An Investigation of Synthesized Samarium Oxychloride in Molten LiCl-KCl

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Abstract

The spectroscopic and electrochemical properties of synthesized samarium oxychloride were investigated as they relate to the pyrochemical reprocessing of used nuclear fuel in the molten LiCl-KCl eutectic. A qualitative, *in situ* investigation of oxychloride formation was conducted using electroanalytical voltammetry and Raman spectroscopy. Electroanalytical properties of samarium in trivalent chloride and oxychloride form were investigated using cyclic voltammetry. Electrochemical relationships developed for aqueous systems, and their applicability to the reaction couples of interests, were evaluated using the Randles-Sevcik equation. The diffusion behavior of chloride and oxychloride samarium is discussed in terms of electrochemical current response. Synthesized oxychloride was also analyzed using various solid-state characterization techniques to better understand its chemical properties. The nature of oxychloride formation, solvation in the molten eutectic, implications in electrochemical processing, and the management of nuclear material in high-temperature systems are discussed.

Keywords: SmOCl, XRD, TEM, and Raman spectroscopy.

Introduction

As the international community transitions to more sustainable and environmentally-friendly energy sources, nuclear power remains one of the cleanest sources of electricity in terms of greenhouse gas (GHG) emissions. The International Atomic Energy Agency's (IAEA) *Climate Change and Nuclear Power 2018* report projects nuclear energy's role in electricity markets to grow anywhere from 24-184 % in terms of generating capacity by 2050.¹ Technological improvements in power plant design, passive safety features, proliferation-resistant fuel cycles, and analytical nuclear material management methodology will allow for nuclear energy to penetrate emerging electricity markets.² Nuclear power plants are considered to be in their third technological generation as of 2019, with a Generation-III+ fleet of reactors currently being commercialized. Generation-IV nuclear power plants and fuel cycles drift away from aqueous systems in favor of higher-temperature materials, such as molten salts. Securing nuclear material and optimizing process conditions for economically viable power and fuel production remain the main obstacles to advanced system commercialization.³

Molten chloride salts are candidate materials for nuclear power plant cooling, fueled-salt power reactors, and the electrochemical processing of nuclear material. Used nuclear fuel (UNF) is not reprocessed internationally on a large scale; however, a few nations recycle UNF using a process termed PUREX (Plutonium Uranium Redox Extraction). PUREX relies on aqueous media to separate, pure uranium and plutonium streams that exhibit dangerously high enrichment levels. PUREX is riddled with problems associated with radiolysis and criticality that manifest in the form of waste management and proliferation concerns.^{4, 5} The pyrochemical reprocessing of UNF employs the molten LiCl-KCl eutectic salt at 500 °C to electrochemically deposit uranium, plutonium, and transuranic (TRU) chlorides in metallic form on a combination of solid and liquid metal electrodes.^{5, 6} The impure and high temperature nature of plutonium streams in the pyrochemical flowsheet create a more proliferation-resistant process.⁷ Although the fuel is refined and consolidated in metallic form, electrolytic reduction unit operations can incorporate existing

light water reactor (LWR) oxide fuel into a closed nuclear fuel cycle employing the pyrochemical process.⁶ Electroanalytical and spectroscopic investigations of actinide and lanthanide chloride analytes in the molten LiCl-KCl eutectic produce information regarding analyte chemistry, electrochemical separation efficiency, and process scale-up.⁸⁻¹⁵ The proposed process flowsheet for the pyrochemical reprocessing of UNF, reported by Williamson et al., is shown in Figure 1.⁶

Figure 1: Proposed pyroprocessing flowsheet published by Williamson et al.⁶ reports a variety of unit processes (electrorefiner, oxidant production, lanthanide drawdown, U/TRU drawdown) that require concrete understanding of analyte behavior before optimization can be pursued. Figure used with permission from Dr. Williamson.

Oxychloride chemistry plays an important role when addressing lanthanide and actinide chemistry in molten chloride salts. Oxychloride formation, predominantly in the form of precipitates, can have negative effects on process efficiency along with creating nuclear material management concerns regarding hold up and material loss. Oxychloride precipitation has also been proposed as a method for co-precipitation and consolidation of nuclear material in molten salt.^{16, 17} Furthermore, also oxychloride formation presents a potential for nuclear material buildup due to moisture or impurities in alternative electrochemical processes related to the nuclear industry, specifically the conversion of plutonium pits in

high-temperature molten salt.¹⁸ The literature data regarding oxychloride formation in the LiCl-KCl molten eutectic is limited and requires further investigation to fully understand solvation mechanisms, effects on electroanalytical measurements, and characterization of relevant reaction products.^{16, 17, 19}

This paper presents a synthesis method for, and characterization of, samarium oxychloride (SmOCl) in the molten LiCl-KCl eutectic at 500 °C. Additionally, solid state characterization is reported to confirm the synthesis of SmOCl before the *in situ* analysis of the analyte using electroanalytic measurements and polarized Raman spectroscopy. Cyclic voltammetry (CV) results are reported and discussed in terms of current response and empirical relationships applicability. CV and *in situ* Raman also provide a qualitative evaluation of oxychloride formation in the molten LiCl-KCl eutectic. The results are discussed in term of engineering implications related to nuclear material management in high-temperature molten salt systems.

Experimental

General features

All molten salt studies were conducted in ultra-high purity argon atmosphere (Airgas 99.99%) inside an inert glovebox maintained under 1 ppm moisture and oxygen content. The electroanalytical and *in situ* Raman spectroscopy setup has been previously presented by the authors for low concentration lanthanide studies in the same eutectic system.²⁰⁻²³ The experimental apparatus employed for both spectroscopic and electroanalytical molten salt investigations is shown in Figure 2.

Figure 2: Experimental setup employed for spectroscopic and electroanalytical investigations in molten LiCl-KCl eutectic consists of precision alignment stages for electrochemical and spectroscopic focusing, electrode alignment mounts, fiber cabling for 532 nm laser excitation, a polarized Raman probe, and a high-temperature ceramic cylindrical furnace.

Uncertainties associated with thermal gradients were mitigated with an insulating ceramic furnace cap fabricated with electrode alignment holes and a laser beam path for Raman analysis. Alumina tubes were installed to ensure electrode alignment is repeatable and precise. Molten salt samples were contained in 55 mL alumina crucibles nested inside stainless-steel Faraday cages that remove electrical current noise produced by the furnace heaters. The system was equipped with a three-electrode electrochemical stage and Raman probe with polarization capability. A 532 nm wavelength laser was utilized for Raman excitation. A K-type thermocouple was installed to provide feedback to the furnace controller with ± 2 °C temperature precision. Electrode positioning and Raman probe focusing were controlled by a high-resolution translation stage with a LabVIEW National Instruments software user interface to ensure accurate and repeatable placement of electrodes inside the molten salt matrix and to ensure the laser excitation converges in the solution to excite the bonds associated with dissolved analyte complexes rather than electrodes or crucible walls.

Cyclic Voltammetry Methods

CV is a three-electrode electrochemical method that relies on a cyclic potential sweep to scan a voltage range for analyte-specific redox reactions. Current response can be correlated to analyte concentration if the diffusion behavior of the analyte is well understood.²⁴ The Randles-Sevcik equation can be applied to CV data assuming all diffusion is mass transfer limited, linear in nature, and the redox reaction of interest is reversible.²⁴ The Randles-Sevcik relationship is reported in Equation 1. Once diffusion coefficient values are established, current response has the potential to be correlated to concentration for process monitoring and nuclear security applications.²⁵

$$i_p = 0.4463 \cdot n \cdot F \cdot A \cdot C_i \cdot \left(\frac{n \cdot F}{R \cdot T}\right)^{1/2} \cdot v^{1/2} \cdot D^{1/2} \quad (1)$$

Here i_p is the peak current response, n is the number of electrons transferred during the redox reaction, F is Faraday's constant, A is the surface area of the working electrode (WE), C_i is the bulk concentration of the dissolved analyte of interest, R is the ideal gas constant, T is temperature, v is the potential scan rate, and D is the diffusion coefficient of the analyte of interest.²⁴ The working electrode (WE) and counter electrode (CE) consisted of a 1/16" and 1/8" diameter tungsten rod, respectively. A 5 mol % Ag|AgCl reference couple encased in Pyrex which has been previously deployed for voltammetry experiments in the same eutectic was employed as a reference electrode.¹⁰ The peak current versus square-root of scan rate relationship was studied for both SmCl₃ and SmOCl. Peak currents were measured five times at each of the following scan rates for each CV analysis: 100 mV/s, 150 mV/s, 200 mV/s, 250 mV/s, and 300 mV/s.

Samarium oxychloride synthesis

LiCl-KCl melts were prepared by mixing LiCl (Alfa Aesar 99% pure) and KCl (Alfa Aesar 99% pure) at 46 wt.% and 54 wt.%, respectively.²⁶ Precursor salts utilized to prepare the final eutectic were first baked under vacuum at 200 °C in order to minimize moisture-induced impurities. Anhydrous SmCl₃ (Alfa Aesar, 99.9% pure) was dissolved directly into the molten LiCl-KCl eutectic at 500 °C and agitated for eight

hours. Synthesis of SmOCl was accomplished through the dissolution of O^{2-} ions in the eutectic with the addition Li_2CO_3 to the $SmCl_3$ -LiCl-KCl solutions. The reaction mechanism for SmOCl formation and precipitation in this manner has been reported in the literature by Castrillejo et al.^{19, 27} The dissolution of $SmCl_3$, Li_2CO_3 , and formation of SmOCl are reported in Equations 2, 3, and 4, respectively.

After addition of Li_2CO_3 , melts were agitated until CO_2 gas bubbling halted, indicating the reaction had completed.

$SmCl_3$ was solvated in LiCl-KCl at a concentration of $3.3 \times 10^{-4} \text{ mol cm}^{-3}$, and Li_2CO_3 was added to the solution in an equimolar quantity. Upon completion of the synthesis reaction, the melt was allowed to solidify. Carboxylic acid groups on ethylenediaminetetraacetic acid (EDTA) were deprotonated in DI H_2O in solution through the addition of NaOH. The deprotonated solution was used to rinse off remaining eutectic and pull any unreacted $SmCl_3$ into solution as well. The EDTA forms a 1:1 complex with the unreacted $SmCl_3$, leaving only the SmOCl precipitate behind. Excess EDTA was present to ensure all unreacted $SmCl_3$ was fully chelated. The remaining solution containing the synthesized precipitate was then centrifuged so that precipitate powder could be consolidated. The powder was then allowed to dry before undergoing solid state characterization.

Synthesis is complete once CO_2 bubbling is no longer observed. Li_2CO_3 is added in small increments while the melt is agitated to ensure the salt mixture does not overflow out of the containment crucible due to CO_2 bubbling. Once bubbling has halted, the melt is agitated for an extended period of time to ensure the reaction proceeds to completion. After agitation, the melt is observed to be transparent with a suspension of white precipitate, assumed to be SmOCl. After reaction completion, the melt is cooled and dissolved in the EDTA complex for separation and consolidation.

Solid state characterization

Synthesized precipitate was analyzed using a variety of solid-state characterization methods to confirm the formation of SmOCl. X-ray diffraction (XRD) patterns were obtained from the collected precipitates using a Rigaku Smartlab X-ray diffractometer. Diffraction patterns were analyzed using a PDXL software package. A Hitachi S-4700 field emission scanning electron microscope (SEM) equipped with energy dispersive x-ray spectroscopy (EDS) was employed to investigate precipitate morphology and elemental makeup, respectively. Transmission electron microscopy (TEM) analysis was carried out using a JEOL-JEM 2100F Analytical TEM. A Thermo Scientific DXR Raman microscope equipped with a 10 mW, 532 nm wavelength laser was employed for solid-state Raman analysis of the precipitate.

Results and Discussion

Synthesis and Solid-State Characterization

The precipitate remains a white color throughout the separation and consolidation operations. Once dry, solid-state characterization is commenced to confirm the presence of SmOCl. The XRD pattern obtained from separated, consolidated, and dried precipitate is reported in Figure 3.

Figure 3: The XRD pattern obtained from separated, consolidated, and dried precipitate indicates the formation of SmOCl with relatively few impurities.

XRD analysis is followed by SEM imaging and EDS elemental analysis. Two different particulate morphologies can be observed in the SEM micrographs. EDS elemental analysis is conducted with respect to the Sm:Cl atomic ratios. SmOCl should exhibit 1:1 Sm:Cl atomic ratios, while SmCl₃ will exhibit 3:1 Sm:Cl ratios. The oxygen ratios are not reliable due to oxygen atmospheric and mounting tape contamination. The two different morphologies observed by SEM are displayed in Figure 4, and the regions of analysis by EDS are indicated.

Figure 4: SEM images of plate-like precipitate particles (left) and fluff-like precipitate particles (right) both illustrate the regions of interest (purple outline) where EDS chemical analysis was conducted.

The EDS results are reported in Table 1 for both morphologies. The platinum content is attributed to the use of platinum to sputter coat samples before SEM-EDS analysis in order to prevent sample charging.

Elemental Emission	Atomic %	
	Plate-Like Morphology	Fluff-Like Morphology
O K	58.61	52.44
Cl K	19.35	23.05
Sm L	20.78	23.67
Pt M	1.26	0.84

Table 1: EDS chemical analysis results for both precipitate morphologies observed in SEM images indicated approximately 1:1 Sm:Cl atomic ratio values.

Both morphologies indicate Sm:Cl atomic ratios approximately 1:1, suggesting both morphologies are SmOCl. These ratios confirm that the bulk precipitate collected is indeed SmOCl as the XRD pattern also suggests.

TEM imaging allows for planar, d-spacing to be measured. TEM imaging and d-spacing measurement results obtained from the precipitate are reported in Figure 5.

Figure 5: TEM diffraction analysis shows the 110-plane d -spacing is in agreement with the measured XRD pattern reported in Figure 3, confirming the precipitate to be SmOCl.

Once focusing on a plane of interest is achieved, a d -spacing measurement is confirmed with the 110-plane associated with SmOCl and d -spacing values for the 110-plane measured using XRD. Solid-state Raman spectra obtained from the precipitate are reported in Figure 6.

Figure 6: Raman spectra obtained from the precipitate show five symmetry modes that confirm the precipitate to be SmOCl.²⁸

Raman spectra indicate the presence of five symmetrical modes labelled in Figure 6. These modes are confirmed to be consistent with the previously reported literature concerning lanthanide oxychlorides.^{28,}

Solid-state characterization results all indicate the precipitate synthesized in the molten LiCl-KCl-SmCl₃ solution is indeed SmOCl, as Equations 2-4 suggest. The TEM images confirm the d-spacing values reported for the 110-plane in the obtained XRD patterns, and the SEM-EDS results show the presence of two different morphologies, both of which can be attributed to SmOCl through Sm:Cl atomic ratio analysis. The solid-state Raman spectra report five symmetrical modes that are consistent with the previously published lanthanide oxychloride literature.^{28, 29}

In Situ Electrochemistry and Spectroscopy

CV experiments conducted on LiCl-KCl with SmCl₃ solvated at low concentrations may produce an additional anodic peak in a slightly more oxidative region than that associated with the traditional SmCl₃ redox couple. A sample CV that contains this additional anodic peak, indicated with an asterisk, is reported in Figure 7.

Figure 7: An additional anodic peak (*) manifests in a slightly more oxidative region than the traditional SmCl₃ redox couple at low concentrations.

The additional anodic peak is hypothesized to be the result of SmOCl formation. The CV reported in Figure 7 is compared with a CV obtained from the molten LiCl-KCl eutectic solvated only with synthesized SmOCl in Figure 8.

Figure 8: A comparison of CV curves obtained from a low-concentration SmCl₃ melt with the additional anodic peak and a molten LiCl-KCl melt containing synthesized SmOCl indicate the additional peak is due to SmOCl formation.

Figure 8 illustrates SmOCl is responsible for the additional anodic peak observed in molten LiCl-KCl melts solvated with low concentrations of SmCl₃. The SmOCl couple also includes a cathodic peak that manifests underneath the more prominent SmCl₃ cathodic peak. The additional cathodic and anodic redox peaks that are the result of SmOCl contamination will create uncertainty in SmCl₃ current response measurements which will have nuclear material management implications in terms of monitoring SmCl₃ content.

In order to better understand the electroanalytical implications of SmOCl formation, the oxychloride was synthesized using the methods outlined in previous sections of this paper and then studied using CV and fiber-based Raman spectroscopy. CV and Raman analysis were first conducted on a molten LiCl-KCl melt solvated with SmCl₃ at a concentration of $3.3 \times 10^{-4} \text{ mol cm}^{-3}$. The equimolar synthesis of SmOCl was then conducted through Li₂CO₃ solvation to convert the SmCl₃ to SmOCl. CV and *in situ*

Raman were conducted to confirm the SmCl_3 is no longer present after synthesis is complete. A more targeted CV analysis was then conducted on the SmOCl in the LiCl-KCl melt. Figure 9 and 10 respectively report *in situ* CV results and Raman spectra of SmCl_3 solvated in the molten LiCl-KCl eutectic that is consistent with the reported literature, and the subsequent disappearance of SmCl_3 Raman indicators post-synthesis of the SmOCl .^{9, 19}

Figure 9: A clear shift in the location and magnitude of the peak current response is observed in the CV acquired post- SmOCl synthesis as compared to the CV acquired before SmOCl synthesis.

Figure 10: The lack of features in the Raman spectra acquired after the SmOCl synthesis indicate the SmOCl is either soluble at levels below the detection limits of the Raman or does not exhibit Raman active modes when solvated in the molten LiCl-KCl eutectic.

The peak current response from SmOCl is less in terms of magnitude than the solvated SmCl₃. Figure 9 illustrates this shift in magnitude as the post-synthesis, SmOCl redox peaks are barely visible compared to the prominent, pre-synthesis SmCl₃ peaks. This reduction in magnitude, along with the observable collection of SmOCl precipitate at the bottom of the melts suggests SmOCl is soluble at low levels in the molten LiCl-KCl eutectic. This low solubility may explain why no Raman indicators are detected post-synthesis in Figure 10; however, this lack of modes may also be attributed to dissolved SmOCl not being Raman active. There is no available literature regarding the coordination chemistry of SmOCl solvated in the molten LiCl-KCl eutectic so that its Raman activity can be determined. Investigations of fundamental coordination chemistry requires techniques such as x-ray absorption fine structure (XAFS) analysis.

The peak current responses from CV associated with SmCl₃ reached values above 100 mA, while the same peak current responses all remained below 10 mA for SmOCl. This difference in magnitude further suggests the low solubility of SmOCl in the molten LiCl-KCl eutectic. The results of CV analysis as a

function of scan rate are summarized for the LiCl-KCl-SmCl₃ (pre-synthesis) and LiCl-KCl-SmOCl (post-synthesis) melts in Figures 11 and 12 respectively.

Figure 11: CV results (left) with respect to scan rate from the LiCl-KCl-SmCl₃ (pre-synthesis) indicate high levels of peak current vs. scan rate linearity (right), and therefore high levels of Randles-Sevcik applicability.

Figure 12: CV results (left) with respect to scan rate from the LiCl-KCl-SmOCl (post-synthesis) indicate lower levels of peak current vs. scan rate linearity (right), and therefore lower levels of Randles-Sevcik applicability.

The linearity of peak current vs. scan rate relationships, both for cathodic and anodic current response, is much higher for SmCl₃ (pre-synthesis) samples than SmOCl (post-synthesis) samples. This difference in linearity is illustrated by the difference in R² values reported in Figures 11 and 12. Randles-Sevcik applicability for analysis is therefore less suitable for the oxychloride species than SmCl₃. The dissolution behavior in terms of ionic state equilibrium also seems to vary between the SmCl₃ and SmOCl₃ samples. Specifically, the SmCl₃ samples produce cathodic peak current responses slightly larger than the anodic responses, suggesting the trivalent samarium that is reduced on the cathodic sweep is not fully oxidized

back into solution. In comparison, the anodic current responses are much larger than the cathodic responses for the SmOCl samples. The literature is limited regarding the nature of oxychloride redox reactions, but this difference in current response relationships suggests the SmOCl could be more likely to undergo spontaneous reduction. Therefore, there is less oxidized species to reduce on the cathodic sweep, producing lower cathodic response. XAFS analysis may help elucidate these equilibrium conditions as well.

The implications of these findings regarding the application of CV for process monitoring and nuclear material management are notable. Carbonate or moisture impurities have the potential to convert solvated trichloride analytes to their oxychloride forms. Correcting for SmOCl is clearly necessary as it is electroactive and produces distinguishable redox peaks in CV curves. Current correction methods must be developed for oxychloride species to account for their contributions to solvated trichloride analysis. Developing these correction methods will not be trivial, as the applicability of Randles-Sevcik relationship loses effectiveness when studying the oxychloride species. Elucidation of ionic states and equilibria associated with oxychloride species must first be investigated before any adjustments to the Randles-Sevcik can be accomplished. These studies would most likely require fundamental coordination chemistry investigations using methods such as XAFS.

Conclusions

A targeted synthesis, solid-state characterization, *in situ* electroanalytical, and *in situ* Raman spectroscopic investigation of SmOCl in the molten LiCl-KCl eutectic was completed. Synthesis was accomplished through carbonate addition to the molten LiCl-KCl-SmCl₃ system. SmOCl was confirmed to precipitate out of solution due to carbonate addition through a variety of solid-state characterization techniques. The SmOCl was then analyzed *in situ* using fiber-based Raman spectroscopy and cyclic voltammetry. Both the Raman and voltammetry results indicated a conversion of SmCl₃ to SmOCl and

change in solution chemistry. The SmOCl was not detectable using Raman either due to its solubility limit being below the Raman's detection limits or its solvated form being Raman inactive. CV investigations into the SmOCl produced redox peaks that suggest current corrections will be necessary for SmOCl when using CV for process monitoring and nuclear material management purposes in the molten LiCl-KCl eutectic.

Conflicts of Interest

There are no conflicts to declare.

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