

Molten Salts Discussion Group

Newsletter January 2006

Christmas Research Meeting 2005

The MSDG Christmas Meeting was held on Monday 19 December at the University of Nottingham London office, a new venue for the group. The 31 participants listened to 12 presentations in convivial surroundings. Marcelle Gaune-Escard and Douglas Inman were unable to attend this meeting but did send season's greetings and their best wishes for 2005 to the MSDG and its members. The day finished with the traditional wine and cheese and the opportunity to review the events of 2005.

The papers include 6 on ionic liquids, 5 on higher temperature systems and one that encompassed both temperature ranges thus rendering any suggestion of a rift in the ionic liquid/molten salt communities utterly ridiculous.

Brønsted acidity in ionic liquids

L.Crowhurst & T.Welton

The pH scale is applicable only to aqueous systems and hence a different approach has to be taken when considering acidities in ionic liquids. The effect of different ionic liquids on Brønsted acid properties have been investigated by physical measurements (Hammett acidities) and by monitoring the impact of ionic liquids on specific acid catalysed reactions. For most systems, the Hammett activities for acids in ionic liquids are low compared to the neat acids. The acidity of solutions of strong acids in ionic liquids depends on the characteristics on the anion.

Supported Liquid Phase Catalysis: An old success with molten salts - a new era with ionic liquids ?

R.Fehrman, A.Riisager, S.B.Rasmussen, K.M.Eriksen, M.Haumann, & P.Wasserscheid

Progress in the potential uses of ionic liquids for major industrial catalytic processes was outlined, in particular with reference to SO₂ oxidation and the hydroformylation of alkenes. The polarity of ionic liquids can be tuned to a specific reaction but it is the combination very low vapour pressure and large liquidus range that make supported ionic liquid phase catalysis (SILP) so attractive for industrial scale processes. A recent development has been the carbonylation of methanol to form acetic acid using a Rh-SILP catalyst.



A patent application for the process has been submitted and a publication describing the success of this development is in the press.

Electropolishing of stainless steel using ionic liquids

K.McKenzie, A.P.Abbott, K.S.Ryder & G.Capper

The processes currently used for the electropolishing of stainless steels have many disadvantages, these include use of concentrated sulphuric acid and phosphoric acid, poor current efficiency and many environmental, health and safety concerns. A new treatment in an ionic liquid, based on choline chloride and ethylene glycol, has been developed and is in regular use on an industrial scale. The mechanism of Electropolishing seems to be different from that found in aqueous systems. A protocol for recycling the spent ionic liquid has been developed.

Kinetics of the Friedel-Crafts reaction in ionic liquids

D.Rooney, C.Hardacre, P.Nancarrow, J.Thompson & D.Milroy

The Friedel-Crafts benzoylation of anisole with benzoic anhydride to yield 4-methoxybenzophenone has been carried out in a range of ionic liquids using a variety of different catalysts, e.g. homogeneous metal triflate, indium chlorides and zeolites. For both metal triflate and zeolites a complex exchange of ligands results in the formation of a free acid catalyst. This acid is reversibly deactivated by complexation with the product as part of a 2 cycle mechanism. The equilibrium constant for this complexation has been measured and a rate equation of the form $r = k \cdot A^m \cdot B^n$ derived.

Environmental control of chemical reactivity: Diels-Alder reactions in ionic liquids

V.L.Mestre & T.Welton

Reactions of acrylonitrile, methyl acrylate and acrolein with cyclopentadiene have been studied in a variety of ionic liquids and organic solvents. The ratio of the *endo* and *exo* products depends on the solvent used. The rate and selectivity were found to be dependent on the dienophile and on the solvent. In general, high *endo* selectivity and rate enhancements were observed when the reactions were carried out in ionic liquids. These improvements can be rationalised by considering the solvent effects based on polarity, hydrogen bonding ability and solvophobic interactions. Various solvent parameters were employed to illustrate the behaviour of the different solvents.

Nanoscale electrocrystallization of metals, alloys and semiconductors from ionic liquids

W.Freyland

Ionic liquids are suitable electrolytes for the electrodeposition of materials such as metals (e.g. Ti, Al, Mg) or semiconductors (e.g. Ge, Si) which cannot be deposited from aqueous solutions and are much more difficult to fabricate from high temperature molten salts. By combining the electrodeposition with in-situ scanning probe methods, detailed information about the microscopic and electronic structure can be obtained. Thus, the electrocrystallization of Zn on Au(111) and AlSb on Au(111) have been studied. There are usually four stages of an electrocrystallization process: a charge transfer reaction; a diffusion controlled step; formation of critical nuclei; phase formation and growth. However, the deposition of Zn on Au(111) appears to proceed via spinodal decomposition rather than nucleation and growth.

Calculated phase diagram for the {CeI₃-NaI} system

A.T.Dinsdale & S.A.Mucklejohn

The thermochemical properties of the {CeI₃ - NaI} system are needed to help understand the chemistry of metal halide discharge lamps, especially those developed recently as part of the NumeLiTe - a project to develop a highly efficient roadlighting system. To date there have been no published reports for the phase diagram of the {CeI₃ - NaI} system, the properties were therefore estimated by reference to the experimental data reported for similar systems. Data for the pure components were taken from the SGTE thermochemical database. The calculated phase diagram predicted a eutectic at $x(\text{NaI}) = 0.7$, $T = 705 \text{ K}$

Thermochemical investigations on metal halide salt systems for lighting applications

T.Markus

The group at Julich, formerly headed by Klaus Hilpert and now led by Torsten Markus following the former's retirement, has investigated the properties of a vast array of metal halides and binary metal halide systems. Recent studies have included Knudsen effusion - mass spectrometry measurements for the {CeI₃ - NaI} system which confirmed the presence of gas phase complexes NaCeI₄ and Na₂CeI₅. Activity measurements from the mass spectrometry study were supplemented by DTA data. Assessment of the combined data gave an optimised phase diagram with a eutectic at $x(\text{NaI}) = 0.7$, $T = 734 \text{ K}$.

Electrochemical deposition of iron in molten salts

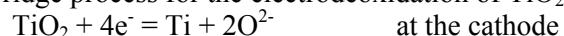
T.Murakamia, G.M.Haarberg, H.Karoliussen, E.Kvalheim & S.Pietrzyk

The ULCOS project is evaluating various options for the production of steel which emit lower amounts of greenhouse gases than the current used process, i.e. reduction of Fe₂O₃ with carbon. The options include: use of natural gas; use of biomass material; use of hydrogen; electrolysis. The latter depends on the solubility of Fe₂O₃ in the electrolyte. The solubility in {CaCl₂ - NaCl} can be increased by the addition of AlF₃ or MgCl₂ but Fe³⁺ is not stable in these melts. Although Fe³⁺ is stable in fluoride melts such as {NaF - KF} and {LiF - NaF - KF}, the solubility is low. The solubility of Fe₂O₃ in {CaCl₂ - KF} at 1123 K was found to be 0.72 mol per cent and 0.45 mol per cent in {CaCl₂ - KF - NaF} at 1183 K. The iron deposited from galvanostatic electrolysis of Fe₂O₃ in {CaCl₂ - KF} at 1144 K had a columnar structure and contained impurity levels of FeO and CaF₂. This and similar experiments had current efficiencies of more than 90%.

Thermodynamic, kinetic, and microstructural aspects in the electrochemical reduction of titanium dioxide

C.Schwandt, D.T.L.Alexander & D.J.Fray

The FFC Cambridge process for the electrodeoxidation of TiO₂ to Ti can be summarised by:



This reduction has been shown to proceed through a series of reactions that involves the formation and subsequent decomposition of a series of Ca-containing intermediate species. A plot of current against time shows a current peak followed by a drop in the current and a long tail. During this current peak the cathode assembly gains weight, this is due to the formation of CaTiO_3 . The reduction proceeds through CaTi_2O_4 to TiO and eventually to Ti . There is a critical concentration of CaO in the electrolyte needed to prevent reactions which result in the release of $\text{Cl}_2<\text{g}>$.

Metal powder production by the FFC Cambridge process

D.Hodgson

The company's (Metalysis) priority is the production of tantalum from Ta_2O_5 on a commercially viable scale. The electrodeoxidation of Ta_2O_5 in $\{\text{CaCl}_2 - \text{CaO}\}$ by the FFC Cambridge process goes through a series of complex chemical steps which includes the inclusion of CaO into the Ta_2O_5 precursor to form $\text{CaTa}_2\text{O}_{11}$. Several other intermediates have been identified (including CaTa_2O_6 , $\text{Ca}_2\text{Ta}_2\text{O}_7$). Tantalum metal can be produced in laboratory and pilot plant quantities. The company has a design for a 100 kg batch reactor which forms part of the plan to scale up production. Although carbon anodes are currently used they have inherent disadvantage including the possibility of carbide formation and changing cell geometry as the carbon is eroded. The search for a suitable inert anode continues.

Molten salt and ionic liquids events in 2005

T.R.Griffiths

Trevor's conference season ran from May to September and involved attendance at: IT3 (Incineration & Thermal Treatment Technologies) in Galveston; Rare Earth Research Conference in Keystone, Colorado; Actinides 2005 in Manchester, MSDG Summer Meeting in Cambridge; MS7 in Toulouse. Scientific, cultural and social events were highlighted by a series of digital images and a well informed, light hearted commentary. Of particular interest was the growing concern over the worldwide shortage of radiochemists.

Annual General Meeting 2005

The following appointments were made at the AGM.

Chairman	Derek Fray
Honorary Secretary	George Chen
Honorary Treasurer	David Kerridge
Newsletter Editor	Stuart Mucklejohn
Committee members	Andrew Doherty Louise Slevin Robert Watson
Co-opted member	Trevor Griffiths
Corresponding member	Rasmus Fehrmann
Honorary Auditor	Tony Wilson

MSDG Summer Meeting 2006

The MSDG Summer Meeting will be held in Fitzwilliam College, University of Cambridge on Monday & Tuesday 10 - 11 July.

EUCHEM 2006

The EUCHEM conference on molten salts and ionic liquids will be held in Hammamet, Tunisia 16 - 22 September. The deadline for registration is 15 February, see <http://iusti.polytech.univ-mrs.fr/EUCHEM2006>

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@msm.cam.ac.uk).