Molten Salt Discussion Group
Christmas Research Meeting 2016

Final Programme & Abstracts

Burlington House, London

19 December 2016
Authors’ Abstracts

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MSDG Christmas 2016 Research Meeting Programme

MONDAY December 19th

09:00 – 09:55  Registration/coffee

09:55 – 10:00  Chairman’s welcome by Professor George Z. Chen

10:00 – 11:15  Technical Session 1. Chair George Z. Chen

10:00 – 10:30  The Molten Salt Reactor Experiment: Designed, started, built and successfully operated in the 1960s
A film by the Oak Ridge National Laboratory just released after 50 years
Trevor R Griffiths
Energy Process Developments Ltd
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10:30 – 10:50  Structural Investigations of Ionic Liquid Mixtures
Cameron C. Weber1, Nicholas J. Brooks1, Fiona Cameron1, Franca Castiglione2, Cara M. Doherty3, Andrew Dolan1, Jeraimie Griffith1, Jason P. Hallett1,4, Anita J. Hill5, Patricia A. Hunt1, Richard P. Matthews1, Michele Mauri5, Andrea Mele2, Roberto Simonutti5, Ignacio J. Villar-Garcia1,6 & Tom Welton1

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10:50 – 11:10  Electro-reduction of solid silicon dioxide to solid silicon in molten chlorides: engineering energy efficiency, purity, microstructures and functionalities
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11:10 – 11:30  Coffee and Poster Session.

Metal-Free Hydrogenation in Ionic Liquids

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The nano-scale segregation of ionic liquids probed by molecular dynamics simulation

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Corrosion of Ti₃AlC₂ MAX phase in molten LiCl-KCl eutectic

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Solid State Manufacture of High Entropy Alloys: Preliminary Studies

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Recent progress in black silicon photovoltaics

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Carbonate Oxidation of Electrorefining Salts

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Investigating the effect of water on the band of ionic liquids

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Effects of ionic liquid pretreatment severity on pulp, saccharification yield and lignin structure isolated from *Salix*

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The thermal decomposition of sodium carbonate and calcium carbonate in molten sodium chloride and the molten salt synthesis of sodium silicate and calcium silicate.

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Effect of LiF Addition on Current Efficiency for Aluminium Electrolysis from Cryolite-Based Molten Alumina Electrolytes

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11:30 – 11:35 The Inman Lecture Introduction by Professor George Z. Chen
11:35 – 12:15 Low Temperature Synthesis of Structural and Functional Materials from Molten Salt
Shaowei Zhang
College of Engineering, Mathematics and Physical Sciences, University of Exeter
12:15 – 13:35 Technical Sessions 2: Chair Robert Watson
12:15 – 12:35 Improved Electrolytic Production of Titanium Alloys in Molten Salts via Compounding the Oxide Precursors
D.Hu¹, A.J.Stevenson² & G.Z.Chen¹,²
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12:35 – 12:55 Ionic liquids as media for photon upconversion: a modelling study

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12:55 – 13:15 Thermoelectrochemical Cell with Molten Carbonate Electrolytes and Symmetrical Gas Electrodes

Geir Martin Haarberg¹, Sathiyaraj Kandhasamy¹, Signe Kjelstrup², and Asbjørn Solheim³

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13:35-14:00 Lunch

14:00 – 14:30 MSDG Annual General Meeting

14:30 – 15:30 Technical Session 3: Chair Stuart Mucklejohn

14:30 – 14:50 Cleaning of industrial off-gases by ionic liquid filters

P. K. Kaas-Larsen, P. Thomassen, L. Schill, S. Mossin, A. Riisager, and R. Fehrmann*

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14:50 – 15:10 Calcium Reduction of Spent Electrorefining Salt

Clare Stawarz, Robert Watson

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15:10 – 15:30 Development of quantitative spectroelectrochemical techniques for the study of molten chlorides

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15:30 – 15:50 Tea break and Poster Session

15:50-16:50 Technical Sessions 4 Chair Andrew Doherty

15:50–16:10 Anodic Dissolution of Vanadium in Molten LiCl-KCl-TiCl₂
K. Milicevic¹, J. Gussone², J. Haubrich² & B. Friedrich³

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16:10-16:50 Early Times in Molten Salt Research

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16:50 – 19:00 Wine and cheese

19:00 Close of Meeting.
LECTURES
The Molten Salt Reactor Experiment: Designed, started, built and successfully operated in the 1960s
A film by the Oak Ridge National Laboratory just released after 50 years

Presented by Trevor R Griffiths

Energy Process Developments Ltd

In the 1960s I had the privilege and excitement of working at ORNL on two occasions on the molten Salt Reactor project as a member of the Metals and Ceramics Division. My participation was in the group led by Pedro Smith and involved studying the spectra of transition metal complexes in molten halides, using the first ever digitised uv vis nir spectrophotometer and installed with reverse beam optics, all designed by ORNL engineers. This meant that molten salt systems could now be measured at temperatures up to 800°C without having to restrict them to a light-tight enclosure.

As an “alien” I was restricted in what I could see or be told of certain aspects of the reactor (guards with guns at the entrance to certain corridors!). Neither was I allowed to see the reactor being build. This 20 minute film now tells the complete story that I was never allowed to see or fully know before.
Structural Investigations of Ionic Liquid Mixtures

Cameron C. Weber1, Nicholas J. Brooks1, Fiona Cameron1, Franca Castiglione2, Cara M. Doherty3, Andrew Dolan1, Jeraime Griffith1, Jason P. Hallett1,4, Anita J. Hill3, Patricia A. Hunt1, Richard P. Matthews1, Michele Mauri5, Andrea Mele2, Roberto Simonutti3, Ignacio J. Villar-Garcia1,6 & Tom Welton1

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The structures of ionic liquids (ILs) are remarkably complex due to the interplay between strong Coulombic forces and other, weaker, interactions such as a hydrogen bonding and π-π stacking [1, 2]. The level of complexity increases further when mixtures of these ILs are considered as there is now the potential for preferential interactions between specific ions either through the formation of ion-pairs or through preferential hydrogen bonding interactions. The existence, magnitude and dynamics of preferential interactions in IL mixtures remains controversial with proposals that there are preferences for certain anions to occupy specific locations around the cation [3], whereas others have suggested that ion locations are randomly assigned within a charge alternating structure regardless of their identity [4]. The existence of preferential hydrogen bonding interactions between different ions is also not clear as the NMR spectroscopy of IL mixtures supports such a preference whereas IR spectroscopy indicates the absence of any preferential hydrogen bonding interactions between specific ions [5]. Surprisingly, despite the structural complexity of IL mixtures and the uncertainty surrounding the nature of these structural effects, the physical properties of many IL mixtures can be predicted from those of their constituents as most IL mixtures exhibit nearly ideal mixing behaviour [6, 7].

In order to reconcile these findings and to gain greater insight into the structural changes that occur as ILs are mixed, we have conducted a detailed study of the structures of IL mixtures containing a common 1-butyl-3-methylimidazolium ([C6C1im]+) cation with different anions using Small Angle X-ray Scattering (SAXS) and NMR spectroscopy as well as molecular dynamics simulations and quantum chemistry calculations [8]. The free volume of these mixtures was also probed using Positron Annihilation Lifetime Spectroscopy (PALS) and 129Xe NMR. This presentation will use these results to unify the apparent conflicts in the understanding of the structures of IL mixtures and to highlight the relative importance of these structural factors in determining the thermodynamics of mixing and the physicochemical properties of IL mixtures.

References
Electro-reduction of solid silicon dioxide to solid silicon in molten chlorides: engineering energy efficiency, purity, microstructures and functionalities

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Silicon plays an important role in metallurgical, photovoltaic and information industries and shows great application potential for energy storage. The current carbothermal reduction methods for large-scale silicon production are inadequate to sustain their applications in terms of energy efficiency, purity, microstructure and functionalities. Alternatively, electro-reduction of solid SiO₂ in molten chlorides was recently reported as a more affordable and efficient silicon production[1-2]. Focusing on the interfacial phenomena during the course, the author (1) developed a quantitative kinetic model for the direct solid-solid reactions[3-4]; (2) verified the co-existing dissolution-electrodeposition mechanism[5-6]; (3) specified the factors affecting the purity and microstructure of the electrolytic silicon[7-8] and (4) prepared hollow-nanostructured SiGe alloys with enhanced lithium storage capability[9]. We hope that the above results could form the scientific grounds on a more affordable and controllable preparation of nanstructured and high-purity silicon with intriguing functionalities.

Fig.1 Schematic illustration on one-step and template-free preparation of SiGe nanotubes by molten salt electrolysis of solid mixture between SiO₂ and GeO₂.

References
Low Temperature Synthesis of Structural and Functional Materials in Molten Salts

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Abstract. Compared to conventional synthesis techniques, the so-called molten salt synthesis (MSS) technique shows a number of advantages: 1) the synthesis reaction can be completed at a relatively low temperature and in a short time; 2) in principle any kind of precursor can be used as a starting raw material; 3) the resultant product powders are generally homogeneous and well-dispersed, and have high surface reactivity; 4) grain shapes (spheroidal, platelet-shaped or lath/needle-shaped) and sizes (nanoscale to microscale) can be controlled/tailored; 5) the process is easy to perform, scalable and at a relatively low cost. Because of these advantages, MSS has attracted a great deal of research interest and been used extensively, in particular in recent years, to synthesise a range of structural and functional materials for many important applications. In this talk, the main work on MSS of structural and functional materials carried out at Exeter will be reviewed. The presentation starts with a brief background introduction, which is followed by a discussion on the two important MSS mechanisms, “dissolution and precipitation” and “template-growth” mechanisms. Their effects on MSS process as well as resultant products will be compared. The third part of the presentation focuses on MSS governed by the “template-growth” mechanism. Microstructures, properties and potential applications of some novel materials (such as spinel platelets, carbide nanorods/platelets/foams, and g-C3N4 nanotubes) synthesised via this route, will be introduced. Furthermore, the work on the in-situ formation of functional coatings or mono-dispersed nanoparticles, on different substrates (such as graphene or carbon nanotube) will be presented. Their applications in some important areas such as in armour, aerospace and hydrogen generation will be reviewed. In the fourth part of the presentation, the work on MSS controlled by the “dissolution and precipitation” mechanism will be highlighted. Microstructures, properties and applications of some nanomaterials (such as mullite whiskers, Si3N4 nanoplatelets, and SiC nanofibers) formed via this route will be introduced. In addition, the latest work on MSS of other non-oxide ceramics such as transition metal borides, sulphides and nitrides, and porous graphene (for water-treatment), will be presented. Finally, future work on MSS of other new materials will be suggested.

Fig. 1 Schematic of a typical MSS process.
Improved Electrolytic Production of Titanium Alloys in Molten Salts via Compounding the Oxide Precursors

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Direct electrochemical reduction of solid TiO$_2$ in molten CaCl$_2$ was demonstrated more than a decade ago at both laboratory and kilogram pilot scales [1]. While it is now undergoing technical improvement and scaling up for commercialisation, many laboratory investigations have commonly revealed a key intermediate step in the process: formation of various perovskite phases [2-3] due to chemical and electrochemical reactions at the cathode as shown below,

\[
\text{TiO}_2 + \alpha \text{Ca}^{2+} + \beta \text{O}^{2-} + 2(\alpha - \beta) \text{e} \leftrightarrow \text{Ca}_\alpha\text{TiO}_{2\beta}
\]

where $1 \geq \alpha \geq \beta \geq 0$. Proposed as “in situ perovskitisation” [3], the above reaction is a chemical reaction for $\alpha = \beta$, but an electrochemical one for $\alpha > \beta$. It is now commonly accepted that in situ perovskitisation combines Ca$^{2+}$ into the solid phase in the oxide cathode, leading to volume expansion and blockage of some of the pores, hence slowing down the overall electrochemical reduction process. In this presentation, we show electro-co-reduction of TiO$_2$ with metal co-oxides (such as TiVO$_4$) to produce Ti-6Al-4V. The presence of metal co-oxide can mitigate the impact of in situ perovskitisation, making the Ti-6Al-4V production more efficient than that of pure Ti production. As shown in Figure 1, after 20 hours electrolysis, the Ti-6Al-4V sample exhibits a better extent of sintering when compared to that of the pure Ti sample, which implies its higher metallisation speed.

![Fig.1 Photographs of pellet-shaped metal oxide precursors (a) before and (b) after electrolysis at 3.2 V 1173 K in molten CaCl$_2$ for 20 hours SEM images of electrolytic (c) Ti-6Al-4V and (d) Ti obtained from the pellets in (b).](image)

References

Ionic liquids as media for photon upconversion: a modelling study

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Photon upconversion (UC) is the process of converting low-energy photons into high-energy photons. Triplet–triplet-annihilation-based UC (TTA-UC) is particularly interesting for solar energy harvesting and other biological photosensitized processes since it can turn low-energy photons from the visible part of solar radiation into higher-energy photons at the other end of the visible spectrum, which are much more efficient in such processes.

Air-stable, non-volatile ionic liquids are able to overcome two major challenges encountered in the manufacturing of photovoltaic cells with upconversion materials: the deactivation of the triplet states caused by molecular oxygen and the volatility of the solvent. Moreover, the efficiency of the TTA process is also enhanced by relatively high triplet diffusion rates caused by the fluid but structured nature of the IL media.

The use of MD simulations (fig. A) and the resulting structure analyses (fig. B) allowed the rationalization of the underlying molecular processes that permit high TTA yields in IL-based upconversion materials, namely the recognition that such yields are not caused by the nanosegregation between polar and non-polar domains in the IL —the chromophores are not oriented in any particular way within the non-polar domains— but mainly due to the anchoring of the chromophore-grafted anions to the continuous polar network at regular spaces.
Thermoelectrochemical Cell with Molten Carbonate Electrolytes and Symmetrical Gas Electrodes

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Waste heat generated in industrial processes for production of metals and alloys by metallurgical and electrochemical methods may be used to generate electricity.

Commercial thermoelectric generators based on semiconductor materials have limited power efficiency. Alternative thermoelectric cells using molten salt electrolytes and symmetrical gas electrodes may be developed for power production without the use of expensive and critical materials.

Experiments were carried out in the molten Li$_2$CO$_3$-Na$_2$CO$_3$-K$_2$CO$_3$ system at different compositions at temperatures from 550 - 850 °C. Reversible electrodes with respect to carbonate ions were established by using gas mixtures of O$_2$ and CO$_2$. Solid MgO particles were added to the molten electrolyte in order to provide for more accurate potential measurements. Two identical electrodes of platinum or gold were located at different temperatures for determining the Seebeck coefficient based on potential measurements. Seebeck coefficients up to ~1.5 mV/K were obtained.

The possibility to combine a thermoelectrochemical cell and a battery or a fuel cell in a hybrid electrochemical power generating system is an interesting option which will be explored in future experiments.
UNDERSTANDING HALOMETALLATE IONIC LIQUIDS
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Early ionic liquids (ILs) included aluminum based anions, principally [AlCl\textsubscript{4}]\textsuperscript{-}, more recently chlorometallate ILs with a larger range of metals (or main group elements) have been synthesised M=Fe, Co, Ni, Cu, Al, Ga, In, Sn, Sb, Bi. Moreover, ILs have been produced with other halides, exchanging Cl for Br or I. Halometallate ILs have been proposed for a large range of applications including; clean metal deposition, electrochemical applications, semiconductor synthesis, liquid magnetic materials, nanostructure synthesis, battery electrolytes, heat storage fluids, lubricants and as active or passive solvents for catalysis. Thus there is a diverse and expanding range of potential application areas for this technology.

Halometallate ILs are produced by adding solid MX\textsubscript{n} (M is a metal, X is a halide) to a traditional IL such as [C\textsuperscript{+}]X\textsuperscript{-} (C\textsuperscript{+} is an organic cation), a reaction occurs and the anion [MX\textsubscript{n+1}]\textsuperscript{-} is formed. If more MX\textsubscript{n} is added, then there is a “shortage” of X\textsuperscript{-} ions and dimers [M\textsubscript{2}X\textsubscript{2n+1}]\textsuperscript{-}, trimers [M\textsubscript{3}X\textsubscript{3n+1}]\textsuperscript{-} or larger clusters [M\textsubscript{n}X\textsubscript{m+n+1}]\textsuperscript{-} can form. If less MX\textsubscript{n} is added then there is an excess of X\textsuperscript{-} ions. If a mixture of metals and halides is employed clusters with a more complex stoichiometry can form. The speciation within such ILs is difficult to determine.

Recently a series of novel halobismuthate ILs were reported.\textsuperscript{[1]} These ILs exhibit a very high density, and a high thermal stability, they are easy to prepare and generate a range of colours from clear through yellow to deep red. When the halide anion is varied, mixed halide ions of the form [BiX\textsubscript{4}]\textsuperscript{-}, [BiX\textsubscript{3}X\textsuperscript{3}]\textsuperscript{-}, [BiX\textsubscript{2}X\textsuperscript{2}]\textsuperscript{-} and [BiX\textsuperscript{3}]\textsuperscript{-} can form within the IL. More complex combinations within the dimer anions are also possible. Experimental studies have characterized some properties of these ILs, but have not yet been able to completely unravel the nature or speciation of the anionic complexes present. We have computationally investigated (employing DFT methods) the halobismuthate ILs, characterizing the relative stability and structures of the mixed anionic species, the bonding within the cluster anions and the nature of the cation-anion interactions. The aim is to provide additional information which can be combined with that from experimental studies to better understand and characterize these ILs.

\begin{figure}
\centering
\includegraphics[width=0.7\textwidth]{molecular_orbitals.png}
\caption{Molecular Orbitals from [Bi\textsubscript{3}Cl\textsubscript{3}]\textsuperscript{2-}}
\end{figure}

Cleaning of industrial off-gases by ionic liquid filters

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Atmospheric pollution and climate changes is now recognized to be severely influenced by emission of acidic gases such as NOx, SOx and COx from combustion of fossil fuels in, e.g. power plants, cement factories and ships. Accordingly, 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 NOx with ammonia, SO2 wet-scrubbing by lime obtaining gypsum and CO2 wet-scrubbing with organic amines. The latter leads to particular concern about, e.g. intensive energy requirements for desorption, corrosion of steel pipes and pumps, CO2 absorption capacity and thermal decomposition of the amine.

The structures of ionic liquids (ILs) are well-ordered even in the liquid state with regular cavities which can host selected solute species depending on the IL ion composition or contain reversible binding functionalities. This makes the materials promising for selective, reversible absorption of gaseous pollutants in, e.g. industrial off-gases [1,2].

In this work we demonstrate how more environmental friendly ILs as amino acid based ones can be applied as selective, high-capacity absorbents of CO2, exemplified by a tetraalkylphosphonium prolinate IL. In the context of CO2 removal, ILs are considered environmentally friendly because they are not emitted to the environment due to their negligible vapor pressure. In addition, an imidazolium nitrate IL is also investigated regarding absorption of NO. Only few publications deal with possible interferences of other flue gas components with the IL absorbers. Thus we here also investigate the interaction of the selected ionic liquids with SO2, CO2, NO and air.

Furthermore, different porous, high surface area carriers like mesoporous silica have been applied as supports for the ionic liquids to obtain Supported Ionic Liquid-Phase (SILP) absorber materials. These materials benefit from low mass transport resistance of the often very viscous ILs by the distribution of the liquid as a thin film (or small droplets) on the surface of the highly porous carrier materials enabling fast absorption/desorption rates of the particular gas to be removed by the SILP absorber [3]. These powderly SILP materials may also be extruded with appropriate binders to multichannel rotating filters that might be installed in the flue gas duct of the industrial unit for reversible selective gas absorption. The gaseous pollutant is then desorbed and obtained in concentrated form for further processing on site to e.g. commercial grade mineral acids or stored in underground reservoirs.

References
Calcium Reduction of Spent Electrorefining Salt

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Spent Electrorefining (ER) salt from the pyrochemical processing of plutonium at AWE is currently stored on site awaiting a suitable recovery route. Restrictions on the materials storage and disposal mean reprocessing is required to find a more suitable storage form and recover the plutonium metal. A Calcium Reduction process is currently being developed at AWE to treat spent ER salt residues.

The process aims to reduce the Pu$^{3+}$ species in the spent salts to plutonium metal via the addition of calcium metal. The product is a consolidated plutonium button or plutonium rich salt and salt residues that contain considerably lower levels of plutonium than before processing. In total, nine experiments have been carried out at AWE to demonstrate calcium reduction as a potential plutonium recovery process. Of the nine experiments carried out; three experiments were on spent ER salt with no ceramic fines and six on spent ER salt containing ceramic fines. Alongside the experiments carried out on the two different salt feeds, varying levels of calcium were used in different runs to identify a suitable excess amount of calcium for the process.

Findings from the AWE experiments show a high removal of plutonium in both types of spent ER salt, with or without ceramic fines. The product metal in all cases has made a plutonium button or a consolidated plutonium salt phase. The salt after assay and initial analysis has shown to contain very low levels of plutonium, between 85 – 99 % removal.

Figure 1: Photograph of the spent ER salt containing ceramic fragments after the calcium reduction process. This experiment used 30 % excess calcium. Two phases can be seen in the salt block. The white layer contains almost no plutonium, the darker layer is plutonium rich where partial reduction of the plutonium occurred.
Anodic Dissolution of Vanadium in Molten LiCl-KCl-TiCl₂

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The mechanism of anodic dissolution of pure vanadium in a titanium enriched alkali chloride molten salt was investigated to determine whether it can be used as an ion source for a continuous Ti-V alloy deposition process. This study represents the first step towards the preparation of ternary Ti-Al-V alloys. Cyclic voltammetry was performed and potentials for dissolution experiments were determined. Additionally, the influence of anode morphology on the dissolution process, as a consequence of pre-treatment, was investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

Results indicate that anodic vanadium dissolution is possible, but hindered by the electroless formation of a thin titanium layer. Additionally, a secondary reaction, namely the oxidation of Ti²⁺ ions, takes place, lowering the current efficiency of the process. Morphology investigations revealed the risk of grain detachment (material loss) from the vanadium electrode, which is critical in direct dissolution, whereas under indirect dissolution conditions, passivation impedes the controlled process. Thus, electrolysis with coarse grained vanadium electrodes is best carried out in the direct dissolution range.

Figure 1: Cyclic voltammogram of Vanadium anode with morphology SEM insets in different dissolution areas
Metal-Free Hydrogenation in Ionic Liquids

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Hydrogenation reactions conventionally rely on scarce and/or toxic metals such as palladium, platinum or nickel as catalysts. Recently, sterically hindered Lewis acid/base pairs, known as Frustrated Lewis Pairs (FLPs), have been shown to facilitate the heterolytic splitting of hydrogen and to facilitate the catalytic hydrogenation of various functionalities including imines, alkenes, ketones and aldehydes [1-4]. This approach enables the use of hydrogenation catalysts featuring earth abundant main group elements such as boron. However, the scope of FLP catalysis using boranes is limited by the propensity of the strong Lewis acids required to activate hydrogen to form adducts and by the correspondingly poor nucleophilicity of the resultant borohydrides. This imposes limitations on functional group tolerance, substrate scope, solvent selection, and necessitates rigorously dry conditions to maintain the activity of the catalyst.

One of the limiting factors in the search for less Lewis acidic boranes which generate more nucleophilic borohydrides is the thermodynamics of the hydrogen activation equilibrium (Scheme 1). As ionic liquids (ILs) are capable of strongly dissociating ionic solutes [5, 6] and, with appropriate ion selection, can be designed to be non-coordinating, we have investigated their use as solvents for FLP chemistry with a view to ultimately increasing the scope of metal-free hydrogenation chemistry. This presentation will outline our results on the feasibility of metal-free hydrogen activation in ILs as well as the effect of IL solvation, including a comparison with molecular solvents. The influence of IL solvation on the catalytic hydrogenation of imines will also be discussed and compared to molecular solvents.

**Scheme 1.** An example of metal-free hydrogen activation using a FLP.

References
The nano-scale segregation of ionic liquids probed by molecular dynamics simulation

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The diverse structure and morphology of ionic liquids (ILs) at a molecular level is complex and can exhibit nano-scale segregation. A systematic study has been done in order to understand the complex nature of ionic liquids as pure substances as well as in mixtures/solutions of IL plus neutral organic molecules.

The results involve the discussion of the structure factors, \( S(q) \), in the low-\( q \) range (1.6 \( \leq q/\text{nm}^{-1} \leq 2.0 \)); the confirmation of the periodicity of the polar network of the ionic liquid and its relation to the so-called intermediate peaks; and the characterization of the polar network and the nonpolar regions that are formed along the series. The lowest-\( q \) peaks of the structure factor spectra (prepeaks) can be appointed to distinctive separations between strands of the IL polar domain that are intermediated by nonpolar regions. Moreover, the second lowest \( q \)-peaks suggest the medium-range ordering of the polar network itself. [1]

The first part of this study is related to the investigation of the nano-segregation and self-aggregation of pure and mixtures of ionic liquids in bulk phases (isotropic liquid or formation of liquid-crystalline phases). [2] The second part is dedicated to the analysis of the structuration of ILs at the IL/vacuum interface (Figure 1). [3]

Figure 1: Simulation snapshots depicting different types of structural/boundary features. The polar moieties of the IL are represented as a blue and red (cations and anions, respectively), the non-polar alkyl side chains of the cations as grey space-filled atoms, the fluorinated domains are depicted as green spheres and air/vacuum phases as a white background. (a) 1-hexyl-3-methylimidazolium bis-(trifluoromethylsulfonyl) imide, \([C_6C_1im][Ntf_2]\); (b) 1-dodecyl-3-methylimidazolium tetrafluoroborate, \([C_{12}C_1im][BF_4]\); (c) liquid–vacuum surface of IL slab of the 1-hexyl-3-methylimidazolium perfluorobutylsulfonate, \([C_6C_1im][C_4F_9SO_3]\).

References
Corrosion of Ti$_3$AlC$_2$ MAX phase in molten LiCl-KCl eutectic

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Molten salt reactors are Generation IV nuclear reactors where the fuel is dissolved in an alkali chloride or fluoride salt at temperatures in excess of 500°C. The structural materials used must possess high strength at such temperatures and resist chemical attack in high neutron and gamma fluxes. The M$_{n+2}$AX$_n$ phases, a class of layered ternary carbide and nitride materials with a mixture of ceramic and metallic properties, are strong at high temperatures and resistant to chemical attack and radiation damage. However, their resistance to reaction in alkali halides has undergone limited research. Bulk Ti$_3$AlC$_2$ has been synthesised and exposed to LiCl-KCl eutectic (LKE) in order to investigate its resistance to chemical attack. Fully dense samples >95wt.% Ti$_3$AlC$_2$ have been consistently produced using mechanical alloying followed by spark plasma sintering. Samples have been exposed to LKE under argon followed by characterisation via scanning electron microscopy (Figure 2) and glancing-angle X-ray diffraction. Additionally, electrochemical experiments have been performed in-situ including measurement of the open-circuit potential and cyclic voltammetry.

Figure 2 – Backscattered electron image of the outer region of a cross-section of Ti$_3$AlC$_2$ which has been exposed to molten LiCl-KCl eutectic. The sample surface is on the right-hand side of the image.

References

Solid State Manufacture of High Entropy Alloys
Preliminary Studies

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Abstract

Metalysis, for the past ten years, have, through their solid state salt electrolysis process, manufactured tantalum, titanium and titanium alloy powders for a number of high performance applications. This low energy and environmentally friendly process is now being used to manufacture the next generation of High Entropy Alloys (HEAs).

The manufacture of HEAs involves, in most cases, high temperatures which melt and put all the constituent alloying elements into the liquid phase. This can lead to numerous problems and restrict the number of HEAs which can be made, in particular, the alloys where one needs to combine low melting point elements with refractory elements and also where there are significant liquid density differences between the constituents causing melt segregation.

The aim is to present the preliminary work carried out by Metalysis showing how the solid state diffusion process based on molten salt electrolysis lends itself to the manufacture, on an industrial scale, low tonnage quantities of the next generation of HEAs. Metalysis will focus production on the HEAs whose constituent alloying elements have large differences in both their melting points and liquid densities, for example, tungsten, niobium, tantalum, molybdenum, vanadium, titanium and aluminium.
Recent progress in black silicon photovoltaics

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Solar photovoltaics (PV) are a huge area of research with 95% of current world market dominated by solar cells made from silicon. At present, silicon used in PV cells reflects around 40% of the incident light. Obviously if this is increased, the efficiency of the cells will increase. Porous black silicon offers the potential to radically increase the amount of light captured due to its specialised surface texture [1]. Its highly porous and dense nanostructure makes it particularly useful as an anti-reflection layer (ARC) and boost the performance of crystalline silicon solar cells by minimising reflection light losses at the front cell face. Black silicon can be made via several time-consuming and expensive routes, involving hazardous chemicals. By de-oxidising silica surfaces on the front of commercial Si wafers in a bath of molten calcium chloride salt, similarly textured surfaces can be made quickly and at a fraction of the cost [2]. Here we present recent work on the development of a molten salt black silicon solar cell, using an emitter layer prepared via thermally-driven diffusion.

References

Carbonate Oxidation of Electrorefining Salts

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Spent electrorefining salts contain about 10wt% Pu (presumed to be PuCl₃ and uncoalesced Pu metal) in a NaCl-KCl matrix. A salt distillation process under reduced pressure is proposed to separate the salt matrix from the plutonium species. To prevent any plutonium species being transferred all the plutonium needs to be present as an oxide. An oxidation process using Na₂CO₃ is being investigated. The proposed reactions taking place are:

\[
2\text{Pu}^{3+} + 3\text{CO}_3^{2-} \rightarrow 2\text{PuO}_2 + \text{CO} + 2\text{CO}_2 \quad (1)
\]

\[
\text{Pu} + 2\text{CO}_3^{2-} \rightarrow \text{PuO}_2 + 2\text{CO} + 2\text{O}^{2-} \quad (2)
\]

Trials took place using CeCl₃ or PuCl₃ in NaCl-KCl to demonstrate the process. A 100% stoichiometric excess of carbonate based on equation 1 was found to be necessary to ensure complete reaction.

Two initial trials used spent electrorefining salts from which visible alumina crucible fragments were removed. A 100% excess of Na₂CO₃ was used, assuming all the plutonium was present as PuCl₃. The salt was heated to 735±10°C in a magnesia crucible and stirred at 120rpm with a pitched bladed tantalum stirrer for 2 hours. In both trials the salt separated into a white upper layer and a dark lower layer, with the salt cleaving across the interface between the two phases, in the previously reported studies the salt cleaved along the interface. In one run non-destructive assay showed the plutonium concentration of the white salt phase was 230ppm Pu and the black salt phase about 20% Pu. There was no significant weight loss on the process implying very little carbonate reacted. XRD of the feed salt did not identify any Pu species and product salts were shown to contain a Pu-O compound, provisionally identified as Na₂PuO₄.

Two further trials have been completed where the salt was initially melted. This resulted in most of the plutonium from the feed salt concentrating in a dense lower phase, with the upper phase containing a lower Pu concentration. The salts were then reacted at 735°C with a 100% excess of Na₂CO₃ assuming all the Pu in the upper salt was PuCl₃. This produced a lower black salt phase and a white upper salt phase, Figure 1. The process weight loss was commensurate with all the PuCl₃ having reacted according to Eqn 1.

![Figure 1. After carbonate oxidation Pu lean salt (left) and Pu rich salt (right).](image)

On melting the electrorefining salts it is postulated a reaction takes place between PuCl₃, Pu metal and Al₂O₃ ceramic fines to form insoluble Pu-O species.

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Investigating the effect of water on the band of ionic liquids

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Ionic liquids, liquids solely composed of mobile cations and anions, are promising materials for a range of applications such as solvents for biomass deconstruction\textsuperscript{1}, materials for gas capture,\textsuperscript{2} and as electrolytes for batteries and supercapacitors\textsuperscript{3}. The electronic structure of ionic liquids determines key properties such as thermal stability, the electrochemical window and reactivity. Therefore, knowledge of ionic liquid electronic structure is important for tuning ionic liquid properties to a particular application. Ionic liquid-water mixtures give excellent solvent performance for the dissolution of biomass.\textsuperscript{4} Previously, we have thoroughly characterised the valence band of neat 1-butyl-3-methylimidazolium thiocyanate ([C\textsubscript{4}C\textsubscript{1}Im][SCN]) using a combination of resonant Auger electron spectroscopy, variable $h \nu$ X-ray photoelectron spectroscopy (XPS) and DFT calculations.\textsuperscript{5}

In this work we have carried out XPS on ([C\textsubscript{4}C\textsubscript{1}Im][SCN])\textsubscript{x}(H\textsubscript{2}O)\textsubscript{1-x} mixtures using a liquid microjet (Figure 1). Liquid microjet XPS results have been combined with DFT calculations in order to elucidate the effects of water on the valence band electronic structure of ionic liquids. For all ([C\textsubscript{4}C\textsubscript{1}Im][SCN])\textsubscript{x}(H\textsubscript{2}O)\textsubscript{1-x} mixtures the highest occupied molecular orbital (HOMO) was found to be localised on the [SCN]$^-$ anion of the ionic liquid. Increasing concentrations of water led to an increasingly stable HOMO. DFT calculations were found to be in excellent agreement with our experimental results.

We believe this is the first time that the valence band of water mixtures has been measured. Most liquid-phase studies have been on aqueous systems. Our work greatly understanding of solvation in a very different to water. Our wide range of concentrations allow us to judgements on [SCN]$^-$ solvated by water ($x = 0.03$) and by other ions ($x = 1$). Additionally, our work provides a benchmark for our computational methods, allowing us many solvent water molecules are necessary to capture structure of the bulk liquid system.

![Figure 3. Valence band spectra for ([C\textsubscript{4}C\textsubscript{1}Im][SCN])\textsubscript{x}(H\textsubscript{2}O)\textsubscript{1-x} mixtures (i.e. $x = 1.00$ is the neat ionic liquid) recorded at $h \nu = 600$ eV.](image)

References

Effects of ionic liquid pretreatment severity on pulp, saccharification yield and lignin structure isolated from *Salix*

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Introduction
Pretreatment of lignocellulosic biomass is crucial for biomass valorisation to bioethanol and chemicals or materials [1]. The Ionomolv process uses low-cost ionic liquids such as triethylammonium hydrogensulfate [TEA][HSO₄] to fractionate lignocellulose by dissolving lignin and hemicellulose [2]. The hardwood *Salix* has gained interest as a feedstock for bioethanol production. However, using hardwoods is still challenging due to their complex cell structure [3]. The focus of this study lies on identifying the pretreatment conditions that give the highest glucose yields as well as the impact the pretreatment has on the pulp composition. The changes of lignin structure with pretreatment severity are also investigated.

Results and discussion
Pretreatment of *Salix* was performed using [TEA][HSO₄] with two different acid/base ratios (a/b) at 120 °C, 150 °C and 170 °C for varying pretreatment times which resulted in a cellulose-rich pulp and a lignin fraction. It was found that an increase in pretreatment severity removes more lignin and improves glucose release after enzymatic hydrolysis. Additionally, a significant decrease in hemicellulose content and high delignification of the pulp was observed at elevated reaction temperatures. The a/b of the IL was found to have a significant impact on the pretreatment outcome as well as on the saccharification yields. Under the same pretreatment conditions, using [TEA][HSO₄] with a/b > 1 lead to higher hemicellulose removal and higher delignification. However, the excess acid also causes an increase in glucan degradation, which gets more significant with increasing severity of pretreatment. Interestingly, the glucose release after pretreatment is also greatly affected by the choice of IL for pretreatment (see Fig. 1), especially for pulps isolated after longer pretreatment times. It was observed that the a/b ratio of the IL not only influences the properties of the pulp but also those of the isolated lignin. Lignin recovered from pretreatment with excess acid IL showed a lower amount of β-O-4 and β-β linkages with the differences getting more pronounced with increasing severity of the pretreatment.

Conclusion
This study shows that the hardwood *Salix* can be successfully pretreated using [TEA][HSO₄] leading to high glucose release and highlights the impact that a/b ratio of ILs has on the isolated pulp and lignin as well as the saccharification yields. The difference in structure of the isolated lignin gives the opportunity to engineer the lignin properties solely by changing pretreatment conditions and a/b of the IL.

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References