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Ceramic Ion Filters for Mixed Waste Separations

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S5: Ion Conducting Ceramics
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Pyroprocessing: A Hot Mess

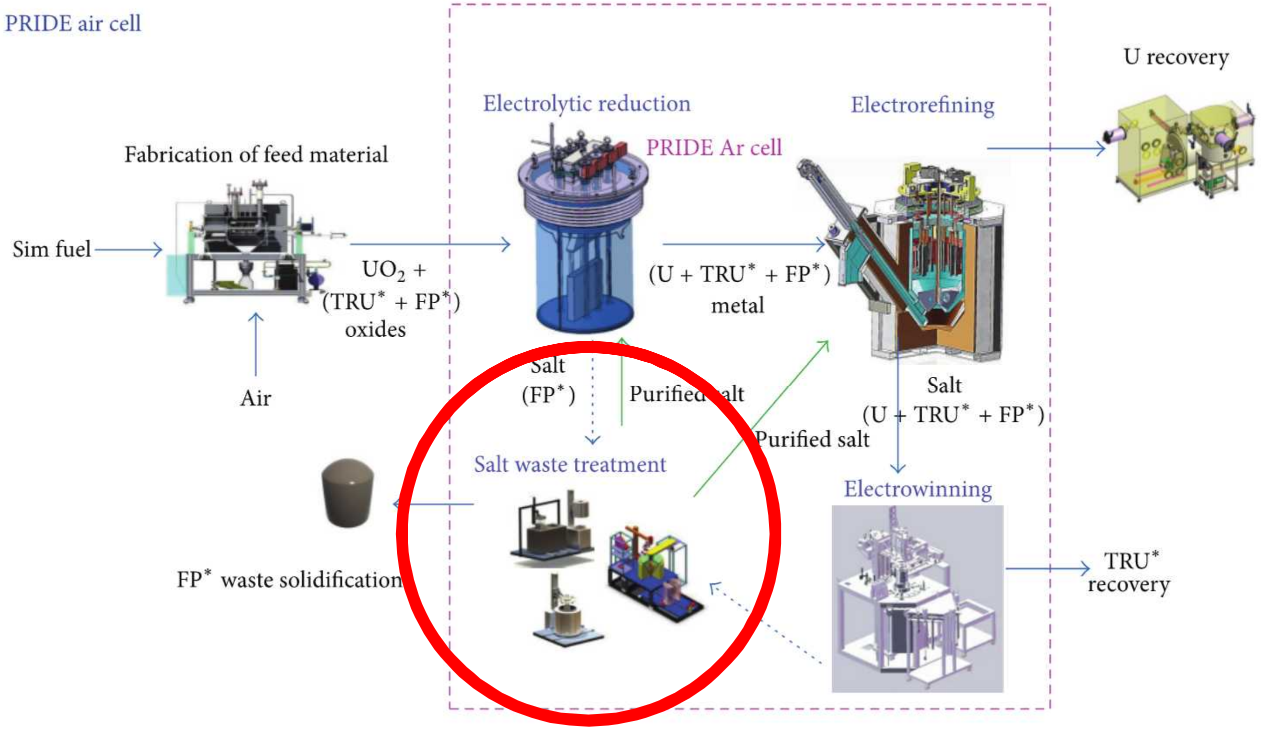
Pyroprocessing is a promising technology to electrochemically recycle spent nuclear fuel.

Coordinated oxidation and reduction reactions in molten salts separate 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.



TRU*: transuranic elements surrogates
FP*: fission products surrogates

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

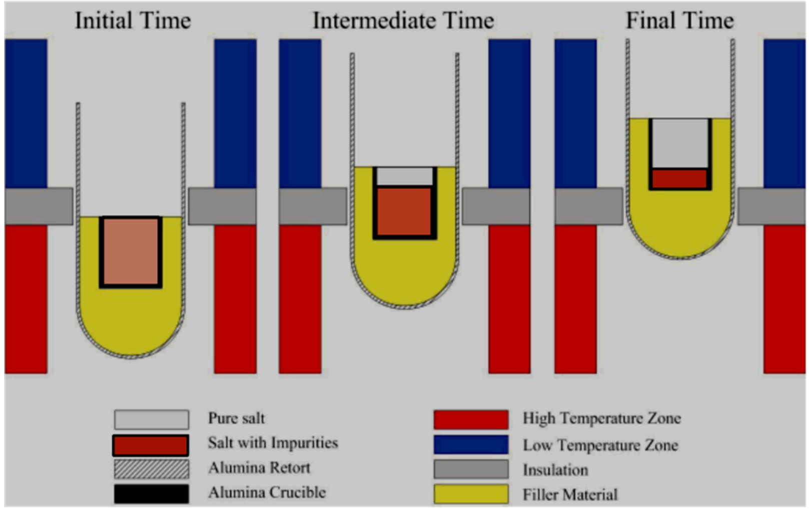
- The accumulation of waste products (e.g., fission products, transuranics, etc.) in KCl-LiCl molten salt can impact the electrorefining process.
  - Changes in ionic conductivity (impacts efficiency of uranium ion transport)
  - Changes in eutectic melt properties
- Removing waste products from the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

Current approaches to removal of fission product waste includes extraction with zeolites or consolidation through zone freezing.

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

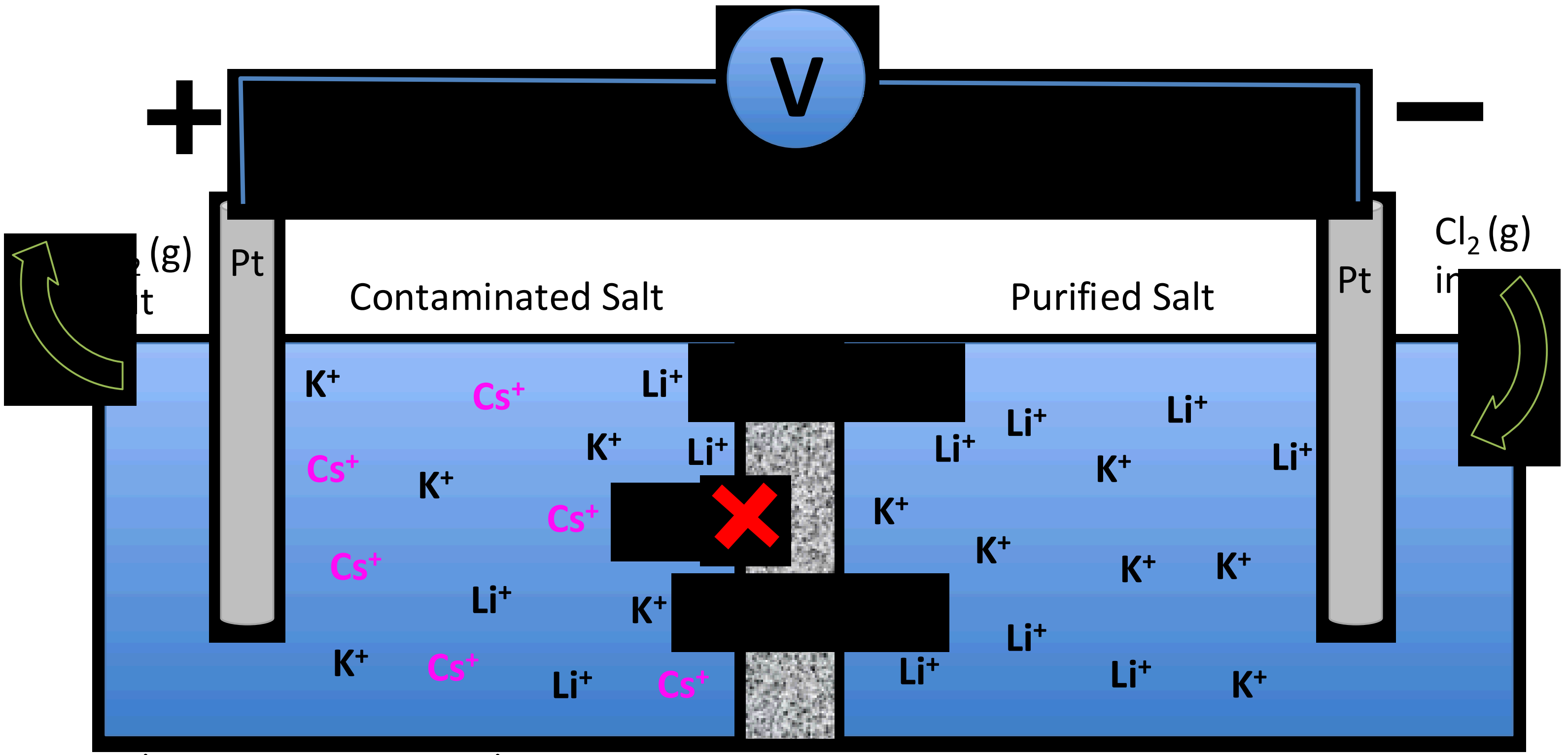
www.molecularsieve.org/image/Zeolite_Molecular_Sieve_4A.gif

Zone Freezing



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

An Electrochemical Approach



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

This electrochemical approach uses ion-selective ceramics as “filters” to isolate and concentrate contaminant ions such as Cs^+ in LiCl-KCl eutectic molten salts.

Advantages of the Electrochemical Approach

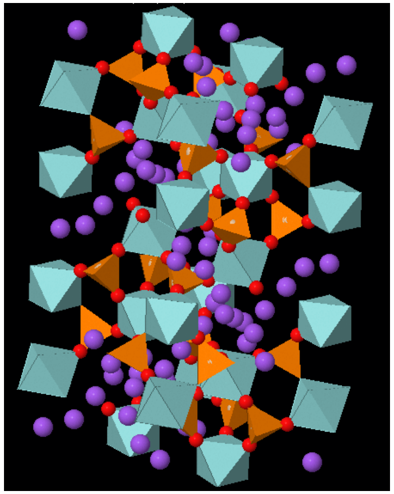
- Potentially compatible with existing electrochemical materials setup.
- Electrochemical process allows high degree of control over degree of purification.
  - In-situ quantification of contaminant concentration
  - Control heat load in final waste form
- Not expected to require changes to current waste stream.

Ceramics are Key!

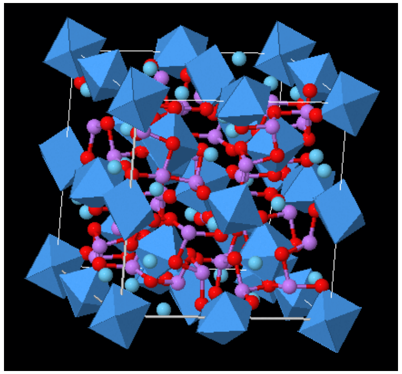
- **Critical Ceramic Criteria:**
    - High Li^+ and K^+ conductivity
    - Selectivity against Cs^+ transport
    - Chemical, electrochemical, and structural stability in molten LiCl-KCl
    - Temperature stability (> 500^oC)
    - Radiation resistant

Candidate Ceramics

- "NaSICONs" – Super Ion CONductors (e.g., KSICON: $KZr_2P_3O_{12}$)
  - Lattice is chemically, structurally flexible
  - High Na^+ 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

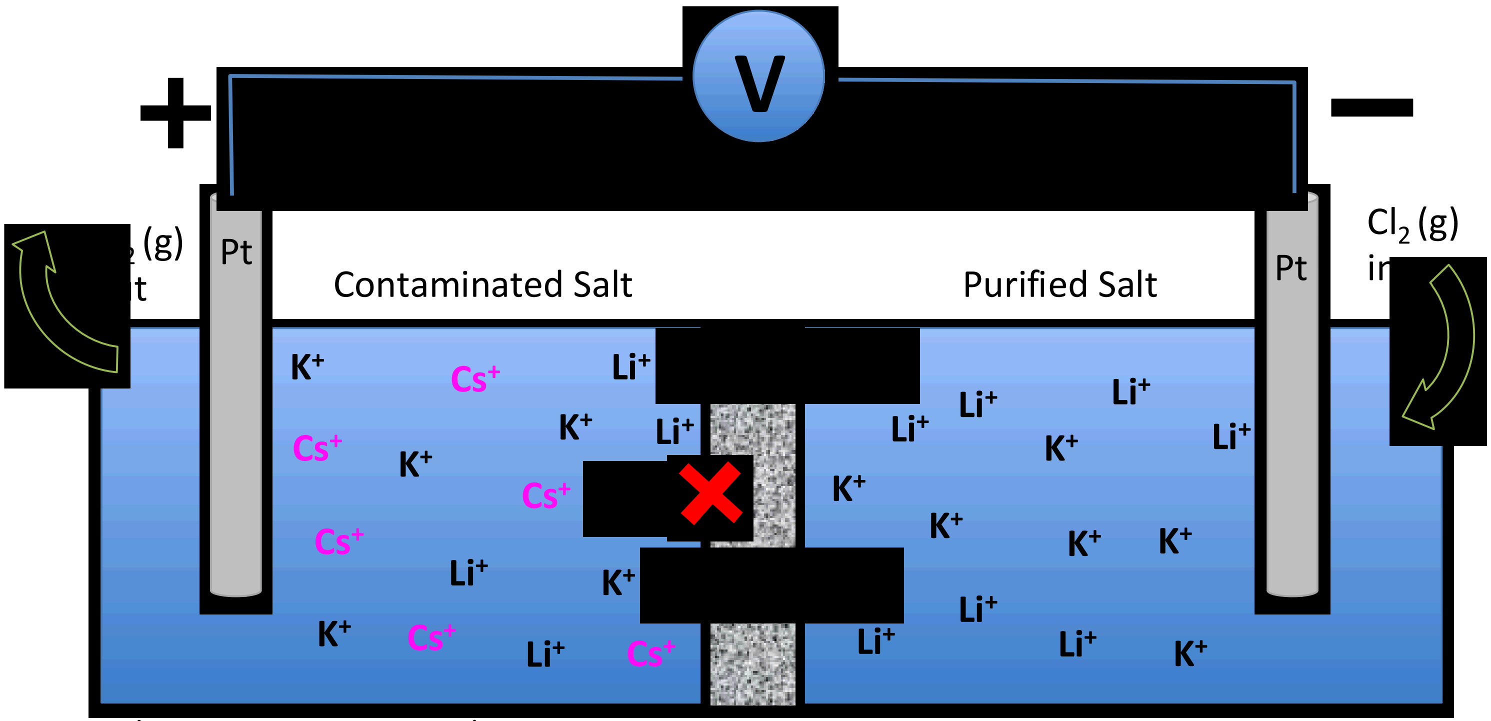


- LLTO – Garnet structured Lithium Lanthanum Tantalates ($Li_5La_3Ta_2O_{12}$ and $Li_6BaLa_2Ta_2O_{12}$)
  - Chemically flexible lattice
  - Favors Li^+-transport; conductivity (~10^{-5}-10^{-4} S/cm) at room temperature



A Technical Complication

Chlorine chemistry at 500°C poses significant materials compatibility (and human compatibility) challenges…

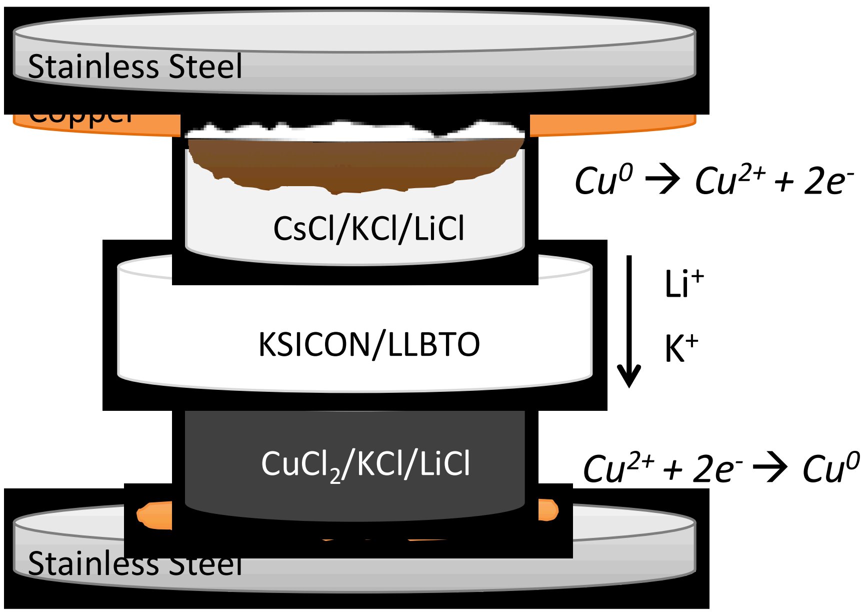


$2Cl^{!}$ " $Cl_2 + 2e^{!}$ $Cl_2 + 2e^{!}$ " $2Cl^{!}$

Through proper materials engineering, these problems are addressable, but an safer variant of the process was desirable.

A Safer Alternative

Pellet stacks that use copper oxidation/reduction for charge balance.

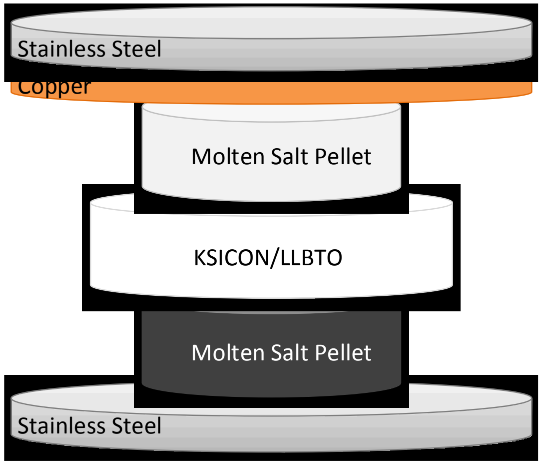


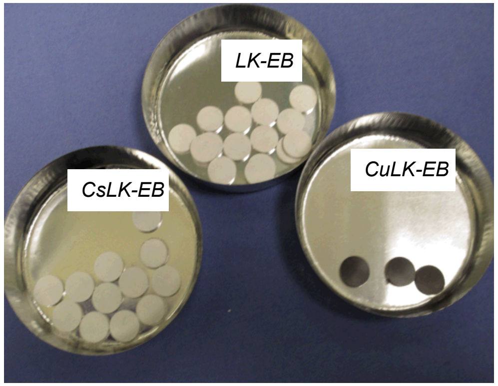
Excess chloride at the anode is compensated by Cu dissolution (oxidation).

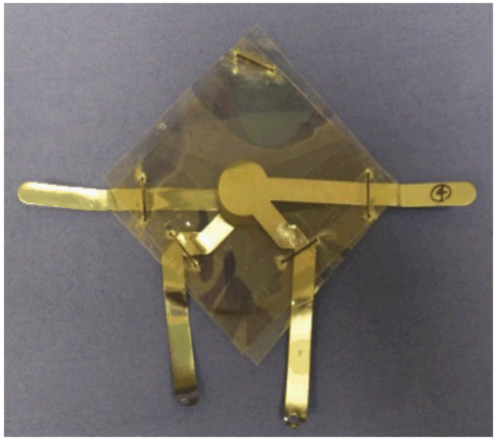
Excess positive charge at cathode (from Li^+, K^+) are compensated by Cu^{2+} reduction from $CuCl_2$.

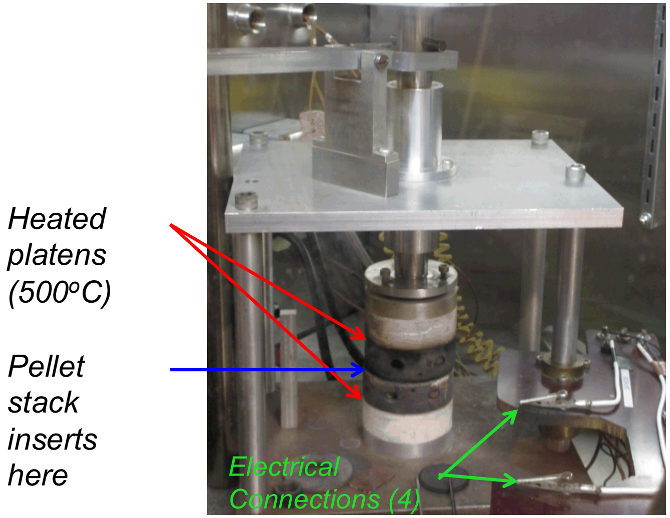
Pellet Testing materials/configuration

Borrowing from thermal battery technologies at SNL allowed for ready testing of the “pellet stack” configuration.



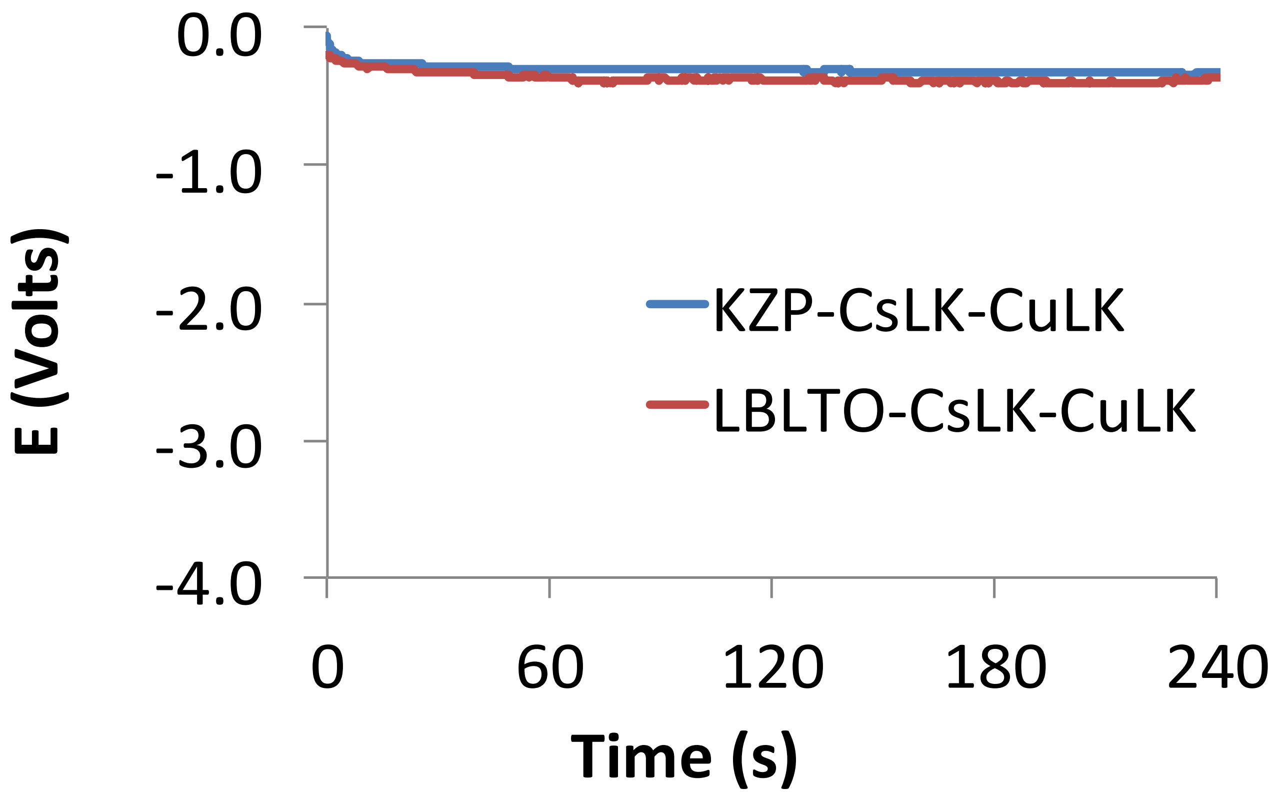




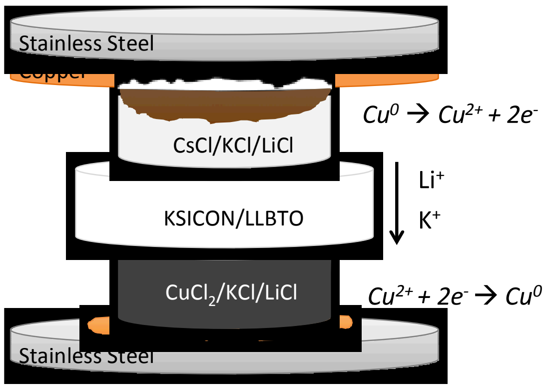


Initial Galvanostatic Discharges

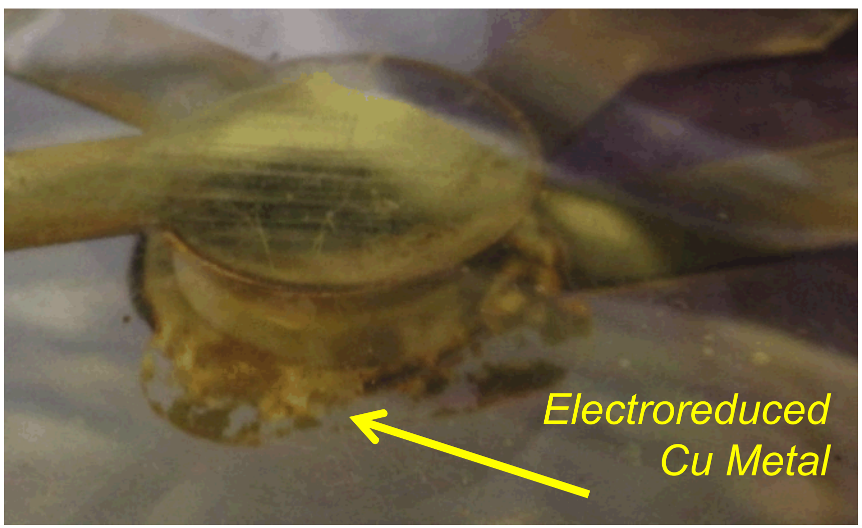
Galvanostatic discharge at 100mA/cm^2 shows effective charge transport with minimal overpotential.

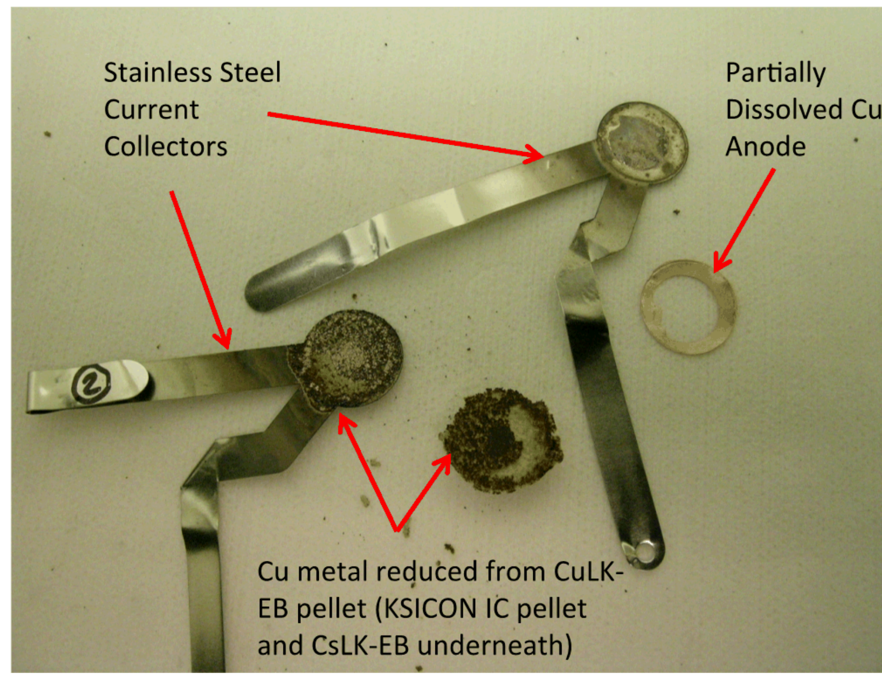


Macroscopic Material Transport during Discharge



Examination of discharged cells reveals significant mass transfer, evidenced by Cu dissolution and deposition.

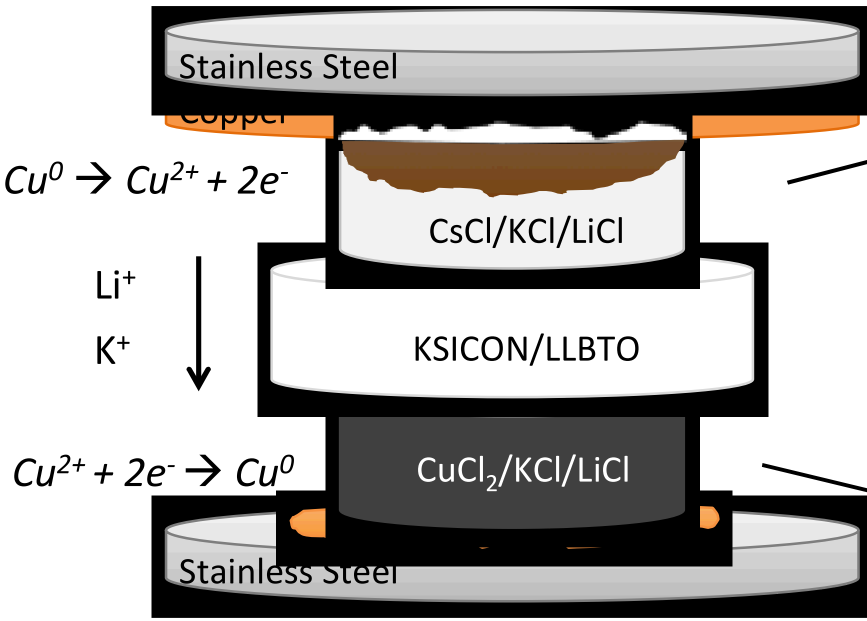


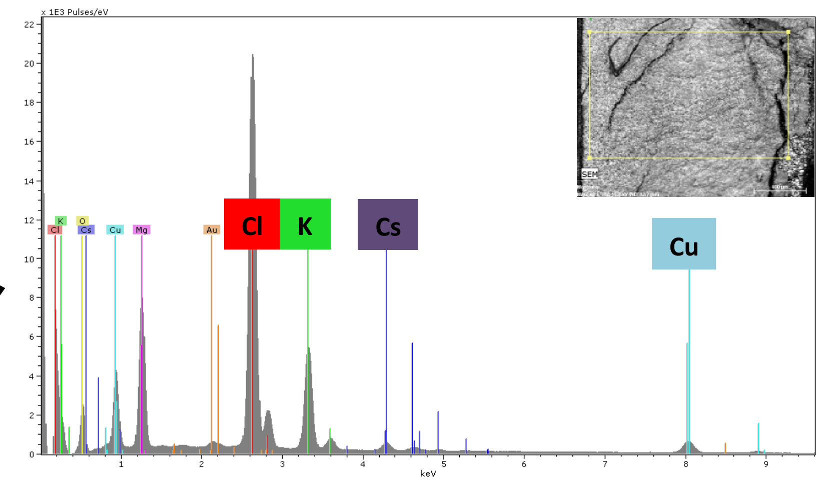


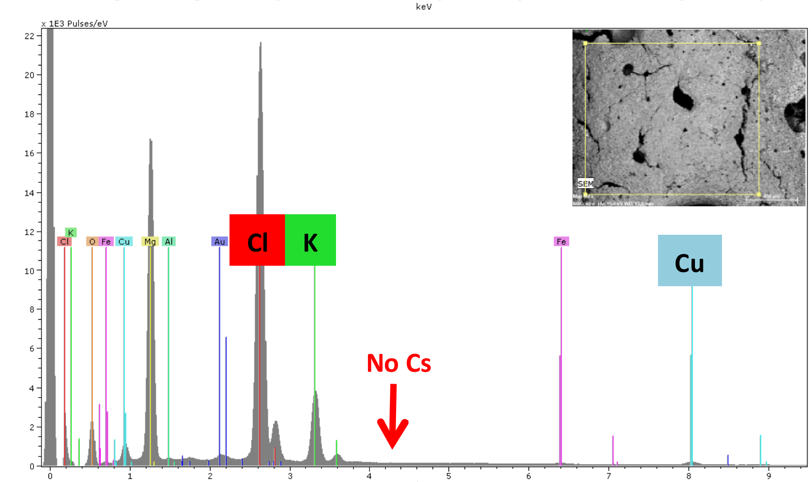
Macroscopic Material Transport during Discharge

"Qualitative" Ionic Selectivity

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





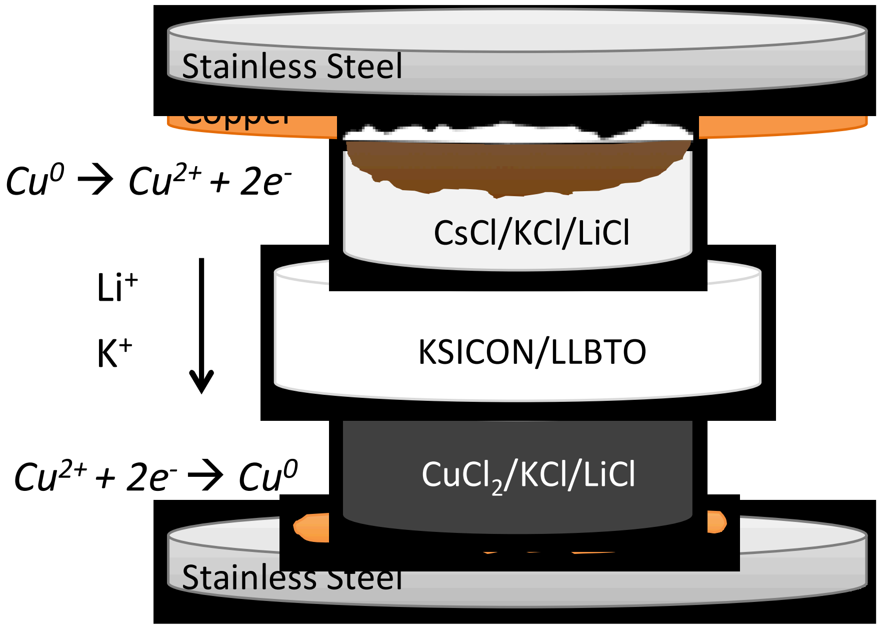


Quantitative Ionic Selectivity

Elemental Analysis (ICP) shows negligible Cs in cathodic molten salt after galvanostatic discharge.

Elemental concentrations dissolved in deonized water (ppm)

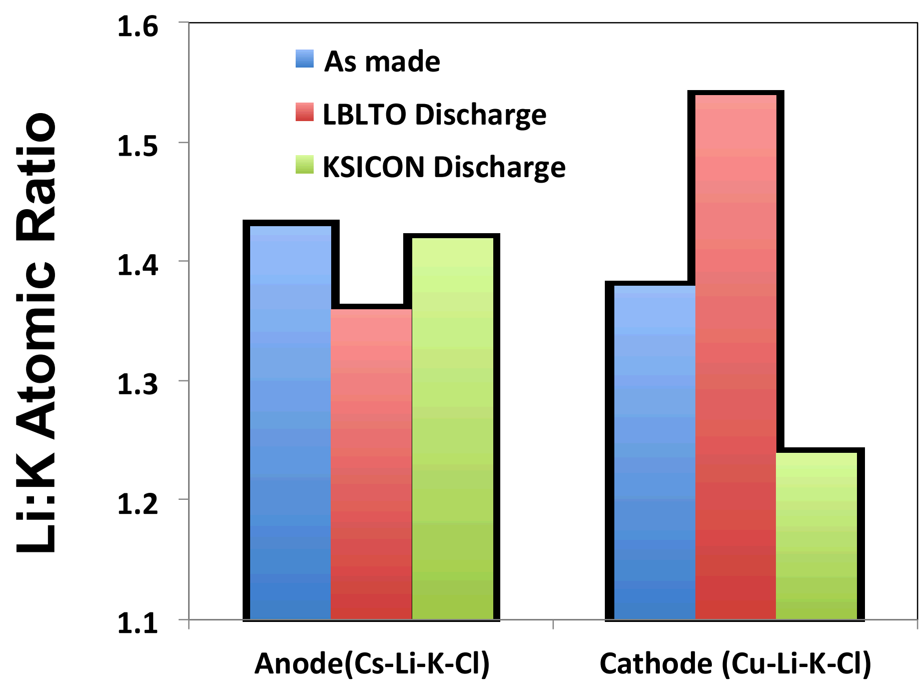
LBLTO	**Li**	**K**	**Cs**
Anode (Cs-Li-K-Cl)	630	2600	660
Cathode (Cu-Li-K-Cl)	740	2700	1.1
KSICON	**Li**	**K**	**Cs**
Anode (Cs-Li-K-Cl)	960	3800	860
Cathode (Cu-Li-K-Cl)	440	2000	3



Trans-ceramic Ion Transport

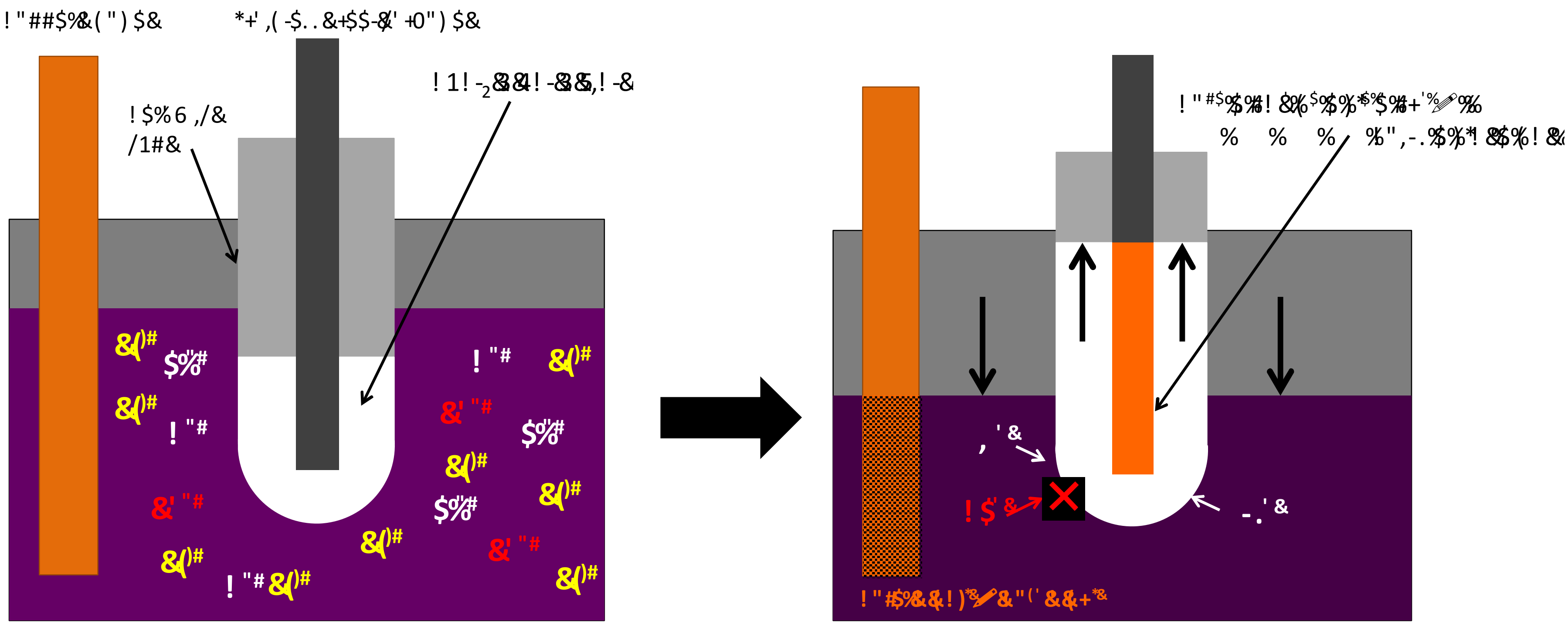
Elemental Analysis (ICP) also reveals which ionic species move preferentially through the ceramic separators.

- LBLTO preferentially transports Li^+
- KSICON moves both Li^+ and K^+, but K^+ from KSICON lattice is expelled into cathodic molten salt



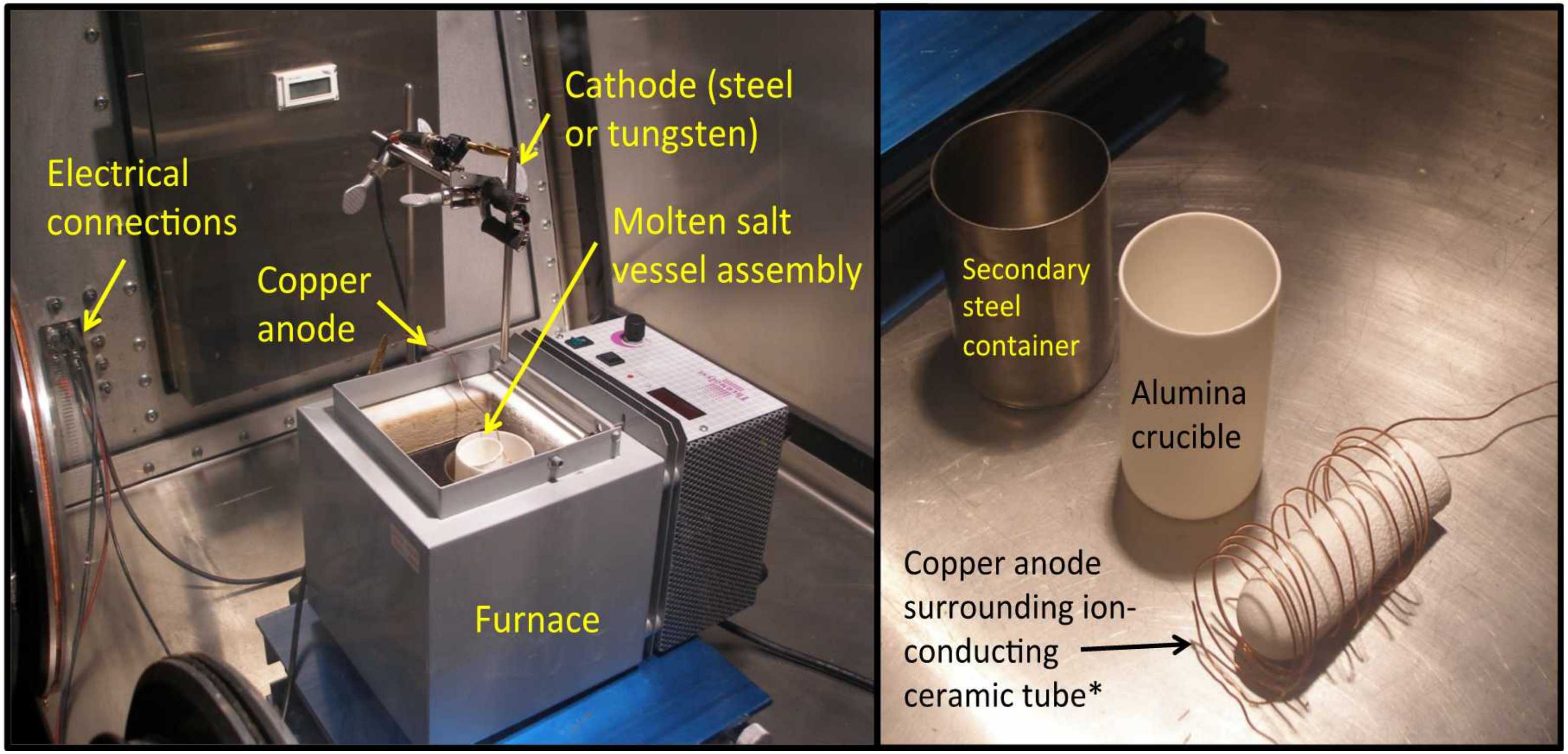
A Volumetric Variation

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



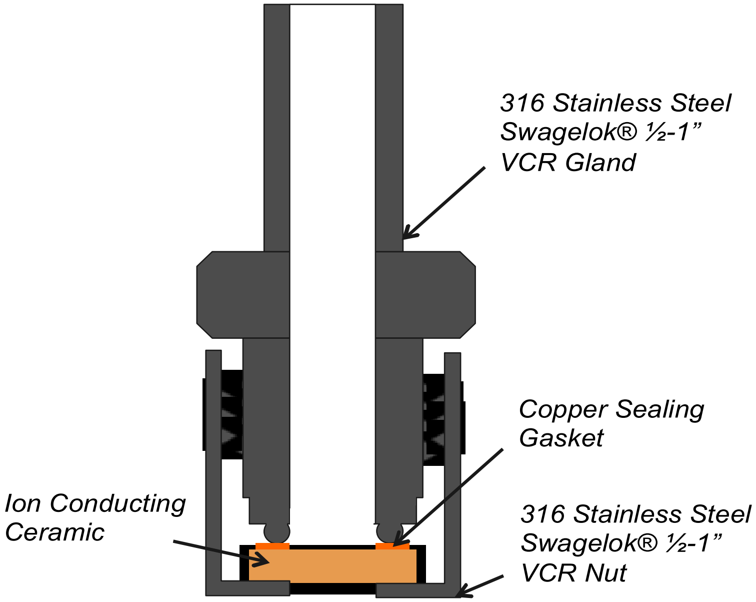
Volumetric Reactor Design

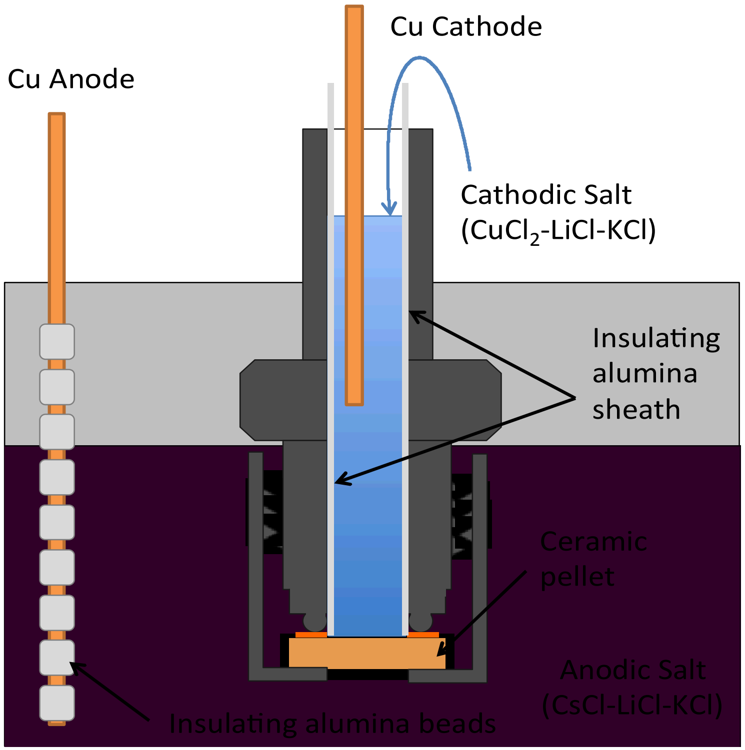
Volumetric reactions require an air-free environment, a reactor capable of heating separated salt volumes to 500°C and a system to electrochemically drive and interrogate the system.



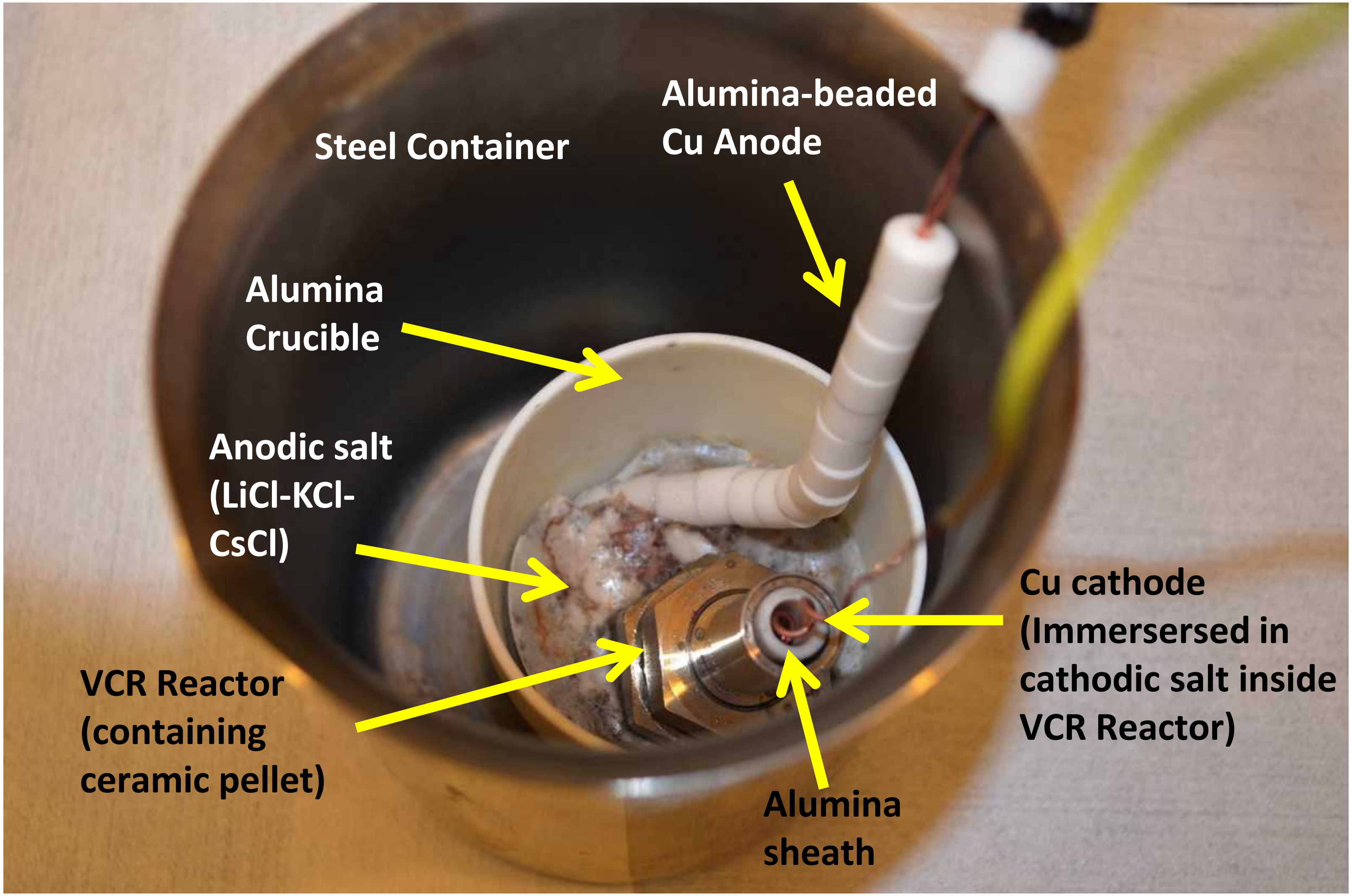
An Engineering Solution

Using Swagelok VCR fittings, we could create a volumetric reactor design using ceramic pellets!





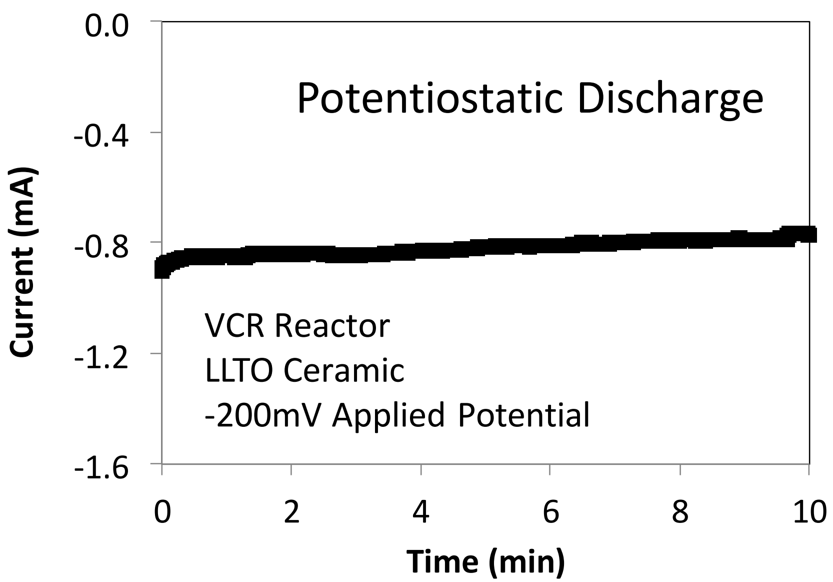
An Assembled Volumetric Reactor

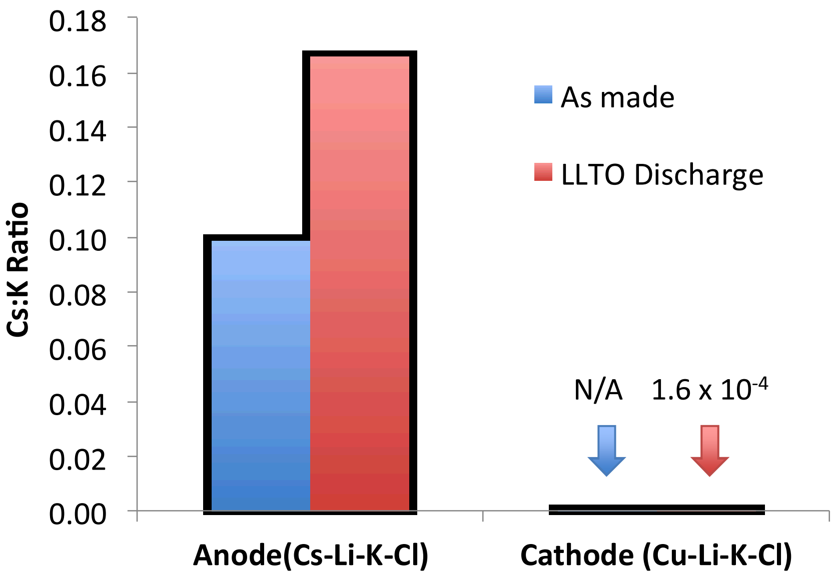


Characterizing Volumetric Purification

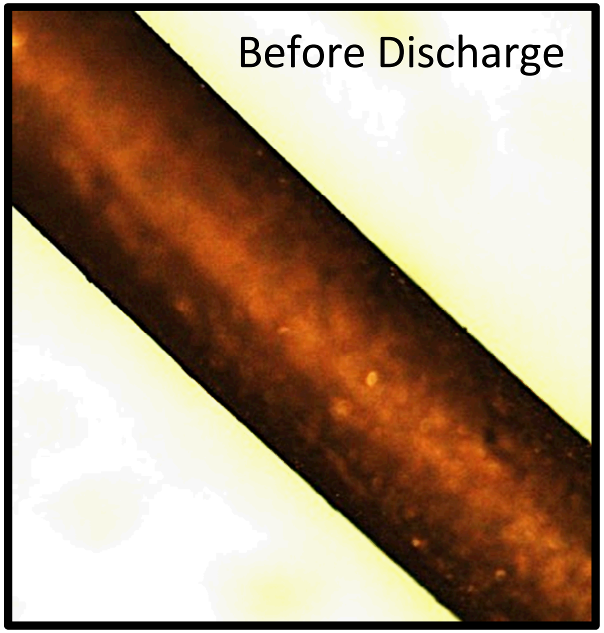
Using potentialstatic discharge this time, significant current passing through the LLTO ceramic was observed.

Elemental Analysis of anodic and cathodic salts shows K^+ and Li^+ (Li^+ not shown) transport, but no significant Cs^+ transport.





Cathodic Copper Deposition



Key Points

If you remember nothing else…

Electrochemical isolation of contaminant waste from eutectic molten salts is feasible using ceramic ion conductors.

If you remember a little more…

- Selective ion transport through LLTO-based and NaSICON-based ceramics allowed concentration of Cs^+ out of contaminated LiCl-KCl waste
- Although charge balance would ideally be achieved through reduction and oxidation of chlorine and chloride, copper served as a suitable substitute for proof of principle.
- This process was demonstrated using "pellet stacks," but more significantly, it was demonstrated in volumetric scale with VCR reactors.
- This approach offers a potentially new way to recycle and consolidate molten salt waste generated by pyroprocessing
  - Potentially compatible with existing electrochemistry and waste streams
  - Highly controllable process allowing regulation of contaminant concentration and subsequent heat load.

Acknowledgements

Thank you!

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