

Molten Salts Discussion Group

Newsletter January 2012

Christmas Meeting 2011

The MSDG Christmas Meeting was held on Monday 19 December at 15Hatfields, the conference centre at the Chartered Institute of Environmental Health in London.

The meeting was opened by the Director of Policy, Andrew Griffiths (brother of Trevor Griffiths) who welcomed the MSDG and gave a brief summary of some of the work the Institute had been undertaking recently concerning risk assessments.

After the safety briefing and introduction from Derek Fray, the scientific proceedings began with an invited lecture from Koen Binnemans of the Department of Chemistry at Katholieke Universiteit Leuven in Belgium.

The meeting was attended by 30 participants, the 12 oral presentations were followed by the traditional wine & cheese party. The AGM was held between lunch and the start of the afternoon scientific session.

The MSDG thank Trevor Griffiths for arranging to hold the meeting hosted at 15Hatfields.

Papers

Liquid metal salts

Koen Binnemans, Neil R. Brooks, Stijn Schaltin, & Jan Fransaer

'Liquid metal salts' are low-melting ionic metal salts and they can be considered as metal-containing ionic liquids. 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/dm² or even higher. The great advantage of this type of complex 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.

Chemical and electrochemical processing of Plutonium in chloride melts

Tim Paget

The recovery of Plutonium from spent nuclear fuel is a challenging task. Plutonium is very dense, very reactive, has 6 solid phases ($T_M = 641^\circ\text{C}$) and presents severe hazards with respect to its highly radioactive nature, the risk of criticality and it is highly toxic. Molten salt processes offer a number of potential advantages over traditional aqueous/solvent extraction techniques for the treatment of spent nuclear fuel and are being actively developed by several nations. AWE has operated a Pu recovery system using molten salts for some years. The processes used are very effective for metal recovery. Recent research has led to several process improvements, for example: changes to the design of the crucibles which had been unchanged since the 1960s; recovery of spent anodes; salt recovery.

Ionic liquid catalysis for upgrading biomass to value-added chemicals

Anders Riisager, Tim Ståhlberg, Shunmugavel Saravanamurugan, Peter Fristrup, Wenjing Fu & John M. Woodley

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 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 food flavoring agents, plasticizers, succinic acid & its and derivatives.

High energy site exchange in the $^1\text{H-NMR}$ spectrum of pyrrolidinium based ILs

Andrew Dolan, Tim Gorman, Agnieszka Brandt & Tom Welton

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 hydrogen sulphate 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.

Spectroscopy and electrochemistry of K_2TaF_7 and K_2NbF_7 in Ionic Liquids

Olga Babushkina

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 - $(1-x)\text{K}_2\text{MeF}_7$ ($x = 0.80 - 0.20$) 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 $\text{TaF}_6^- \leftrightarrow \text{TaF}_7^{2-}$ 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 $\text{TaF}_6^- \rightarrow \text{TaF}_7^{2-}$ as the temperature increases from 20 to 200°C.

Anode processes on Carbon in molten chloride electrolytes with dissolved oxides

Geir Martin Haarberg, Reidar Tunold & Espen Sandnes

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 $\text{NaCl-Na}_2\text{O}$, and in binary melts of the type $\text{NaCl-MCl}_2\text{-MO}$ with 0 - 7 mol% oxide, ($\text{M} = \text{Ca, Sr and Ba}$) at temperatures from 800 to 825°C. The techniques of linear polarization, cyclic voltammetry and electrochemical impedance spectroscopy were used. The gaseous products were found to be Cl_2 , CO and CO_2 , and the exit gas composition was determined by gas chromatography. The experimental results presented concentrated on the $\text{NaCl-CaCl}_2\text{-CaO}$ system.

Molten salts & nuclear energy

Marcelle Gaune-Escard

Since the disaster which affected the Fukushima nuclear complex there has been several international summits trying to reassure people about the safety of nuclear energy. Since the inception of nuclear power, i.e. for ~fifty years, the industry has given the impression that there is only one and only way to exploit fission - in pressurized water-cooled reactors (PWR). It is not, however, the only method capable of producing electricity: there are other recipes to trigger a nuclear fission reaction and to maintain that reaction by controlling it. It is possible to take Thorium ore and convert the fuel into liquid, rather than solid rods, mix it all in a cooling fluid which is a molten salts 'syrup' at ambient pressure, and not water at high pressure. The roots for this approach are in the Oak Ridge National Laboratory's Molten Salt Reactor program which was abandoned in 1965. Recently there has been a resurgence of interest in the Thorium cycle and Molten Salt Reactors. This has, for example, recently attracted much interest in the French press and media. In July 2010 The International Thorium Energy Organization announced the International Thorium & Molten Salt Technology Inc. (IThEMS) plan to build the world's first commercial Thorium Molten-Salt Reactor power generator. To make this a reality the company says it needs to secure an additional \$300 million investment. The first step to commercially available Thorium-fuelled energy will be

through a 10 MW FUJI generator. The plant was designed by Professor Kazuo Furukawa, it was with much sadness that the molten salts community noted the death of Professor Furukawa on 14 December 2011.

The Oak Ridge National Laboratory molten fluoride reactor: The foundation of modern molten salt chemistry ?

Trevor R. Griffiths

The Oak Ridge National Laboratory (ORNL) in Tennessee was built to be one of the major sites for the Manhattan Project to build the world's first atomic bomb. The laboratory's main contribution was to develop techniques for enriching ^{235}U and then to produce it in quantity. ORNL was shortly thereafter, in the 1950s, 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. Although water and gas cooling are obvious candidates, they 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 . In trying to resolve the many problems encountered in designing and bringing the reactor into being, it can be therefore be argued that this successful reactor was the source and foundation on which the subsequent 'explosion' of molten salts & ionic liquids chemistry is based.

The Weinberg Foundation

Laurence O'Hagan

The Weinberg Foundation, named after Alvin Weinberg a former director of Oak Ridge National Laboratory and a great advocate of the molten salt reactor, was formed in September 2011 as a not-for-profit organisation dedicated to driving the uptake of safe, clean and affordable energy. Inspired by the compelling evidence behind the Thorium cycle as a viable alternative to Uranium and driven Weinberg's vision of safe & abundant nuclear power, the Foundation was established to act as a communications, debating & lobbying hub to promote Thorium energy.

Further information is available on the Foundation's website: www.the-weinberg-foundation.org

Evaluation of carbonate oxidation for the treatment of waste pyrochemical salts

G.T.Taylor & T.Wilson

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 process 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(III) chloride, as a non-radioactive simulant for plutonium chloride, using two molten salt systems, $\{\text{NaCl-KCl}\}$ or CaCl_2 . 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 90% have been achieved with cerium chloride in $\{\text{NaCl - KCl}\}$, 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.

Supported Ionic Liquid Phase (SILP) catalysts and gas absorbers

Rasmus Fehrmann

Emission of acidic gases such as NO_x and SO_x and CO_x from energy production by fossil fuels in power plants is a major concern in relation to atmospheric pollution and climate change. 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 SO_2 wet-scrubbing while organic amines are being used as absorbents in CO_2 scrubbers. This leads to concern about, for example, intensive energy requirements for desorption, corrosion of steel pipes and pumps, CO_2 absorption capacity and thermal decomposition of the amine. Ionic liquids can be tuned by design to perform as selective, high-capacity absorbents of environmentally problematic flue gases including SO_2 , NO , NO_2 and CO_2 . Reversible absorption has been obtained for several different ionic liquids at varying 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 showed that CO₂, NO, NO₂ and SO₂ can be reversibly and selectively absorbed using different ionic liquids and that SILP absorbers are promising materials for industrial flue gas cleaning.

The anodic processes of chloride and bromide ions in ionic liquids

Linpo Yu, Xianbo Jin & George Z.Chen

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-methylimidazolium 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 cyclicvoltammograms. Although the Cl₃⁻ ion was observed on the gold electrode and Br₃⁻ was investigated in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM]NTf₂), the oxidation of the chloride ion did not lead to chlorine gas evolution in our study on different electrode materials and in different ionic liquids. The retention of the Cl₂, Cl₃⁻ and Br₂, Br₃⁻ species in [BMIM]PF₆ was determined by cyclicvoltammetry and UV-Vis spectrometry. These findings suggest the possibility of direct electro-reduction of solid metal halides to metals because of the capability of ionic liquids for transferring halide ions.

Derek Fray closed scientific part of the meeting by thanking all of the speakers and the participants for their enthusiastic contributions to the discussions. He also drew people's attention to the Alloy Phase Diagram International Commission (APDIC) 4th World Round-Robin Seminar: Phase Equilibria - Materials for the Future. This is a satellite event of the IOM3 Materials Congress, Monday 25 June 2012 to be held at 1 Carlton House Terrace, London, UK. (Contact: Dr Andy Watson, University of Leeds, E-mail: a.watson@leeds.ac.uk)

The incoming MSDG chairman, Andrew Abbott, closed the meeting by thanking Derek Fray for his service as chairman of the Group over many years.

Annual General Meeting 2011

The following appointments were made at the AGM.

Chairman	Andrew Abbott
Honorary Secretary	Andrew Doherty
Honorary Treasurer	Robert Watson
Newsletter Editor	Kartik Rao
Committee members	George Chen Trevor Griffiths Peter Licence Stuart Mucklejohn Carsten Schwandt
European member	Rasmus Fehrmann
International member	Marcelle Gaune-Escard
Honorary Auditor	Tony Wilson

Forthcoming conferences

Ninth International Conference on Molten Slags, Fluxes and Salts (MOLTEN12)
27 - 30 May 2012, Beijing, China

See: <http://hy.csm.org.cn/MOLTEN12/en/>

13th International Symposium on the Science & Technology of Light Sources (LS13)
24 to 29 June 2012, Troy, USA

See: Website to be announced

APDIC 4th World Round-Robin Seminar: Phase Equilibria - Materials for the Future
A satellite event of the IOM3 Materials Congress, Monday 25 June 2012, London, UK
See: <http://www.iom3.org/events/congress2012>
Contact: Dr Andy Watson, University of Leeds, E-mail: a.watson@leeds.ac.uk

3rd International Round Table on Titanium Production in Molten Salts, in conjunction with the 2012 Molten Salts Discussion Group Summer Research Meeting
17 to 19 July 2012, Fitzwilliam College, University of Cambridge, UK
See: <http://www.ch.qub.ac.uk/msdg>

EUCHEM Conference on Molten Salts & Ionic Liquids
05 to 10 August 2012, Celtic Manor, Wales, UK
See: <http://www.euchem2012.org>

3rd Asian Pacific Conference on Ionic Liquids & Green Processes
17 to 19 September 2012, Beijing, China
See: <http://apcil12.org/dct/page/65540>

PRiME 2012 - Pacific Rim Meeting on Electrochemical & Solid-State Science
Joint meeting incorporating the 222nd Meeting of The Electrochemical Society & the 2012 Fall Meeting of The Electrochemical Society of Japan
07 to 12 October 2012, Honolulu, Hawaii
See: <http://www.electrochem.org/meetings/biannual/222/222.htm>

MSDG Support Fund

Members are reminded that bursaries to help towards the cost of attending meetings on molten salts and/or ionic liquids are available from the MSDG. Those interested in applying for a bursary should contact the Chairman, Andrew Abbott (E-mail: apa1@leicester.ac.uk).

S.A.Mucklejohn, Ceravision Limited, 28 Dec 2011; Revised 04 Jan 2012
News_0112.doc