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Fuel Cycle Research and Development

Ion-Selective Ceramics for Mixed Waste Separations

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Oak Ridge National Laboratory
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Research Team at SNL

- **Erik Spoerke (PI, KSICON lead)**
  - Jill Wheeler (Technologist, NaSICON synthesis)
  - Leo Small, Ph.D. (Post-doc, electrochemist)
- **Jon Ihlefeld, (LLTO lead, electronic ceramic characterization)**
  - Mia Blea (Technologist, LBLTO synthesis)
- **Harlan Brown-Shaklee (Ceramic Processing)**
- **Mark Rodriguez (XRD)**
- **Amy Allen and Bonnie McKenzie (SEM)**

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Salt Purification for Pyroprocessing

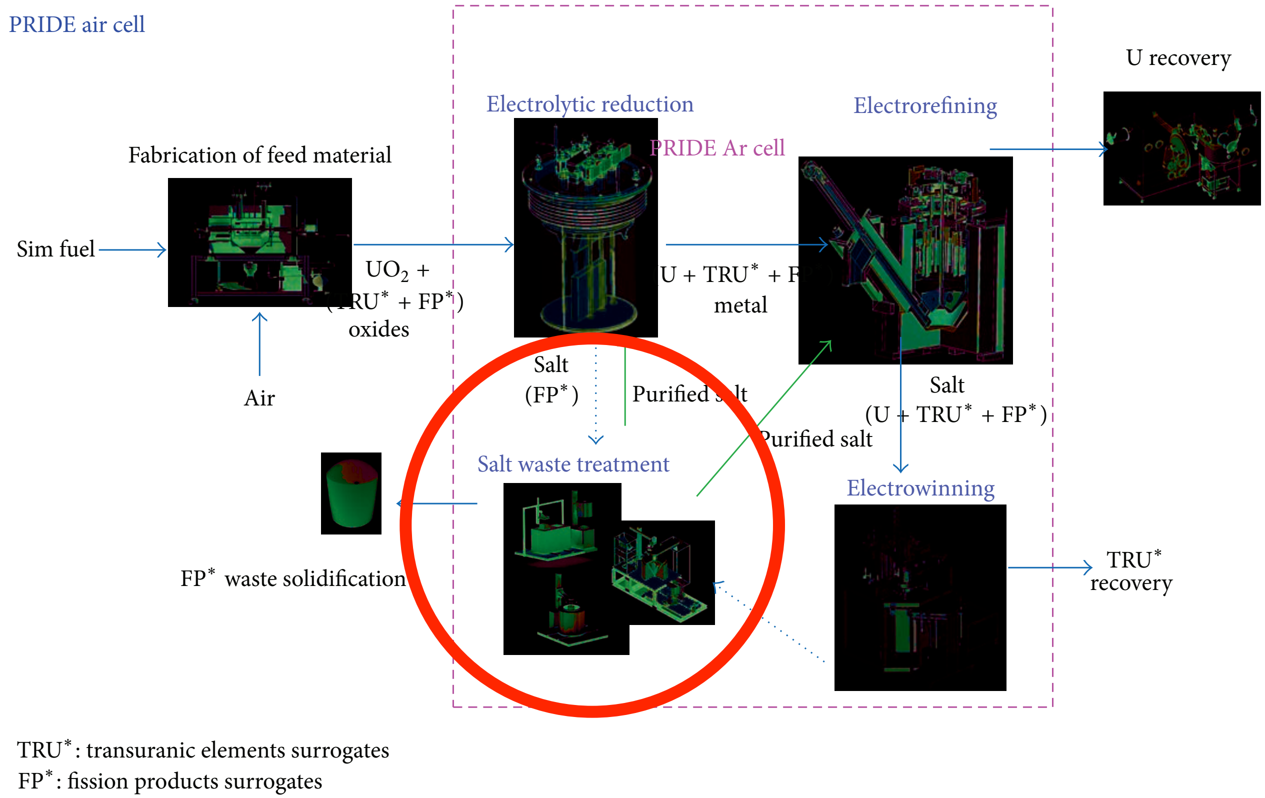
Pyroprocessing is a promising technology to electrochemically recycle nuclear fuel.

This process is based on coordinated oxidation and reduction reactions to separate and extract target recyclable elements.

<u>Consider the Electrorefiner:</u>

Uranium is electrochemically oxidized (anode) and dissolved into a eutectic KCl-LiCl molten salt 56 wt% KCl, 44 wt% LiCl) .

Uranium is then reduced at the cell cathode where it can be collected and processed into a purified product.



Lee, H. et al. Current Status of Pyroprocessing Development at KAERI. Sci. and Tech. Nuc. Install. ***2013****, 1-11 (2013).*

Motivation: Recycling LiCl-KCl Molten Salts

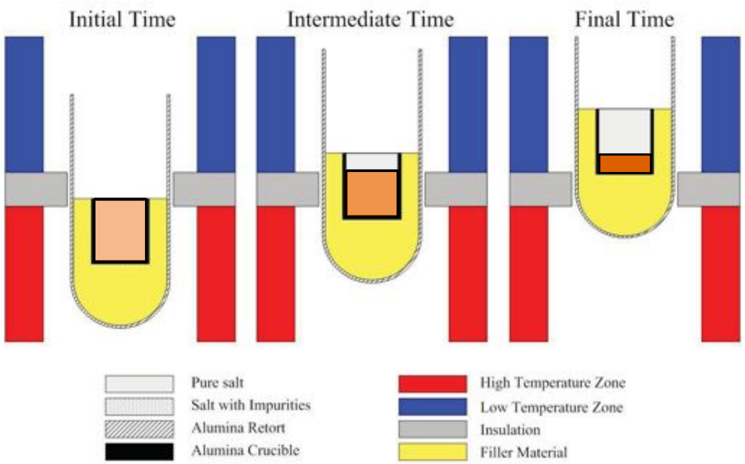
- **The accumulation of waste products (e.g., fission products, transuranics, etc.) in KCl-LiCl molten salt can impact the electrorefining process.**
  - Changes in ionic conductivity (important for efficiency uranium ion transport)
  - Changes in eutectic melt properties
- **Removing waste products from the salt:**
  - Key to recycling high conductivity salt electrolytes
  - Stands to significantly reduce waste volume (reduction of HLW)
- **There is significant interest in removing "short-lived" hot fission products such as Sr and Cs.**

Current Molten Salt Purification Approaches

Ion extraction with alumino-silicate zeolites (e.g., Zeolite 4a)

www.molecularsieve.org/image/Zeolite_Molecular_Sieve_4A.gif

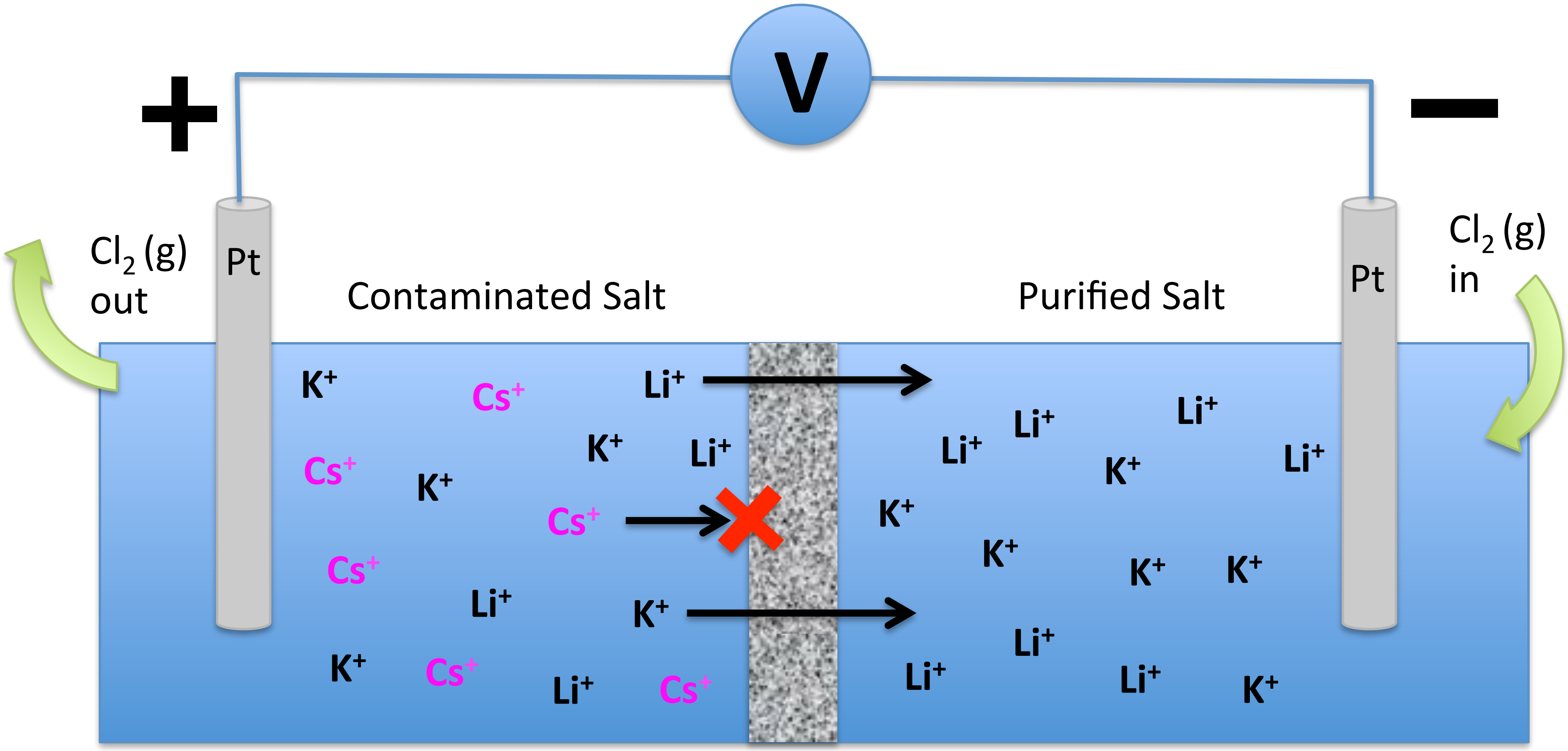
Zone Freezing



Williams, A. Zone-Freezing Study for Pyrochemical Process Waste Minimization Master of Science thesis, University of Idaho/Idaho National Laboratory, (2012).

We are exploring an alternative electrochemical approach to Cs^+ from LiCl-KCl eutectic molten salts.

Electrochemical Approach to Salt Purification



$$2Cl^- \rightarrow Cl_2 + 2e^-$$

$$Cl_2 + 2e^- \rightarrow 2Cl^-$$

Ion Conducting Ceramic Selection

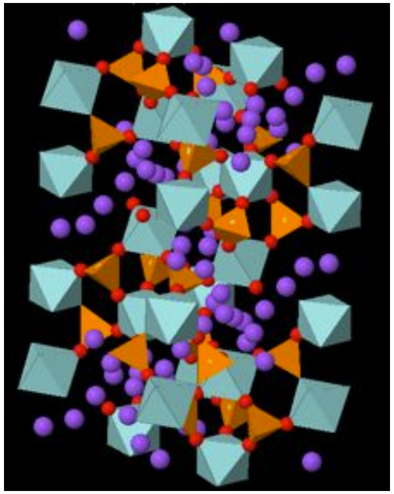
- **Critical Criteria:**
  - **High Li^+ and K^+ conductivity**
  - **Selectivity against Cs^+ transport**
  - **Chemical, electrochemical, and structural stability in molten LiCl-KCl**
  - **Temperature stability (> 500^{o}C)**
  - **Radiation resistant**

FY13 Progress Summary

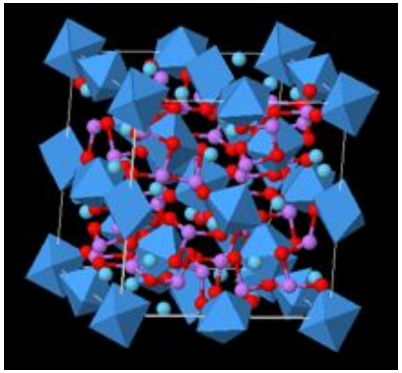
- Electrochemical salt purification scheme developed.
- Successful synthesis of KSICON and LBLTO ion conductors.
- Both ceramics demonstrate promising stability against molten salts between 400^{o}C to 500^{o}C.
- Preliminary data indicate selectivity against Cs transport for both ceramics
- Initial impedance data show promising potassium conductivity in KSICON samples
- Prototype test equipment was identified to enable electrochemical testing of candidate ceramics.

Candidate Ion Transport Ceramics

- **"NaSICONs" – Super Ion CONductors (e.g., KSICON: $KZr_2P_3O_{12}$)**
  - Lattice is chemically, structurally flexible
  - High conductivity ~10^{-4} S/cm at room temperature (modified versions as high as 10^{-3}) in NaSICON
  - Expected to be stable against molten salts
  - Designed to facilitate Li^+ and K^+ transport



- **LLTO – Garnet structured Lithium Lanthanum Tantalates ($A_5La_3Ta_2O_{12}$)**
  - Chemically flexible lattice
  - Favors Li^+-transport; conductivity (~10^{-5}-10^{-4} S/cm) at room temperature



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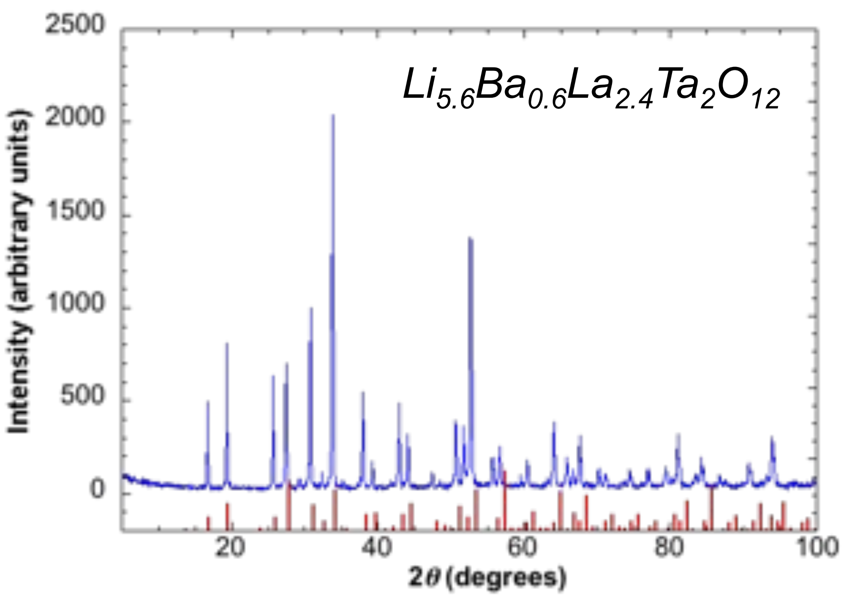
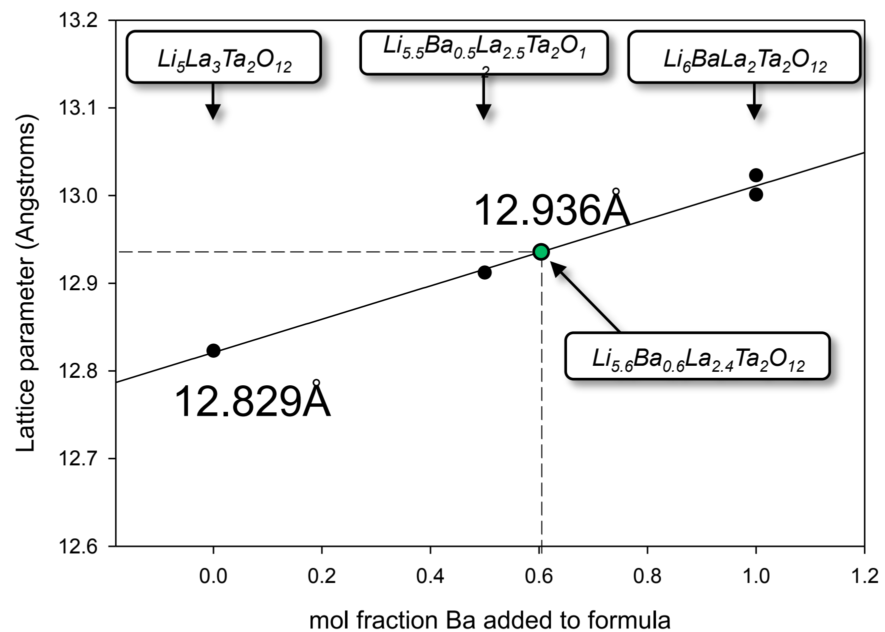
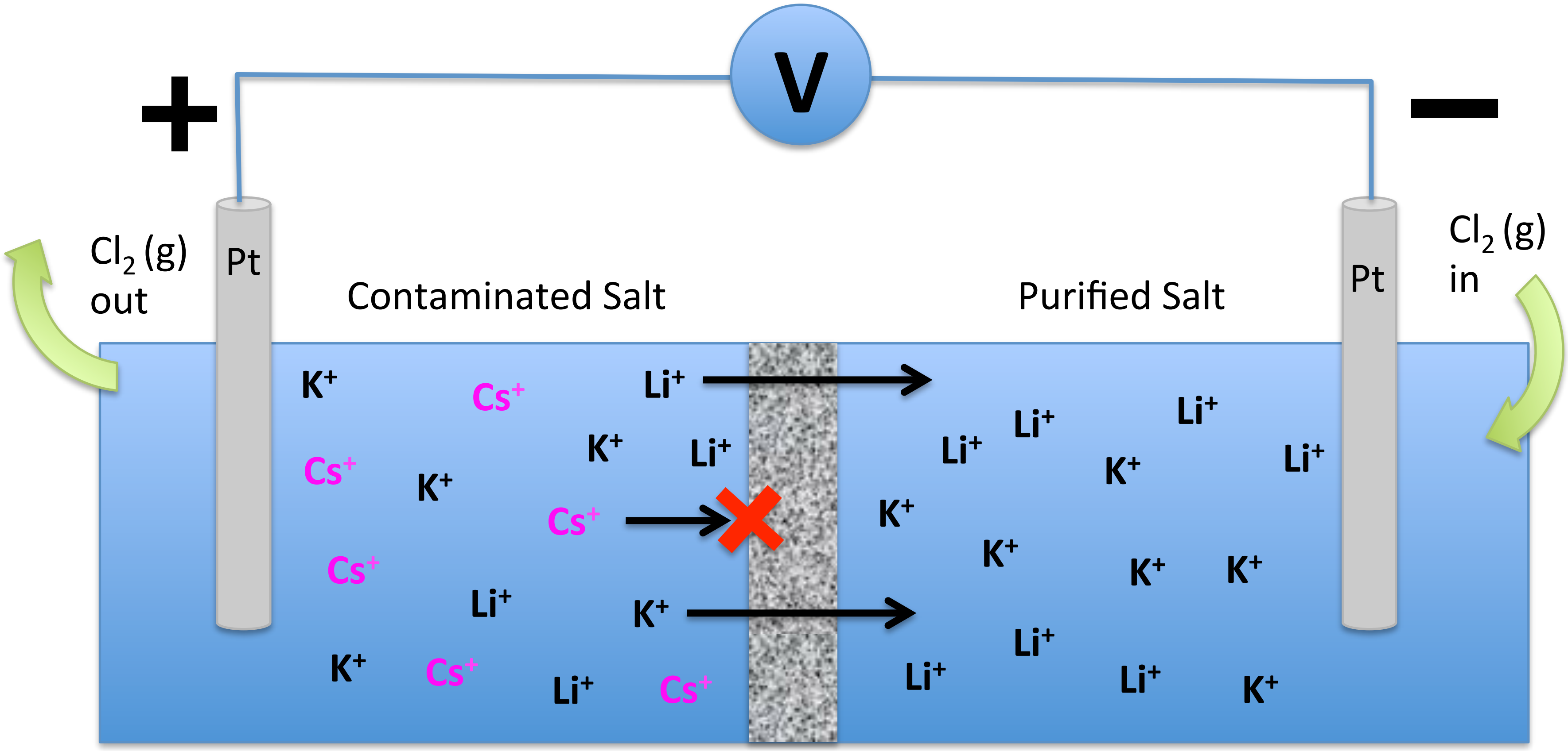
Ba-substitution: LBLTO

- **LBLTO: $Li_6BaLa_2Ta_2O_{12}$**
  - Substitution of Ba^{2+} (r =1.49Å) for La^{3+} (r =1.174Å) expands the crystal polyhedra, and makes ion transport more favorable.
  - Expanded lattice may also promote K^+-transport.





Chlorine Chemistry at 500°C Poses Significant Materials Compatibility Challenges



$$2Cl^{-} \rightarrow Cl_2 + 2e^{-}$$

$$Cl_2 + 2e^{-} \rightarrow 2Cl^{-}$$

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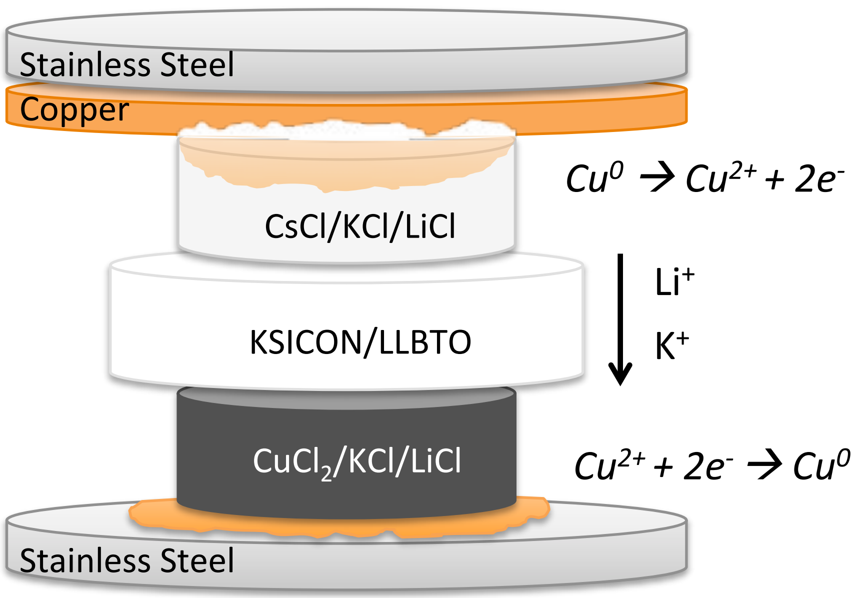
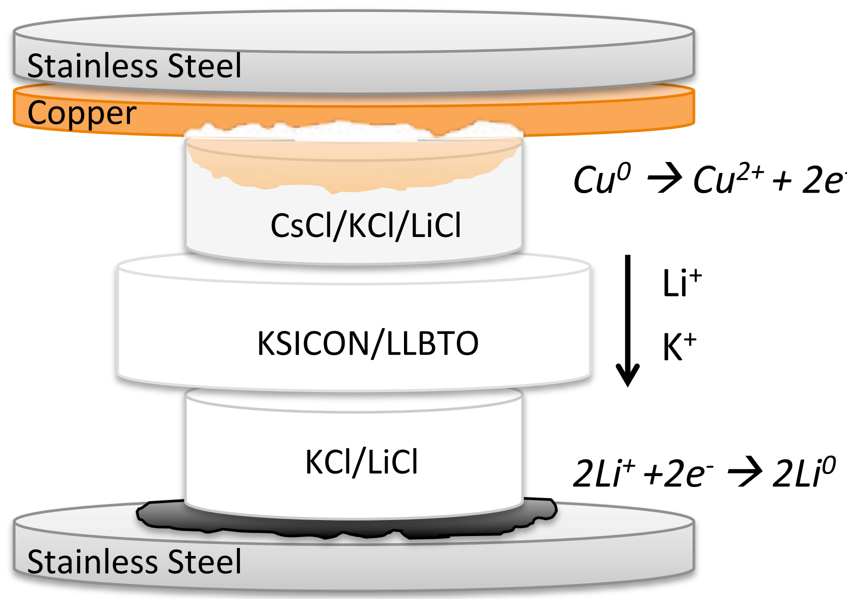
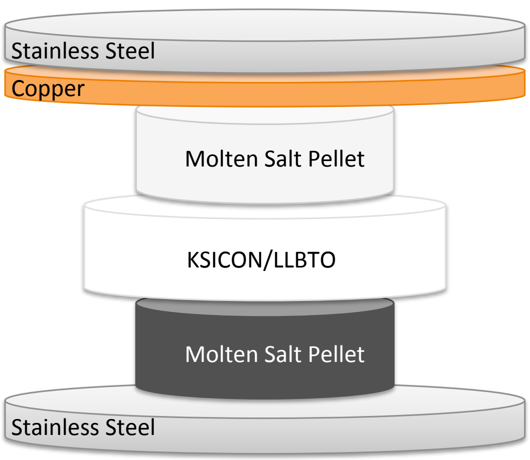
Consider a "Safer" Alternative

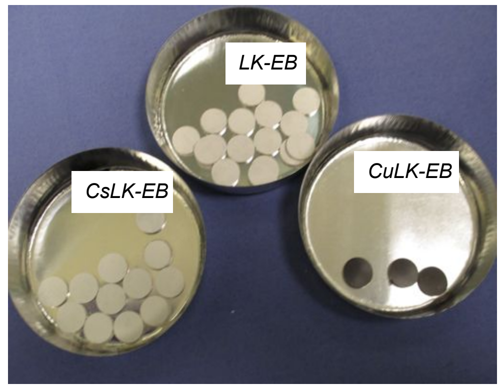
Pellet stacks with Cu-substitution for chloride charge balance equation.

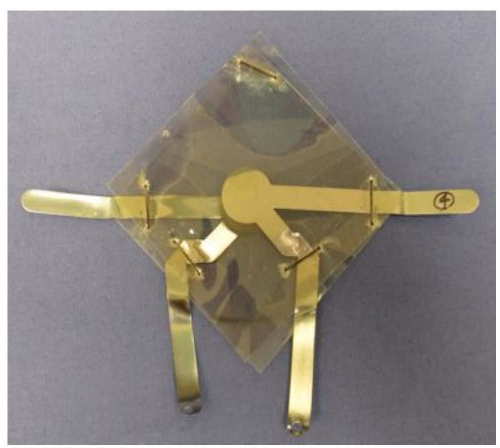




Pellet Stack Test Configuration

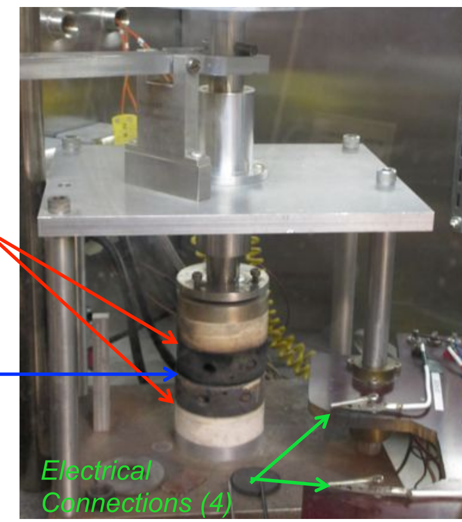




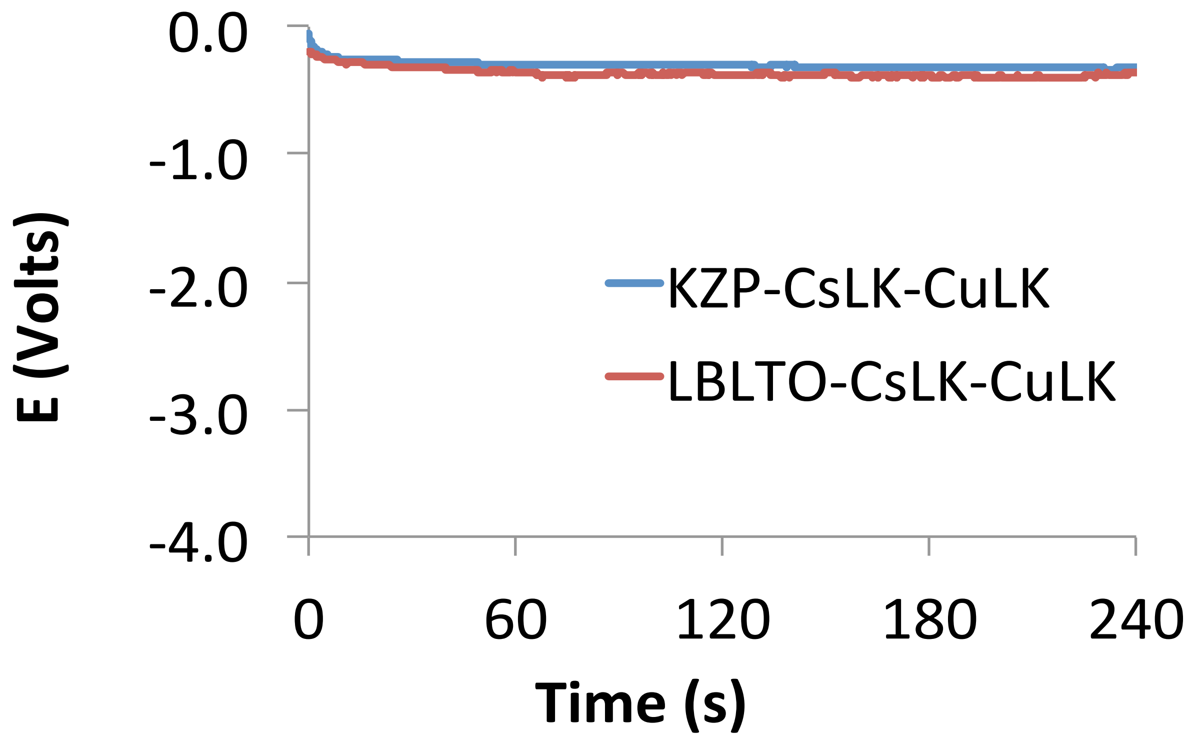


Heated platens (500^{o}C)

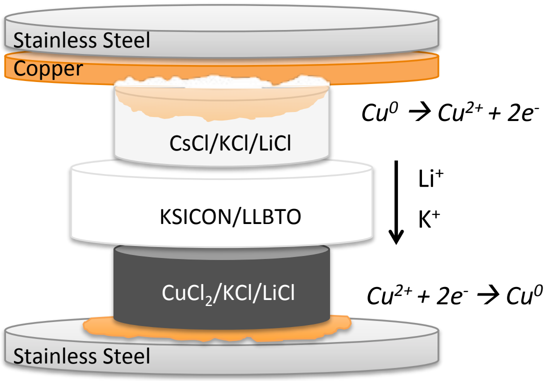
Pellet stack inserts here

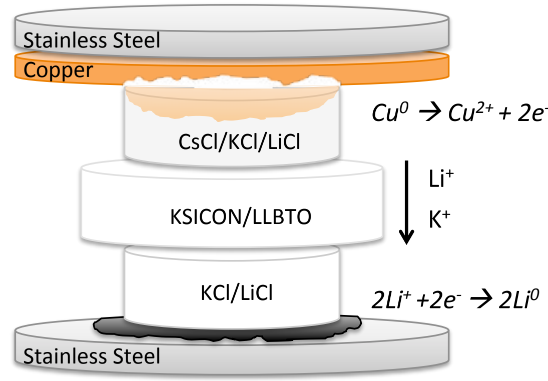


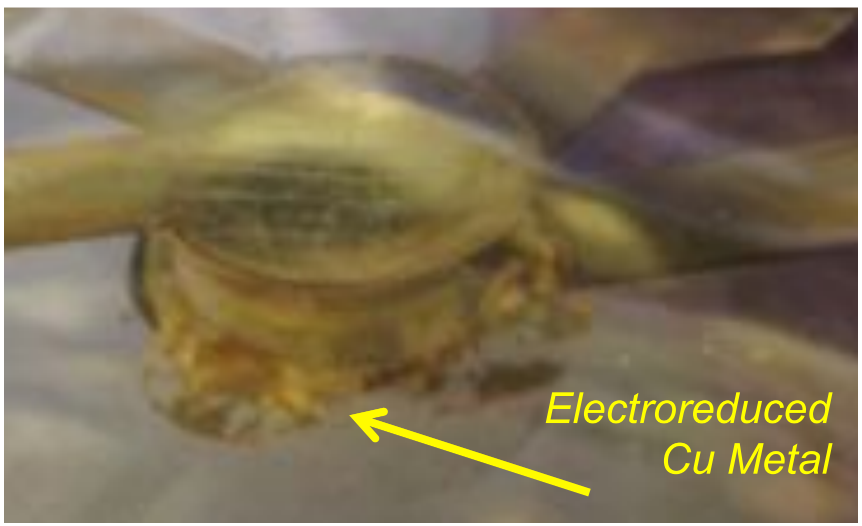
Galvanostatic Discharge through KSICON and LBLTO Ceramics

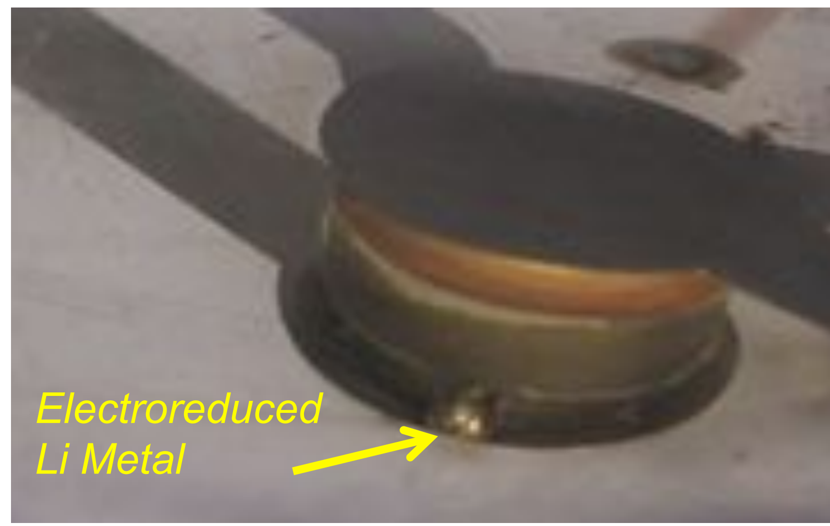


Material Transfer on Galvanostatic Discharge

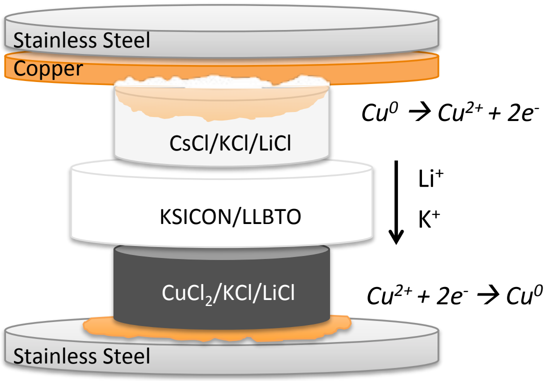


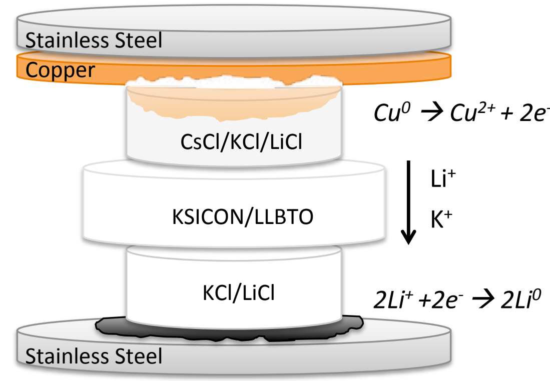


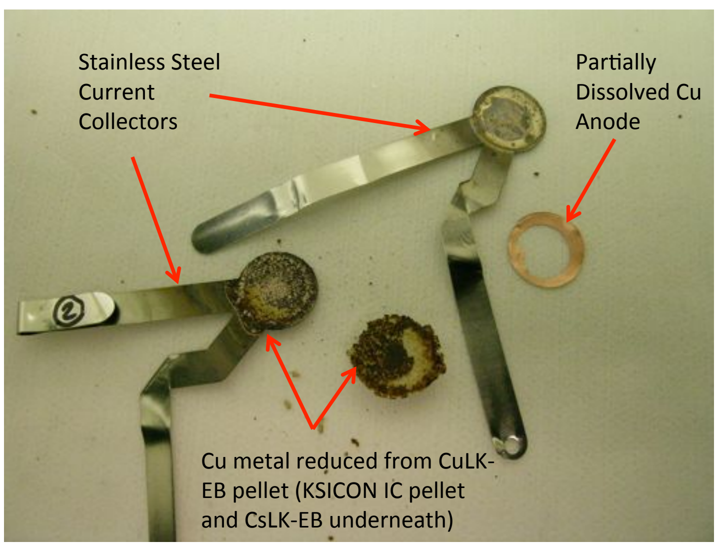


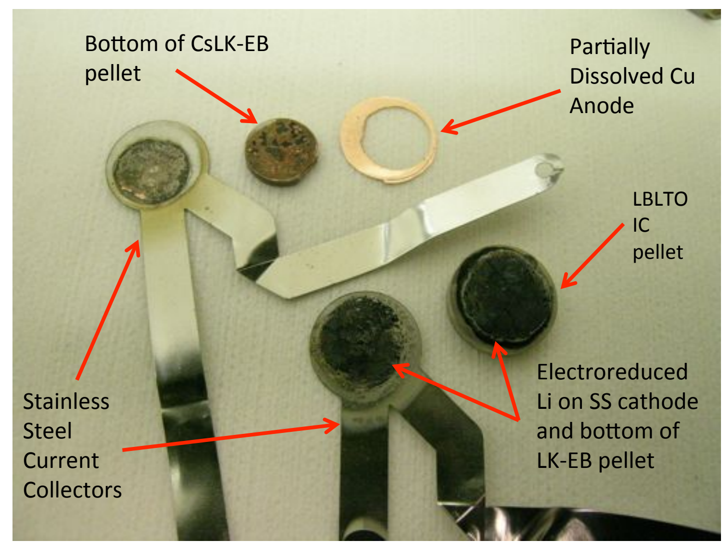


Macroscopic Material Transfer on Galvanostatic Discharge



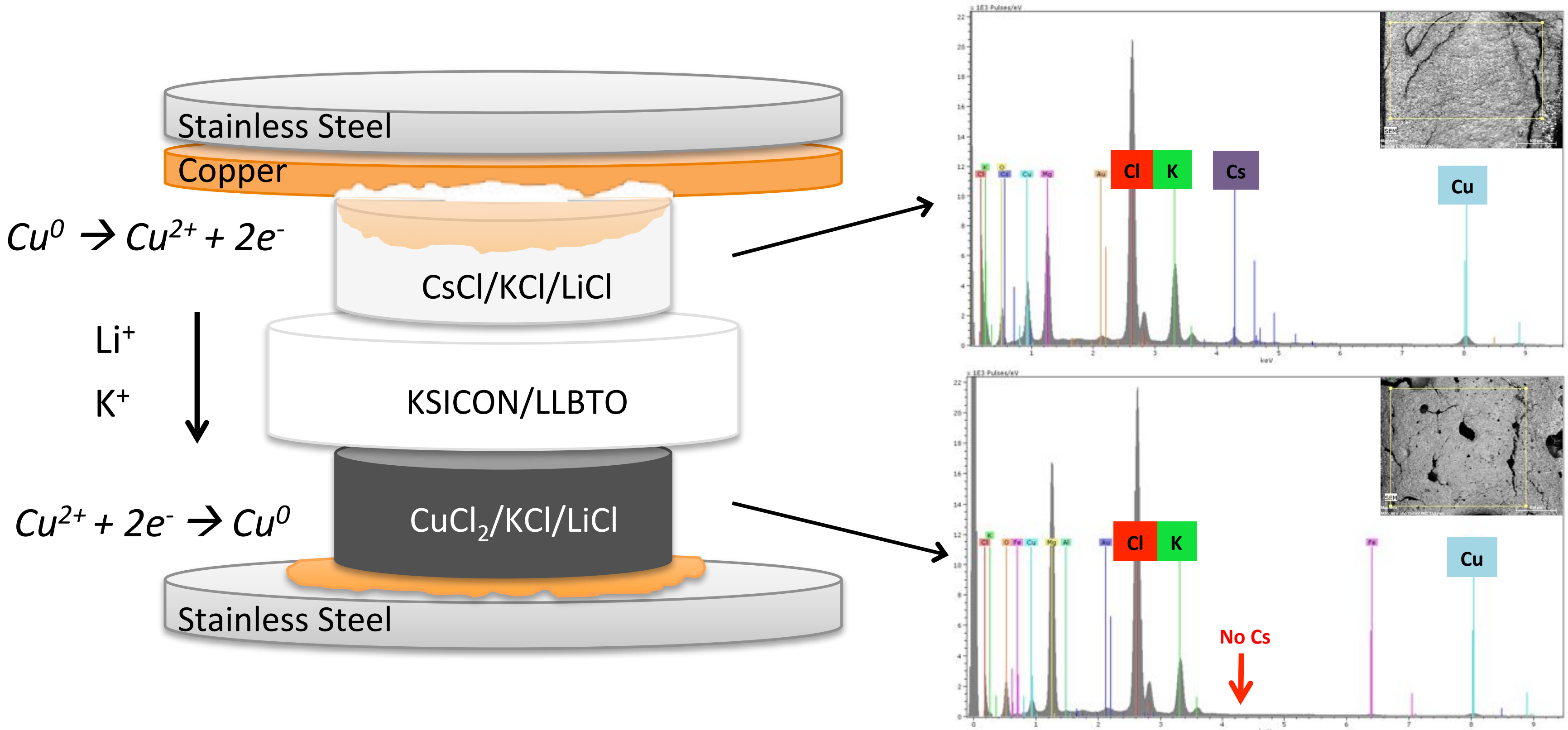






Molten Salt Analysis

Energy dispersive x-ray analysis of molten salts post-discharge reveals effective Cs^+ ion-filtration.



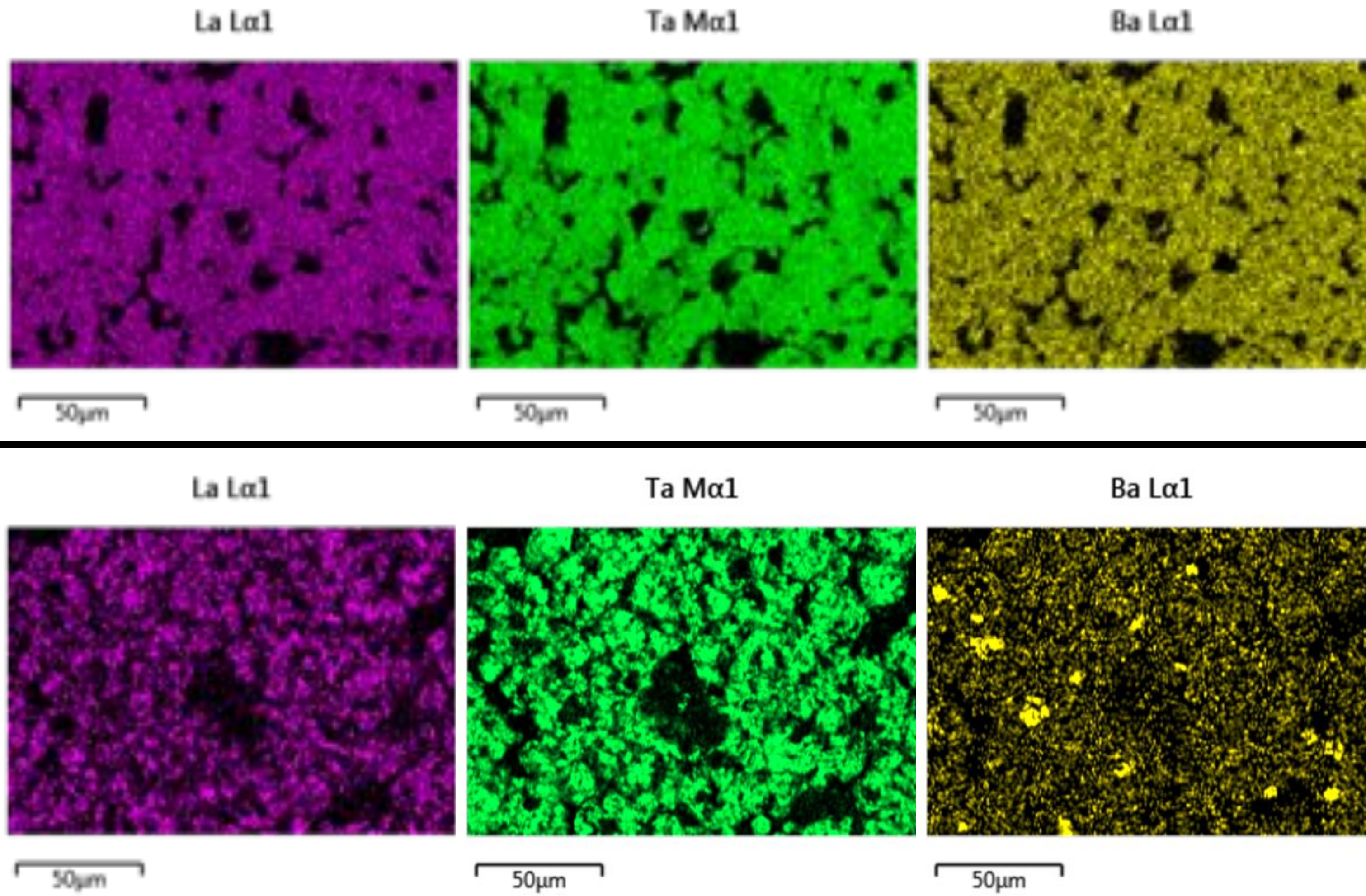
ICP Confirmation of EDXS Selectivity

	Li	K	Cu	Cs	Ratios Li:K	Cu:K	Cs:K	Cu:Li	Cs:Li
Water	<0.2	<10	<0.02	<0.0001					
Lcu	740.00	2700.00	0.04	1.10	0.27	0.00	0.00	0.00	0.00
	106.61	69.05	0.00	0.01	1.54	0.00	0.00	0.00	0.00
LCs	630.00	2600.00	0.12	660.00	0.24	0.00	0.25	0.00	1.05
	90.77	66.50	0.00	4.97	1.36	0.00	0.07	0.00	0.05
Kcu	440.00	2000.00	0.13	3.00	0.22	0.00	0.00	0.00	0.01
	63.39	51.15	0.00	0.02	1.24	0.00	0.00	0.00	0.00
KCs	960.00	3800.00	0.13	860.00	0.25	0.00	0.23	0.00	0.90
	138.31	97.19	0.00	6.47	1.42	0.00	0.07	0.00	0.05
Original Ratios									
Cs-Li-K-Cl	Li:K	Cs:Li	Cs:K						
	1.46	0.07	0.10						
Cu-Li-K-Cl	Li:K	Cu:Li	Cu:K						
	1.38	0.25	0.34						

Ba-segregation in LBLTO is an issue…

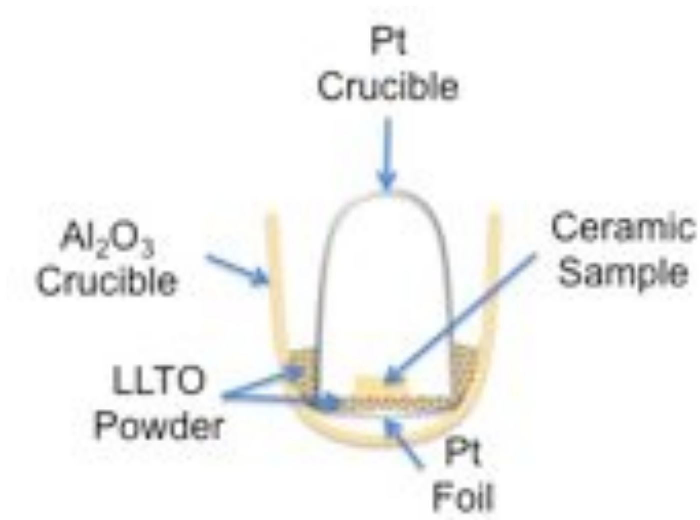
LBLTO as made

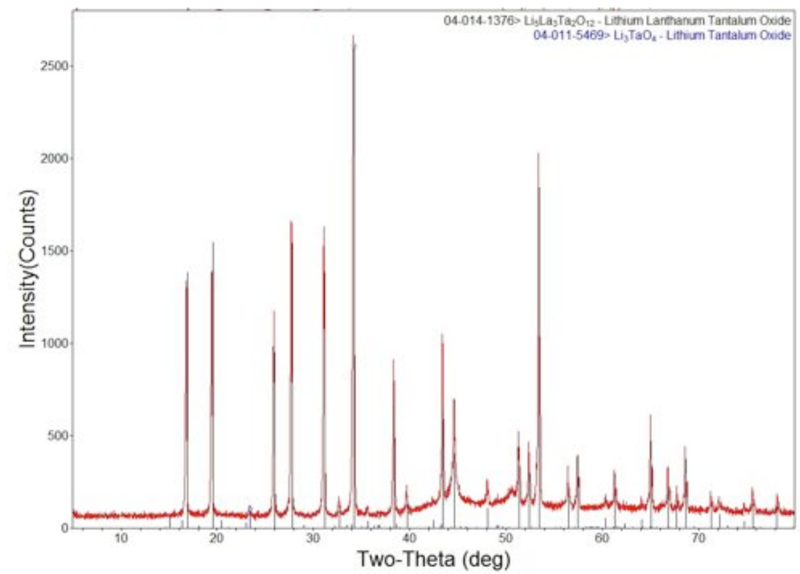
LBLTO after 4 hours at 650^{o}C in LiCl



Optimizing LLTO

Specimens were "sealed" in Pt-crucibles and sintered to 98.4% relative density at 1300°C

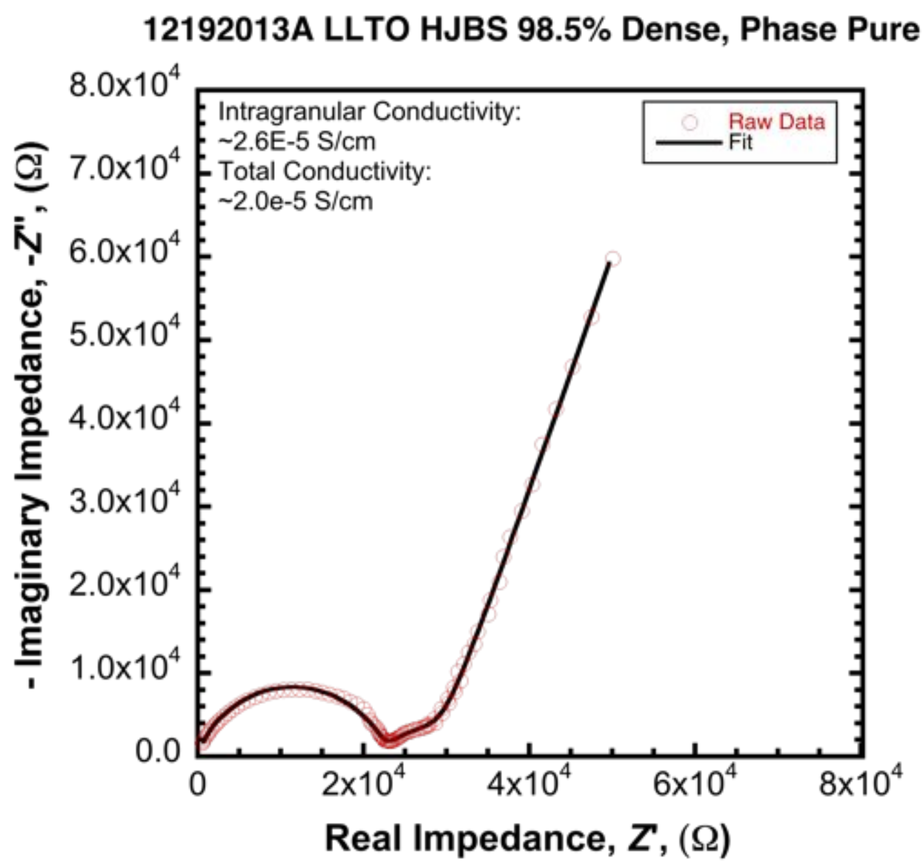




- *New processing route for LLTO processing developed (SNL SD# 13096, March, 2014).*
- *Pellets were pressed from ball milled mixed phase reaction products.*
- *Sealed crucible produced dense ceramic specimens with only trace minor phase.*

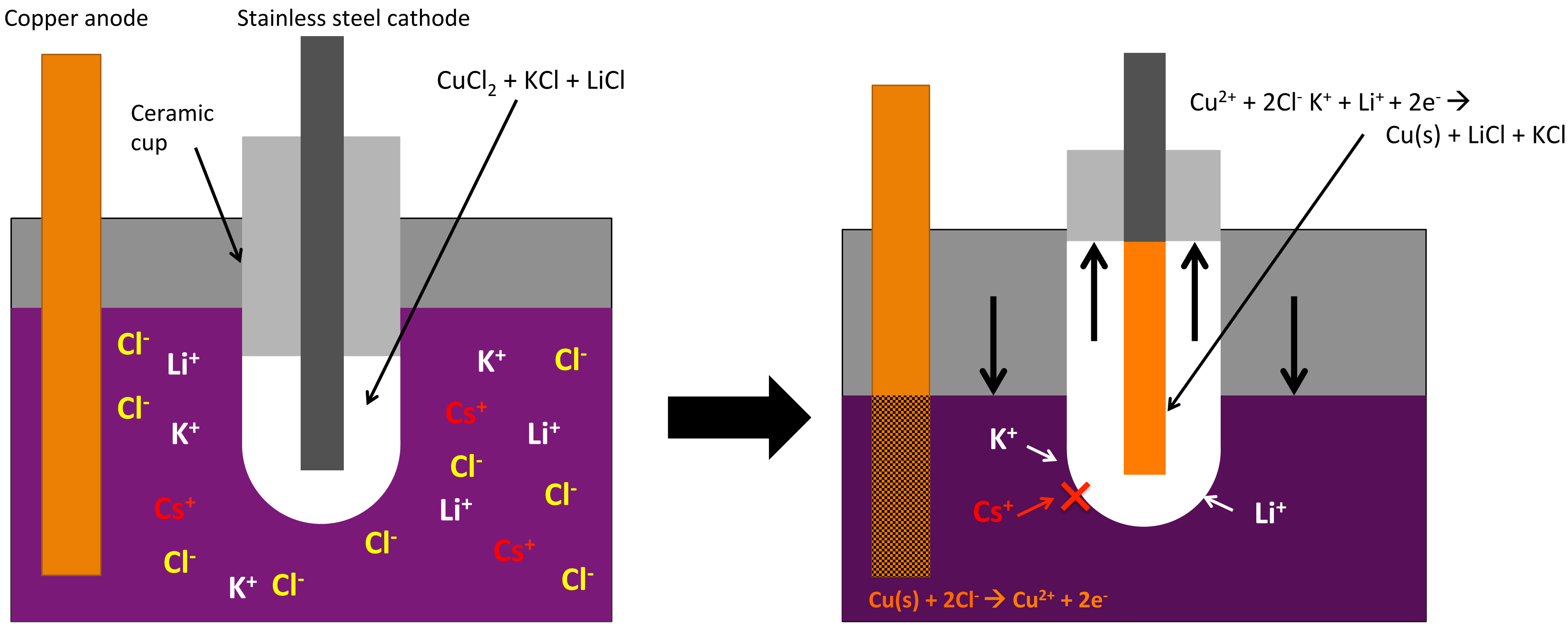
Characterizing Dense LLTO

- **Impedance measured at room temperature using a HP 4192A instrument between 5Hz and 13 MHz**
- **Two ZARCs + CPE used in fit to raw data**
- **Conductivities calculated from resistances of ZARC elements**
- ***Conductivity values are significantly higher than any LLTO in the literature (~10X)***
  - Comparable to Ba-substituted compounds
  - Density Issue in literature materials?



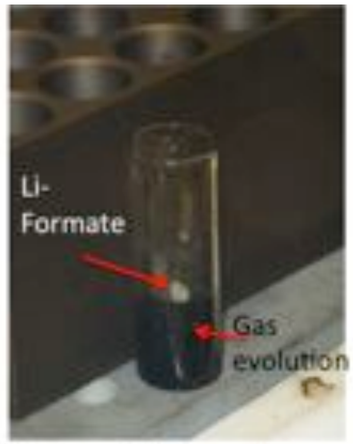
Scaling Up: Volumetric Purification

To make this process viable for larger scale purification, a modified purification scheme is needed…



Resolving residual $CuCl_2$

Initial $KCl\text{-}LiCl\text{-}CuCl_2$ molten salt at 400°C



Addition of Li-Formate (LiCOOH) to $KCl\text{-}LiCl\text{-}CuCl_2$ molten salt at 400°C rapidly evolves CO_2 and H_2 gases.

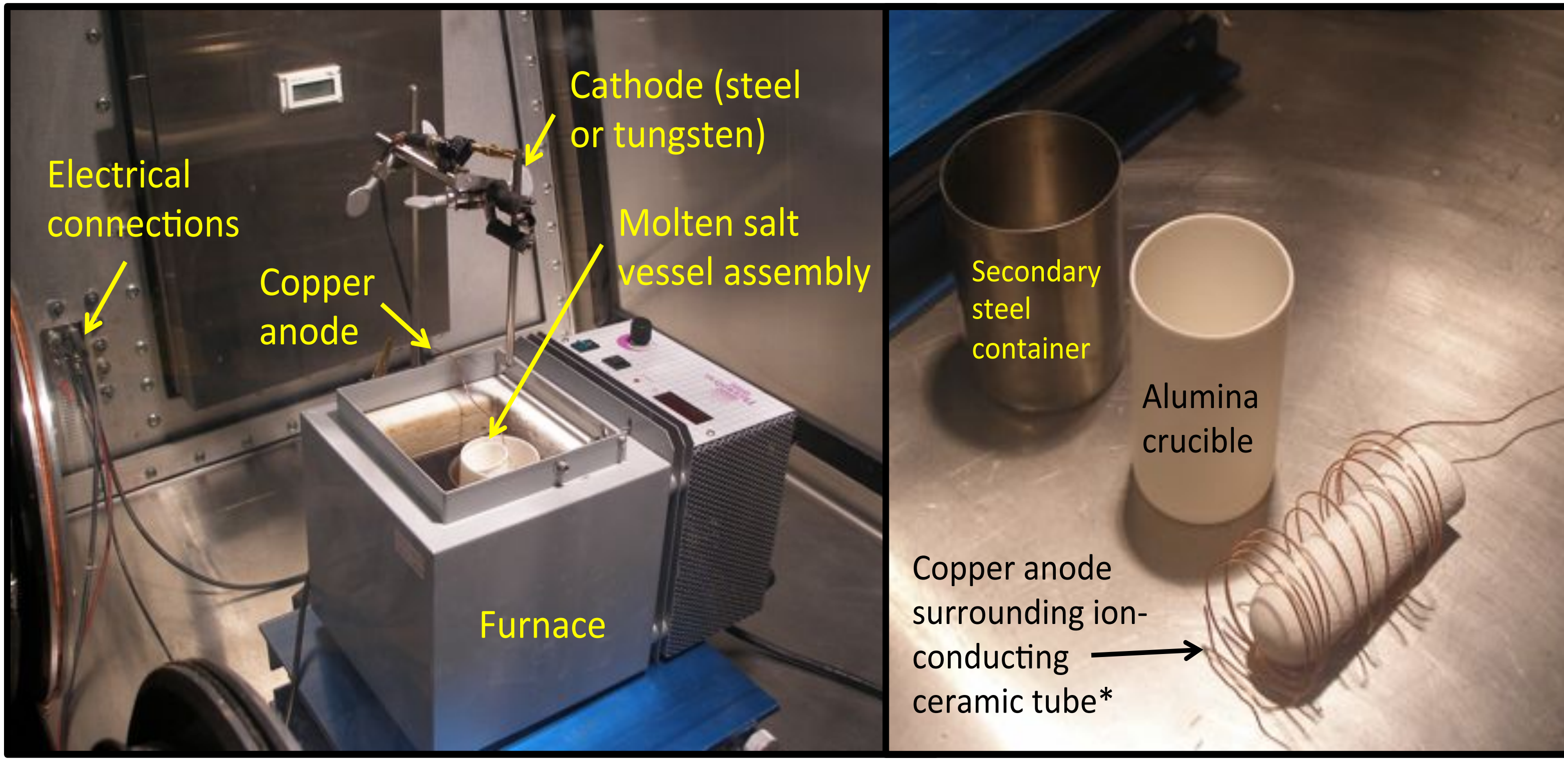
Reddish color resulting from Cu-metallization in $KCl\text{-}LiCl\text{-}CuCl_2$ molten salt at 400°C

In cooled salt, Cu metal (reddish-orange) and purified LiCl-KCl salt (white) are visible (left).

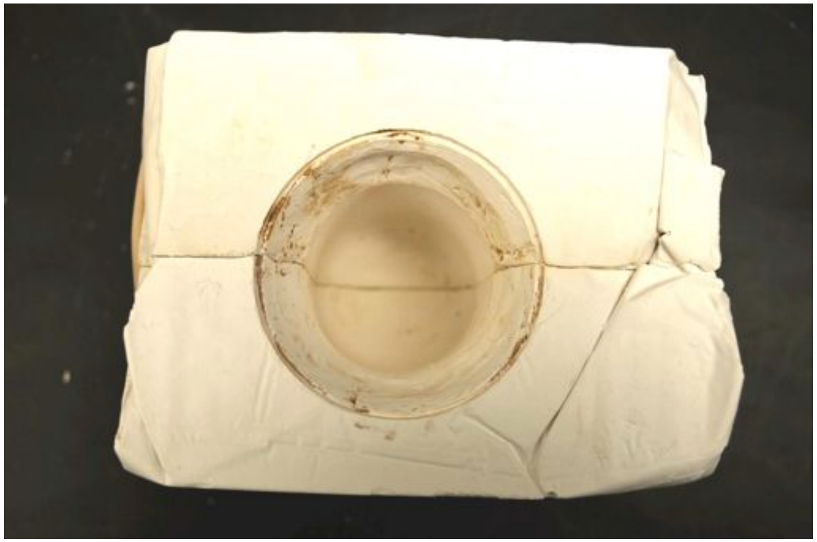
Overall reaction:

$$2LiCOOH + CuCl_2 \rightarrow 2LiCl + Cu(s) + 2CO_2 + H_2$$

Volumetric Reactor Assembly



Slip Cast Mold for Ceramic Tube Synthesis



Plaster mold will enable ceramic slip casting to produce 50mm OD (40-46mm ID) unsintered crucibles. Sintered crucibles will be ~40mm OD with ~2-3mm thick walls.

Calcined Powder → (*50 vol. %*) → *Disperse in H_2O* → (*De-Air*) → *Pour in Mold* → *Remove Mold* → *Dry Ceramic* → *Sinter in Crucible*

Green LLTO Ceramics

Unfired "Green" Ceramic Tubes

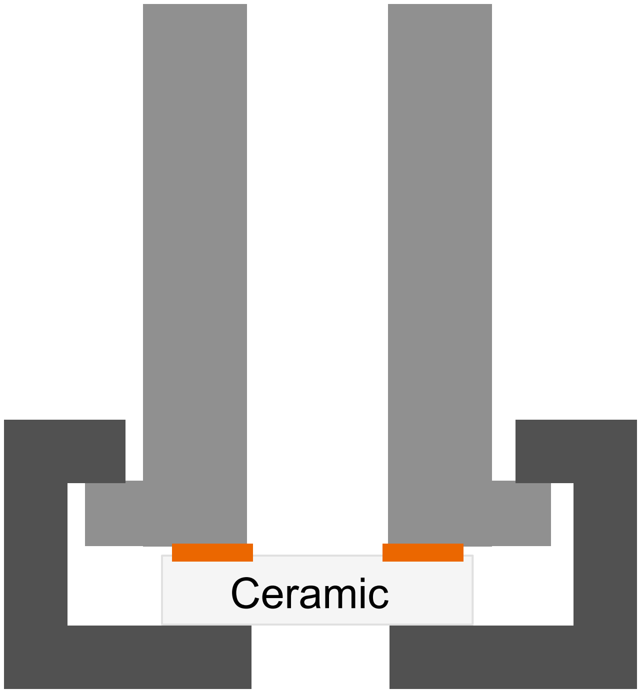
Fired LLTO Ceramic Tube

Initial “Fired” LLTO Ceramic

A Backup Alternative

In the event that the ceramic tube processing does not prove tractable within FY14, a secondary, pellet-based scheme will be employed to demonstrate volumetric salt purification.

This approach will use a VCR fitting with a copper gasket to seal polished ceramic pellets into a steel tube.



Paths Forward

- **Continue efforts to produce ceramic tubes for volumetric testing**
  - LLTO
  - $KZr_2P_3O_{12}$ (Also consider: $K_4Zr_2Si_3O_{12}$ and $K_3Zr_2PSi_2O_{12}$
- **Begin volumetric testing using steel tube fixtures**
- **Evaluate testing of ceramic tubes in volumetric test configuration**
- **Characterize salt purification efficiency of electrochemical process**
- **Refine ceramic chemistry to optimize purification process.**

Thanks!

Thanks to Stephen Kung, Mark Williamson, and Terry Todd for continued support of this effort.

Thanks, also, to Kevin McMahon and Brad Couch for program and technical guidance.

This work was funded by the United States Department of Energy Office of Nuclear Energy under the Fuel Cycle Research and Development Program

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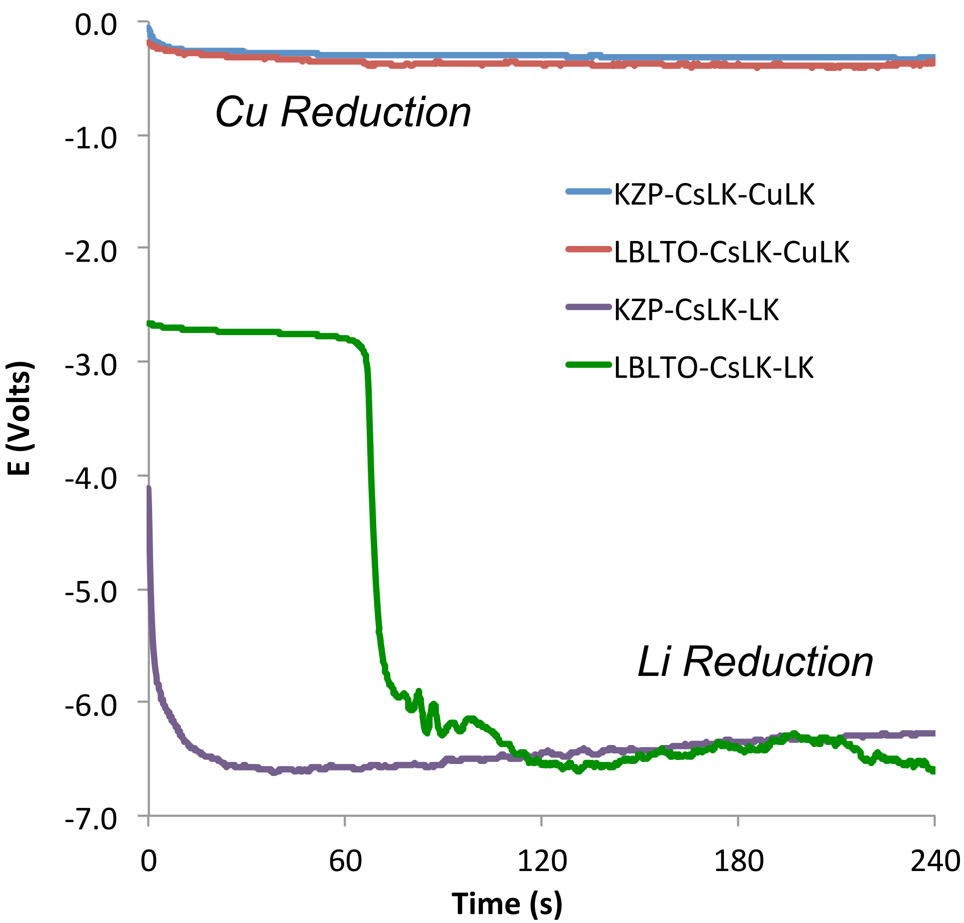
Comparison of LBLTO with other Li-ion conductors

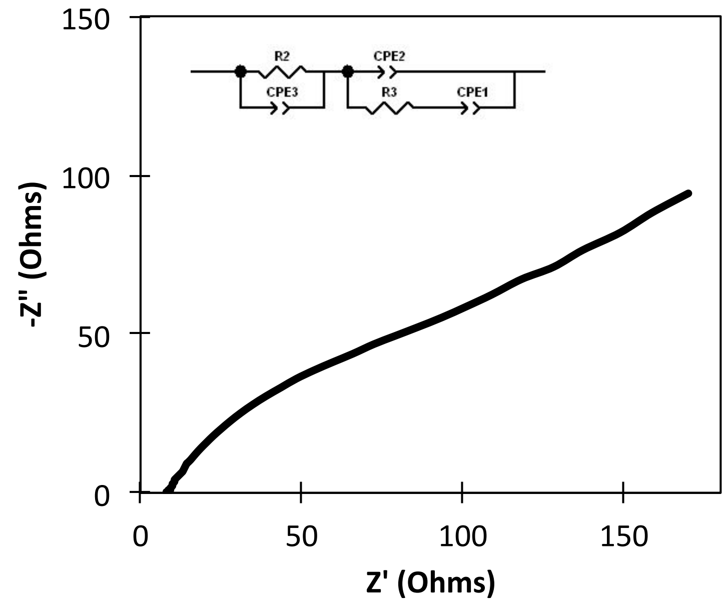
Backup Slides

EB Pellet Compositions

	LiCl	KCl	CsCl	$CuCl_2$
LK-EB	44	56	0	0
CsLK-EB	40.1	48.7	11.2	0
CuLK-EB	32.7	41.6	0	25.7

Electrochemical Behavior of



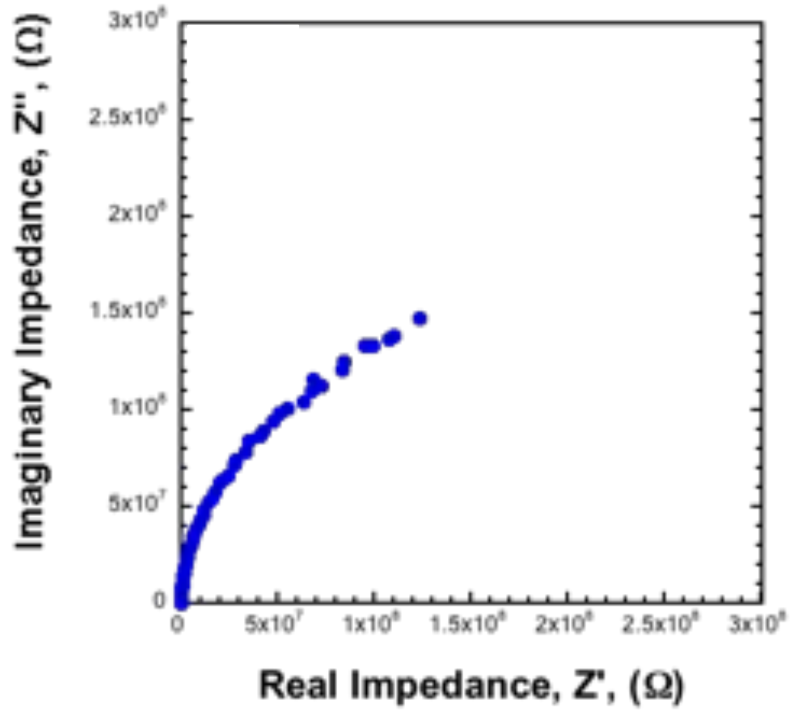


Potassium Conductivity

Preliminary impedance spectroscopy data provide insight into potassium conductivity of KSICON.

The high frequency (1MHz) real portion of the impedance was attributed to K^+ conductivity within the grains of the material.

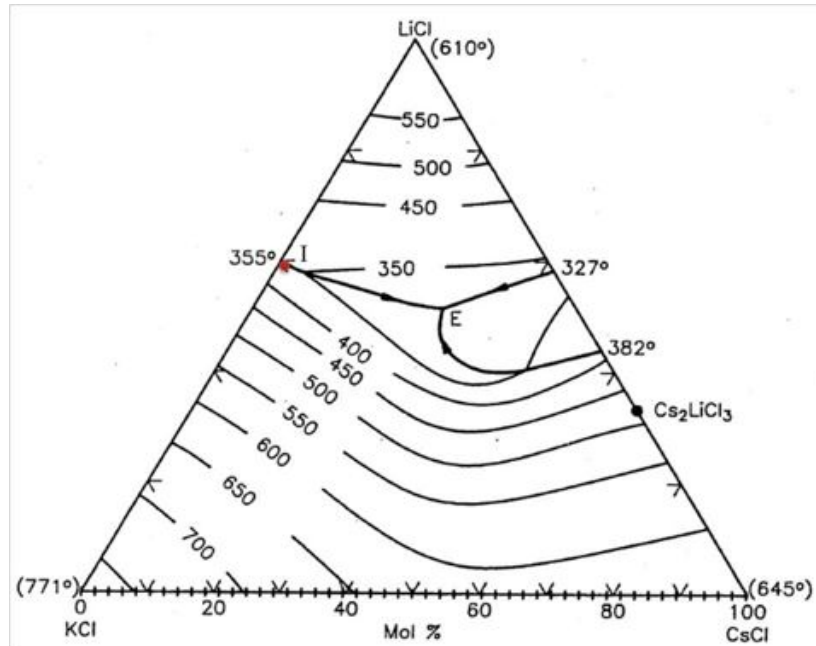
This value was used to approximate grain conductivity of **~2 x 10^{-4} S/cm**. (Consistent with values expected for Na-transport in NaSICON)



Powers *et al. J. Electrochem. Soc.* (1975) **122**, p226.

Evaluating Cs-selectivity in eutectic salts

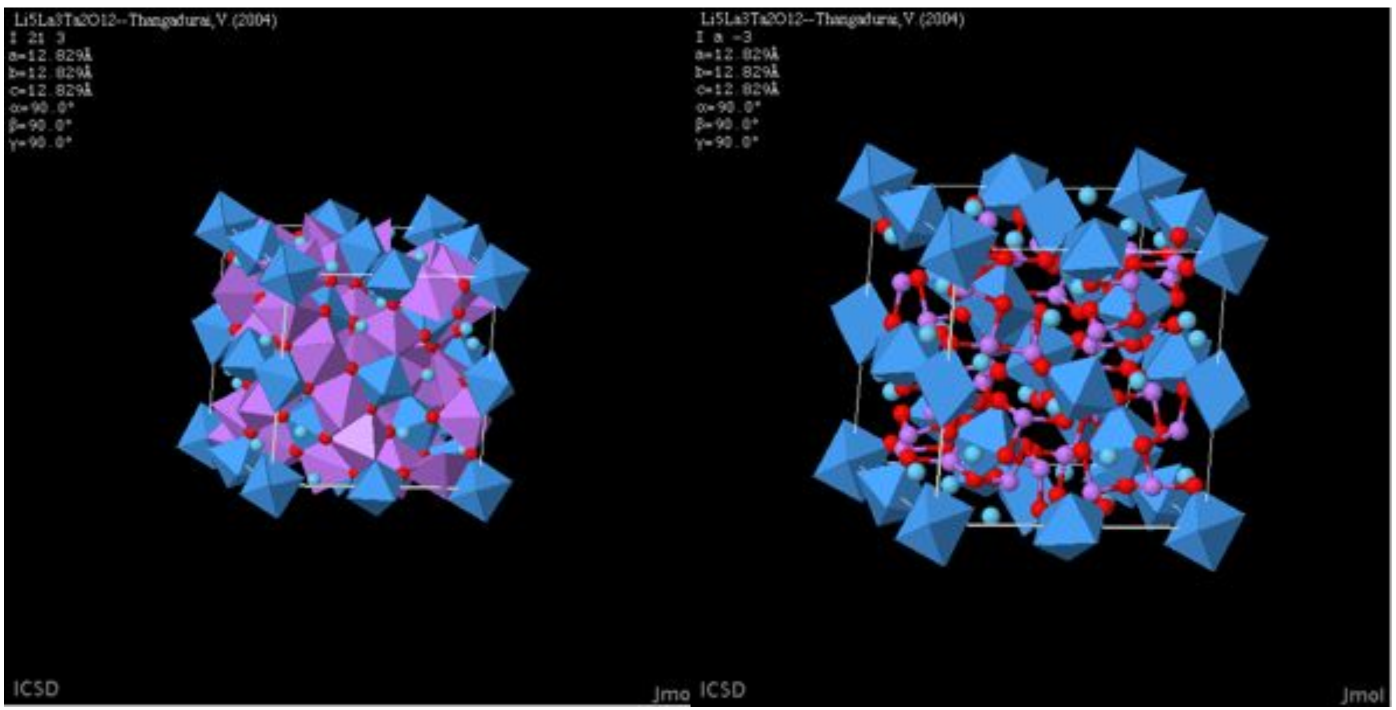
- **Ternary KCl-LiCl-CsCl (18wt% - 25wt% - 57wt%) were prepared**
- **Melting temperature reduced (~260°C vs 355°C)**
- **Samples were immersed in these salts at 400°C for 30-60 minutes to test stability and evaluate Cs^+ diffusion into these structures.**



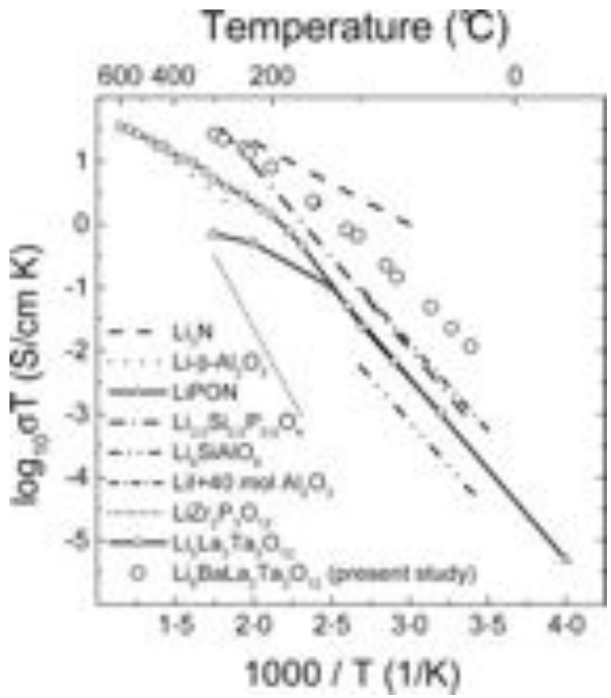
Williams, A. Zone-Freezing Study for Pyrochemical Process Waste Minimization Master of Science thesis, University of Idaho/Idaho National Laboratory, (2012).

LLTO ($Li_5La_3Ta_2O_{12}$) Ion Conducting Ceramics

Lithium ions in $Li_5La_3Ta_2O_{12}$ and related materials move within a 3-D network of octahedrally and tetrahedrally coordinated Li-sites in this lattice (though it is believed that transport along the octahedral sites is more favorable).



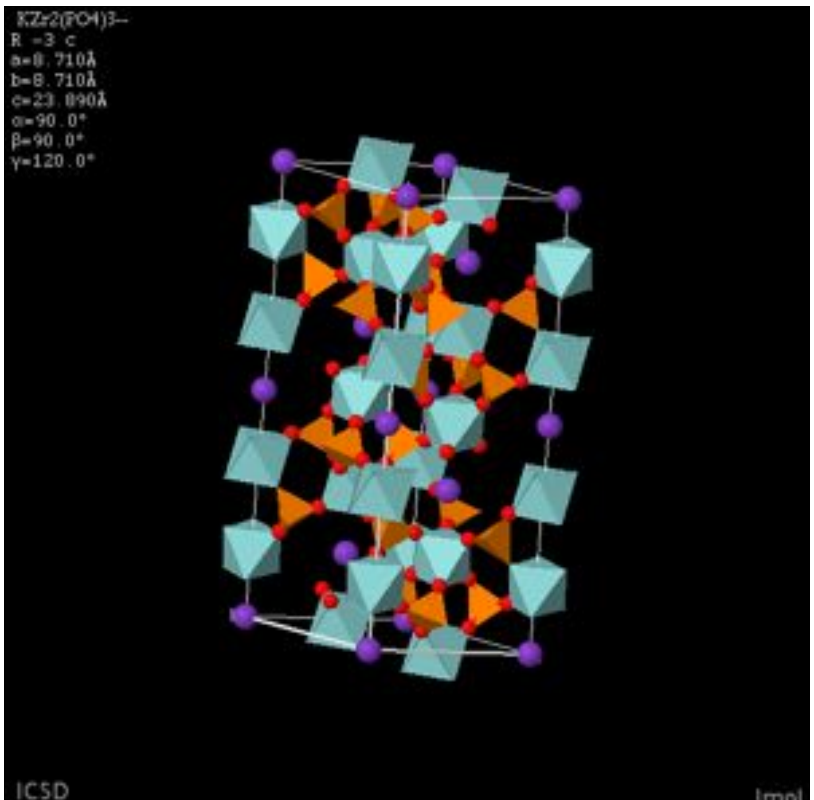
Comparison of LBLTO with other Li-ion conductors

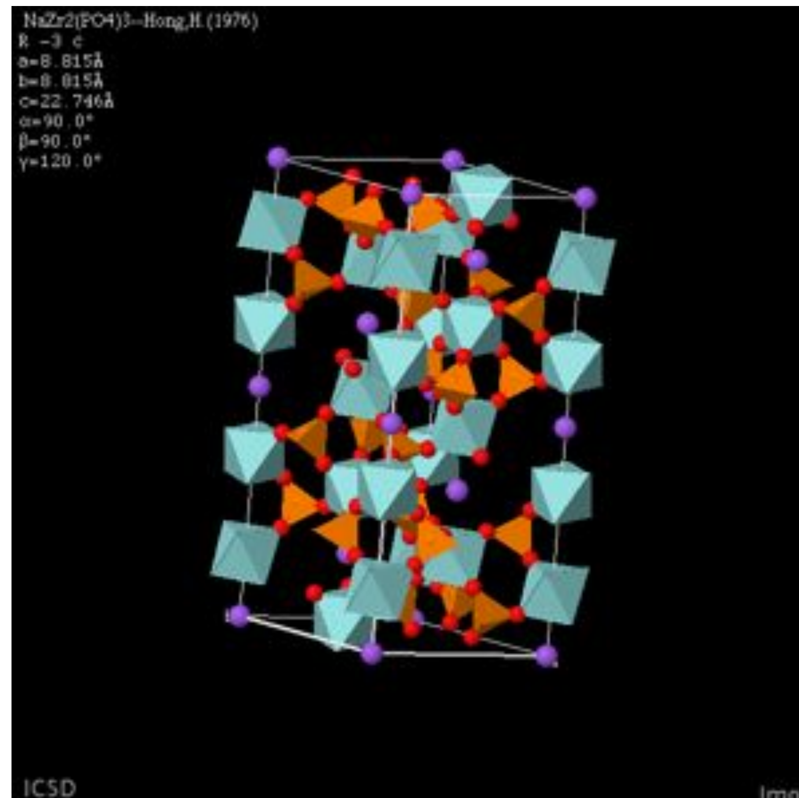


V. Thangadurai, *et al. Adv. Funct. Mater.* (2005) **15** (1), p107.

Consider KSICON

KSICON is a potassium-substituted variant of NaSICON with an expanded c-axis and a contracted a-axis.



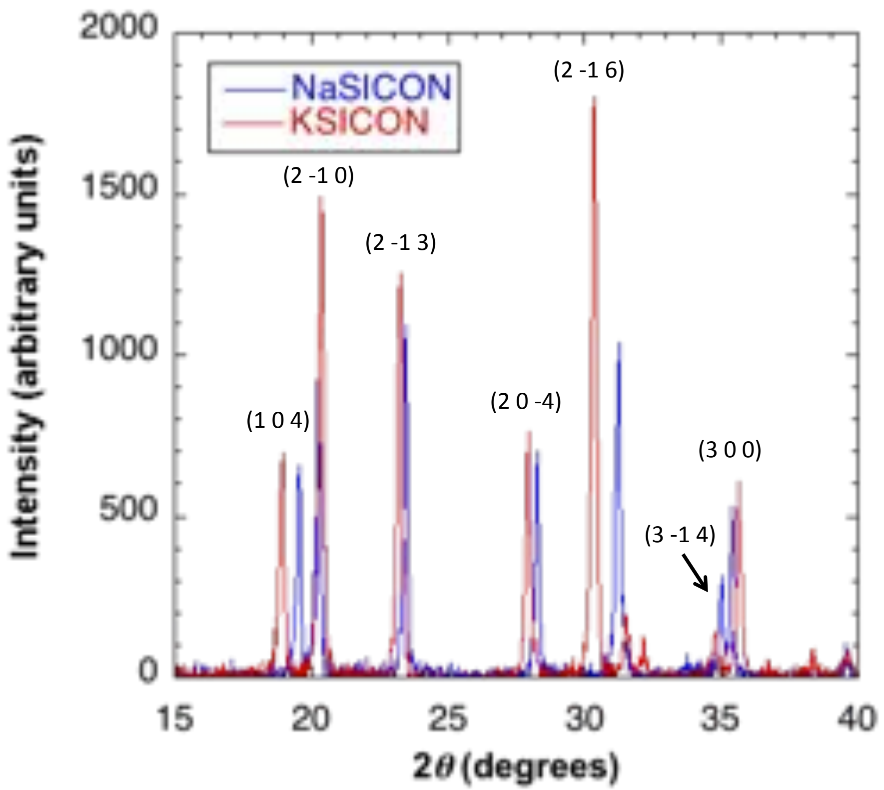


Confirming KSICON synthesis

X-ray diffraction shows the synthesis of KSICON and illustrates anticipated changes in lattice parameter.

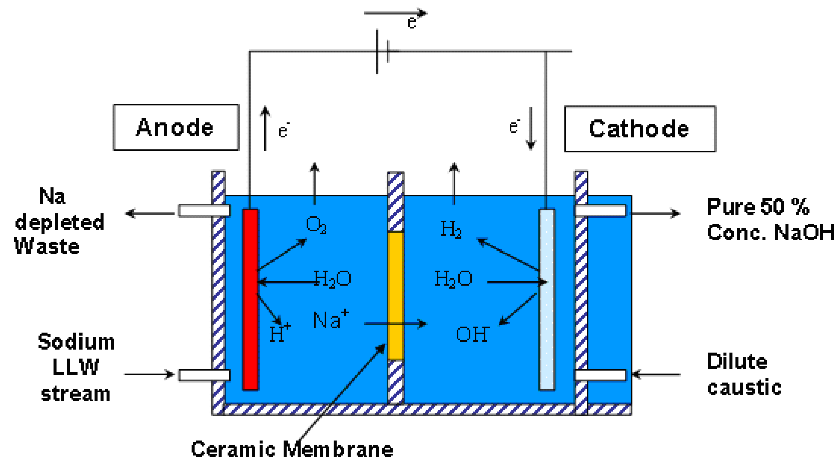
$c_{NaSICON}$ = 22.746Å,
c_{KSICON} = 23.890Å;

$a_{NaSICON}$ = 8.815Å,
a_{KSICON} = 8.710Å



NaSICON for Na-Removal From Aqueous Waste

Schematic for removal of Na from aqueous waste streams.



Anode: $2H_2O = O_2 + 4H^+ + 4e^-$

Cathode: $4H_2O + 4e^- = 2H_2 + 4OH^-$

Overall: $2H_2O = 2H_2 + O_2$

M.S. Fountain, *et al*. "Caustic Recycle from Hanford Tank Waste Using NaSICON Ceramic Membrane Salt Splitting Process." PNNL-18216, prepared for the Department of Energy, Feb, 2009.

Reduction Potentials

Reduction potentials:

$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36
$Li^+ + e^- \rightarrow Li_{(s)}$	-3.05
$K^+ + e^- \rightarrow K_{(s)}$	-2.93
$Cs^+ + e^- \rightarrow Cs_{(s)}$	-2.92
$La^{3+} + 3e^- \rightarrow La_{(s)}$	-2.52

Recent Impedance Data