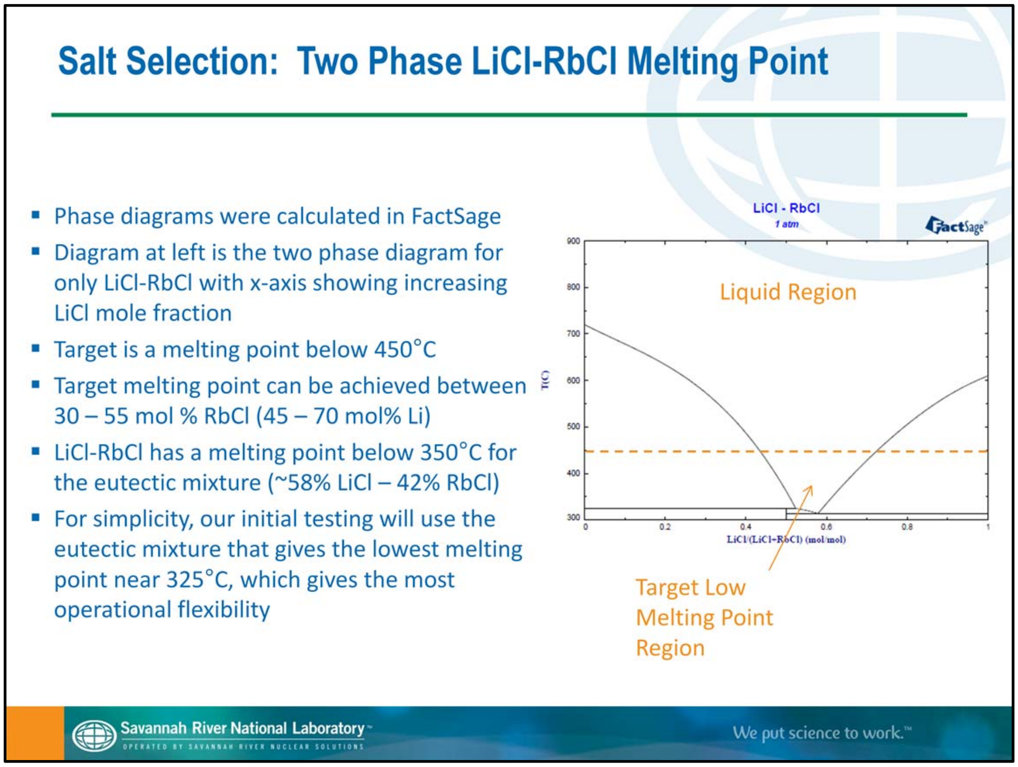


There were 3 main requirements that Susana indicated they wanted to try and meet:

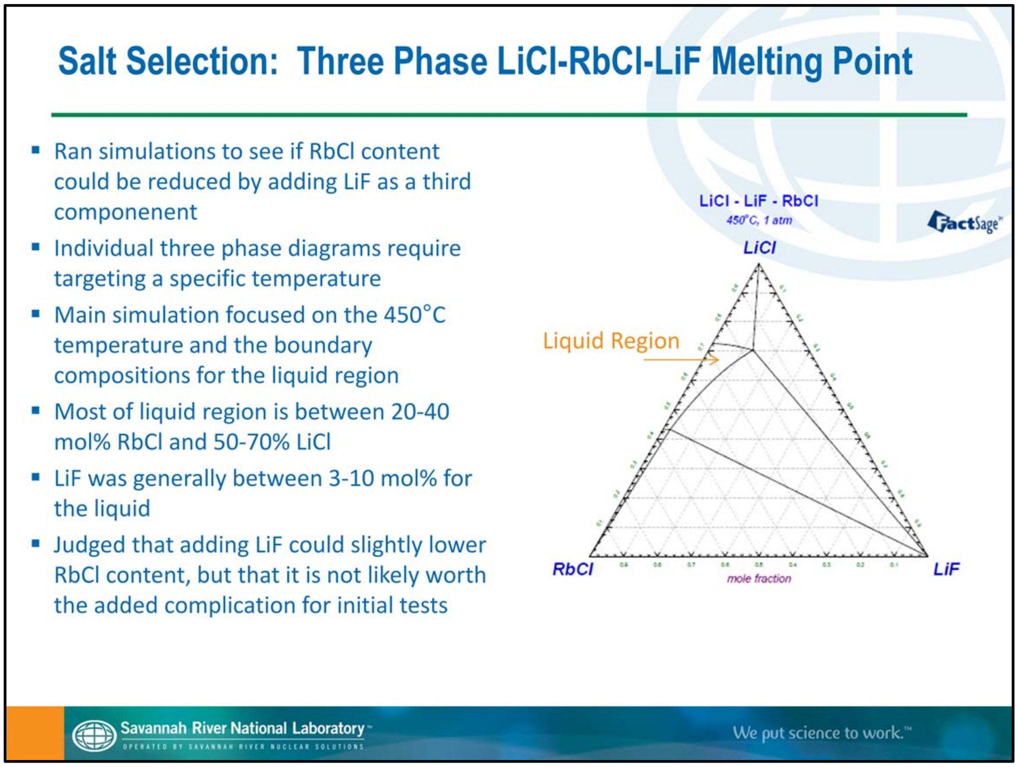
1) that the salt needs to be stable and not contaminate the Li blanket,
2) that salt components should have a low neutronics impact if they get in the reactor, and

3) a melting point below 450°C is needed.

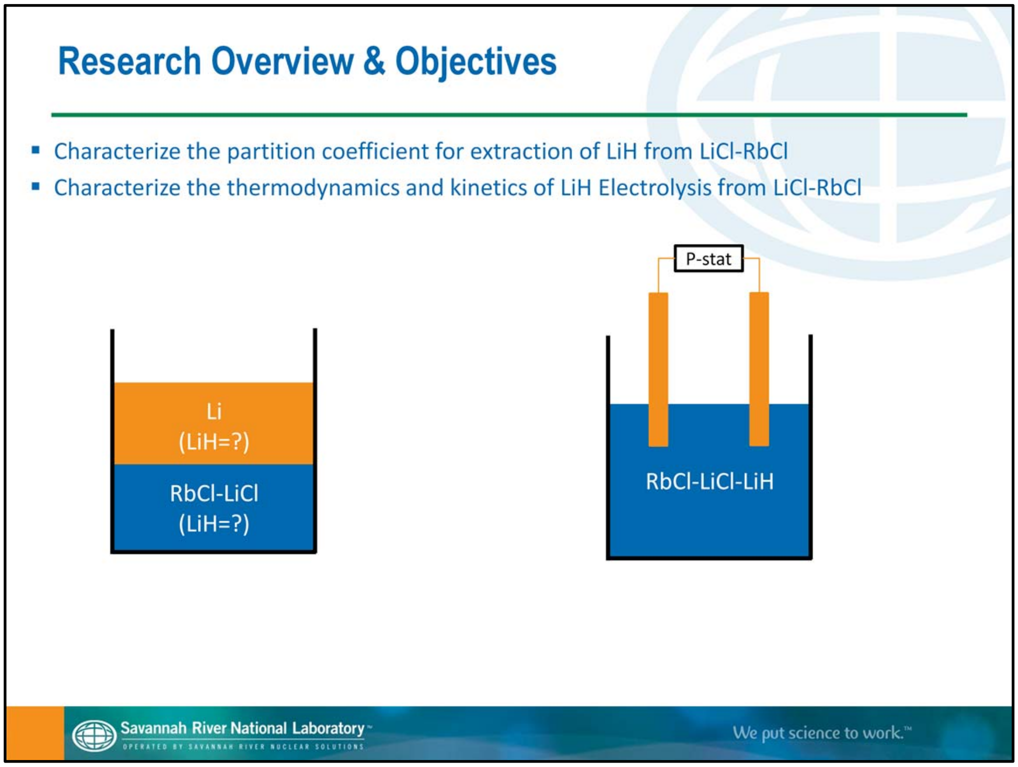
- Main cations considered were alkali metal and alkali earth metals and we settled on chlorides as an anion that would have acceptable neutronics while being stable.
- Quickly ruled out all the alkali earth metals except for Sr and Ba due to their high equilibrium potentials relative to Li. Susana indicated 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.



- 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.



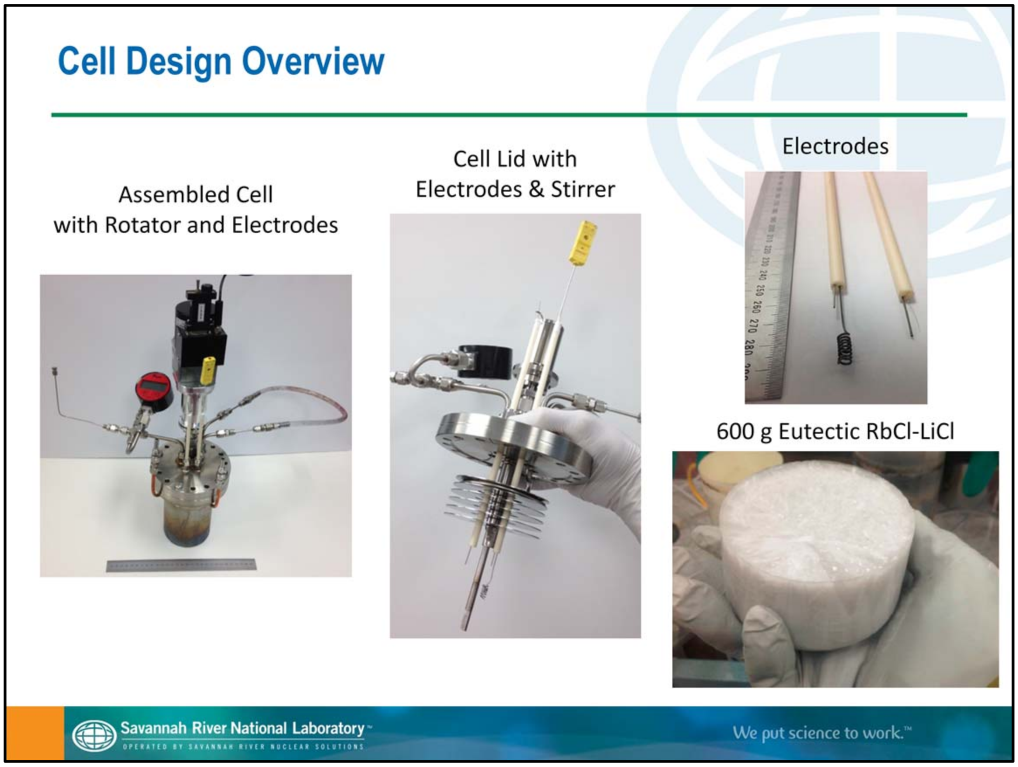
- We simulated adding LiF to see if it would significantly lower the amount of RbCl needed in the salt mixture to achieve a melting point of 450°C. The basic thought for considering this is that there may be advantages in terms of neutronics of having as large a fraction of lithium ions as possible in 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.



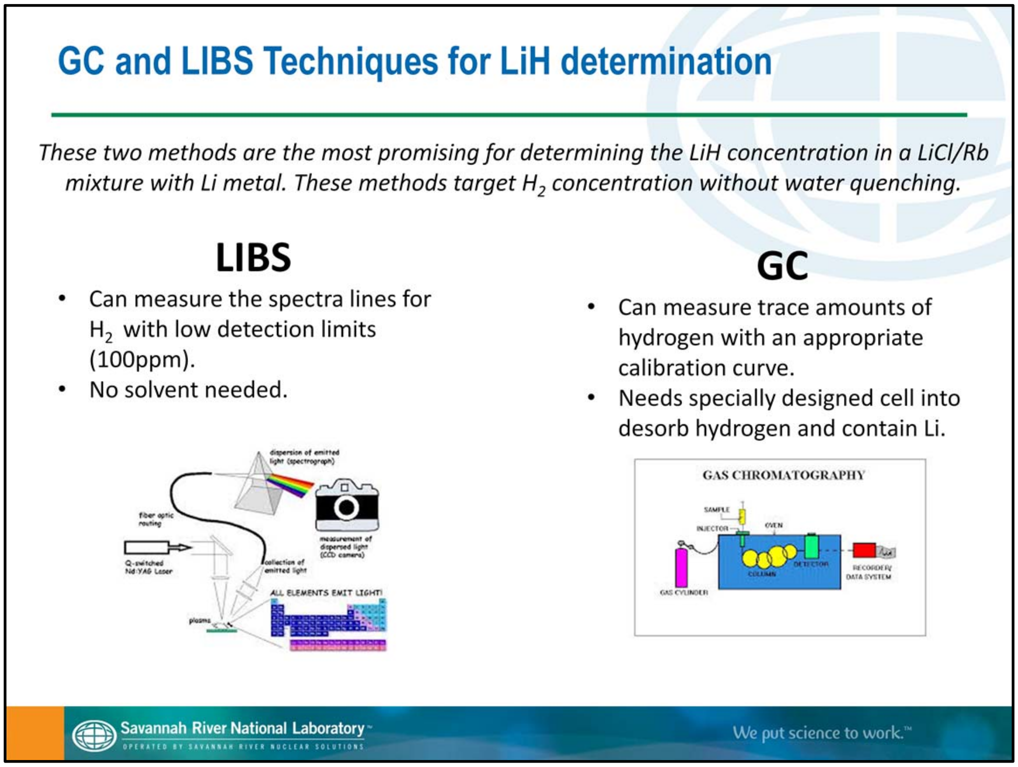
The research of SRNL has two main parts:

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.



- 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



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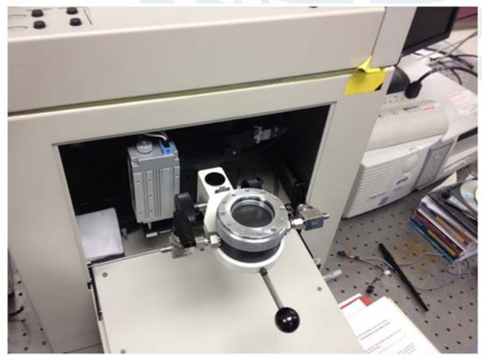
LIBS Instrument

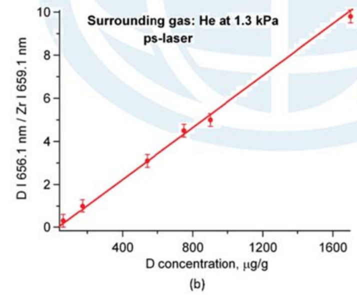
A laser ablation system was modified to act as a laser induced breakdown spectrometer.



- 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)

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



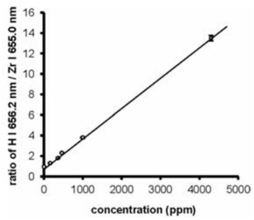


Figure 19. Calibration curve obtained from zircaloy-4 samples with error bars indicating deviations around 1.3%. Reprinted with permission from Kurniawan et al. (89). Copyright (2007) American Chemical Society.

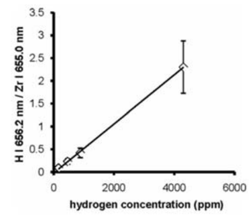


Figure 42. Calibration curve from zircaloy-4 samples of 0, 161, 461, 1,000, and 4,300 ppm hydrogen concentrations with the data obtained from the averaged results over 100 shots under +10 mm defocused condition. The gate delay and gate width of the OMA system were set at 5 and 50 μs, respectively. Reprinted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

Extra Slides