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Ion Selective Ceramics for Waste Separations:

Input for Annual Accomplishments Report

Fuel Cycle Research & Development

Prepared for
U.S. Department of Energy Office of Nuclear Energy
Material Recovery and Waste Form Development Campaign

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FCT Quality Assurance Program Document

FCT Document Cover Sheet

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"Ion-Selective Ceramics for Waste Separations" aims to develop an electrochemical approach to remove fission product waste (e.g., Cs^+) from the LiCl-KCl molten salts used in the pyroprocessing of spent nuclear fuel. Consolidation and concentration of contaminants such as Cs^+ and Sr^{2+} in molten salts would substantially reduce the volume of high level waste that must be packaged for disposal. We recently generated two reports describing the laboratory-scale application of ion-selective ceramics (LLTO ($Li_5La_3Ta_2O_{12}$) and NaSICON-type materials (e.g., $KZr_2P_3O_{12}$)) as "filters" to recycle 500°C LiCl-KCl molten salts and concentrate Cs^+ contaminants in a reduced volume of salt.[1,2] Under electrochemical bias, Li^+ and K^+ were selectively transported across the membrane to make purified salt, while Cs^+ contaminants were blocked from transport. Na^+ ions are also expected to be transported, while divalent contaminants,[3] such as Sr^{2+}, Ba^{2+}, or Sm^{2+} would also be expected to be excluded, concentrated in the waste salt. Charge balance of these reactions was maintained through the oxidation and reduction of copper at the anode and cathode of the cell, respectively. This process is schematically illustrated in Figure 1, though, the copper-based charge balance chemistry is replaced by chlorine/chloride reduction/oxidation. In Figure 1, a closed-end ceramic tube separates volumes of contaminated and non-contaminated salt, allowing selective transport of Li^+ and K^+ through the ceramic. Balancing cation transport with chlorine reduction results in increased volume of purified LiCl-KCl salt outside the tube, and concentrated CsCl salt inside the tube. The focus of effort in FY15 was to identify critical technical issues associated with scaling this approach for potential industrial use.

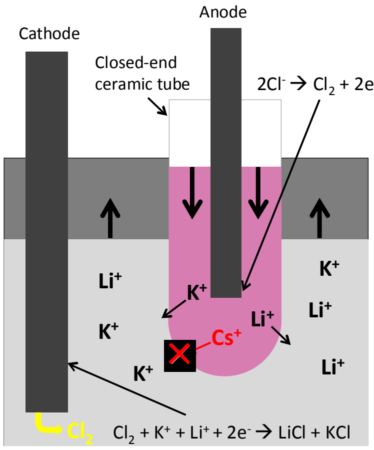

Fig. 1. Schematic of process to use a closed-end ceramic tube to isolate Cs-contamination from LiCl-KCl molten salt. Cl^- ions (present in all salts) not shown for clarity.

In considering the technical challenges of implementing this process for pyroprocessing salt remediation, a number of assumptions were made. First we assume an annual salt waste (LiCl-KCl, containing 12% NaCl) production volume of 15 metric tons (MT), based on projections by Simpson,[3,4] and this waste is conservatively assumed to have a representative (though not expressly definitive) contamination level of 2.5% CsCl[3] (accounting for other contaminants would slightly *decrease* the required electrochemical capacity of the system). The limit for CsCl concentration was determined by estimating the melting temperature (<500°C) of the Cs-enriched molten salt,[5] leading to an estimated target waste CsCl content as high as 60 mole percent CsCl (~80 weight percent). This dramatic consolidation of contaminant would require transporting more than 99% of the Li^+, K^+, and Na^+ ions out of the waste salt. Applying a current density of $100 mA/cm^2$, utilizing 50 waste-filled ceramic separator tubes (25 cm long, 4 cm diameter), and running 12 hours daily, 15MT of waste salt could be treated in under 1 year (11.7 months). This timeframe is proportionately decreases if the number (or size) of ceramic tubes (and electrodes) is increased, the number of hours per day is increased, or the current density is increased.

There are several critical design elements that must be considered to effectively integrating these ceramic tubes, molten salts, electrodes, and charge compensating chemistry into a functional reactor. First, a vessel capable of maintaining an isolated atmosphere, possibly a highly corrosive chlorine atmosphere, must be created to contain the assembly. Candidate formable steel alloys may include Haynes 556 and Haynes 214, available through Haynes, International (Kokomo, IN), and reported to exhibit excellent corrosion resistance in chlorine-bearing and chloride molten salt environments at temperatures well above the 500°C anticipated working temperature.

Realizing large-scale salt treatment will also require the reliable manufacture of numerous formed ceramics, ideally closed end tubes. We have consulted with representatives from Ceramatec, Inc (Salt Lake City, UT), who specialize in alkali-conducting NaSICON ceramic materials, similar to the KSICON ceramics explored in this program. As shown in Figure 2, they have developed production-scale capabilities to create a range of NaSICON ceramic discs, plates, and tubes, including closed-end tubes, adhering to strict tolerances for ceramic thickness, uniformity, and phase chemistry. Ceramatec would be a logical partner in the production of formed KSICON or LLTO ceramics for use in this technology.

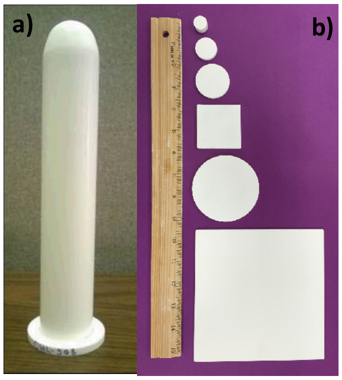

Fig. 2. a) A closed-end ceramic tube (4 cm diameter) and b) sheets, discs, and cylinders made from NaSICON ceramics. Images from Ceramatec, Inc.

Another key concern is the incorporation of chemically, thermally, and radioactively stable seals, particularly if a chlorine atmosphere is to be maintained in the reactor. Seals will also need to electrically isolate the anode and cathode and effectively join reaction vessel ports with components such as salt inlet plumbing, thermocouples, gas inlets, overpressure relieve connections, and pressure gauges. Ultimately, selection of the appropriate glass seals with system-compatible thermal expansion, chemical inertness, and thermal stability will require specific technical study and evaluation. Phosphate, borate, and silicate glass seals used for solid oxide fuel cells may prove to be qualified candidates, as these materials are commonly used to create metal-metal and metal-ceramic seals, are suitable for temperatures exceeding 500^{o}C, and are stable against highly oxidizing environments.[6,7]

Achieving high rate electrochemical reactions will require high surface area anodes and cathodes that are stable against corrosion in chlorine and molten chloride salt environments. The corrosion resistant Haynes alloys mentioned above would logical choices, readily formed/welded and compatible with the aggressive environment and potential sealing chemistries. The cathode should also be constructed to allow chlorine gas introduction (actively or passively) to the molten salt through the electrode, maximizing reactive surface area for ideal reaction kinetics.

The technical issue of electrochemical charge compensation (e.g., chlorine versus copper or other suitable metal) should also be carefully considered. The chlorine-mediated approach does provide an elegant and relatively straightforward electrochemical strategy, and it does not stand to introduce any new chemical contaminants to the waste stream. Chlorine chemistry at 500^{o}C, however, challenges the chemical stability and ultimate safety of the system, impacting the selection of every component of the reactor and potentially introducing additional development and manufacturing costs. In contrast, the copper-mediated approach eliminates the highly corrosive, potentially hazardous chlorine atmosphere. It does, however, increase the chemical complexity of the system, and copper would have to be removed from the final waste salt, perhaps precipitated using lithium and potassium formates as shown previously.[1]

Successful adoption of these components and processes is likely to require a graded scale-up approach. Although our research-scale efforts have demonstrated feasibility of the approach using lab scale volumes (typically less than 100g), it would be recommended that the chemical kinetics be optimized by scaling to a 1kg pilot scale, ideally utilizing as many of the large-scale components (e.g., ceramic tubes, electrodes, etc.) as possible. In addition, small scale studies of glass sealing stability, corrosion resistance of all materials, the chlorine-gas delivery, and ultimately the radiation stability of the system must all be explored prior to large scale implementation. While there is significant promise in the use of this technology to reduce waste salt volumes, significant technical development and optimization must be done before that promise can be realized.

1) Spoerke, E. *et al.* "Ion Selective Ceramics for Waste Separations." (U.S. DOE Office of Nuclear Energy 2014). **2)** Spoerke, E. *et al.* "Ion Selective Ceramics for Waste Separations: End of Fiscal Year Project Assessment." (US DOE Office of Nuclear Energy 2013). **3)** Williamson, M. (personal communication with E. Spoerke) (2015). **4)** Simpson, M. Projected Salt Waste Production from a Commercial Pyroprocessing Facility. *Science and Technology of Nucelar Installations* **2013**, 1-8 (2013). **5)** Sangster, J. & Pelton, A. D. Thermodynamic Calculation of Phase Diagrams of the 60 Common-Ion Ternary Systems Containing Cations Li, Na, K, Rb, Cs and Anions F, Cl, Br, I. *J. Phase. Equilibria* **12**, 511-537 (1991). **6)** Zhu, Q., Peng, L. & Zhang, T. in *Fuel Cell Electronics Packaging* (eds K Kuang & K Easler) Ch. 2, 33-60 (Springer US, 2007). **7)** Paulsen, O. *Rigid bonded glass ceramic seals for high temperature membrane reactors and solid oxide fuel cells* Ph.D. thesis, Norwegian University of Science and Technology, (2009).

Publications and Patents:

Publication:
M.A. Rodriguez, J. Griego, H.J. Brown-Shaklee , M. A. Blea-Kirby, J. F. Ihlefeld, and E.D. Spoerke "X-ray Powder Diffraction Study of La_2LiTaO_6." (2015) *Powder Diffraction.* **30**(01) 57-62.

Non-Provisional Patent:
E.D. Spoerke, J. Ihlefeld, J.S. Wheeler, K. Waldrip, H. Brown-Shaklee, L Small, and D.R. Wheeler. "Electrochemical Ion Separation in Molten Salts." US Appln No.: 14/660,696. (3/17/2015).

Provisional Patent:
H.J. Brown-Shaklee, J. Ihlefeld, E.D. Spoerke, M. A. Blea-Kirby. "Methods for Producing Dense Lithium Lanthanum Tantalate Lithium Ion Conducting Ceramics." US. Appln No.: 62/110,834 (2/2/2015).

Presentations:

1. E.D. Spoerke, J.S. Wheeler, H.J. Brown-Shaklee, J. Ihlefeld, M. Blea-Kirby, L.J. Small, L. E. Johnson and K. Waldrip. "Ceramic Ion Filters for Mixed Waste Separations", Electronic Materials and Applications 2015, Orlando, FL, Jan., 2015.

2. H.J. Brown-Shaklee, M. A. Blea-Kirby, J. Griego, M.A. Rodriguez, J. Ihlefeld, E.D. Spoerke. "High Density $Li_5La_3Ta_2O_{12}$ (LLTO) ceramics for ion-selective fission waste processing." Electronic Materials and Applications 2015, Orlando, FL Jan., 2015.