

Molten Salts Discussion Group

Newsletter March 2009

Christmas Research Meeting 2008

The MSDG had a new venue for the Christmas Meeting held on Monday 15 December, 15 Hatfields, the conference centre at the Chartered Institute of Environmental Health. The meeting was opened by the Director of Policy, Andrew Griffiths (brother of Trevor Griffiths) who welcomed the MSDG and outlined the work and responsibilities of the Institute. Andrew also described the concept and design of the conference facilities. These were opened in 2007 after extensive refurbishment which adopted recycling as a key part of the design and running of the centre. The Institute are very proud that 15 Hatfields is generally regarded as the most eco-friendly conference centre in London.

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

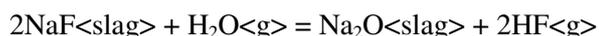
The meeting was attended by 24 participants and the nine presentations were followed not by the traditional wine & cheese party but by an informal supper and drinks at The Mad Hatter. As usual at the Christmas Meeting, the AGM was held between lunch and the start of the afternoon scientific session.

Although the MSDG will not hold a meeting during the summer of 2009, the committee hope many members will attend the symposium on Molten Salts and Ionic Liquids at the IUPAC 42nd Congress in Glasgow, 02 to 07 August.

Regeneration of fluorides from a spent potlining slag: A riddle

Harold Øye, Vladimir Blinov & Tor Grande

Due to its NaF and NaCN content, spent potlining (SPL) from Al-cells is becoming one of the major environmental concerns for the aluminium industry. However, SPL also represents a major recycling opportunity. The newly started ELKEM SPL recycling process is one of several technically feasible alternatives for treatment and recycling of SPL. In this process, the fluorides are recovered by pyrohydrolysis of a silicate slag remaining from the first step which produces pig iron by carbothermal reduction. The expected reaction for the pyrohydrolysis is:



Experimental results however cannot be explained by this reaction. High temperature mass spectrometry studies have shown that fluorides evaporate as $\text{Si}(\text{OH})_x\text{F}_y$ and $\text{NaAl}(\text{OH})_x\text{F}_y$, species not previously reported.

Reversible gas absorption by ionic liquids

R.Fehrmann, A. Riisager, P. Harris, & R.W. Berg

Ionic liquids are a promising class of materials that might be suitable for selective, reversible absorption of gaseous pollutants in, e.g. power plant flue gases and other exhaust or industrial off-gases. Thus absorption of gases like such as SO_2 , NH_3 , NO_x and CO_2 offers outstanding opportunities for pollution reduction. Recent studies of the reversible gas absorption of NH_3 and SO_2 by $[\text{BMIM}]^+$ (1-butyl-3-methylimidazolium) and $[\text{TMGH}]^+$ (1,1,3,3-tetramethylguanidinium) cation-based ionic liquids have used UV-VIS and Raman spectroscopy to describe the interaction between the solvent and the solute SO_2 molecules. Ionic liquids exhibit a marked tendency for glass formation rather than crystallisation which prevents single crystal X-ray structural investigations. $[\text{TMGH}]\text{Cl}$ has an absorption capacity molar ratio of 3 for $\text{SO}_2\langle\text{g}\rangle$ at 1 bar, 25°C. This is the highest capacity for SO_2 absorption in any ionic liquid found so far. The SO_2 -saturated ionic liquid provided crystals suitable for X-ray investigation. The compound crystallizes in the cubic system, space group $\text{Pc}bn$.

*Tin filled Carbon nanotubes for Lithium-ion batteries*Rajshekar DasGupta & Derek J. Fray

There is a continuing need to develop batteries with higher energy densities. Currently, the most widely used anode in lithium-ion batteries is based on graphite, LiC_6 , which has a theoretical capacity of 372 mAh/g. Graphite anodes with some lithium alloys have higher theoretical capacities and the corresponding value for tin is 992 mAh/g. However, there is a large volume change associated with tin which results in the anode structure failing after approx. 10 recharging cycles. Tin-filled carbon nanotubes, however, might prove sufficiently resilient to be able to cope with the volume changes. Samples of nanotubes and nano-particles were produced using a novel switching electrolysis method in molten LiCl-SnCl_2 . The ability of the system to produce tin-filled nanotubes is related to the electrolyte composition. After characterisation by SEM, TEM, HRTEM and EDAX samples were tested in lithium-ion batteries. These tests are continuing and the results to date with the nano-particles look particularly promising.

*Phase diagram and electrical conductivity of the AgBr-NdBr₃ binary system*Marcelle Gaune-Escard, P. Kolodziej, M. Szymanska-Kolodzie, I. Chojnacka & L. Rycerz

This work is part of a long term study of the properties of lanthanide(III) halide mixtures. Systems with silver halides are of interest as superionic conductors and for use in mid-IR solid state lasers. Phase equilibria in the (AgBr-NdBr₃) system were investigated by DSC. The system has a eutectic at $x(\text{AgBr}) = 0.845$ with a eutectic temperature of 647 K. The compound $\text{AgNd}_3\text{Br}_{10}$ was also identified, it decomposes in the solid state at 634 K. The work was complemented by measurements of the electrical conductivities of the pure components and liquid mixtures. The behaviour of the melt can be explained by the formation of the complex ion NdBr_6^{3-} .

*Bridging the gap between ionic liquids & molten salts: The gas phase of salts based on the bistriflamide anion*José Nuno Canongia Lopes, João P. Leal, Manuel E. Minas da Piedade, Alina A. Tomaszowska, José M. S. S. Esperança, Luís Paulo N. Rebelo, & Kenneth R. Seddon

Ionic liquids were originally considered to be involatile but recently it has been shown that some ionic liquids can be distilled at reduced pressures without decomposition and their vapour pressures and enthalpies of vaporization could be determined by experimental and simulation techniques. Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FTICR-MS) was used to study the vaporisation of some aprotic ionic liquids based on the bistriflamide anion, $[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$, the vapour consists exclusively of neutral anion-cation pairs. This is in contrast to the alkali metal halides which have significant fractions of aggregates larger than ion-pairs, particularly dimers. A study of the distillation of $\text{M}[\text{N}(\text{SO}_2\text{CF}_3)_2]$ ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) salts has shown that the vapour phases consist of neutral ion pairs. However, the observation of large charged aggregates generated through a sequence of ion-molecule reactions is closer to what might be expected for alkali metal halides.

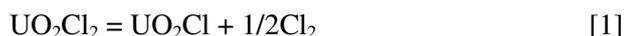
*Use of Nickel anodes in molten salts and the application to metallurgical problems*Derek J. Fray & Tony Cox

It is desirable to have inert anodes for electrochemical processes in molten salts. The Hall Heroult process for the reduction of alumina, for example, uses carbon anodes which produce CO and CO₂. However, it is very difficult to find materials that are compatible with halide melts. Sodium hydroxide is less corrosive and the Castner process was used between 1890 and 1920 to produce sodium from sodium hydroxide with nickel anodes. These nickel anodes did not appear to suffer any degradation during the process. Sodium is added to aluminium-silicon alloys to improve the properties of the alloy by changing the microstructure. This addition can be carried out by the electrolysis of sodium hydroxide in a sodium beta-alumina tube with a nickel anode. This method is far superior to that previously used, i.e. immersing sodium pellets into the molten aluminium-silicon alloy. Another huge opportunity for this type of approach is the electrochemical reduction of iron oxide in sodium hydroxide with nickel anodes for the production of steel. This would dramatically reduce the CO and CO₂ emissions for steel production from the currently employed blast furnaces. Early experiments have shown this approach to be highly promising.

*A spectroelectrochemical study of Uranium(V) species in alkali chloride melts*Trevor Griffiths, V. A. Volkovich, D. E. Aleksandrov, B. D. Vasin, T. K. Khabibullin, & I. B. Polovov

The aim of this work was the study of the thermal stability and decomposition of uranyl(VI) species in chloride melts. The measurements included high temperature electronic absorption spectra and

electrochemical properties. The thermal decomposition [1] of UO_2Cl_2 in chloride melts under high vacuum was found to be faster in systems containing CsCl.



The outcome of electrochemical and chemical reduction of UO_2^{2+} ions in LiCl, 3LiCl-2KCl, NaCl-KCl and NaCl-2CsCl melts at 550 - 850°C depended on the electrochemical properties of the reductant. Electrochemical reduction of UO_2Cl_2 in NaCl-2CsCl at 550°C resulted in formation of UO_2Cl and UO_2 . The chemical reduction of UO_2Cl_2 with Te, Pd, Ag, Mo, Nb or Zr in alkali chloride melts also gave UO_2Cl and UO_2 through the formation of a variety of complex ions. For example, reduction by Mo with glassy carbon electrodes gave MoCl_6^{3-} and $\text{UO}_2\text{Cl}_4^{3-}$ ions. The higher the Cs content of the melt, the more the dissolution of uranium.

Shape retention in the electro-reduction of oxide preforms to the Ti-6Al-4V alloy in molten CaCl₂

Di Hu & George Z. Chen

The alpha-beta alloy Ti-6Al-4V is the workhorse alloy of the titanium industry due to its excellent combination of high specific strength, which is even maintained up to approximately 400°C, fracture resistant characteristics and exceptional corrosion resistance. The Ti-6Al-4V alloy is used in aerospace frames, military equipment & armour, engine components, petroleum refining, chemical & electrochemical processes and marine applications. Recently this alloy has also been used in sporting industry goods, particularly in high performance golf clubs. As the most commonly used titanium alloy, Ti-6Al-4V accounts for over 45% of the total titanium production. Despite the increased usage and production of Ti-6Al-4V, it is still much more expensive when compared to many other metals because of its high melting point, complexity of extraction and the difficulties of fabrication & machining. The FFC-Cambridge process, which has the potential to directly produce titanium alloys, offers the not only the possibility of reducing the cost of producing Ti-alloys but also has the potential to make near-net shape components. Preforms of $\text{TiO}_2\text{-Al}_2\text{O}_3\text{-V}_2\text{O}_5$ with special shapes were first sintered at 900°C and then directly reduced to the Ti-6Al-4V alloy in molten CaCl_2 using the FFC-Cambridge process. The products retained the overall shape of the sintered preforms. The products typically had oxygen contents of approximately 2000 ppm.

A brief report on EUCHEM 2008 and other events in relation with molten salts and ionic liquids in 2008

Rasmus Fehrmann

EUCHEM 2008 in Copenhagen was very successful with 220 participants from 37 countries and 6 continents. The meeting, held in a converted 18th century warehouse, attracted good sponsorship and was complemented by a varied social program. The scientific part of the conference consisted of 8 keynote lectures, 42 oral presentations from participants and 173 posters.

Venues for the next two EUCHEM conferences will be: 2010 Germany (Chairman - Peter Wasserschied); 2012 Belfast, Northern Ireland (Chairman - Ken Seddon).

Annual General Meeting 2008

The following appointments were made at the AGM.

Chairman	Derek Fray
Honorary Secretary	George Chen
Honorary Treasurer	Robert Watson
Newsletter Editor	Stuart Mucklejohn
Committee members	Andrew Doherty Trevor Griffiths David Kerridge Peter Licence
European member	Rasmus Fehrmann
International member	Marcelle Gaune-Escard
Honorary Auditor	Tony Wilson

Annual subscriptions

The 2009 annual subscription to the MSDG for RSC members is £2.00.

Promotion for George Chen

The MSDG congratulates George Chen on his promotion to Professor of Electrochemical Technologies at the University of Nottingham.

Forthcoming conferences

215th Electrochemical Society meeting

24 to 29 May 2009, San Francisco, USA

See: www.electrochem.org/meetings/biannual/215/215.htm

COIL-3: 3rd Congress on Ionic Liquids

31 May to 04 June 2009, Cairns, Australia

See: www.coil-3.org

17th Symposium on Thermophysical Properties

21 to 26 June 2009, Boulder, USA

See: <http://symp17.nist.gov/>

IUPAC Congress 2009

The MSDG committee's proposal to hold a symposium on molten salts and ionic liquids at the IUPAC Congress 2009 has been accepted. Derek Fray will be the symposium convener. The congress will be hosted by the RSC in Glasgow 03 to 07 August 2009. There will not be a MSDG Summer Meeting in 2009.

See: www.rsc.org/ConferencesAndEvents/RSCConferences/IUPAC2009/

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, Derek Fray (E-mail: djf25@cam.ac.uk).