

Molten Salt Discussion Group

Christmas 2011 Research Meeting

Programme & Abstracts

19th December 2011
15Hatfields London

Programme

Monday 19th December

09:00 - 09:55 Registration with Tea/coffee & Danish pastry

09:55 – 10:00 Welcome by Andrew Griffiths (Chartered Institute for Environmental Health) and Professor Derek Fray (Chairperson of the MSDG)

10:00 – 10:40 Invited Lecture

(Chairperson : Professor Derek Fray)

Professor Koen Binnemans

Department of Chemistry, Katholieke Universiteit Leuven, Belgium

Liquid Metal Salts

10:40 – 12:30 Technical Session 1

(Chairperson :Dr Trevor Griffiths)

10:40 – 11:00 **Tim Paget**

AWE, Aldermaston, Reading, RG4 4PR, UK.

Chemical and Electrochemical Processing of Plutonium in Chloride Melts

11:00 – 11:30 **Anders Riisager**

Chemistry, Technical University of Denmark

Ionic liquid Catalysis for Upgrading Biomass to Value-added Chemicals

11:30 – 12:00 **Andrew Dolan¹, Tim Gorman², Agnieszka Brandt¹, Tom Welton¹**

1 Department of Chemistry, Imperial College, London, UK.

2 University of York, York, UK,

High energy site exchange in the 1H-NMR spectrum of pyrrolidinium based ILs

12:00 – 12:30 **Olga Babushkina**

CEST, Austria

Spectroscopy and Electrochemistry of Ionic Liquids with K₂NbF₇ and K₂TaF₇ Salts

12:30 – 13:30 Lunch

13:30 – 14:00 MSDG AGM

14:00 – 15:30 Technical Session 2

(Chairperson : Professor Andrew Abbott)

- 14:00 – 14:30 **Geir Martin Haarberg, Reidar Tunold and Espen Sandnes**
Institutt for Materialteknologi, NTNU, Sem Salands vei 12, Trondheim,
Norway, NO-7491
Anode Processes on Carbon in Molten Chloride Electrolytes with Dissolved Oxides
- 14:30 – 15:00 **Marcelle Gaune-Escard**
Ecole-Polytechnique, CNRS UMR 6595. Marseille, France
Molten Salts and Nuclear Energy
- 15:00 – 15:20 **Trevor Griffiths**
Redston Trevor Consulting Ltd., Leeds, LS17 8RF, UK.
***The Oak Ridge National Laboratory Molten Fluoride Reactor:
The foundation of modern molten salt chemistry?***
- 15:20 – 15:30 **Laurence O'Hagan**
The Weinberg Foundation, Somerset House, Strand, London, WC2R 1LA, UK
The Weinberg Foundation

15:30 – 16:00 Tea, coffee & biscuits

16:00 – 17:30 Technical Session 3

(Chairperson : Professor Geir Martin Haarberg)

- 16:00 – 16:30 **Rasmus Fehrmann**
Chemistry, Technical University of Denmark
Supported Ionic Liquid Phase (SILP) Catalysts and Gas Absorbers
- 16:30 – 17:00 **Geoffrey Taylor**
AWE, Aldermaster, Reading, RG4 4PR, UK
***Evaluation of Carbonate Oxidation for the Treatment of Waste
Pyrochemical Salts***
- 17:00 – 17:30 **Linpo Yu, George Z. Chen**
Dept. of Chemical and Environmental Engineering, University of Nottingham,
Nottingham, UK.
The Anodic Processes of Chloride and Bromide Ions in Ionic Liquids

17:30 – 19:00 Cheese/biscuits plus Tortilla chips/dips & wine

19:00 Close of meeting

Authors' Abstracts

Abstracts presented on the following pages are compiled by the MSDG for the sole purpose of distribution amongst attendees of the 2011 MSDG Christmas Research Meeting and are based on the submitted versions from the authors who are responsible for issues related with the scientific correctness and copyright.

Liquid metal salts

Koen Binnemans,^a Neil R. Brooks,^a Stijn Schaltin,^b Jan Fransaer^b

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“Liquid metal salts” are low-melting ionic metal salts and they can be considered as metal-containing ionic liquids.¹⁻⁴ Liquid metal salts are electrolytes with the highest possible metal concentration, because the metal ion is an integral part of the solvent. A typical example of such an ionic liquid is $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{Tf}_2\text{N}]$, in which the cation is a copper(I) ion surrounded by four acetonitrile molecules. Structurally, this compound can be considered as the inorganic analogue of a tetraalkylammonium compound. It melts at 60 °C. This ionic liquid allows electrodepositing metallic copper at very high current densities of 25 A/dm³ or even higher. The great advantage of this type of complexes is that the metal ion is part of the cation and this cation is attracted by the negatively charged electrode where the electrodeposition takes place. High current densities can be achieved, because the cathodic electrochemical decomposition reaction is the deposition of the metal. A similar complex with silver(I) instead of copper(I) turned out to have a more complex composition, in the sense that silver is present both in the cation and anion: $[\text{Ag}(\text{MeCN})_4]_2[\text{Ag}(\text{Tf}_2\text{N})_3]$. This complex could be used for the electrodeposition of silver coatings of a high quality. The acetonitrile ligands can be replaced by other ligands such as pyridine, 2,2'-bipyridine, and 1-alkylimidazoles. Especially the transition metal complexes of 1-alkylimidazoles proved to be interesting from a structural point of view. The cobalt(II), nickel(II) and copper(II) complexes of 1-methylimidazole all have similar stoichiometries and crystal structures. However, the melting point of the copper(II) complex $[\text{Cu}(\text{MeIm})_6][\text{Tf}_2\text{N}]_2$ (48 °C) is much lower than that of $[\text{Ni}(\text{MeIm})_6][\text{Tf}_2\text{N}]_2$ (147 °C) and $[\text{Co}(\text{MeIm})_6][\text{Tf}_2\text{N}]_2$ (137 °C). This difference is attributed to the Jahn-Teller effect, leading to a less symmetric cation in the case of the copper(II) complex, and thus to a less efficient packing. This distortion is very evident from the crystal structure of the complex.

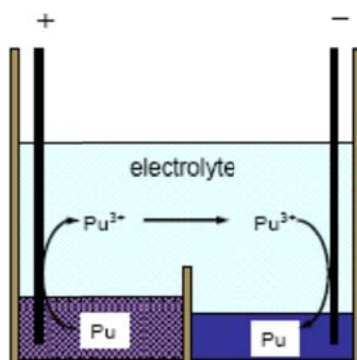
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Chemical and Electrochemical Processing of Plutonium in Chloride Melts

Tim Paget
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Molten salt techniques offer a number of potential advantages over traditional aqueous/solvent extraction technologies for the treatment of spent nuclear fuel, and are being actively developed in a number of nations. AWE has operated a plutonium recovery flowsheet using molten salts for a number of years. The processes used are very effective for metal recovery.



A schematic of the electrorefining process used at AWE to purify plutonium

Efforts are underway to improve process efficiency, reducing dose and residue arisings.



Breakout of the crucible following an electrorefining run

This presentation provides an overview of the techniques in use at AWE and describes some of the research and development activities underway to support plutonium recovery. Work undertaken and supported by AWE is helping to maintain expertise in molten salts within the UK.

Ionic liquid Catalysis for Upgrading Biomass to Value-added Chemicals

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The impending exhaustion of fossil resources and climate change has prompted an intensified research for establishing new and better pathways for obtaining carbonaceous chemicals and fuels from renewable sources. Carbohydrates constitute in this context an essential source representing 75% of the world's renewable biomass with cellulose (a glucose polymer) being the most abundant.

In a future carbohydrate-based chemical industry furanic compounds like 5-(hydroxymethyl)furfural (HMF), formed by the triple dehydration of hexoses (i.e. glucose and fructose), is expected to play a key role. HMF is primarily considered to be a starting material for its diacid counterpart 2,5-furandicarboxylic acid (FDA), which is a very attractive monomer replacement of terephthalic acid in polyesters and plastics. Secondly, reduction of the furan ring yields compounds suitable as solvents or fuels. Furthermore, rehydration of HMF led to formation of levulinic acid which is yet another important renewable platform chemical that can serve as a valuable source to produce, e.g. food flavoring agents, plasticizers and succinic acid and derivatives. Despite the obvious potential of HMF as key intermediate chemical, efficient and industrial suitable synthetic routes to HMF are still not accomplished nor are upgrading technology for processing HMF into other industrially useful chemicals.

The current presentation will address the unique potential offered by applying ionic liquid systems in valorization of biomass resources, and highlight new catalytic systems relying on ionic liquids which are viable for converting hexose carbohydrates into HMF and important derivatives hereof, including FDA and alkyl levulinates.

High energy site exchange in the ^1H -NMR spectrum of pyrrolidinium based ILs

Andrew Dolan¹, Tim Gorman², Agnieszka Brandt¹, Tom Welton^{1*}

1: Department of Chemistry, Imperial College London

2: Department of Chemistry, York University

The activation energy of the ring flip of salts and Ionic Liquids (ILs) based on the N-methylpyrrolidinium cation were investigated after the synthesis and characterisation of N-methylpyrrolidinium hydrogensulphate showed the ring protons had not coalesced in the room temperature proton spectrum, both in solution and neat.

This led to further synthesis of a range of ILs to investigate this phenomenon and attempt to develop some understanding of the cause. NMR spectroscopy was used in a range of solvents and the pure phase, where possible. Investigation showed a wide range of activation energies, from ca. 60 to 80 kJ/mol depending on the anion and the alkyl chain length, however no correlation with any single anion property was satisfactory.

The activation energies of all species investigated were higher than that of N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulphonyl)imide and significantly higher than the (literature) value of the parent molecule, N-methylpyrrolidine.

Spectroscopy and Electrochemistry of K_2TaF_7 and K_2NbF_7 in Ionic Liquids

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Ionic liquids are considered as an alternative media for electrochemical deposition of refractory metals and their compounds at temperatures below 200°C and for the development of energy saving and environmental friendly technologies. Electrochemical and spectroscopic behaviour of K_2TaF_7 and K_2NbF_7 in ionic liquids (x)1-methyl-1-butylpyrrolidinium chloride-(1-x) K_2MeF_7 (x=0.80-0.20) was investigated in respect to electrochemical deposition of tantalum and niobium at temperatures below 200°C. A series of these ionic liquids were investigated using cyclic voltammetry, FTIR, and *in situ* Raman spectroscopy.

FTIR and Raman spectroscopy confirm the existence of equilibrium $TaF_6^- \leftrightarrow TaF_7^{2-}$ species in ionic liquids which shifts towards TaF_7^{2-} as the molar fraction of K_2TaF_7 increases. *In situ* Raman spectra at x=0.65 demonstrate the shift of equilibrium $TaF_6^- \rightarrow TaF_7^{2-}$ as the temperature increases from 20 to 200°C.

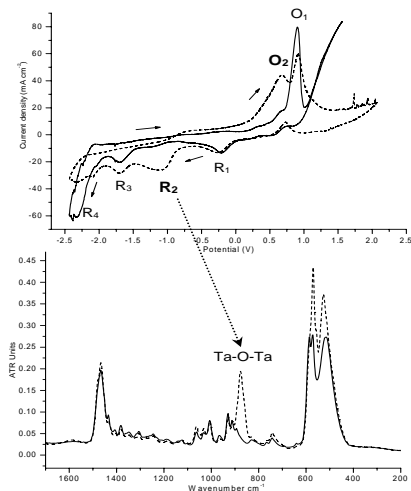


Fig.1 CVs and FTIR spectra,
x=0.40 (oxygen impurities)

As the impurities of tantalum(V) oxohalides play a crucial role in the deposition process, the influence of the additives of Na_2O and air inlet on the electrochemical reduction of tantalum(V) was investigated and correlated with spectroscopic data. Fig 1 presents the CVs of ionic liquid at x=0.40 without oxygen impurities (solid line) and with oxygen impurities (dash line) at 160°C and the corresponding FTIR spectra conforming the presence of oxyhalides species in electrolyte.

Electrochemical behaviour of tantalum(V) in acidic and basic ionic liquids as well as with the additives of alkali metal halides was investigated by means of cyclic voltammetry and will be discussed in details.

FTIR and Raman spectroscopy confirm the existence of equilibrium $NbF_6^- \leftrightarrow NbF_7^{2-}$ species in ionic liquids. In contrast to tantalum(V) containing ionic liquids, the equilibrium between two niobium(V) species is not affected significantly by temperature or composition of electrolytes. The electrochemical behaviour demonstrates the characteristic feature: the electrochemical window for niobium(V) containing ionic liquids is limited by alkali metal reduction.

Acknowledgement. The financial support within the COMET Programme given by the Austrian Government via the FFG (Austrian Research Foundation Agency) and by the Government of Lower Austria is gratefully acknowledged.

Anode Processes on Carbon in Molten Chloride Electrolytes with Dissolved Oxides

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Alkali and alkaline earth metals such as lithium, sodium, magnesium and calcium are produced by electrowinning in chloride melts. Direct cathodic reduction of metal oxides in chloride melts has been proposed for the FFC process. Fundamental data for the anodic process on carbon in mixed chloride/oxide melts are lacking.

Anodes of graphite and glassy carbon were used to study anode processes in NaCl-NaO, and in binary melts of the type NaCl-MCl₂-MO with 0-7 mol% oxide, (M = Ca, Sr and Ba) at temperatures from 800 - 825 °C. The techniques of linear polarization, cyclic voltammetry and electrochemical impedance spectroscopy were used. The gaseous products were found to be Cl₂, CO and CO₂, and the exit gas composition was determined by gas chromatography. The presented experimental results are mainly related to the NaCl-CaCl₂-CaO system.

Molten Salts & Nuclear Energy

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Since the Nuclear Fukushima disaster, the international summits multiply in the hope to reassure people. With, as industrial issue, the survival of an energy source that delivers 16% of planetary electricity for a minimum of CO₂.

Since the inception of nuclear power, that is to say, for fifty years, the industry atom gives the feeling that there is only one and only way to exploit fission.

Conventional PWR pressurized water-cooled reactors are omnipresent all over the world.

This nice PWR recipe has been served for ages at the table of nuclear; it is particularly narrow and bounded! Especially it is not the only one capable of producing electricity: there are other recipes to trigger a nuclear fission reaction and maintain that reaction by controlling it! It would be possible to take in place of uranium, thorium ore and convert the fuel in liquid rather than solid rods, mix the all in a cooling fluid which is a molten salts syrup at ambient pressure, and not water at high pressure.

This presentation will only mention the enthusiasm for this architecture which has singularly deep and solid roots. In fact, the revelation of this little wonder machine has occurred. at the end of 1950's in the Oak Ridge prestigious laboratories...(another talk will give more details on the Molten Salts Reactor Experiment – MSRE).

This presentation will deal with what has happened since then.

The Oak Ridge National Laboratory Molten Fluoride Reactor: the foundation of modern molten salt chemistry?

Trevor R. Griffiths

Redston Trevor Consulting Ltd., Leeds LS17 8RF

The Oak Ridge National Laboratory in Tennessee, USA, was built to be one of the major sites for the Manhattan Project to build the world's first atomic bomb. The lab's main contribution, as most know, was to develop techniques for enriching U235 and then to produce it in quantity. What is less well known is that ORNL was shortly thereafter, in the 1950s, also chosen to be the site for developing and testing various designs for nuclear reactors.

The basic principle is that a nuclear reactor, maintained at criticality, generates heat and this heat must and could be taken away and usefully employed to generate steam to drive turbines, thereby providing electricity. Thus a crucial feature was the effective removal of this heat energy. Water and gas cooling are obvious candidates but are not the best conductors of heat. It was recognised that molten salts are amongst the best candidates, being good heat conductors; stable to radiation; thermally stable and of low viscosity at 700°C; and fission products formed can be controlled and readily removed.

A description of the Oak Ridge Molten Salt Reactor will be given, with pictures, and indications of considerations and problems encountered in designing and bringing the reactor into being in a pre-computer era. Personal reminiscences will be included.

It can be therefore be argued that this successful reactor was the source and foundation on which the subsequent "explosion" of and in the field of molten salts and ionic liquids chemistry can be based.

Evaluation of Carbonate Oxidation for the Treatment of Waste Pyrochemical Salts

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Molten salt carbonate oxidation is being evaluated for the treatment of the salts generated during pyrochemical operations with plutonium. Potentially, carbonate oxidation could be part of a processing flowsheet designed to recover the plutonium and condition the salt for disposal. Its role would be to convert plutonium species, such as the chloride salt or free metal, to plutonium oxide. This would optimise the subsequent separation of the plutonium from the salt.

Carbonate oxidation has been performed with cerium chloride, as a non-radioactive simulant for plutonium chloride, using two molten salt systems, i.e. equimolar sodium chloride / potassium chloride or calcium chloride. The oxidation yield was measured by dissolving the salt in mild acid and weighing the filtered insoluble solid material, which was shown to be cerium dioxide by Raman spectroscopy and X-ray diffraction. The amount of unreacted and/or partially oxidised cerium chloride was determined from the cerium content of the aqueous filtrates.

Oxide yields of up to about 90% have been achieved with cerium chloride in sodium chloride / potassium chloride, using twice the theoretical stoichiometric amount of sodium carbonate. Less than 1% of the added cerium chloride remained in a form that was soluble in mild acid. The oxidation of pieces of cerium metal was slower than the oxidation of cerium chloride, but a 70% yield was achieved by extending the reaction time. Also, yields with cerium chloride in calcium chloride were initially much lower than those in sodium chloride / potassium chloride. However, a yield of about 80% was achieved by using 6x the stoichiometric amount of potassium carbonate. Work to improve processing efficiency is ongoing.

It was thought possible that the excess carbonate in the product of oxidation could cause problems during subsequent processing. It has been shown that these could be avoided by reacting any excess carbonate with magnesium chloride at the end of the oxidation step. Furthermore, it has been confirmed that the product of carbonate oxidation contains a lower, grey cerium-rich layer and an upper white, cerium-poor layer. Segregation of the two layers would reduce the amount of material requiring subsequent processing.

Supported Ionic Liquid Phase (SILP) Catalysts and Gas Absorbers

Rasmus Fehrmann

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Catalysis in ionic liquids may be carried out regarding many all ready industrially established homogeneous catalytic processes like hydroformylation of alkenes, carbonylation of alcohols and alkoxy carbonylation of alkenes traditionally carried out in volatile organic solvents. The non-volatile ionic liquids that might be used for these catalytic processes opens up for supporting them on high area porous carriers forming Supported Ionic Liquid Phase (SILP) catalysts. Such catalysts might be used in fixed-bed continuous flow process designs and thus enable heterogenisation of the homogeneous catalytic process whereby problems regarding separation of the catalyst and the product phase might be avoided. The advantages of the SILP catalyst process design will be demonstrated for selected important industrial processes.

Emission of acidic gases such as NO_x and SO_x and CO_x from e.g. energy production by fossil fuels in power plants, is a major concern in relation to atmospheric pollution and climate changes. Therefore, these gases have to be effectively removed from flue gases. Presently this is mainly achieved by relatively energy intensive and resource demanding technologies via selective catalytic reduction (SCR) of NO_x with ammonia, by gypsum formation after SO₂ wet-scrubbing while organic amines are being used as absorbents in CO₂ scrubbers. This leads to concern about, e.g. intensive energy requirements for desorption, corrosion of steel pipes and pumps, CO₂ absorption capacity and thermal decomposition of the amine. In this work, we demonstrate how ionic liquids (IL) can be tuned by design to perform as selective, high-capacity absorbents of environmentally problematic flue gases like, e.g. SO₂, NO, NO₂ and CO₂. Reversible absorption has been obtained for several different ILs at different temperatures and flue gas compositions. Furthermore, different porous, high surface area carriers have been applied as supports for the ionic liquids to obtain Supported Ionic Liquid-Phase (SILP) absorber materials. The results show that CO₂, NO, NO₂ and SO₂ can be reversible and selective absorbed using different ILs and that SILP absorbers are promising materials for industrial flue gas cleaning. Absorption / desorption dynamics can be tuned by temperature, pressure, gas concentrations and the properties of the porous carrier.

References :

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Tuning Ionic Liquids for High Gas Solubility and Reversible Gas Absorption. J. Huang, A. Riisager, R.W. Berg and R. Fehrmann, *J. Molec. Catal. A*, 279, 170-176, **2008**.

The Anodic Processes of Chloride and Bromide Ions in Ionic Liquids

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The electro-oxidation processes of chloride and bromide ions on Pt-disk electrodes (diameter: 100 and 60 μm) were investigated in a typical room temperature ionic liquid, 1-butyl-3-methyl-imidazolium hexafluorophosphate ([BMIM]PF₆) in the presence of high concentrations of chloride and bromide ions by addition of 1-butyl-3-methylimidazolium chloride and bromide ([BMIM]Cl and [BMIM]Br), or tetrabutylammonium chloride and bromide (Bu₄NCl and Bu₄NBr). The difference in sources of the halide ions led to similar cyclic voltammograms (CVs) in shape as compared in **Fig. 1**. Although the tri-chloride (Cl₃⁻) was observed on gold electrode¹ and tri-bromide (Br₃⁻) was investigated in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM]NTf₂)², the oxidation of the chloride ion did not lead to chlorine gas evolution in our study on different electrode materials and different ionic liquids.³ The retention of the Cl₂, Cl₃ and Br₂, Br₃ species in [BMIM]PF₆ was determined by cyclic voltammetry and UV-Vis spectrometry.⁴ These findings suggest the possibility of direct electro-reduction of solid metal halides to metals,⁴ because of the capability of ionic liquids for transferring halide ions.

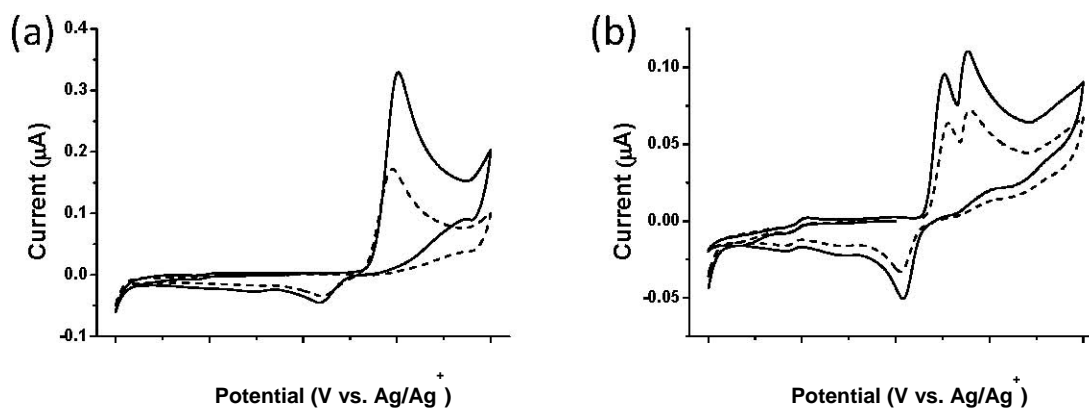


Fig. 1. Comparison of CVs recorded on a Pt-disk electrode (diameter: 100 μm) in [BMIM]PF₆ in the presence of (a) 0.33 M [BMIM]Cl (solid line) and 0.17 M Bu₄NCl (dash line), and (b) 0.30 M [BMIM]Br (solid line) and 0.21 M Bu₄NBr (dash line). Scan rate: 50 mV/s.

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