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Electrolytic Tritium Extraction in Molten Li-LiT

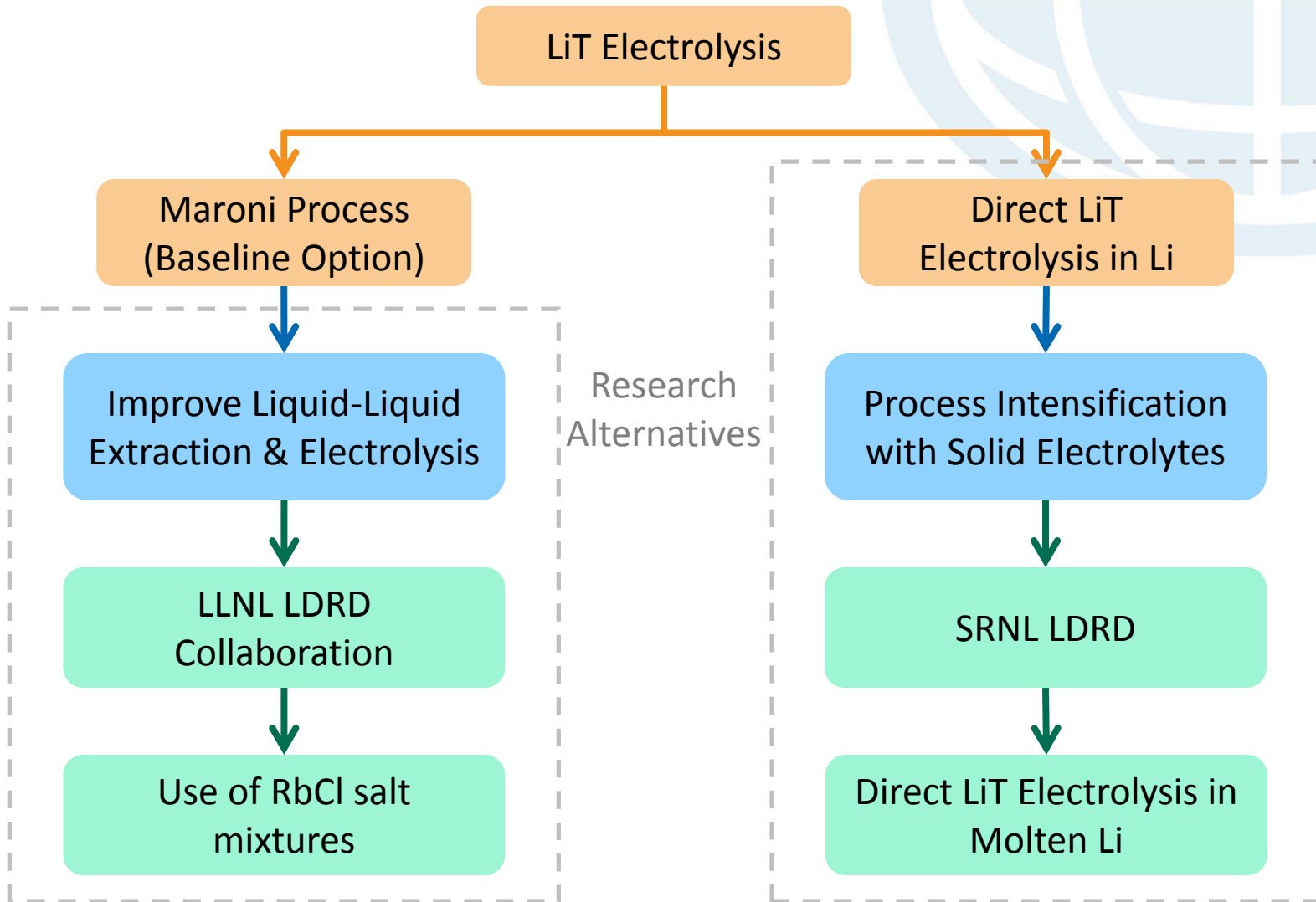
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SRNL-STI-2015-00605*



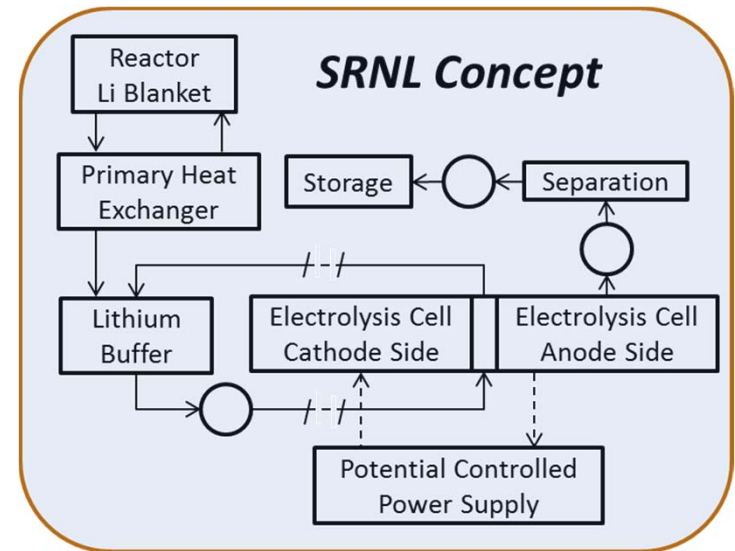
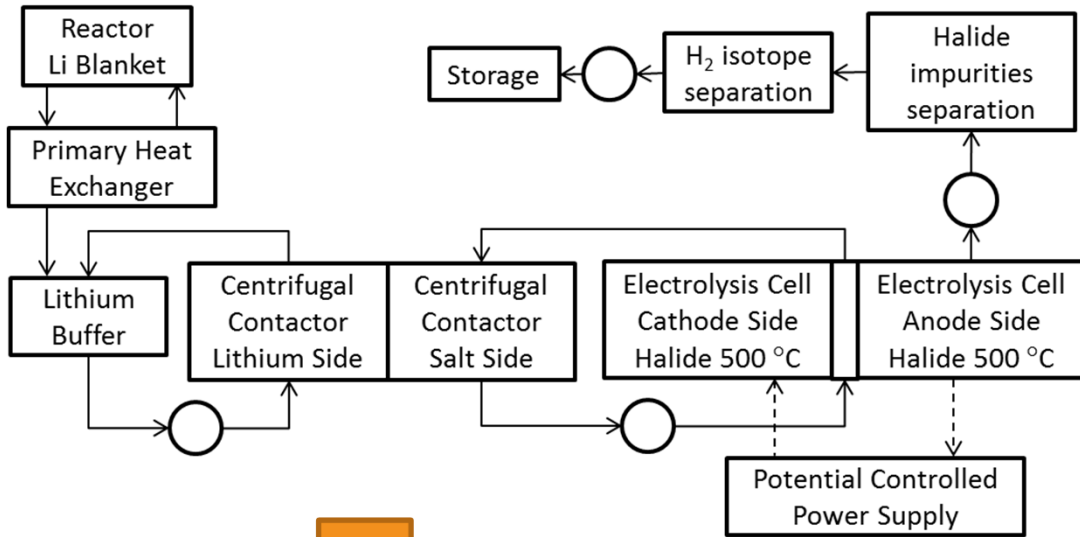
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LiT Electrolysis Options



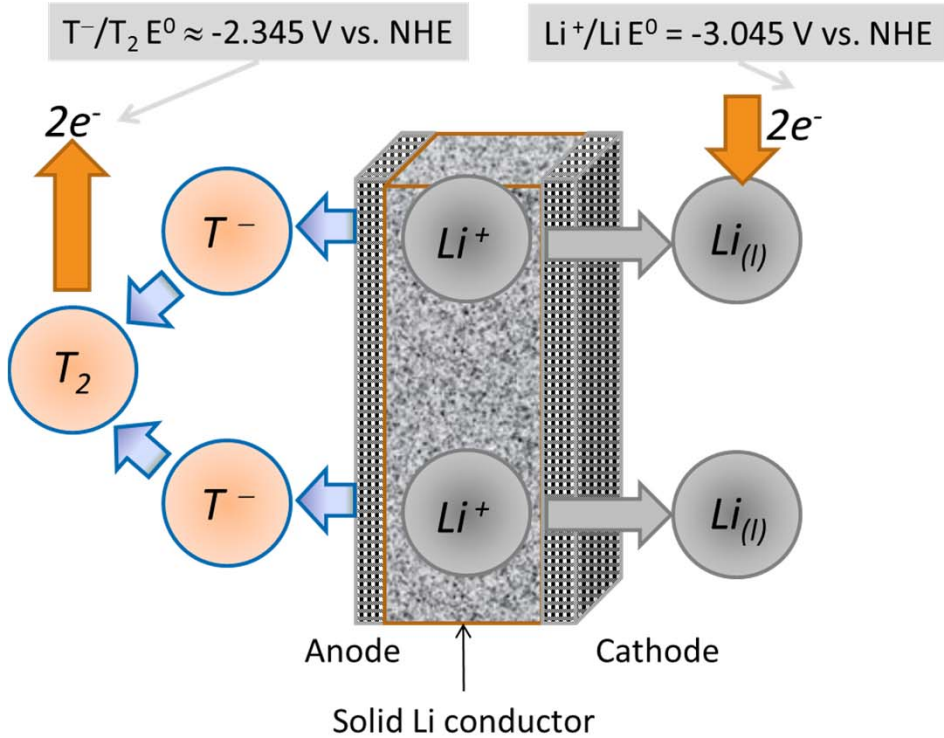
Tech: Approach: SRNL Direct LiT Electrolysis Concept

Maroni Process

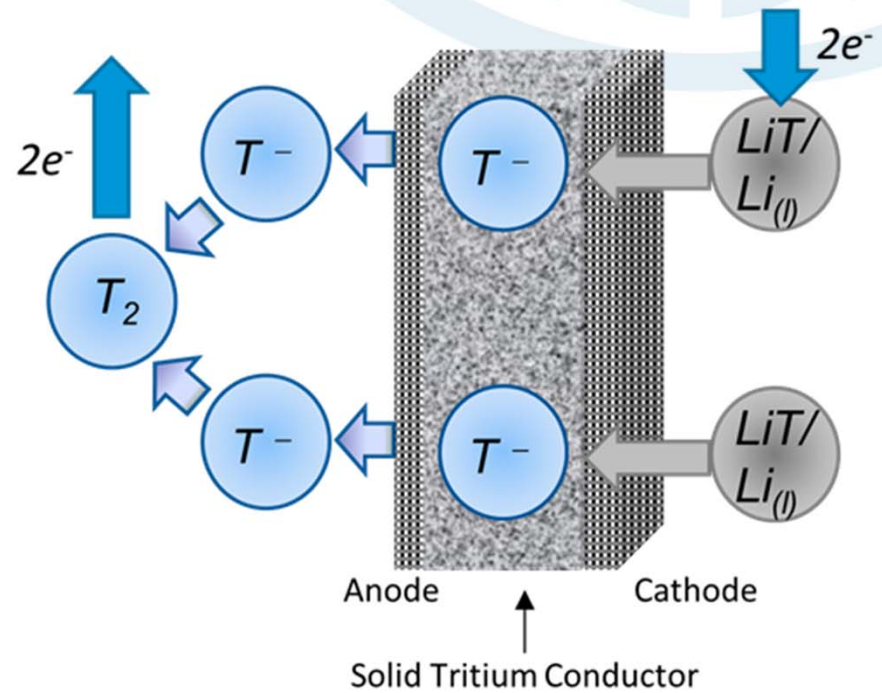


Tech. Approach: SRNL Solid State Conduction Process

Lithium Conducting Electrolyte

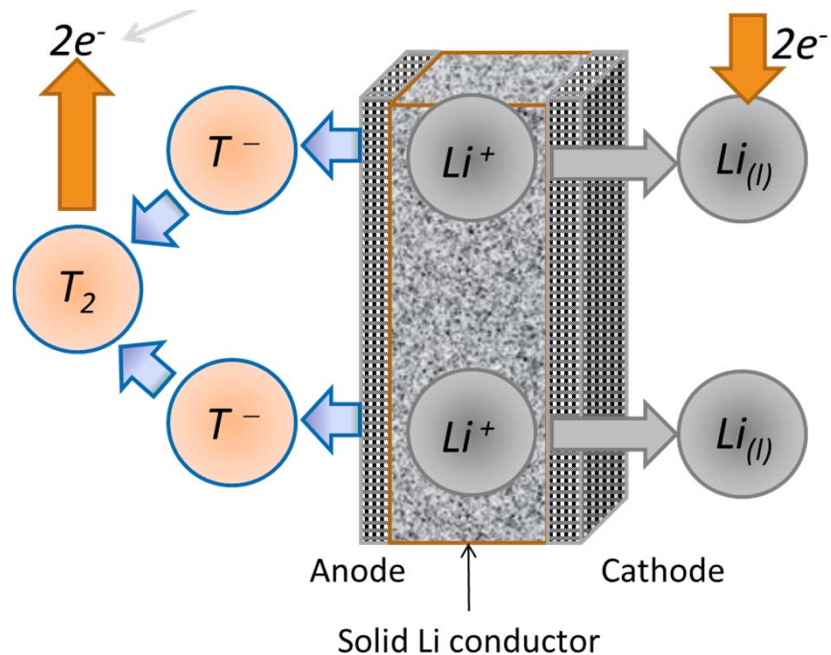
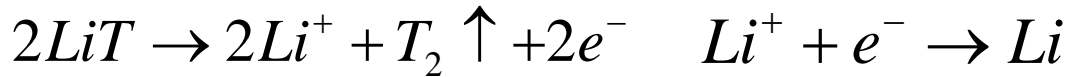


Tritium Conducting Electrolyte



Tech. Approach: SRNL Solid State Conduction Process

Lithium Conducting Electrolyte



$$E_{400^\circ C}^0 = -2.82V$$

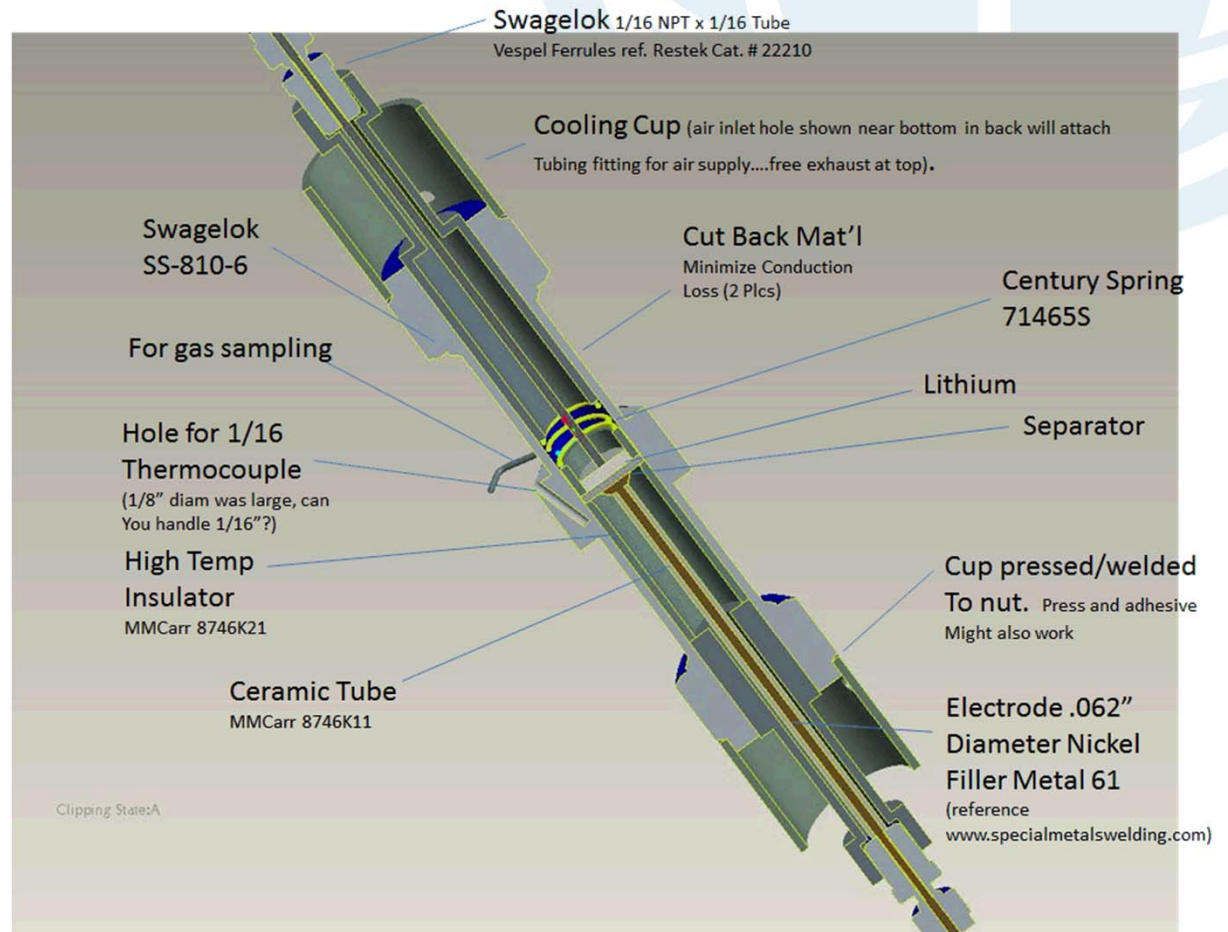
$$E_{400^\circ C}^0 = -3.22V$$

- Metallic Li means blanket material in electrolysis vessel becomes a large electrode
- LiT will be reacted at the rate at which hydrogen molecules encounter each other in blanket
- Rate of electrolysis will likely be faster than the rate at which molecules find metal electrodes in a molten salt system
- Parasitic current from Li reaction at 600 mV will likely only be 6 mA/cm² or 0.36 mW/cm² of reaction area for a 100 micron thick electrolyte with 0.0001 S/cm conductivity

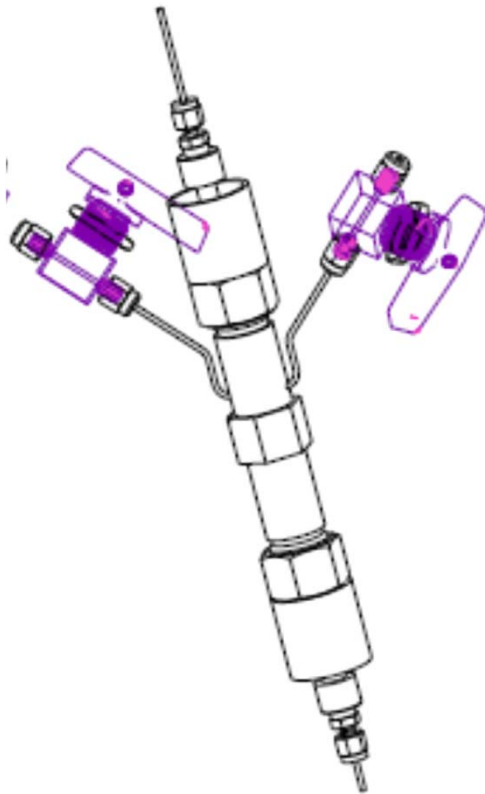


Results: High Temperature Cell Design

- 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



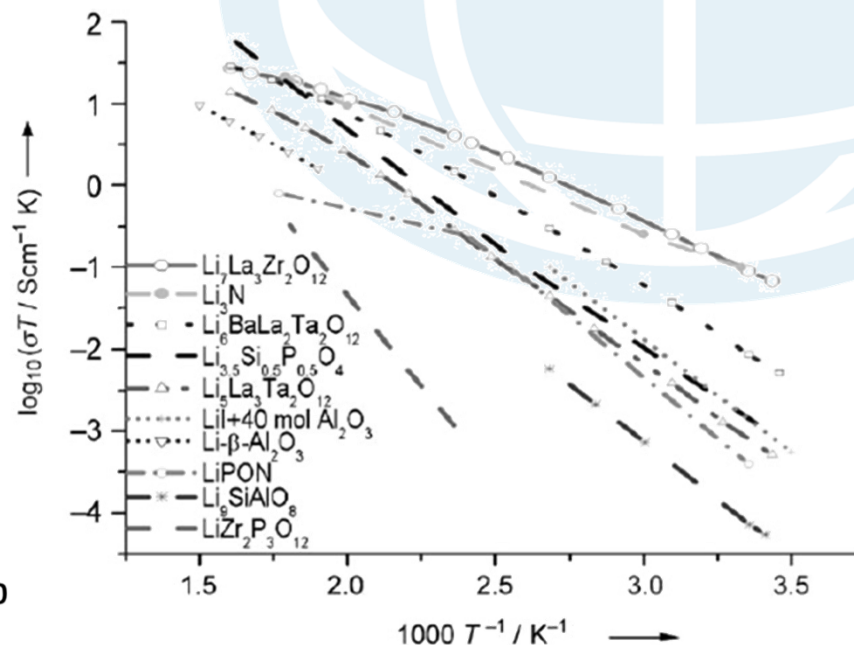
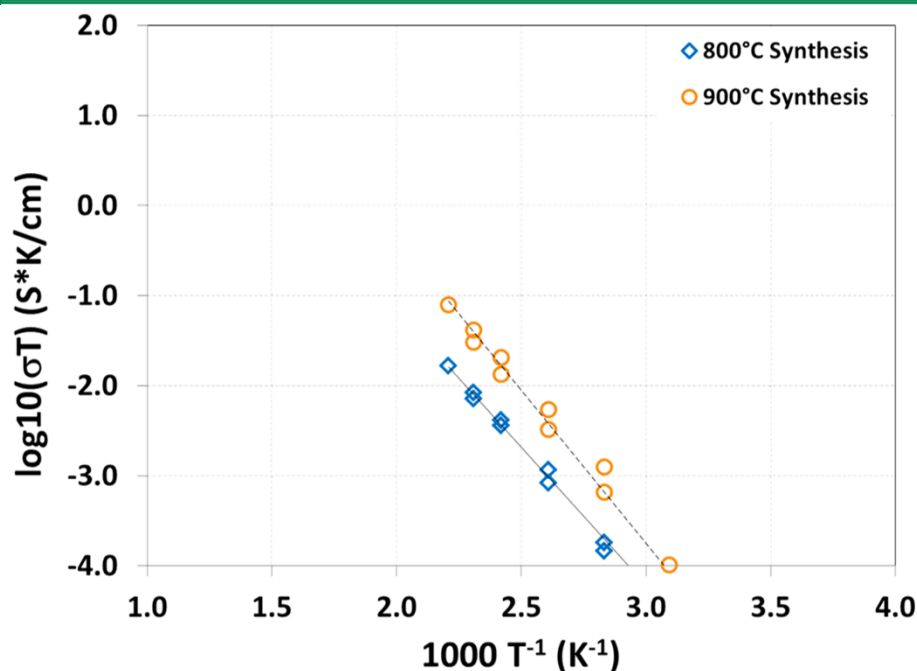
Results: High Temperature Cell Photographs



- 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



Results Comparison of LLZO Lithium Ion Conductivities

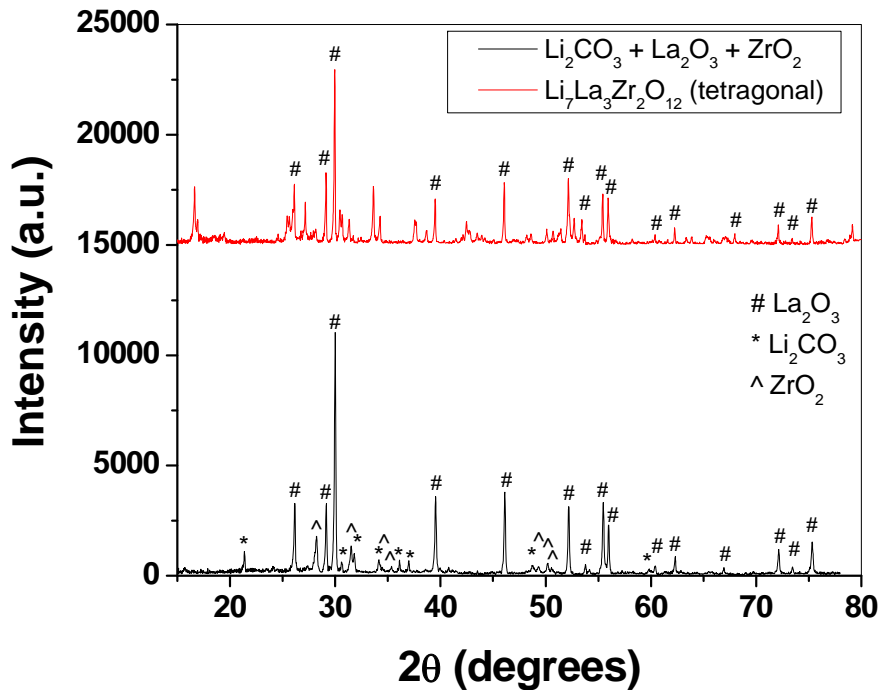


- Pellets have been synthesized by adapting literature methods using a Li_2CO_3 precursor for lithium in the solids
- An important step in the synthesis of lithium lanthanum zirconate is the sintering of the pellet
- Initial attempts with sintering temperatures of 800°C and 900°C have been attempted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



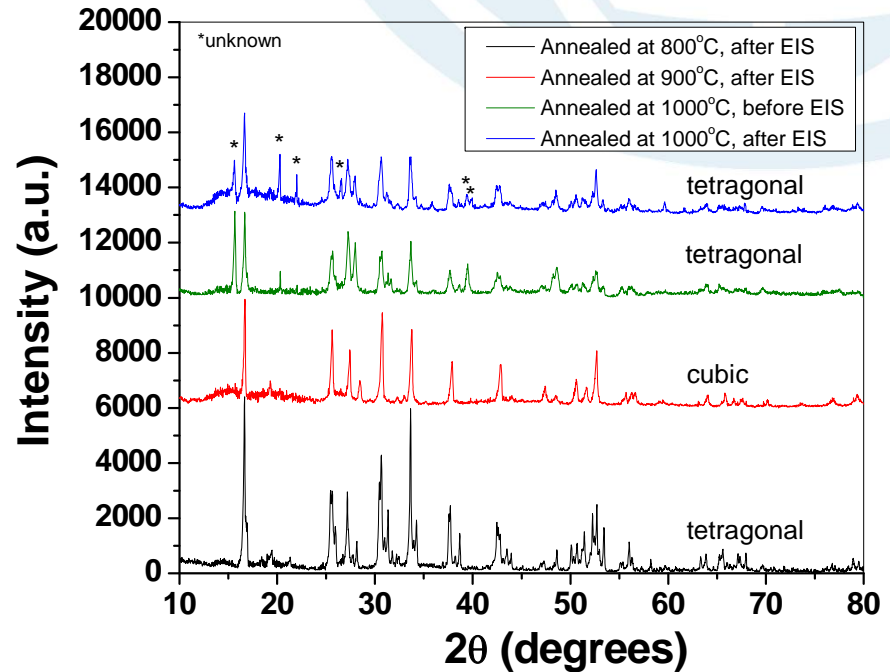
Technical Progress: XRD study of the electrolyte

Initial synthesis of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$



Excess La_2O_3 is present in the sample and is likely due to the loss of Li_2CO_3 during the annealing/synthesis process. In order to consume the excess La_2O_3 in the as prepared material, additional Li_2CO_3 was added to the pellets before the sintering step at 800-1000°C.

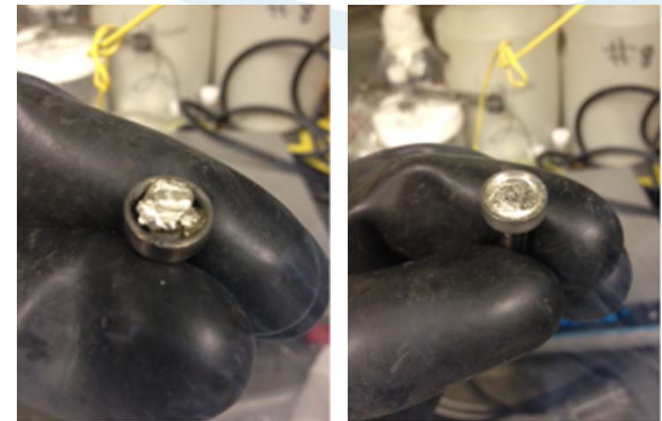
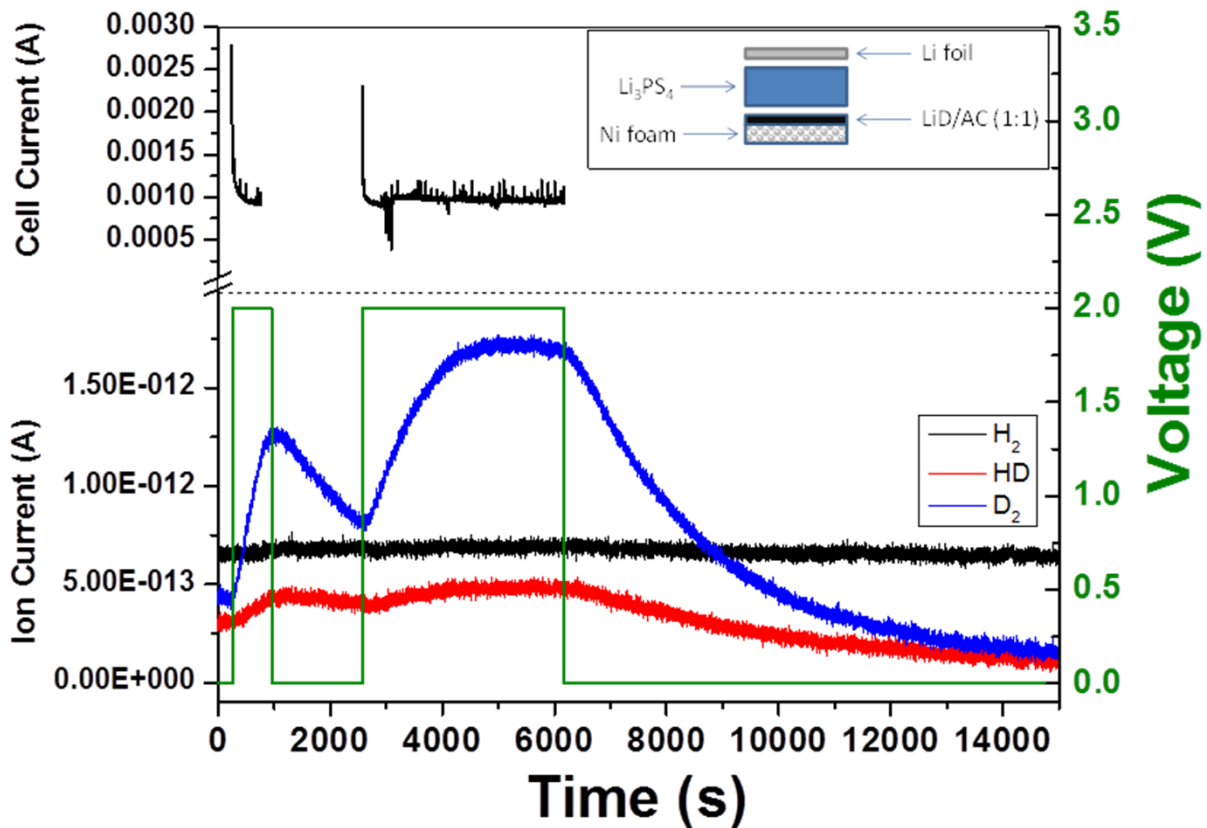
$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ before and after EIS measurements



The formation of the unknown phase after additional sintering of the pellets could be due to the incorporation of Al into the structure from the Al_2O_3 crucible used for the sintering process



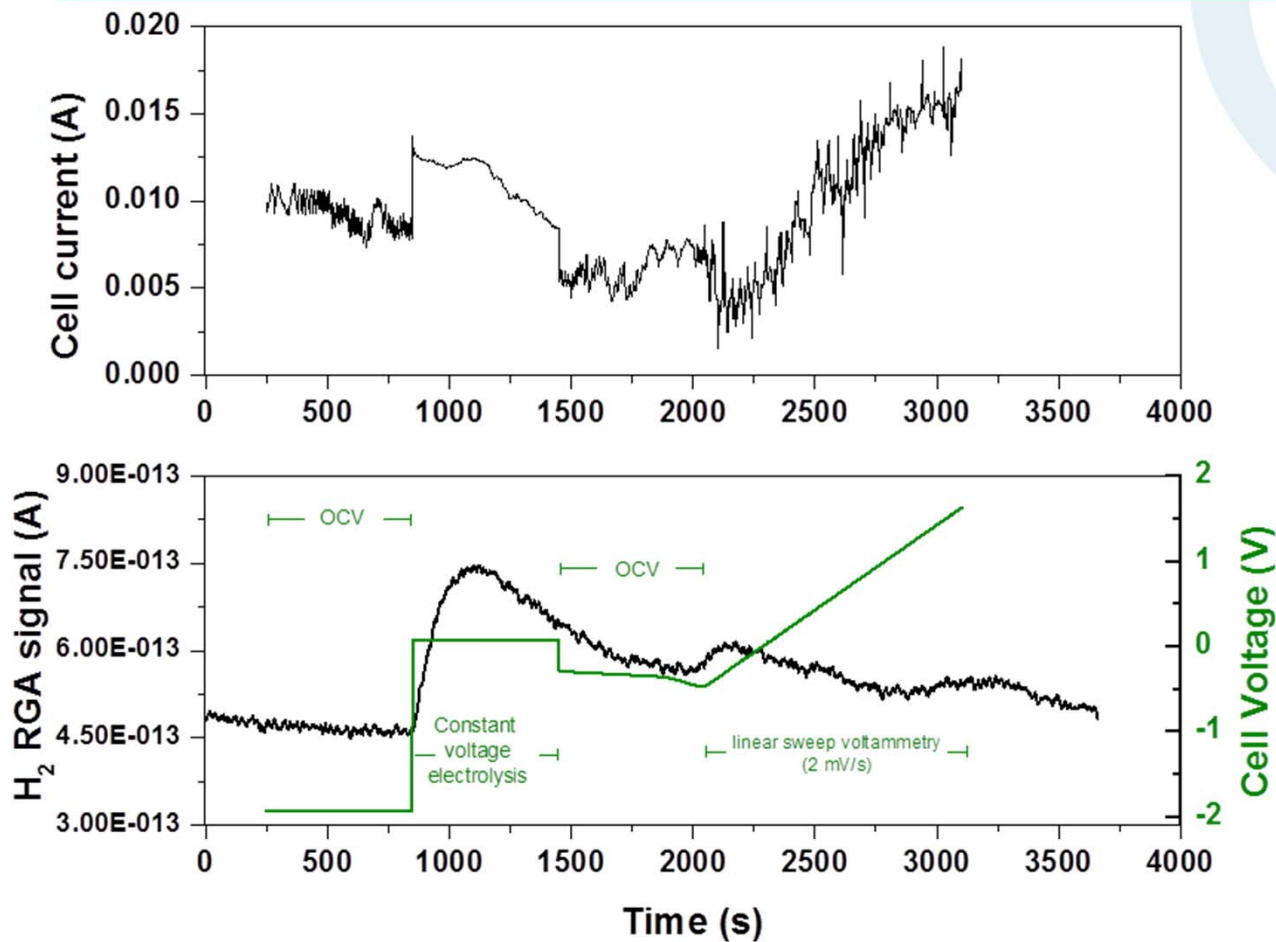
Achieving TRL 3 for the Electrochemistry



- Constructed cell for LiH electrolysis at conditions where Li is molten
- Showed that during electrolysis of LiH a signal in an RGA from H₂ is detected
- Electrodes and materials not degraded by cell operation



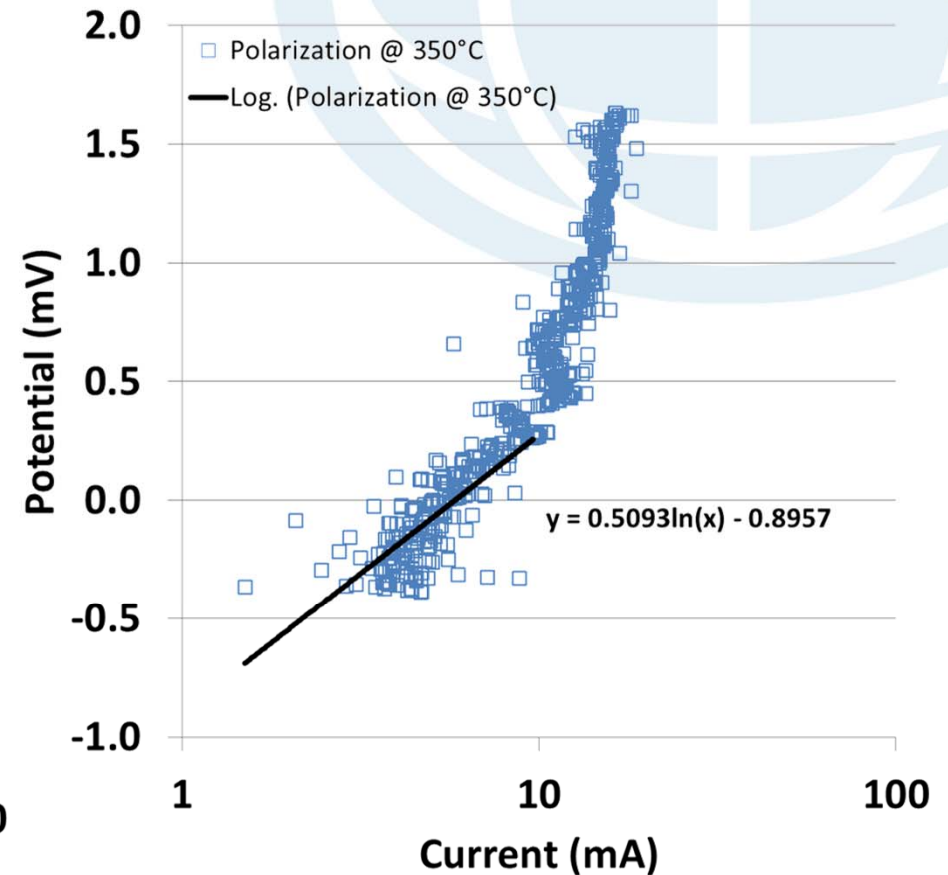
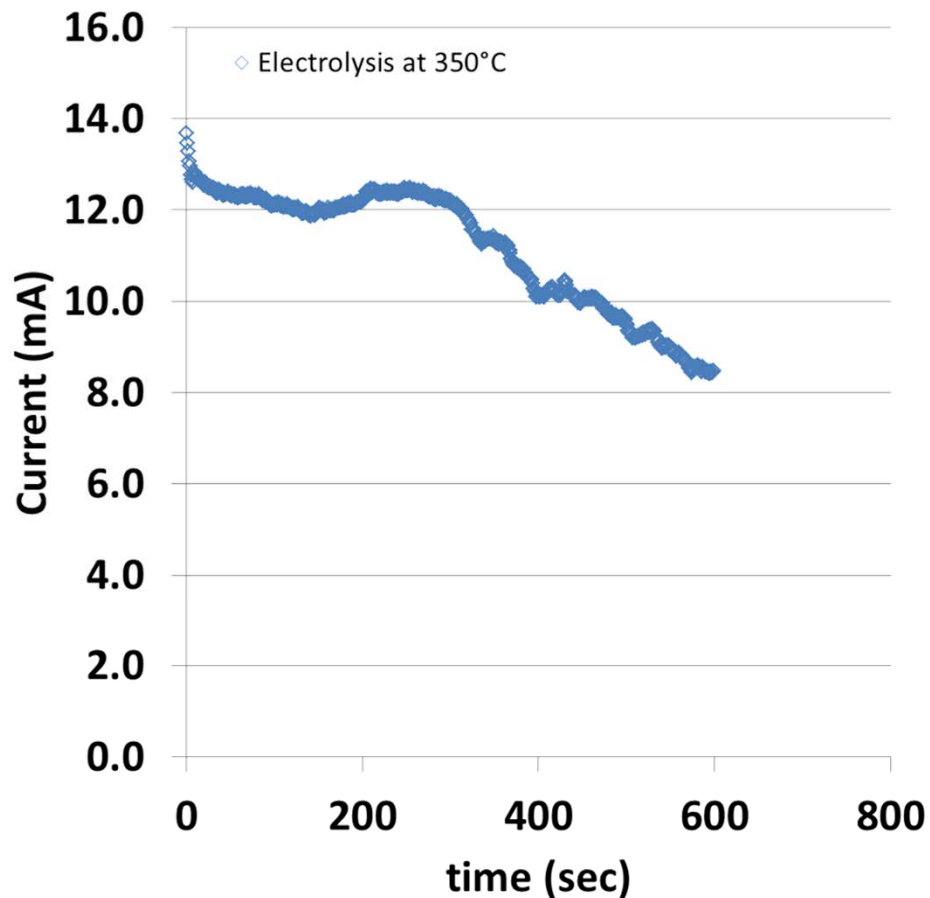
2nd Kinetics Characterization (Electrolysis First)



- Characterized the kinetics of the reaction in a second test
- The highest concentration of hydrogen came out near the start of the scan
- Electrolysis current was 12 mA



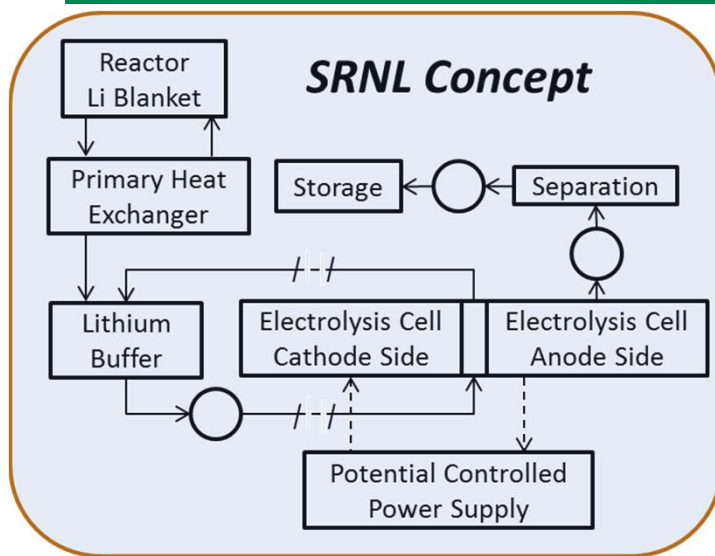
2nd Kinetics Characterization (Electrolysis first)



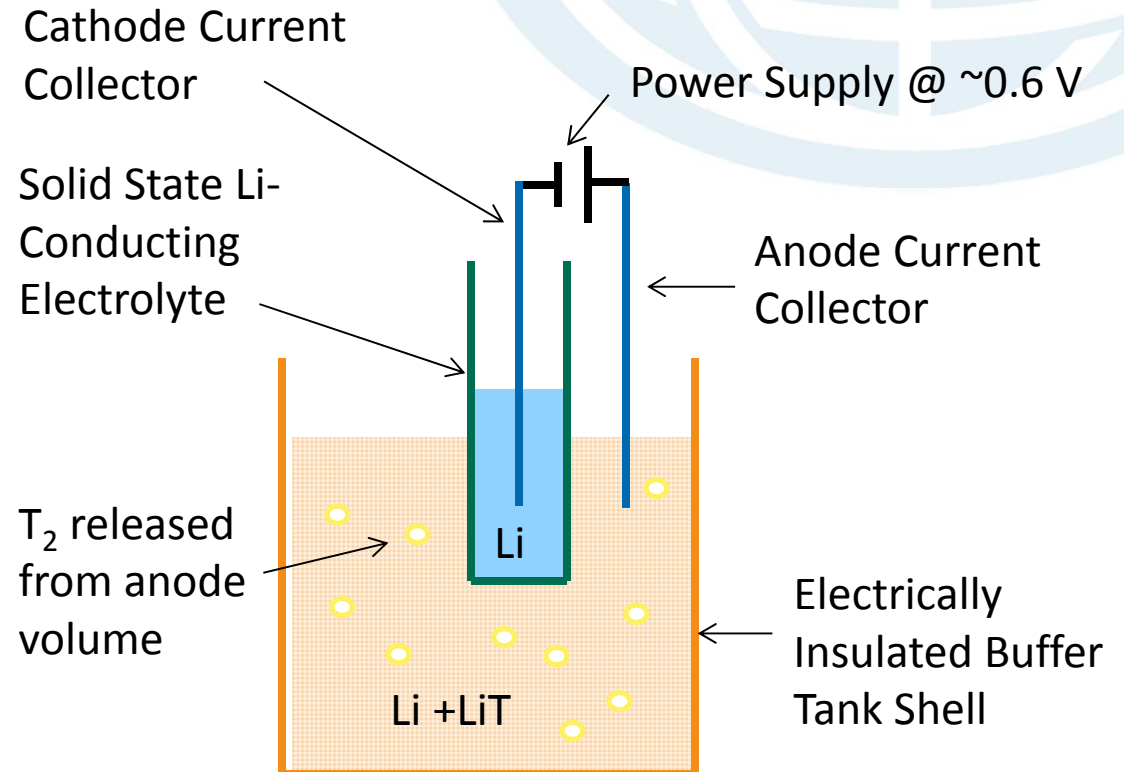
- Current increased quickly to over 10 mA
- Electrode potentials much more equal after 10 minute electrolysis due to Li transport
- Exchange current of 2.4 mA and current reaches plateau near 16 mA due to conduction



Tech: Approach: SRNL Direct LiT Electrolysis Concept



Lithium Buffer Tank



1. Step 1: Electrolyze LiT through reaction in the volume
2. Step 2: Transport Li cathode material back to bulk through flow or reverse reaction
3. Step 3: Repeat cycle



Process Modeling of LiT Electrolysis Scale-Up (1 tonne/hr)

LiT Conc (ppm)	Cell Voltage (V)	Electrolyte Conductivity (S/cm)	Electrolyte Thickness (cm)	Cell Area (cm ²)	Cell Power (W)	Li Transported (g/hr)	T ₂ Produced (g/hr)
1	1	0.0001	0.01	900	9	2.34	0.303
100	3	0.0005	0.01	6000	2700	234	30.3
1000	3	0.001	0.005	14000	25200	1474	303
10000	3	0.005	0.005	30000	270000	16287	3029

- Process modeling was performed to understand the energy requirements and electrode areas needed for decomposing different concentrations of tritium
- Looked at increasing LiT concentrations from 1 – 10,000 ppm of LiT and assumed incremental improvements in LiT cell properties that would be expected when moving to larger systems with more regular production
- The electrode area and power increased, but were not values that are unreasonably large for the amount of tritium being produced
- With LiT concentrations of 10,000 ppm, it would take 270 kW of power to produce 75 kg per day of T₂



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

