

Actinide, Lanthanide and Fission Product Speciation and Electrochemistry in High and Low Temperature Ionic Melts

Anand I. Bhatt,^a Hajime Kinoshita,^a Anne L. Koster,^a Iain May,^{a*} Clint A. Sharrad,^a Vladimir A. Volkovich,^{a,b} O. Danny Fox,^c Chris J. Jones,^c Bob G. Lewin,^c John M. Charnock^d, Christoph Hennig^e

^aCentre for Radiochemistry Research, Department of Chemistry, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK. Iain.May@man.ac.uk

^bDepartment of Rare Metals, Ural State Technical University – UPI, Ekaterinburg, 620002, Russian Federation.

^cBritish Nuclear Fuels plc, Research and Technology, Sellafield, Seascale, Cumbria, CA20 1PG, UK.

^dCLRC Daresbury Laboratory, Daresbury, Warrington, Cheshire, WA4 4AD, UK.

^eESRF, ROBL-CRG, BP 220, Grenoble Cedex, France.

Abstract. *There is currently a great deal of research interest in the development of molten salt technology, both classical high temperature melts and low temperature ionic liquids, for the electrochemical separation of the actinides from spent nuclear fuel. We are interested in gaining a better understanding of actinide and key fission product speciation and electrochemical properties in a range of melts. Our studies in high temperature alkali metal melts (including LiCl and LiCl-KCl and CsCl-NaCl eutectics) have focussed on in-situ species of U, Th, Tc & Ru using X-ray absorption spectroscopy (XAS, both EXAFS and XANES) and electronic absorption spectroscopy (EAS). We report unusual actinide speciation in high temperature melts and an evaluation of the likelihood of Ru or Tc volatilisation during plant operation. Our studies in lower temperature melts (ionic liquids) have focussed on salts containing tertiary alkyl group 15 cations and the bis(trifluoromethyl)sulfonylimide anion, melts which we have shown to have exceptionally wide electrochemical windows. We report Ln, Th, U and Np speciation (XAS, EAS and vibrational spectroscopy) and electrochemistry in these melts and relate the solution studies to crystallographic characterised benchmark species.*

INTRODUCTION

Developing novel methods for the safe treatment of irradiated nuclear fuel is a key challenge facing the nuclear industry. Worldwide research and development is focused on advancements to the current proven PUREX technology, minor actinide partitioning and transmutation, and the development of alternative fuel treatment technologies, including supercritical fluids and pyrochemical separations.

The Application of High Temperature Molten Salt Technology in Nuclear Fuel Processing

There are currently two developed pyrochemical processes operating at the Research Institute for Atomic Reactors (RIAR) in Russia and at the Argonne National Laboratory (ANL) in the US respectively. The two facilities are both able to electrochemically process irradiated nuclear fuel using molten chloride melts – a NaCl-KCl eutectic at the RIAR and a LiCl-KCl eutectic at the ANL. Advanced molten salt technologies are currently being developed at both the ANL, [1-3] the RIAR, [4] and at several research institutes in

Japan and across Europe (including the CEA). [5-9]

The Potential Application of Ionic Liquids in Nuclear Fuel Processing and Waste Management

Ionic liquids are currently being investigated as novel solvent systems for a whole range of chemical processes. [10-11] These ionic melts are generally classified as salts with melting points < 100°C and tend to be comprised of inorganic anions and organic cations. There is much current interest in the use of ionic liquids for solvent extraction processes in the nuclear industry, with studies into {UO₂}²⁺, Sr²⁺ and Cs⁺ extraction. [12-14] The replacement of alkali metal chloride melts with lower temperature ionic liquids in an electrochemical process is also attractive with the obvious decrease in operating temperature and the potential for greatly reducing corrosion issues. Previous studies focused on chloroaluminate melts, [15-16] although the hygroscopic nature of such melts probably inhibits large scale operation. Recently, however, it has been shown that tertiary alkyl

ammonium or pyrrolidinium cation and bis((trifluoromethyl)sulfonyl)amide ($[\text{N}(\text{SO}_2\text{CF}_3)_2]$, TSFI) anion based salts appear to be less moisture sensitive and to have electrochemical windows wide enough to undertake the electrodeposition of uranium and plutonium. [17-19]

Current BNFL/CRR Research Programme

For the past 10 years BNFL have undertaken a research and development programme with the use of ionic melt technologies for the electrochemical separation of uranium and plutonium in an attempt to meet the challenge of providing a more cost effective, and waste minimised, future irradiated nuclear fuel management strategy. Since 2000 the Centre for Radiochemistry Research (CRR) have undertaken chemical research to help underpin this BNFL programme with many of the key results summarised in this paper.

HIGH TEMPERATURE MOLTEN SALT STUDIES

Experimental

Detailed experimental methods are described elsewhere. [20-23] XAS measurements were recorded in absorbance mode on station 9.3 (U L_{III} -edge and Ru K-edge) and in fluorescence mode (Tc K-edge and Ru L_{III} -edge) on station 16.5, both at the CLRC Daresbury Laboratory. Electronic absorption spectroscopy (EAS) and other supporting analysis was undertaken at the CRR laboratories.

Uranium Speciation in Molten Salts

Previous Research

Probing actinide speciation in high temperature melts is extremely challenging due to both the harsh chemical environment, limiting the spectroscopic techniques available, and the radiological hazards, which inevitably restrict most studies to low specific activity nuclides such as ^{238}U . Until recently we have been restricted to electronic absorption spectroscopy which, though a useful tool for determining oxidation state, is limited in its usefulness in probing coordination environment. [20] It might be anticipated that simple anionic chloride complexes dominate actinide speciation in alkali and alkaline earth chloride melts. However,

a recent Raman spectroscopy study has indicated that $\text{ThCl}_4\text{:CsCl}$ melts contain oligomeric Th species with bridging chlorides. [24] EAS has also provided evidence for $\{\text{NpO}_2\}^+:\{\text{UO}_2\}^{2+}$ cation:cation complexes in a CsCl melt [25] and a peroxide bridged $\{\text{UO}_2\}^{2+}$ dimer in a NaCl:CsCl melt. [26] There is thus clearly the potential for the formation of actinide complexes with unusual coordination environments in the ionic melt systems of relevance to the pyrochemical processing of irradiated nuclear fuel.

XAS (X-ray absorption spectroscopy) is an element specific technique that can gain insight into oxidation state and coordination environment in a wide range of different matrixes. It has thus found a wide range of application for the determination of metal speciation, particularly with reference to the actinides. [27] Recently, an XAS study of U^{III} in a LiCl-KCl melt at 550 °C has been undertaken. [28] In this study EXAFS (Extended X-ray Fine Structure) data was collected to an E_{max} of 17.7 keV and they obtained information on the first coordination sphere, which was fitted with 7.3 Cl⁻ ligands a 2.82 Å. However, in this study there was no evidence for the formation of any oligomeric species.

In situ XAS Measurements

We have previously devised a furnace set-up that allows us to record *in situ* EAS measurements [20] and we have recently adapted this system to allow us to undertake *in situ* XAS (EXAFS and XANES) measurements. [21][23] Currently we are only able to obtain data in absorbance mode and our salt systems are restricted to low absorbing alkali metal halides (*i.e.* LiCl, LiCl-KCl and LiCl-BeCl₂). Uranium was introduced into the melt either by direct dissolution of UO_2Cl_2 , UCl_4 or UCl_3 or by *in situ* chlorination (by HCl or Cl₂) of UO_2 or UO_3 .

Preliminary results obtained from probing the U L_{III} edge reveal that we can use the XANES spectrum to distinguish between uranium in the +III, +IV, +V and +VI oxidation states [21] (and also see Fig. 1). EXAFS data fitting is in good agreement for classical 6 coordinate uranium species (e.g. $[\text{U}^{III}\text{Cl}_6]^{3-}$, $[\text{U}^{IV}\text{Cl}_6]^{2-}$, $[\text{U}^{\text{V}}\text{O}_2\text{Cl}_4]^{3-}$ and $[\text{U}^{\text{VI}}\text{O}_2\text{Cl}_4]^{2-}$) but there is also often evidence for longer range interactions. We believe that these represent U-alkali metal and U-U interactions indicating that oligomeric species

may be present in these high temperature melts. Selected EXAFS data is presented in Fig. 2.

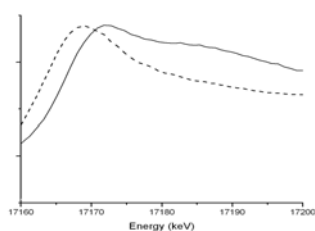


Fig. 1. Low energy edges of X-ray absorption spectra of LiCl/KCl eutectic melts at 575 °C containing mainly U^{IV} (obtained by the reaction of UO_2 with HCl - dashed line), and U^{VI} , (obtained by the reaction of UO_3 with HCl - solid line).

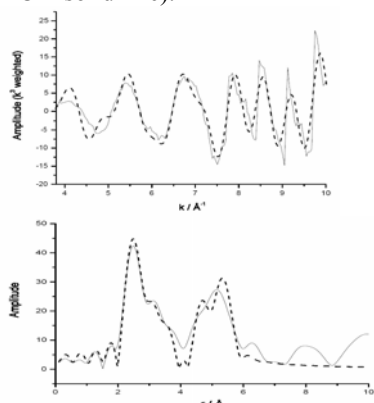


Figure 2. Fitted EXAFS spectrum and Fourier transform of UO_2 exposed to HCl in LiCl/KCl eutectic – quenched (experimental – solid line; theory – dashed line). Data can be fitted with the following model: $6 \times Cl - 2.60 \text{ \AA}$; $6 \times K - 3.12 \text{ \AA}$; $4 \times Cl - 3.49 \text{ \AA}$; $8 \times U - 4.20 \text{ \AA}$; $18 \times U - 4.96 \text{ \AA}$

Selected Fission Product Speciation in Molten Salts

There has been interest in applying molten salt technology to the reprocessing of irradiated oxide fuel. One potential method of dissolution of oxide fuel in a high temperature melt is chlorination (either by HCl or Cl_2) which has the potential to bring additional fission products into the molten solution, including ^{99}Tc and ^{103}Ru and ^{106}Ru . Our interest in chemistry of these two elements lies in the fact that both merit specific consideration during conventional PUREX process operations, with $[TcO_4]^-$ coextraction through solvent extraction operations [29-30] and care required to avoid the formation of volatile RuO_4 during the vitrification process. [31]

We have previously reported a detailed study into the speciation of Tc and Re in a range of high temperature melts which have shown that Re is not always a good non-radioactive analogue for Tc in these systems. [22] The reaction between Re metal, ReO_2 , ReO_3 and TcO_2 with HCl and Cl_2 were studied in LiCl-KCl, NaCl-CsCl and NaCl-KCl melts using *in situ* EAS, with the quenched melts also probed by XAS. In summary, we have shown that $[ReCl_6]^{2-}$ is the dominant species formed for Re for all experimental conditions with TcO_2 also reacting with HCl in a range of melts to form only $[TcCl_6]^{2-}$. However, the reaction between TcO_2 and Cl_2 leads to the formation of volatile chlorides and/or oxychlorides with $[TcO_4]^-$ remaining behind in the melt.

Recently, we have extended this study to Ru, studying Ru and RuO_2 dissolution by HCl and Cl_2 in NaCl-KCl, LiCl-KCl, NaCl-CsCl and LiCl. *In situ* EAS has not been particularly informative and we have not yet conclusively been able to assign the broad absorbance bands that are observed. However, *in situ* EXAFS measurement in LiCl and LiCl-KCl have yielded more information and the data fit is consistent with the formation of $[RuCl_6]^{3-}$ as the major species irrespective of initial Ru starting material, ionic melt or chlorination method. Typical EXAFS data is given in Fig. 3.

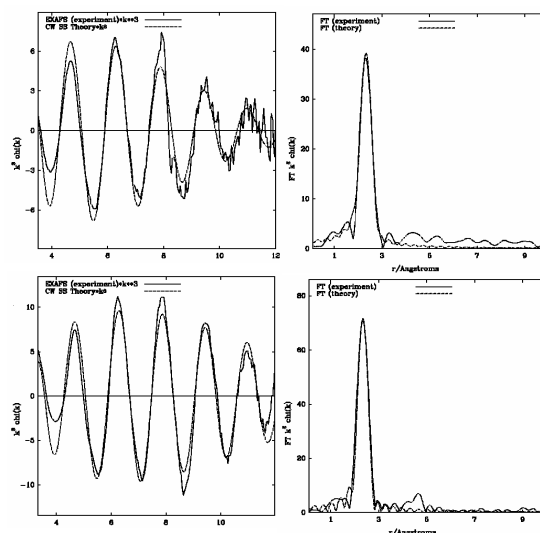


Fig. 3. RuO_2 Chlorination by HCl in LiCl-KCl at 400°C. Top, *in-situ* EXAFS with Fourier transform. Bottom, quenched melt EXAFS with Fourier transform. Both sets of data could be fitted with six chlorines at 2.39 \AA , corresponding to $[Ru^{III}Cl_6]^{3-}$.

IONIC LIQUID STUDIES

Experimental

Detailed experimental methods are described elsewhere. [32-33] XAS measurements were undertaken on station 16.5 at the CLRC Daresbury Laboratory and at the ROBL-CRG beamline at the ESRF. Synthetic chemistry, spectroscopic characterisation, X-ray crystallography and electrochemical measurements were all undertaken at the CRR laboratories.

Synthesis of novel ionic liquids and electrochemical window measurements

Our initial aim was focused on developing novel ionic liquid systems with wide enough electrochemical windows to undertake the electrochemical deposition of U and Pu metal. Initial studies focused on the Group 15 salts of general formula $[\text{Me}_4\text{X}][\text{TFSI}]$, where X = N, P and As. Their electrochemical windows were measured both in the molten state (at 160 °C) and as supporting electrolytes in MeCN. [32] All had electrochemical windows wide enough to potentially undertake U and Pu metal deposition, as observed by through the observation of the Li^+/Li^0 couple. [32] We have since extended this study to ionic liquids with lower symmetry cations, including $[\text{BuNMe}_3][\text{TFSI}]$, which is a liquid at room temperature. [33] All the ionic liquids were synthesized by metathesis reactions between Group 15 based alkyl cation halides and $\text{Li}[\text{TFSI}]$. For all the room temperature measurements the ferrocenium/ferrocene couple was used as an internal standard, [34] with a typical measurement shown in Fig. 4.

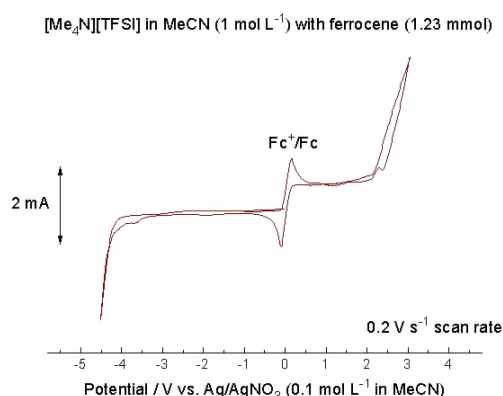


Fig. 4. Cyclic voltammogram showing the electrochemical window of $[\text{Me}_4\text{N}][\text{TFSI}]$ in MeCN.

F-element Speciation

Due to the presence of electron withdrawing CF_3 groups it would be expected that TFSI would be a weakly coordinating anion (Fig. 5). This may explain why, until recently, the only X-ray structural study of coordinated TFSI is in the Cu complex, $[\text{Cu}(\text{CO})(\text{TFSI})]$, where the ligand coordinates through the central nitrogen. [32] There have, however, been more recent reports indicating that TFSI is a flexible ligand, with several possible coordination modes. [36-38]

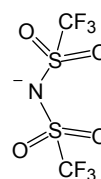


Fig. 5. The TFSI anion

We have recently structurally characterized $[\text{La}(\text{TFSI})_3(\text{H}_2\text{O})_3]$ as a benchmark trivalent f-element complex. [33] The three TFSI ligands coordinate to the La^{III} centre through bidentate sulfonyl oxygens. We have also been able to prepare a range of additional solid state TFSI complexes with other f-element cations, including Eu^{III} , Sm^{III} , Th^{IV} , U^{IV} and $\{\text{UO}_2\}^{2+}$, all characterised by a range of analytical and spectroscopic techniques.

In situ speciation in TFSI based ionic liquids have been limited to EAS and XAS measurements. We have undertaken extensive XANES and EXAFS measurements on a range of uranium complexes in TFSI based melts. EAS has been used to confirm oxidation state purity in solution. The results confirm that TFSI is a weak ligand, for example it unable to displace coordinated chloride anions from UCl_4 . A recent EXAFS study into $\{\text{UO}_2\}^{2+}$ solvent extraction into a TFSI based ionic liquid with nitrate and CMPO gave no evidence for the coordinated TFSI. [12] However, we have found evidence for TFSI remaining coordinated to U^{VI} with $[\text{UO}_2(\text{TFSI})_2]$ appearing to remain intact when dissolved into $[\text{BuNMe}_3][\text{TFSI}]$.

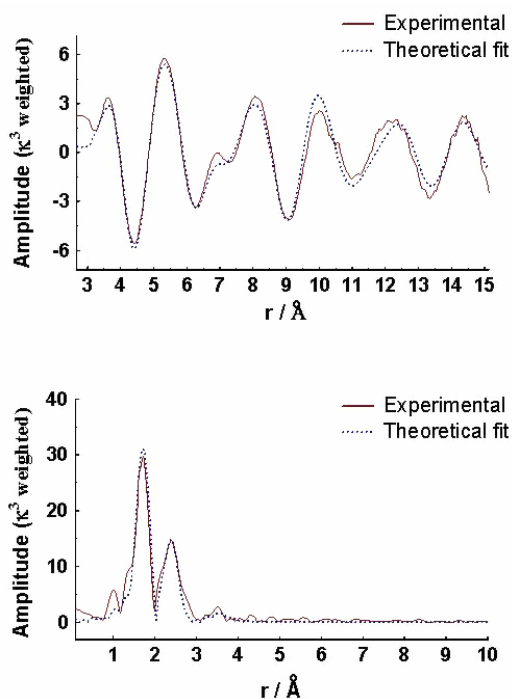


Fig. 6. EXAFS spectrum, and fourier transform of $[\text{UO}_2(\text{TFSI})_2]$ dissolved in $[\text{BuNMe}_3][\text{TFSI}]$. The data has been fit with two U-O_{uranyl} at 1.77 Å, four U-O_{TFSI} at 2.44 Å and two U-S_{TFSI} at 3.59 Å.

The EAS of a Np^{IV} -TFSI complex dissolved in $[\text{BuNMe}_3][\text{TFSI}]$ indicate oxidation to $\{\text{NpO}_2\}^+$ despite our best attempts to eliminate oxygen and moisture from the system, indicating that TFSI is not effective at stabilizing the lower oxidation state. Two major bands are observed around the region for the major $\{\text{NpO}_2\}^+$ f-f transition (at 969 and 980 nm respectively), [36] indicating the presence of more than one species in solution.

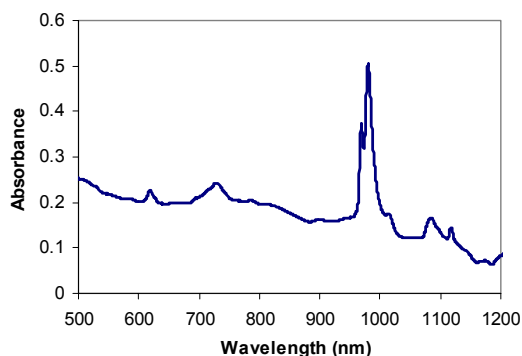


Fig. 7. EAS of Np^{IV} -TFSI dissolved in $[\text{BuNMe}_3][\text{TFSI}]$, indicating formation of $\{\text{NpO}_2\}^+$ species.

F-element Electrochemistry

Electrochemical studies have been undertaken in several of ionic liquids with a series of f-element cations, including La^{III} , Eu^{III} , Sm^{III} , Th^{IV} , U^{IV} , $\{\text{UO}_2\}^{2+}$ and $\{\text{NpO}_2\}^+$. In most cases reduction of Ln^{III} (or Ln^{II}) to Ln^0 or An^{III} to An^0 was observed although often plating and stripping behaviour was not observed, probably due to the presence of moisture in the solvent system leading to the immediate formation of oxide upon reduction to the metallic state. In addition, electrochemical features attributed to higher oxidation state processes (e.g. $\text{U}^{\text{VI/IV}}$, $\text{Np}^{\text{VI/IV}}$) were also observed at more positive potentials. Typical cyclic voltammograms showing the $\text{U}^{\text{IV/III}}$ and $\text{An}^{\text{III/O}}$ couples for U in $[\text{BuNMe}_3][\text{TFSI}]$ are shown in Fig. 8.

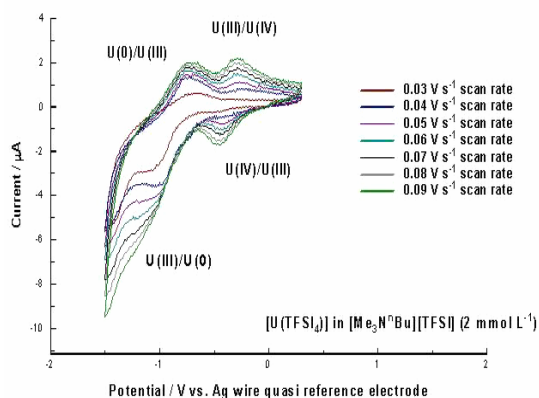


Fig. 8. Cyclic voltammograms of $\text{U}[\text{TFSI}]_4 \cdot x\text{H}_2\text{O}$ in $[\text{BuNMe}_3][\text{TFSI}]$.

CONCLUSIONS

Basic chemical research can underpin the development of novel ionic melt technologies for the electrochemical separation of U and Pu from irradiated nuclear fuel. Our higher temperature melt studies have focused on *in situ* speciation of uranium and key fission products. The application of XAS spectroscopy has given new insight into U, Tc and Ru speciation and yields complementary information to EAS. We plan to further develop our application of this technique and develop new spectroscopic techniques for high temperature studies, including Raman spectroscopy.

In lower temperature ionic liquid studies we have focused on the development of ionic liquid

systems that can possibly be applied to actinide electrochemical separation. Electrochemical studies, backed by an understanding of solution speciation, indicate that it may be possible to electrochemically separate out actinides using this technology. Further studies are required to develop novel ionic liquid solvents that can be used for bulk electrodeposition of U and Pu.

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