

Ion Selective Ceramics for Waste Separations:

***Performance and Design of Ion
Selective Ceramic Membrane
for Molten Salt Recycle***

Fuel Cycle Research & Development

***Prepared for
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SUMMARY

This report summarizes FY14 research efforts at Sandia National Laboratories committed to the program “Ion-Selective Ceramics for Waste Separations” within the DOE Office of Nuclear Energy’s Fuel Cell Research and Development program. In particular, this report describes a novel approach employing selective ion-conducting ceramics to mediate the electrochemical separation of fission product waste contaminants from molten salts used in pyroprocessing. Building on “proof of principle” studies from FY13 research, the primary technical objectives for FY14 were to develop a technical scheme to electrochemically segregate contaminants such as Cs^+ from LiCl-KCl molten salts and to demonstrate the feasibility of this process using laboratory scale volumes of molten salts. This report provides program motivation, describes a proposed approach for electrochemical molten salt purification using ion-selective ceramics, characterizes materials developed for this application, and presents experimental evidence supporting the feasibility of using this technical approach. Ultimately, there are two critical findings from this research: 1) the electrochemical reactions necessary for electrochemical salt recycling using ion-conducting ceramics are feasible on a volumetric scale, and 2) these volumetric reactions are demonstrated to be capable of isolation and concentration of Cs^+ contaminants in LiCl-KCl molten salts. Continued development of this approach would benefit from further refinement of the electrochemistry to include high temperature chlorine chemistry, advances in the processing of target ceramic materials to create closed-end tubes, and continued expansion of reactor scale. Ultimately, it is anticipated that this electrochemical process would enable controllable molten salt recycling that could be potentially integrated into existing pyroprocessing operations to reduce costly waste disposal volumes.

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ABBREVIATIONS

NaSICON	Sodium Super Ion Conductor ($\text{NaZr}_2\text{P}_3\text{O}_{12}$ or $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$)
KSICON	Potassium Super Ion Conductor ($\text{KZr}_2\text{P}_3\text{O}_{12}$)
LLTO	$\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$
LBLTO	$\text{Li}_6\text{BaLa}_2\text{Ta}_2\text{O}_{12}$
FP	fission product
mL	milliliters
mg	milligrams
A	Ampere
V	Volt
S	Siemen
cm	centimeter
psi	pounds per square inch
wt%	weight percent
mol	mole
rms	root mean square
XRD	x-ray diffraction
SEM	scanning electron microscopy or scanning electron microscopy
EDXS	energy dispersive x-ray spectroscopy
Li	lithium
Cl	chlorine
K	potassium
Na	sodium
La	lanthanum
Ba	barium
Ta	tantalum
O	oxygen
Zr	zirconium
Cs	cesium
H	hydrogen
P	phosphorus
Si	silicon
N_2	nitrogen gas
Ar	argon gas

Fe	iron
LiCl	lithium chloride
KCl	potassium chloride
CsCl	cesium chloride
FeCl ₃	iron chloride
kHz	kilohertz
MHz	megahertz
EIS	electrochemical impedance spectroscopy
EB	electrolyte binder
DC	direct current
VCR	variable compression ratio
ICP	inductively coupled plasma

1. INTRODUCTION

The management of waste products generated during the recycling of spent nuclear fuel remains an important consideration in the development of processes such as pyroprocessing. “Ion Selective Ceramics for Waste Separations” employs ion-selective ceramics in a novel approach to electrochemically “filter” out high-heat generating fission products (FPs), such as Cs^+ or Sr^{2+} that remain dissolved in the eutectic chloride molten salt electrolytes after the electrochemical isolation and extraction of recyclable actinides. Removal of these short-lived, high heat-generating FPs not only allows for the recycling and reuse of the molten salts themselves, but reduces the amount of contaminated salt that must be considered for long-term storage and disposal.

In FY13, the general strategy for this process was outlined, candidate ion-selective ceramics were synthesized and characterized, and small scale proof of principle experiments were conducted to verify the selective ion-transport of these materials at 500°C using molten salt pellets. The focus of FY14 work on this program has been the translation of these proof-of-principle experiments to a volumetric configuration capable of contaminant separation in molten salt volumes. This report will briefly review the ion-filtration approach, provide additional characterization of the systems developed in FY13, introduce two new volumetric waste separation configurations, describe new ceramic materials development, and finally demonstrate promising volumetric electrochemical segregation of waste products.

1.1 Background and Motivation

Pyroprocessing involves electrochemically dissolving spent nuclear fuel in a molten salt electrolyte and subsequently reductively plating out purified uranium that can be recaptured and recycled.¹ Left behind in the molten salt electrolyte, however, are residual fission products, transuranics, and other contaminants that can degrade the electrochemical efficiency of the system and, perhaps more significantly, require the disposal of potentially large volumes of radioactive molten salt waste. Developing a method to efficiently remove these contaminants would facilitate molten salt recycling and reduce the volume of hazardous waste to be packaged for disposal.

In contrast to extraction systems that utilize zeolite-based ion exchange or melt crystallization²⁻⁵ to isolate contaminants from molten salts, the technology described here is based on an electrochemical approach, potentially compatible with existing electrochemical operations used in pyroprocessing, that theoretically facilitates careful control over the degree of contaminant isolation. This level of control would be valuable in addressing concerns over factors such as heat load in salt designated for disposal, particularly with high-heat fission products such as cesium or strontium.

1.2 Technical Approach

This research program has focused specifically on the removal of Cs^+ from LiCl-KCl molten salt, though properly designed, the system could be used to remove multivalent cations from the system as well. Using Cs^+ as a model contaminant, Figure 1 schematically illustrates how this process would work, relying on the selective transport of Li^+ and K^+ cations through an ion-conducting ceramic “filter” and utilizing the oxidation and reduction of chlorine to balance charge in the system.

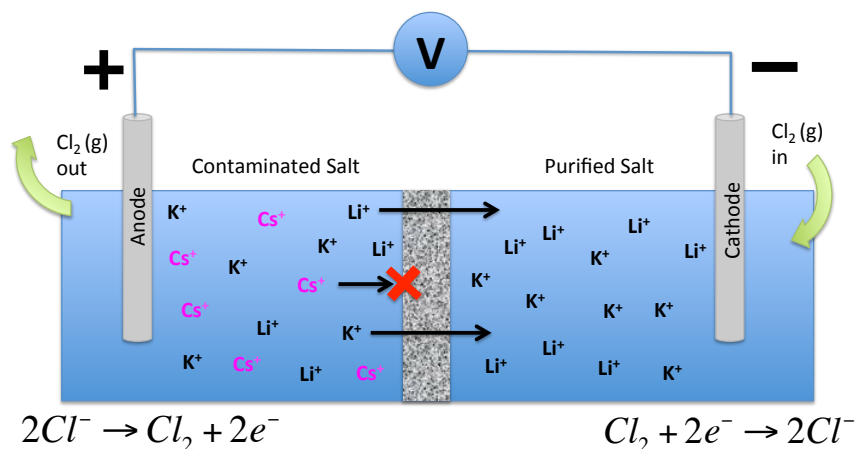


Figure 1. Scheme for electrochemical removal of Cs^+ from LiCl-KCl molten salt. Chloride ions in the molten salt have been omitted for clarity.

To achieve this electrochemical separation, Cs^+ -contaminated LiCl-KCl salt is placed opposite purified LiCl-KCl electrolyte, separated by an ion-selective solid state ceramic electrolyte, as indicated in Figure 1. Under an applied electrical bias, Li^+ and K^+ ions are transported across the ceramic, ion-conducting membrane, while Cs^+ cations are excluded, based on the fact that Cs^+ has a considerably larger ionic radius than either Li^+ or K^+ . ($r_{\text{Li}} = 0.090\text{\AA}$, $r_{\text{K}} = 1.52\text{\AA}$, $r_{\text{Cs}} = 1.81\text{\AA}$). In this way, Cs^+ is effectively filtered and ultimately concentrated on the anode-side of the cell. Ultimately, the resulting heavily Cs^+ -enriched salt would be processed for disposal, but the volume of salt waste would be dramatically reduced. To maintain charge balance on the anodic side of the cell, “excess” chloride ions in the molten salt would be electrochemically oxidized to form chlorine gas. Meanwhile, chlorine gas (Cl_2), ideally that produced at the anode, would be bubbled into the cathode where it would be reduced to chloride ions, balancing the influx of K^+ and Li^+ coming through the ceramic membrane.

1.3 Ion-Conducting Ceramics

The chemical, structural, and electrical properties of the ceramic separator will strongly influence the effectiveness of this approach. This ceramic material must serve as a stable physical barrier between contaminated and purified salts at 500°C , it must be resistant to radiation exposure, it must be electronically insulating, and it must enable efficient, selective ion transport of Li^+ and K^+ . The higher the ionic conductivity through the ceramic, the greater the ionic current through the cell and the faster the salt can be purified. The greater the selectivity, the higher the purity of the recycled salts. In this program, we have targeted two primary candidate materials: NaSICON-type ceramics and garnet-structured lithium lanthanum tantalates (Figure 2) though other candidate ceramics meeting these design criteria may also prove effective.

The general structures of NaSICON and LLTO are shown in Figure 2. The term NaSICON (Na Super Ion CONductor) commonly refers to the ion-conducting ceramic $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$, but more generally belongs to a family of compounds with the basic formula $[\text{M}^{\text{I}}_1][\text{M}^{\text{II}}_2][\text{A}^{\text{VI}}_2][\text{B}^{\text{IV}}_3]\text{O}_{12}$ (most often designated as $\text{M}_x\text{Zr}_2(\text{PO}_4)_3$). These materials comprise a hexagonal framework of corner-linked ZrO_6 octahedra and PO_4 tetrahedra, arranged to create restrictive channels for ionic transport. The size and charge distribution of these channels determines their ion-selectivity and overall ionic conductivity.⁶

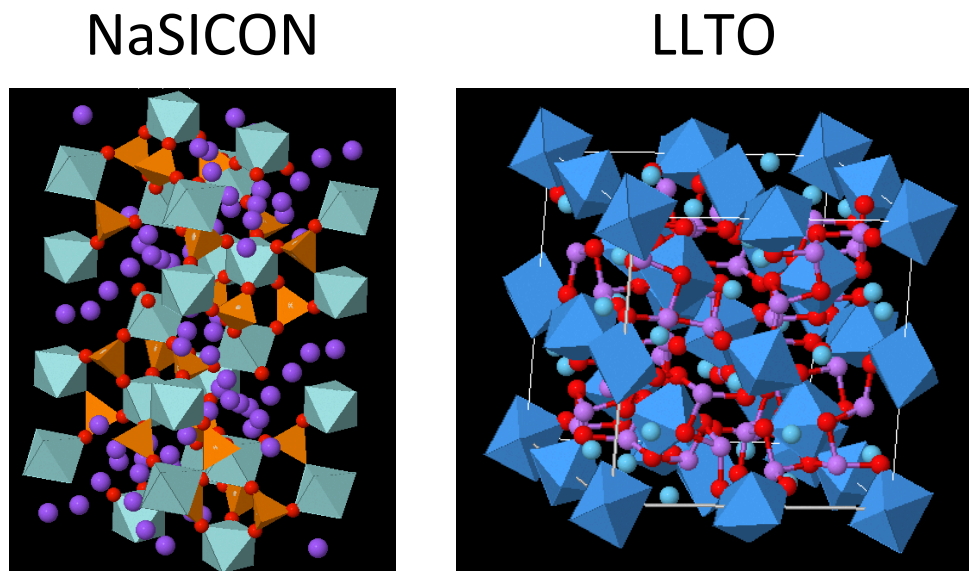


Figure 2. (Left) Molecular structure of $\text{NaZr}_2\text{P}_3\text{O}_{12}$ showing Zr-octahedra (light blue), phosphate tetrahedra (orange) oxygen (red) and Na (purple). Excess sodium is depicted moving through channels in the lattice. (Right) Molecular structure of $\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$ showing Ta octahedra, (blue), oxygen (red), La (blue spheres) and Li (purple).

In the present work, we will focus heavily on the performance of a commercial NaSICON product (Ceramtec, Inc., Salt Lake City, UT) that has been structurally and chemically modified by proprietary means, creating a ceramic exhibiting excellent sodium ion conductivity exceeding 10^{-3} S/cm at room temperature. We have additionally examined a potassium-substituted NaSICON variant, KSICON ($\text{KZr}_2\text{P}_3\text{O}_{12}$), synthesized by our team. This KSICON variant is specifically designed to accommodate the larger K^+ ions (as well as the much smaller Li^+ ions) inherent to our system, but because of relatively lower ionic conductivities, the application of this material in the volumetric purification studies emphasized here has been limited to date. Further studies of this promising material are anticipated in future work.

In addition to the NaSICON structures, we have studied the performance of garnet-structured lithium lanthanum tantalate (LLTO) ceramics (Figure 2) exhibiting high lithium ionic conductivities.⁷⁻⁹ Lithium ions in $\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$ and related materials move within a three-dimensional network of energetically equivalent partially occupied octahedral and tetrahedral coordination sites. Through expansion of these lattice sites, either because of lattice expansion at elevated temperatures, or through substitution with relatively large cations (e.g., substitution of Ba^{2+} ($r=1.49\text{\AA}$) for La^{3+} ($r=1.174\text{\AA}$)),^{8,9} it is anticipated that these LLTO-based ceramics will facilitate both K^+ transport and Li^+ transport, while still excluding the transport of very large Cs^+ ions. It is worth noting, however, that in the event these lattice changes do not promote facile K^+ ion transport, the favorable lithium ion transport properties of this material may still be useful in electrochemically purifying LiCl salts used in pyroprocessing.

1.4 Proof of Principle: Pellet Stack Testing

Initial demonstrations of the feasibility of using ion-selective ceramics to isolate Cs^+ from LiCl/KCl molten salts were done using a “pellet stack” configuration, shown in Figure 3. As detailed in the report by Spoerke, *et al.*,¹⁰ pellets of both anodic and cathodic molten salts, held together with an inorganic binder, were placed on opposite sides of ion-conducting ceramic membranes.

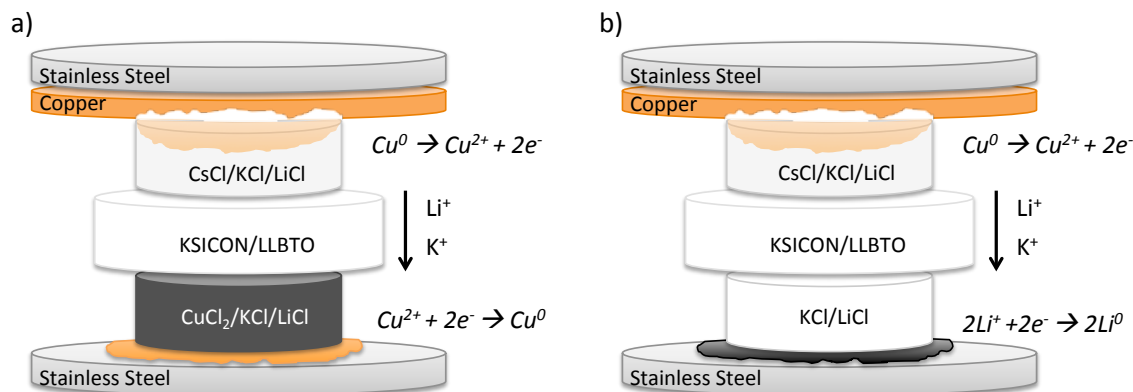


Figure 3. Schematic illustration of electroreduction of copper (left) or lithium (right) in a pellet stack using electrolyte binder pellets and an ion-conducting separator.

Heated to 500°C, galvanostatic discharge experiments showed clear evidence of ion transport (plating of copper or lithium at the device cathode concomitant with dissolution of the copper anode), and initial characterization of the cooled salt pellets showed excellent selectivity against Cs^+ transport for both LBLTO and KSICON ceramics. Further elemental analyses by inductively couple plasma (ICP) analysis of these materials have provided additional insight into the details of ion transport observed. Table 1 below shows the elemental concentrations of molten salt constituents dissolved in water after electrochemical discharge. These data clearly show extremely small quantities of Cs in the cathodic salts after discharge, quantified evidence of promising selectivity against Cs^+ transport through both the LBLTO and KSCICON ceramics.

Table 1. Elemental compositions of molten salt compositions dissolved in water (parts per million by weight).

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

Further analyses of the Li:K ratios in the anodic and cathodic salts informs the relative efficiency of Li^+ and K^+ transport in each ceramic. The graph in Figure 4 shows the Li:K ratios for the molten salts “as made” and after electrochemical discharge. For the LBLTO sample, the Li:K ratio decreased in the anode and increased in the cathode, indicating preferred lithium ion transport as one might expect from a lithium ion conductor. For the KSICON sample, the Li:K ratio did not change appreciably in the anode, but decreased significantly in the cathode. These data suggest that Li and K were transported with relatively equal efficiency from the anode, but that this process involved the expulsion of significant potassium from the KSICON lattice into the cathode, decreasing the observed Li:K ratio. Collectively these data indicate that the LLTO-based materials may be more suitable for Li-ion transport, with excellent selectivity against Cs^+ transport. In contrast, KSICON ceramics offer more balanced transport of both Li^+ and K^+ , though the selectivity against Cs^+ , while still excellent, is not quite as effective as in the LBLTO system. These promising results served as the foundation for designing the volumetric systems described below.

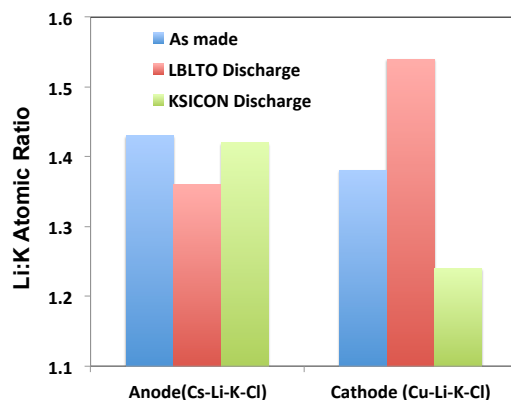


Figure 4. Li:K ratios for molten salt samples “as made” and after galvanostatic discharge in “pellet stack” tests of selective ion transport for LBLTO and KSICON ceramics.

2. VOLUMETRIC PURIFICATION DESIGN

2.1 Reaction Chemistry

The purification configuration in Figure 1 illustrates how the electrochemical separation of Cs^+ from LiCl/KCl molten salts may be achieved using an ion-selective ceramic, relying on the oxidation and reduction of chlorine. While this chemistry is part of a potentially elegant, efficient, and self-contained design for the ultimate realization of this waste separations system, the use of chlorine gas at 500°C introduces engineering challenges that are beyond the scope of the volumetric purification demonstration that was the principle focus of FY14 efforts. Certainly, the chlorine chemistry approach is believed to be feasible, and the materials and processes needed to safely manage this approach are in development. In the meanwhile, we have devised several alternative chemistries that allow preliminary investigation of the volumetric purification process without the added complications of handling chlorine chemistry at elevated temperatures.

2.1.1 Cu-mediated charge balance

The “pellet stack” test configuration highlighted in FY13 and summarized above, proved that charge balance in this electrochemical system could be achieved by oxidizing a copper anode and reducing either dissolved Cu^{2+} or Li^+ in the cathodic molten salt. In the interest of simplifying the chemistry involved, initial volumetric studies in FY14 utilized the symmetric copper chemistry. Copper oxidation at the anode and reduction at the cathode not only provides a symmetric reaction chemistry that requires minimal overpotential to drive, but the reduction of copper metal on the cathode provides clear, qualitative visual evidence that the reaction has occurred. Throughout this report the typical salt concentrations for the anodic and cathodic salts used for copper mediated electrochemistry are as identified in Table 2 below:

Table 2. Initial compositions of electrolyte salts used for volumetric electroreduction studies. All values are weight percents.

	LiCl	KCl	CsCl	CuCl_2
Anode: LiCl-KCl-CsCl	40.1	48.7	11.2	0
Cathode: LiCl-KCl- CuCl_2	32.7	41.6	0	25.7

2.1.2 Metal formate reduction to remove excess copper chloride

Although the use of copper in these systems is intended as a temporary substitute for chlorine, in select applications where chlorine chemistry may not be feasible, alternatives such as copper may be of value. One of the principle disadvantages of potentially introducing dissolved copper chloride into either the cathodic or anodic molten salts, though, is the likelihood of retaining residual copper salts in the final recycled salts or in salts to be packaged to for disposal. To address this concern, we determined that addition of lithium formate and potassium formate reducing agents to the system could effectively precipitate out metallic copper, leaving behind only LiCl and KCl salts. In particular, we demonstrated this process using lithium formate, added to molten salt of LiCl-KCl-CuCl₂. The image series in Figure 5 shows the initially dark brown, Cu-rich molten salt at 400°C. Upon addition of Li-formate, however, the following reaction occurred:



The images in Figure 5 show that as the particle of lithium formate dissolved into the molten salt, it rapidly evolved CO₂ and H₂ gases and transformed the dark brown salt to a reddish, copper-colored salt. Once the reaction was complete and the salt cooled to a solid, the reduced copper was clearly visible, phase separated from the white LiCl-KCl salt. In larger scale systems, it would be expected that the copper metal would sink to the bottom of the reaction vessel, leaving purified salt on top for collection. In addition to serving as an effective means to extract copper from these molten salts, this approach represents a potentially valuable alternative approach to extracting select contaminants from LiCl-KCl molten salts, provided the reduction potentials differ considerably from lithium or potassium.

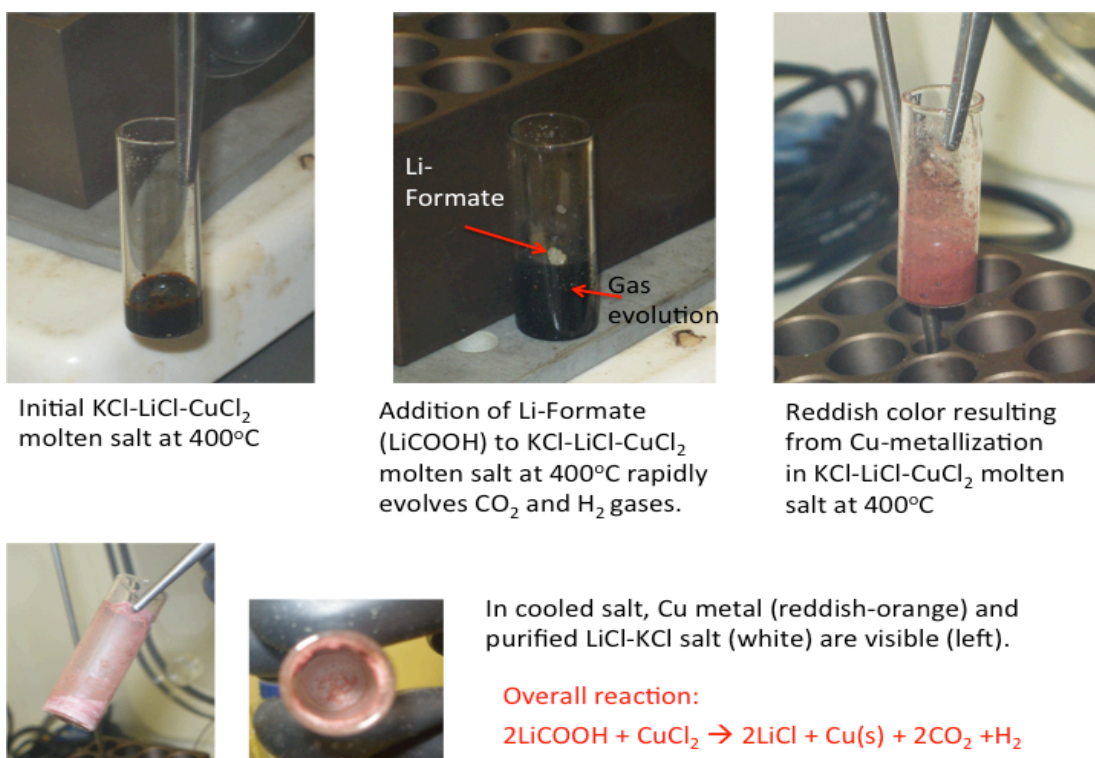
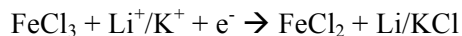


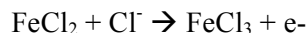
Figure 5. Image series showing the chemical reduction of dissolved CuCl₂ in LiCl-KCl molten salt at 400°C using lithium formate.

2.1.3 Charge balance through ferric/ferrous conversion

Ultimately, it will be desirable to replace copper, which must be physically dissolved and plated to balance charge in this electrochemical scheme, with chlorine. As an intermediate in the development of a feasible volumetric salt recycling system we have identified the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple as a soluble potential alternative to copper. In an iron-mediated system, the reaction in the cathodic salt would be:



Meanwhile, the reaction at the anode would be:



Both the ferric and ferrous chlorides remain soluble in LiCl-KCl molten salts, and this system provides a valuable opportunity to explore how variations in electrode structure and electrolyte interfaces will affect reaction kinetics in the chlorine-based system. To date, preliminary tests using iron-mediated charge balance have been performed using the volumetric reactor design described in Section 2.2.2 with iron chlorides dissolved at approximately 10 atomic % iron in LiCl-KCl molten salts and commercial NaSICON as a separator. These preliminary reactions produced currents comparable to those produced in similar experiments mediated by copper, evidence of approach feasibility. As this system is still under development, however, it will not be a significant focus in this report. Further investigation of these preliminary tests is currently underway to better understand the observed electrochemical behavior.

2.2 Reactor Design

Volumetric salt purification requires consideration not only of the materials chemistry involved, but also the integration of components into function device configurations. Below are two related designs that build around the requirements of electrochemistry and the combined virtues and limitations of the ion-conducting ceramics central to this purification process.

2.2.1 Concentric reactor

Figure 6 below schematically illustrates one configuration of volumetric reactor design that utilizes the concentric arrangement of a molten salt bath and a closed-end ceramic tube (or cups).

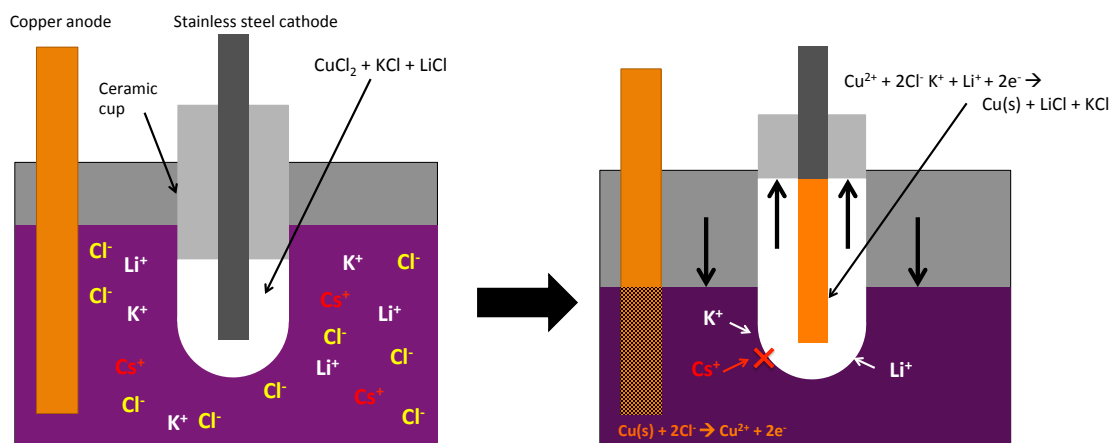


Figure 6. Schematic depiction of a concentric reactor design utilizing closed-end ceramic tubes (or cups) for volumetric salt purification.

This scheme shows the Cs-contaminated anodic salt in a large container. A closed-end ion-conducting ceramic would be placed in this anodic salt volume with the “purified” cathodic salt contained within the closed-end tube. A copper anode would be placed in the external container and an anode (e.g., stainless steel, tungsten, copper) would be placed inside the ceramic tube. Because the tube is closed on the bottom, there are no additional seals required for this system, and it provides inherent electronic separation of the anode and cathode. During the electrochemical discharge process, Li^+ and K^+ would be selectively transported into the ceramic tube interior, while Cs^+ would be concentrated in the anodic salt volume.

Figure 7 presents a photograph of equipment developed in our laboratory to perform these volumetric studies in a controlled atmosphere Ar-glove box utilizing the copper-mediated charge balance chemistry described above. This figure shows a high temperature furnace that has been adapted for use with this reactor scheme. Also shown are a steel cathode, an alumina vessel to contain the external salt volume (as well as a secondary steel container in the event of alumina vessel rupture), and a coiled copper anode. For illustration purposes a cellulose tube is shown where the ion-conducting ceramic would be placed. The anode and cathode are each be connected to two electrical leads (4 total) that connect through ports in the glove box to an external electrochemical workstation used to control and monitor the electrochemistry of the system.

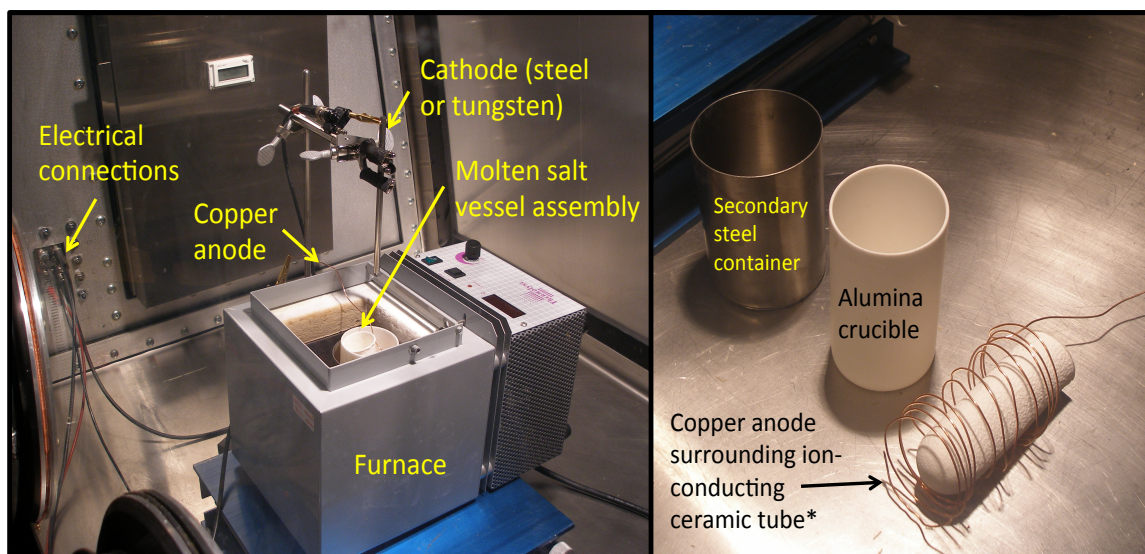


Figure 7. Photographs of reactor components to be utilized for volumetric salt purification using a concentric reactor design. *A cellulose tube is shown in place of the ion-selective ceramic tubes still in development.

Although the chemistry is shown here using copper-mediated charge balance, the system would also be readily amenable to chlorine chemistry. For example, the entire system could be enclosed in a sealed vessel with a chlorine atmosphere that would allow for a self-contained, efficient purification process. As the salt purification process proceeds, the ceramic tube would gradually fill with purified salt, eventually requiring collection, such as from an external drain or by removal and emptying of the ceramic tube.

Critical to this arrangement, however, is the formation of closed-end ceramic tubes. As described below, we have taken preliminary steps toward the development of closed end LLTO ceramic tubes, but ultimately such tubes could be produced by industrial partners such as Ceramatec, CoorsTek, or Ionotec, who have developed mature capabilities to synthesize closed-end tubes from ion-conducting ceramics.

2.2.2 “VCR” reactor

The concentric reactor design above relies fundamentally on the development of closed-end ion-conducting tubes. Since the development and/or procurement of these specialized tubes is still in process and is expected to exceed the timeframe of the FY14 objectives to demonstrate volumetric purification, an alternative approach was developed that utilizes ceramic pellets, already available and proven in lab-scale experiments. The principle challenge to using pellets for volumetric purification lies in forming effective seals against the ceramic parts to prevent mixing of anodic and cathodic salts. To address this challenge, we employed commercial Swagelok® VCR fittings with copper gaskets to seal the ceramic parts, separating anodic and cathodic salts. Figure 8 schematically illustrates both the VCR assembly and its implementation in an adaptation of the concentric reactor scheme from Figure 6.

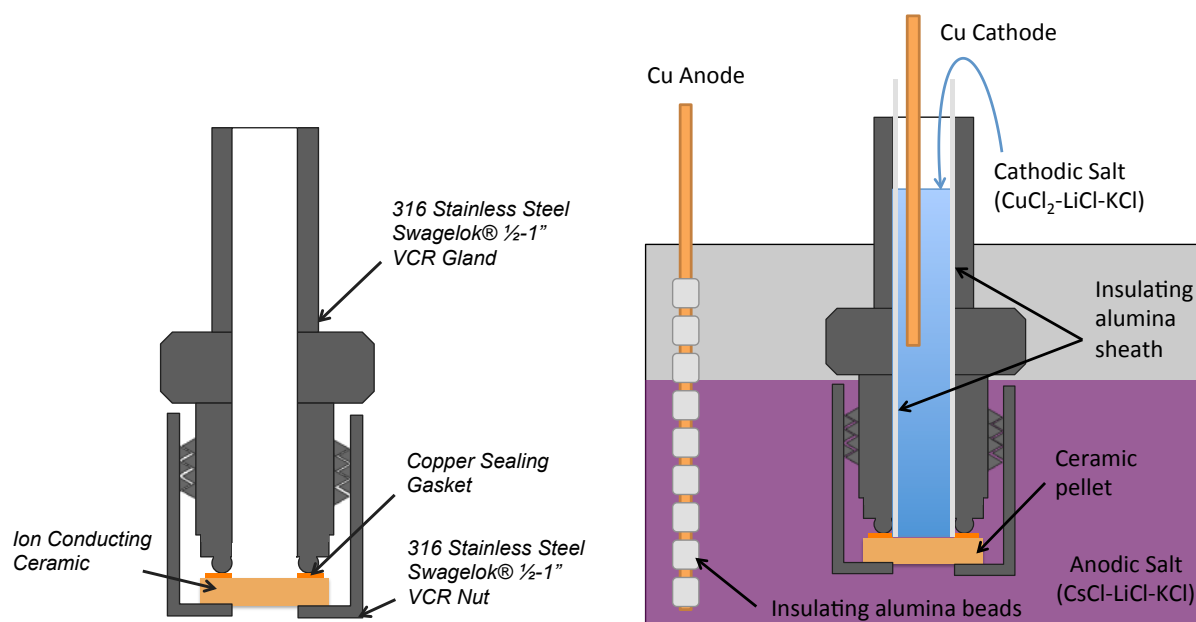


Figure 8. Schematic depiction of a VCR reactor design utilizing ceramic pellets for volumetric salt purification.

Once a flat, dense, uniformly thick ion-conducting ceramic pellet has been sealed in the VCR fixture, the assembled vessel and a copper anode are placed in an alumina crucible prefilled with anodic salt. Cathodic salt is placed inside the top port of the cathodic volume on the VCR assembly and a copper wire anode is placed inside this volume. Key to this process is the electrical isolation of both the cathode and the anode from the stainless steel VCR assembly. It is important that the only pathway for charge transport in this system runs through the ionic ceramic. As a result, an alumina sheath is placed inside the cathodic “chamber” to prevent shorting of the cathode to the VCR fitting, and alumina beads are threaded on the copper anode. These beads prevent electrical shorting, but still allow facile contact between the copper anode and the anodic molten salt. This entire assembly is placed in an insulated furnace within an Ar-atmosphere glove box, the electrical leads are connected to anode and cathode, and the assembly is heated until the salt reaches 500°C. At this point both anodic and cathodic salts are molten and electrochemical experiments can be conducted. Figure 9 shows this assembled structure following an electrochemical experiment and cooling to room temperature.

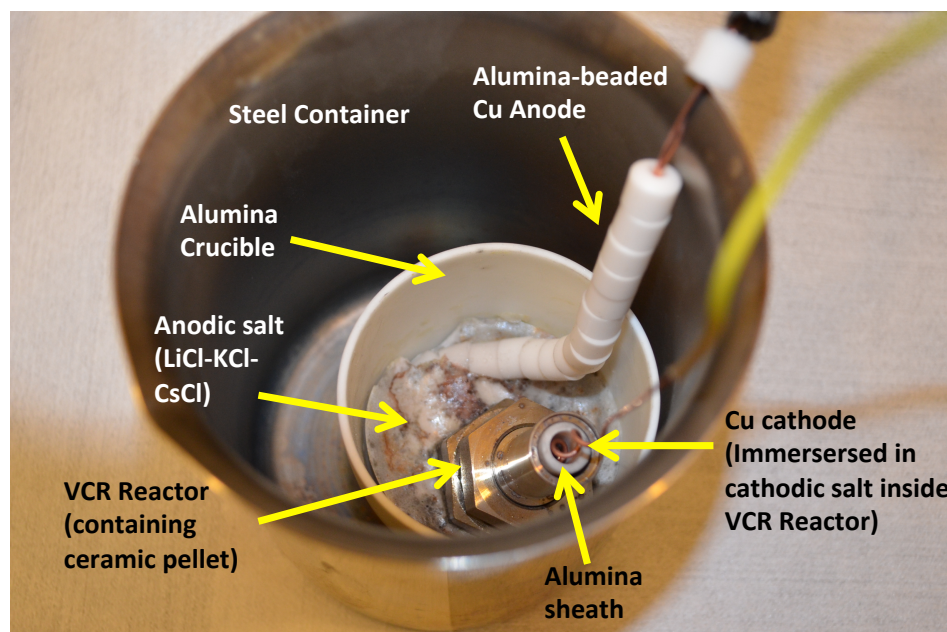


Figure 9. Photograph of a VCR reactor configuration after cooling from an electrochemical test.

Although this configuration does not provide as much surface area for ionic separation as the concentric reactor design described above, and it does require sealing of the ceramic parts within the reactor, this system does offer a number of advantages over the concentric design. First, it can be readily used to study a variety of different ceramic systems without having to developed closed-end ceramic tubes from each material – a potentially significant technical obstacle. In addition, the system is potentially scalable. By increasing the size of the vessel containing the salt, multiple reactors, potentially containing a variety of different ceramic separators could be simultaneously used in parallel. Although this could also be achieved with closed-end tubes, again the relative ease of incorporating different materials into the same reactor scheme is an advantage of the VCR system.

Finally, the VCR fitting apparatus is amenable to integration into a closed system suitable for chlorine-mediated electrochemical purification. Figure 10 below provides a preliminary schematic design of how the VCR fitting may be integrated into such a system using stainless steel tubing and gas-tight Swagelok® unions. Materials compatibility with reactive chlorine chemistry will have to be investigated prior to design implementation, but the VCR-concept does provide a pathway toward initial demonstrations of the electrochemical purification through chlorine oxidation/reduction. The modular, connectable nature of this design makes incorporation of ports, valves, vents, and other reactor access points relatively straightforward. Moreover, because the size of the system can be varied by changing the tubing diameter, or even more easily, the tubing length, the scale of the system can also be readily varied. Examining the implementation of such a system in FY15 will be an important program objective.

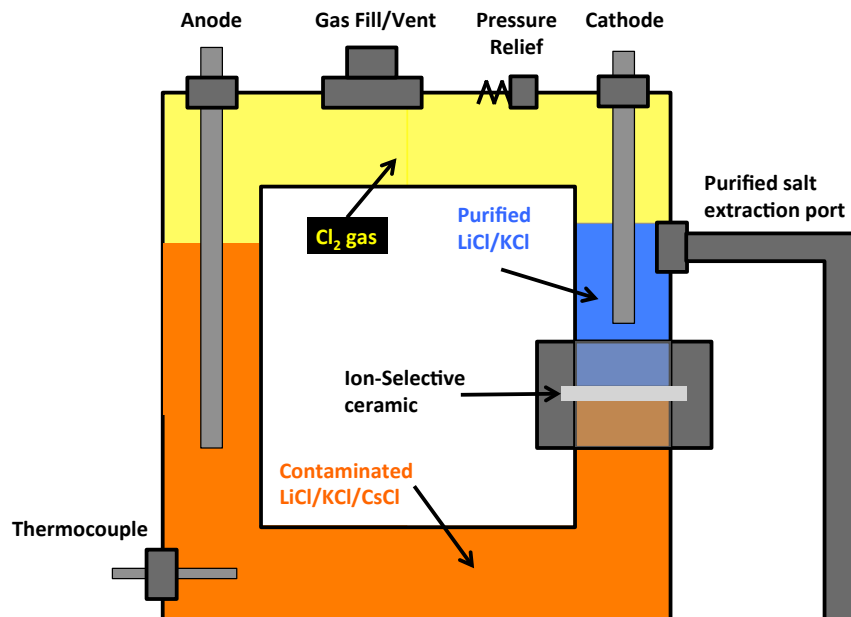


Figure 10. Preliminary schematic of a closed-loop steel tubing-based reactor design incorporating a VCR-reactor for salt purification. *Note, not all valves, unions, or seals are illustrated in this schematic.

3. MATERIALS DEVELOPMENT AND EVALUATION

3.1 Ceramic Development

In FY13, a LBLTO ($\text{Li}_6\text{BaLa}_2\text{Ta}_2\text{O}_{12}$) the barium-substituted variant of the lithium ion conductor LLTO ($\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$) was synthesized to help increase ionic conductivity and potentially facilitate potassium transport in addition to expected lithium transport. Unfortunately, characterization of these Ba-modified samples, particularly after exposure to higher temperatures (e.g., 650°C), revealed significant, undesirable Ba-mobility. As a result, ceramic synthesis efforts refocused on optimization of dense, highly conductive LLTO ceramics that would, at a minimum, serve as robust ionic conductors for separations in LiCl salts. Moreover, one of the principle reasons for introducing Ba into LLTO is the increased ionic conductivity seen in LBLTO. We have recently come to believe, however, that the relatively reduced conductivity reported for bulk LLTO may be related to poor ceramic density. It was anticipated, then, that improving LLTO density would not only improve ceramic integrity but also provide increased conductivity comparable to that of LBLTO.

In addition to LLTO-based materials, NaSICON-based materials were also explored. These activities included both KSICON-based ceramics, synthesized in house at Sandia National Laboratories (SNL) and intended to accommodate facile potassium and lithium transport, and commercial NaSICON pellets obtained from Ceramtec, Inc. (Salt Lake City, UT).

3.1.1 Ceramic Syntheses

For materials prepared at SNL, both NaSICON-type and LLTO-based ceramic test specimens were synthesized using solid-state techniques as described previously.¹⁰ Briefly, solid-state precursors, specific to each compound, were combined and mixed by ball milling with ZrO_2 media in organic solvent (e.g., hexanes, ethanol, etc.) for 24 hours. After removal of the solvent from these mixed powders, materials were calcined, milled once more, and then pressed into pellets for firing under burial powder in capped

crucibles. Significantly, through careful control of reagent stoichiometry throughout the synthesis, a new process was developed that produced almost entirely phase pure LLTO ceramic pellets with densities exceeding 98.5%. Not only are these highly dense ceramic pellets structurally robust, but the ionic conductivity of these materials exceeds any previous reports for LLTO and rivals values generally reported for the more conductive LBLTO (Figure 11). We are currently in the process of advancing IP related to this DOE-NE funded research advance, which we believe is a strong candidate for industrial technology transfer, applicable both to waste separation and robust, electrical energy storage.

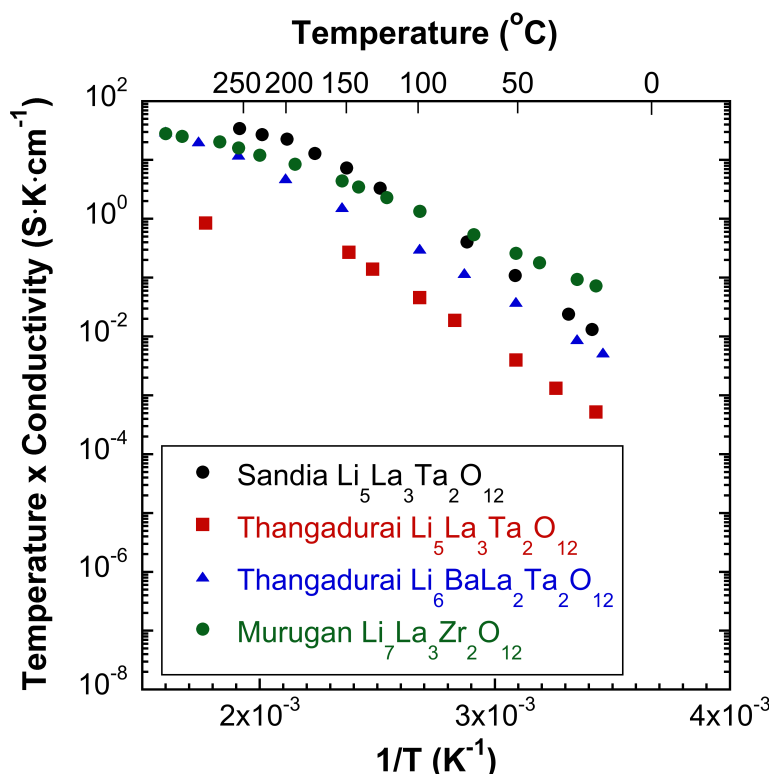


Figure 11. Ionic conductivity of garnet-type lithium ion conductors. Literature values taken from Thanagadurai⁹ and Murugan.¹¹

3.1.2 Secondary LLTO phase formation

In the process of optimizing LLTO synthesis, x-ray diffraction studies revealed a secondary phase forming that was previously not identified in the international crystallographic database. Although this was not a primary focus of the present effort, we were able to identify this material as a monoclinic ordered perovskite, $\text{LiLa}_2\text{TaO}_6$, a new ion conducting phase (Figure 12). The new crystallographic data collected were presented at the 2014 Spring Meeting of the International Center for Diffraction Data (ICDD). (March 17-21, 2014, Concordville, PA), and will be published as a permanent record in the ICDD Database.¹² Further examination of this material as a candidate ion conductor for waste separations will be the focus of future efforts.

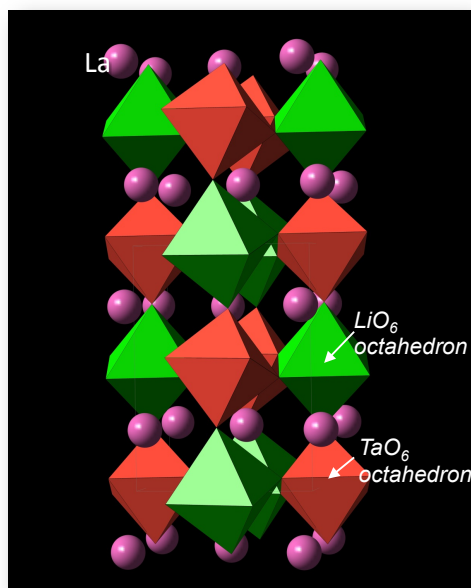


Figure 12. Crystal structure for newly defined $\text{LiLa}_2\text{TaO}_6$ phase.

3.1.3 Ceramic tube synthesis

One of the central components of the concentric reactor design is the closed-end ion-selective ceramic tube. Based on the chemistry developed for the formation of phase-pure, high density LLTO ceramic pellets, a slip-casting approach was used to create LLTO ceramic tubes. Precursor powders were milled in organic solvent, dried, and calcined. A high volume fraction suspension of powders (e.g., 50%) was prepared in water and degassed before pouring into a plaster mold to extract the aqueous phase. After consolidation of the ceramic form, the green ceramic part was removed and allowed to dry before firing in a covered crucible. The images in Figure 13 below show the green tubes as well as a fired ceramic part. Although results to date show promise for the formation of functional closed-end ceramics, this process is not yet mature, and the fired components have not exhibited the structural integrity and density desired for use in the volumetric reactor design of Figure 6. Continued optimization of this process, possibly in collaboration with ceramic part manufacturers would be expected to accelerate future tube development.

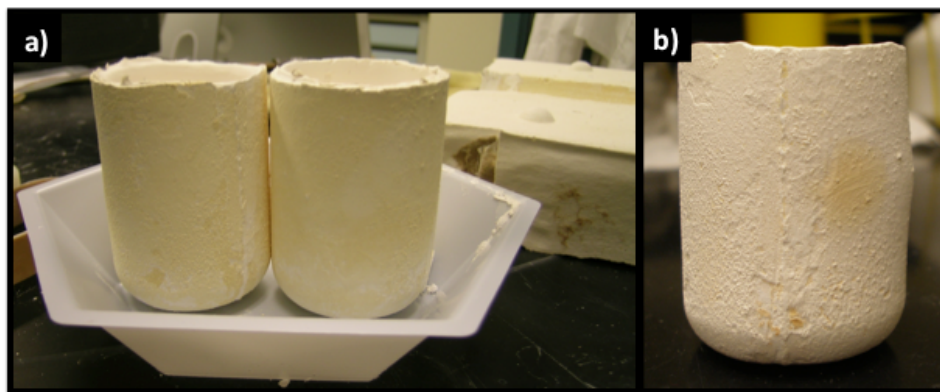


Figure 13. Photographs of a) green LLTO ceramic closed-end tubes produced by slip-casting and b) a fired LLTO ceramic closed-end tube.

3.2 Materials Characterization

The morphology, chemistry, and crystal structure of synthesized materials, both in powder form and as sintered pellets were characterized before evaluating the ion-transport and molten salt stability of these compounds.

3.2.1 Structural characterization

To investigate ceramic microstructure, morphology and qualitative chemical composition, platinum-coated samples examined were examined in a Zeiss Supra™ 55VP scanning electron microscope (SEM) at 10keV, fitted with an Oxford X-Max energy dispersive x-ray spectroscopy (EDXS) detector and AZtec® software. Crystallography of ion-conducting materials was evaluated by x-ray diffraction (XRD), performed on both powder samples and ceramic pellets using a Panalytical X'Pert Pro powder diffractometer or a Siemens D500 theta/theta diffractometer (Cu $K\alpha$ radiation).

3.2.2 Impedance spectroscopy

Gold blocking electrodes were sputter deposited onto the parallel faces of 0.25"-0.625" diameter ceramic pellets to enable impedance measurements. Impedance data were collected using an Agilent 4284A instrument at variable temperatures. An oscillator voltage of 20mV rms was applied over a frequency range from 1kHz to 1MHz and the absolute impedance and phase angle measured.

3.2.3 Chemical Analysis

Chemical analysis of the molten salt compositions both before and after electrochemical testing was performed using inductively couple plasma (ICP) analysis in collaboration with the analytical laboratories at CoorsTek (Golden, CO.) Molten salt samples were either collected from cooled salt volumes or from high temperature melts using a glass pipette (salts cooled in pipette). Samples were dissolved in deionized water and centrifuged or filtered to remove insoluble precipitates (e.g, Cu-based precipitates) before ICP analysis.

4. VOLUMETRIC ELECTROCHEMICAL DEMONSTRATIONS

As mentioned above, the priority of demonstrating the volumetric application of this electrochemical separations approach motivated the use of the VCR-pellet based reactor scheme outlined above. Once closed-end ion conducting ceramic tubes are available for use, the system can be readily adapted to explore this potentially higher capacity application as well.

4.1 Cu-Mediated Electrochemical Separations

The VCR-reactor volumetric electrochemical experiments were set up and run as described in Section 2.2.2. The experiments described below include tests of high density LLTO pellets and commercial NaSICON pellets. Although KSICON materials developed in this program remain of interest, these preliminary studies focused on the use of NaSICON, based on the expectation that the smaller channel size of the sodium-ion conductor (relative to the K^+ -ion conductor may provide improved selectivity against Cs^+ transport. Moreover the commercially available materials offered considerably higher ionic conductivity ($>10^{-3}$ S/cm at room temperature) than the $KZr_2P_3O_{12}$ pellets ($<10^{-4}$ S/cm total conductivity at room temperature) synthesized by our group. Future work will continue to explore the use of the

KSICON variants developed in this program, but for the demonstrations described here, the commercial NaSICON ceramics were used.

Figure 14 below shows the potentiostatic discharge profile for a representative test run on an LLTO pellet using copper-mediated charge balance. These tests were typically run using 30-50g of Cs-contaminated anodic salt and ~5-7g of cathodic salt. The plot in Figure 14 shows the current produced over time when a constant voltage of -200mV was applied across the two cell electrodes. Although previous studies on the “pellet stack” configuration had included galvanostatic discharge experiments, the volumetric studies emphasized here were conducted by applying a specific, constant voltage to drive ion transport. Ultimately, it would be expected that by monitoring the current in these potentiostatic experiments it may be possible to gauge the degree of impurity concentration *in situ*, based on the amount of ionic charge (Li^+ and K^+) passed through the ceramic separator (correlated with the measured current measured in the test cell). The data in Figure 14 show a reasonably smooth current response to the applied voltage over the course of 10 minutes of discharge (though typical tests included multiple 10-20 minute discharges with similar responses).

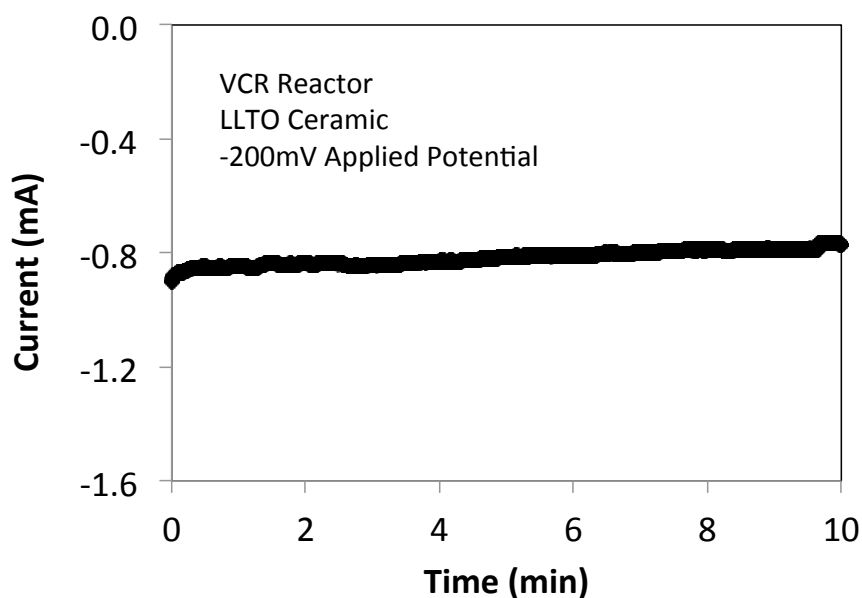


Figure 14. Current response over time for an VCR reactor cell configured with an LLTO ceramic. Constant applied potential was -200mV across the cell. Charge balance was maintained with Cu-chemistry.

Control experiments run using stainless steel coupons in place of the ion-conducting ceramics showed a current response (believed to be due largely to capacitive charging of cell interfaces) more than an order of magnitude smaller than that shown here, supporting the conclusion that the current measured is the result of ion-transport through the ceramic separator. *These data represent compelling evidence to support the feasibility of volumetric electrochemical reactions using the VCR-reactor configuration.*

In addition to demonstrating the feasibility of performing volumetric electrochemical reactions, the objective of these reactions is to segregate and concentrate Cs^+ in the anodic salt. To determine whether or not this process took place during the electrochemical experiments described above, molten salt samples were taken from the cathode and anode after tests performed with both LLTO and commercial NaSICON pellets. These salt samples were dissolved and the elemental compositions determined by ICP. Figure 15 below presents the elemental ratios (based on atomic concentration) of Cs:K for “as-made

salts” as well as salts harvested from LLTO and NaSICON-mediated separations. (Cs:Li data were also collected but led to substantially identical conclusions). Considering first the LLTO samples, the ratio of Cs:K increased substantially at the anode with no significant Cs measured at the cathode (ratio was 1.64×10^{-4}). The increase in the ratio of Cs:K at the anode provides compelling evidence that K^+ was transported from the anode, while the Cs^+ was not, effectively concentrating the Cs^+ in the anodic molten salt. (Similar, corroborating data were observed for the Cs:Li ratio but are not shown for conciseness.) The notable absence of any significant Cs at the cathode is further evidence of the excellent selectivity of the LLTO against Cs^+ transport. It is interesting, however, that the K^+ does appear to have been effectively transported through the LLTO, a ceramic largely known for transport of much smaller Li^+ ions. While this is certainly a boon to the electrochemical purification of the LiCl/KCl molten salts (as opposed to LiCl only), understanding the mechanisms behind this promising result will be the subject of future study.

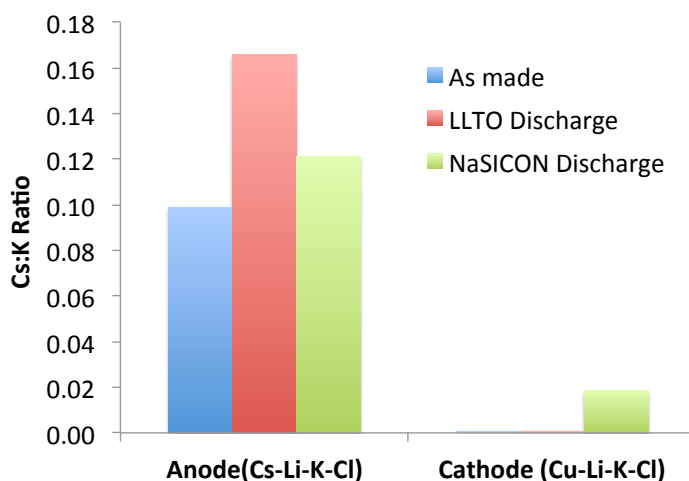


Figure 15. Cs:K ratios determined from anodic and cathodic salts in “as-made” salts as well as after electrochemical separation through LLTO and NaSICON ceramics.

Examining the results from the commercial NaSICON study, the Cs:K ratio also appears to increase at the anode, though not as significantly. This difference may be explained by the significant presence of Cs in the cathode. Clearly the NaSICON structure did not provide the same degree of ion selectivity as the LLTO sample. This result is not terribly surprising, however, owing to the fact that the commercial NaSICON structure has likely been optimized for rapid Na^+ -transport through enlarged crystallographic channels. These enlarged channels would not be expected to provide the same degree of selectivity against the larger Cs^+ .

Collectively, these data not only show that volumetric electrochemical experiments are feasible, but they also confirm that the ion-selective ceramics can be used to segregate and concentrate Cs^+ in LiCl/KCl molten salts. Moreover, understanding and engineering the crystal structures of the ceramics themselves, a significant focus for FY13 and FY14, can have a direct influence on the efficiency of the purification process.

5. SUMMARY AND EVALUATION OF FEASIBILITY

The primary objectives of FY14 research were 1) to develop the materials and processes needed for lab-scale volumetric electrochemical reactions and 2) to demonstrate the feasibility of Cs-segregation from volumes of LiCl-KCl molten salts. Notable, *both of these objectives were met using the VCR-reactor configuration and Cu-mediated charge balance.*

With respect to the first point, we developed two primary volumetric purification schemes, the concentric reactor and the VCR reactor and multiple materials chemistry issues were addressed:

- The concentric reactor scheme promises higher ceramic surface area and thus potentially higher purification rates and does not require “sealing” of the ceramic within the reactor to prevent mixing of the anodic (contaminated) and cathodic (purified) molten salts. This configuration does, however, require the use of closed-end ceramic tubes. Although significant progress was made toward the production of closed-end LLTO tubes, development of these ceramic components is not yet sufficiently mature for effective integration into a functional system. Future collaborations with technical partners such as Ceramtec, CoorsTek, or Ionotec may facilitate accelerated development of LLTO, KSICON, or alternative ionic ceramic candidate materials as closed-end tubes.
- The VCR-reactor configuration takes advantage of commercially-available Swagelok® VCR fittings and more readily processed ceramic pellets available in our laboratory and commercially. This more modular approach introduces significant flexibility for process development, allowing for screening of many more ceramic materials than if each ceramic had to be formed as a closed-end tube. Moreover, this configuration is not only compatible with the facilities developed for the concentric reactor scheme but is also well-suited for integration into a tubing-based volumetric reactor replacing copper redox with chlorine oxidation and reduction for electrochemical charge balance. It is this reactor configuration that was used to demonstrate electrochemical Cs-segregation in lab scale molten salt volumes.
- With respect to the materials chemistry of the system, not only was significant progress made toward the development of phase pure, highly dense and highly conductive LLTO ceramics, but a new lithium lanthanum tantalate was identified and characterized.
- Although the use of copper to mediate charge balance in this system persisted throughout these tests, formate-based chemistries were identified that could be used to remove excess copper from LiCl-KCl molten salts. In addition, an iron-based alternative to copper was presented as an intermediate chemical option until the use of chlorine chemistry can be realized. Development of a chlorine-based system will be a priority for future work on this system.

Considering the second point, the VCR-reactor test configuration not only allowed for electrochemical testing using lab-scale volumes of molten salts, but based on elemental analysis of the anodic and cathodic salts, there is compelling evidence that the *ion-selective ceramics effectively concentrated Cs in the anodic salt.* This result was observed with both LLTO and NaSICON-based ceramics, though the selectivity was demonstrably better with the LLTO.

Collectively, the data presented here provide compelling evidence that with further materials optimization and effective translation to a chlorine-mediated electrochemical system, this technical approach holds promise for efficient, well-controlled recycling of pyroprocessing molten salts. Moreover, the electrochemical nature of the approach makes it potentially compatible with existing pyroprocessing infrastructure with minimal disruption of the existing processes or waste stream development. In addition, because the consolidation and extraction of contaminants is electrochemically regulated, it is

expected that the degree of contaminant concentration in waste salt could be controlled. Such control would facilitate manipulation of, for example, heat loading in waste designate for disposal.

6. FUTURE WORK

Although these results and the schemes proposed form a promising foundation for the advance of this salt recycling technology, there are several key issues that should be addressed in future work if the technology is to advance.

- Translation to chlorine chemistry is an important priority. The chlorine chemistry option reduces the component complexity of the system and avoids introducing additional elements to any waste streams destined for disposal. The highly reactive nature of chlorine gas at 500°C, however, will require significant investigation of materials compatibility between chlorine and the ion-conducting ceramics, the molten salts, and the structural and safety elements of the reactor assembly. Variations of the chlorine chemistry, including dilution of chlorine with inert gases, should be considered to reduce the complications associated with chlorine reactivity.
- Long-term ceramic stability should be investigated. This entails structural, chemical, and functional stability, ultimately in a hot-cell environment. These properties not only affect the potential utility of the system, but they may impact considerations for ultimate disposal of radio-exposed ceramic materials.
- System integration with existing pyroprocessing operations will be a valuable characteristic of this system, and that process will require tailoring the reactor scale and technical configuration for most efficient integration with minimal disruption to ongoing operations.
- The limits of purification capacity, efficiency (purity), and rate will need to be evaluated once larger scale reactors are developed. Extracting the optimal utility of this approach will depend on developing a comprehensive picture of what the limits of the system are.

While these are all important technical priorities, it is also important to consider that continued research in this area is expected to prove rich in scientific insights as well. The development of new materials and/or the novel application of existing materials stand to lend important insights to technical communities focused on ceramic ion-conducting materials. In addition to development of novel salt-recycling systems, the continuation of this work may impact energy storage, hazardous waste remediation, chemical filtration, chemical detection, and a host of other nationally and globally important technologies.

7. NOTABLE PROJECT DELIVERABLES

In addition to the development of the described electrochemical salt recycling technology and the compilation of milestone reports such as this document, efforts to date have produced several other notable deliverables:

- Provisional Patent filed on “Electrochemical Ion Separation in Molten Salts” (March, 2014)
- SNL Technical Advance: Processing method for producing dense $\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$ lithium ion conductor (SNL SD# 13096, March, 2014)
- Submitted manuscript, M.A. Rodriguez, *et al.* “X-ray powder diffraction study of $\text{La}_2\text{LiTaO}_6$ ” for publication in *Powder Diffraction*. (May, 2014)
- Established crystallographic data (new international diffraction database entry) for $\text{LiLa}_2\text{TaO}_6$ (presented at the 2014 Spring Meeting of the International Center for Diffraction Data. March 17-21, 2014, Concordville, PA.)

8. ACKNOWLEDGEMENTS

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