

Molten Salts Discussion Group

Newsletter January 2007

Christmas Research Meeting 2006

The MSDG Christmas Meeting was held on Monday 18 December at the University of Nottingham London Office. The 34 participants were entertained by 12 presentations during a highly informative and stimulating meeting. The day finished with the traditional wine and cheese party and the opportunity to review the events of 2006 and to look forward to 2007.

Forty years in molten salts

J.C.Poignet - Invited speaker

Professor Poignet opened his remarks by reminding the audience that in 1967, when he started his research, experimentalists depended mainly on home made devices and that computers were not widely available. Various molten salts, essentially chlorides and fluorides, from room temperature to over 1000°C, were studied. Fundamental research was devoted to transport properties (diffusion, viscosity, electrical conductivity) and to the cathodic mechanisms of deposition of metals, including solutions of alkali or alkaline earth metals in their molten halides. Most of the industrial problems tackled were linked to metal production, to nuclear problems, to energy storage and to reprocessing of spent materials. The presentation concluded with a survey of the present situation of molten salts research and technology in the Grenoble area.

DeNO_x and deSO_x of flue gases by catalysis, electrocatalysis & selective gas absorption using ionic media

R.Fehrmann, S.B.Rasmussen, J.Huang, A.Riisager, H.Hamma, J.Rogez, J.Winnick & P.Wasserscheid

NO_x emissions are of increasing concern in the industrialized countries and stricter regulations of emission limits are envisaged. Emissions from fossil fuelled power plants are usually reduced by installation in the gas duct of a V₂O₅/TiO₂ based heterogeneous catalyst converting NO_x by NH₃ injection in the flue gas to N₂ and H₂O. However, this SCR (Selective Catalytic Reduction) catalyst operates around 375°C and it has to be placed in a certain position in the flue gas duct. There is therefore a demand for NO_x installations more flexible regarding temperature of operation and possible position in the duct. Also the increased use of biomass (straw, wood pellets etc.) alone or in combination with fossil fuel has been shown to decrease the life time of the V₂O₅/TiO₂ deNO_x catalyst dramatically, due to deactivation by especially potassium salts in the biomass fly ash. A TiO₂ (anatase) supported ionic liquid doped with chromate, molybdate and tungstate complexes, (TMG₂CrO₄, TMG₂MoO₄ & TMG₂WO₄) has been synthesised and has shown much promise as a deNO_x catalyst. Investigations have also been conducted on the use of molten ionic media in electrocatalytic membrane separation, ionic liquid reversible absorption and supported ionic liquid deNO_x catalysis in an attempt to establish a flue gas cleaning process that will operate at a lower temperature than the existing systems.

Ionic liquids in-vacuo

P.Licence

The extremely low volatility of ionic liquids allows them to be examined in a range of analytical instruments that require high vacuum for their operation and which were previously considered unsuitable for liquids. For the first time, high quality X-ray photoelectron spectra (XPS) have been obtained for the several pure ionic liquids as well as the liquids doped with simple metal salts. XPS provides information about the electronic structure of different elements within a compound and has sufficient sensitivity to distinguish between atoms of the same element situated in chemically distinct environments. Under the conditions employed, the ionic liquids studied emitted a surprisingly good photoelectron flux. Hence, excellent XPS data were obtained in a very short collection time (>5 minutes). Furthermore, since ionic liquids are electrically conducting, none of the problems associated with differential charging were encountered and charge neutralisation was not required. The ionic liquids appeared to be very stable during exposure to the X-ray source and there was no evidence of out-gassing after initial pump-down nor beam damage to the sample. Line of sight mass spectrometry (LOSMS) has enabled the determination of enthalpies of evaporation for ionic liquids using the 'dipstick' method for the first time.

Existing thermochemical databases - A possible source for generating new thermochemical data & a means of validating existing data

H.D.B.Jenkins

The importance of thermochemical data is often overlooked and the closure of several laboratories over the past 10 to 20 years has meant the loss of measurement systems and skills. A new approach to estimating thermodynamic data has been developed using volume based considerations. The essence of this method being the linear correlation that has been noted between the standard entropy, S° , of solid materials and their molar volume, V_m . This new approach enables existing thermochemical databases to be used to: generate standard data ($\Delta_f H^\circ$, $\Delta_f G^\circ$, S° , C_p) for solid materials; generate similar data at elevated temperatures; validate data which appear to be unreliable; delineate data for which multiple values exist. One of the examples cited was the determination of $\Delta_f G^\circ$ for copper tungstate, equation [1], this value is not listed in any of the widely available collections of thermodynamic data.



Conferences & symposia on liquids salts in 2006

T.R.Griffiths

Trevor Griffiths' international conference season ran from early July with the MSDG Summer Meeting through September for EUCHEM 06 (Tunisia) to MS15 in October (Mexico). MS15 was dedicated to the memory of Robert Osteryoung, a dedicated, distinguished and highly regarded molten salts researcher. During this conference, the Max Bredig Award was presented to John Wilkes who then presented his address titled 'Molten salts & ionic liquids: Are they not the same thing?' Trevor's talk was illustrated with many digital images and light hearted anecdotes.

Direct electrochemical production of titanium & titanium alloys in molten CaCl₂-based electrolytes

K.Dring

The electrochemical behaviour of titanium oxides in molten CaCl₂-based electrolytes was investigated by cyclic voltammetry using Mo cavity electrodes. Multiple electrochemical processes were observed at potentials positive of the potential corresponding to the formation of Ca at unit activity. An initial process, occurring at potentials approximately 1250 mV positive of the electrolyte reductive limit was attributed to the reduction of TiO₂ to Ti₂O₃, via Ti₃O₅. A concurrent increase in the local CaO activity led to the formation of passivating Ca-Ti-O phases. At potentials approximately 500 mV positive of the potential for unit activity Ca formation, further cathodic processes were observed - the reduction of the passivating phases occurring before the reduction of Ti₂O₃ to TiO could proceed, and, finally, the reduction of TiO to a titanium-oxygen solid solution. Deoxidation of this solid solution was found to occur at potentials near to that for unit activity Ca formation. Voltammetry on mixed oxide powders evoked a substantially different current response that was attributed to the presence of oxide solid solutions with increased oxide ion vacancy concentration.

The electrochemical reduction of chromium sesquioxide in molten calcium chloride under cathodic potential control

C.Schwandt & D.J.Fray

Electrochemical polarisation and reduction experiments which were performed with a three-terminal cell in molten calcium chloride with additions of calcium oxide (~2 mole per cent) were described. Employing a metal cathode, a graphite anode and a pseudo-reference electrode also made from graphite, polarisation measurements were carried out with the aim of validating the performance of the pseudo-reference electrode and to assess the stability of the electrolyte. Using a chromium sesquioxide cathode in conjunction with a graphite anode and a graphite pseudo-reference electrode, electrochemical reduction experiments were conducted under potentiostatic control. The most important findings were: a graphite pseudo-reference electrode has been shown to be suitable for electrochemical experiments in molten salts that take place on a time scale of hours to days; the conversion of chromium oxide into chromium metal has been accomplished under cathodic potential control and in the absence of calcium metal deposition with current efficiencies from 60 to 80 per cent; a significant overpotential has been measured at the anode.

The material testing of anodes for the FFC-Cambridge process

K.C.Tripuraneni Kilby, L.Centeno, G.Doughty, S.A.Mucklejohn, & D.J.Fray

Although graphite anodes are typically used in the FFC-Cambridge process they have the disadvantage of liberating CO<g> and CO₂<g>. These greenhouse gases are particularly undesirable when considering

commercial scale operations and also dissolve in the electrolyte which then gives rise to extensive deposits of carbon in the product and the reactor. An inert anode for this process is highly desirable but the material properties needed are extremely demanding. Factors for consideration include: physical stability at the service temperature; resistance to attack by the molten chloride electrolyte & oxygen; electrochemical stability; electrical conductivity; resistance to thermal shock; robustness; ease of deployment. A protocol was established to examine the suitability of materials for use as inert anodes in the FFC-Cambridge process. A vast array of metals, carbons, ceramics and cermets were evaluated. The most suitable material found to date is tin(IV) oxide. It exhibited a low rate of corrosion, good conductivity and significant quantities of oxygen were detected in the exhaust gas stream during its use as an anode for the FFC-Cambridge process.

Effect of alkali ions on the selective separation of iron and lanthanide/actinides from titani-ferrous minerals
A.Jha, A.Lahiri & E.J.Kumari

The advantages of alkali roasting for the selective separation of iron from ilmenite, equation [1], and anatase were described using the physical chemistry and phase equilibria in the Ti-Fe-Na-O system.



The subsequent precipitation of TiO_2 <Rutile> is strongly dependent on control of pH and the particle size distribution. The role of different alkali ions on the product phase formation, their relative phase stabilities and on the overall kinetics of separation process were also determined. Crystal lattice models were derived to help explain ion transport in the ilmenite, rutile and complex titanate lattices.

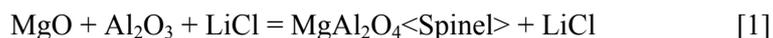
Synthesis of ceramic materials in molten salt

S.Zhang, D.D.Jayaseelan, Z.Li & W.E.Lee

Molten salt synthesis (MSS) of ceramic materials has significant advantages over the costly hydrothermal route. Syntheses can be carried out at low temperatures, reactions are rapid and grain shape & size of the precipitates can be controlled. There are three main types of MSS for ceramic materials:

Type I	Oxide A + Oxide B + Salt
Type II	Oxide A + Salt B
Type III	Salt A + Salt B

Type I reactions are typified by the preparation of high melting oxides such as CaZrO_3 and MgAl_2O_4 .



The morphology of the spinel that is precipitated follows that of the low solubility reactant, Al_2O_3 , in the example above. Preparation of LaAlO_3 can be carried out at 630°C in (KCl - KF) which is approximately 1000°C lower than the temperature required for the corresponding solid-solid reaction.

Electrochemistry in pure molten lead chloride

G.M.Haarberg, L.E.Owe & R.Tunold

Aluminium and magnesium are traditionally prepared on the industrial scale by electrochemical reactions in molten salts. Recently the FFC-Cambridge process has shown that titanium could be prepared in a similar way. Other metals such as iron, zinc and lead are potential candidates for preparation by high temperature electrochemical reductions in the future. The cathodic deposition of liquid lead on substrates of glassy carbon and tungsten was studied in molten lead chloride. The electrochemical techniques of cyclic voltammetry and potential step chronoamperometry were used to study the kinetics of the cathode process. Electrolysis experiments were also carried out over long time periods in a transparent furnace to allow for visual observations. Coloration of the molten lead chloride near the cathode was observed during electrolysis. This is due to the formation of dissolved lead, which is present as a Pb_2^{2+} species. A cathodic background current prior to bulk deposition of lead was observed during voltammetry on glassy carbon electrodes, which is also due to the formation of dissolved lead. Tungsten electrodes were found to facilitate the lead deposition reaction compared to glassy carbon. Linear relationships between current density and potential were observed in steady state measurements. Using a tungsten microelectrode this linear behaviour was measured over a wide region; up to 700 A/cm^2 and 3 V. It is believed that the rate of lead deposition is controlled by migration of Pb(II) complexes in the electrolyte.

Molten salt electrolytes in thermally activated ('thermal') batteries

P.Masset

Thermally activated ('thermal') batteries are primary batteries that use molten salts as electrolytes and employ an internal pyrotechnic source to bring the battery stack to operating temperatures. They are primarily used for military applications such as missiles, ordnance and in nuclear weapons. The electrolyte must be compatible with the other components and the expected performances of the battery. Such batteries operate for a relatively short time (5 to 3600 seconds) but must be highly reliable and have a shelf life of at least 20 years. The batteries typically have a lithium anode and a cathode fabricated from FeS₂. To reach the future electrical needs, especially longer lifetimes, new iodide-based electrolytes were tested. For these systems preparation of the electrolyte (such as LiF - LiCl - LiI), especially the removal of water, was a key factor in ensuring the devices had an operating life of at least 40 minutes.

Derek Fray thanked the speakers, the audience and the session chairmen for their enthusiastic participation to a highly successful day. George Chen's efforts in organising the venue, the program and the catering were widely praised. George emphasised that the meeting would not have been possible without the valuable support and co-operation of Katharine Burn, the Schools Liaison and Office Manager. The Groups thanks Katharine for helping to make the day so successful.

The meeting was closed by the announcement that Georges Zissis and Stuart Mucklejohn had won the International Electrotechnical Commission (IEC) Centenary Challenge for their paper titled 'Standardizing mesopic vision conditions and incidence on light sources science and technology' which featured the use of molten metal halide systems in high intensity discharge lamps.

Professor Klaus Hilpert (08 October 1940 - 30 September 2006)

It is with great sadness that the Group records the recent death of Klaus Hilpert. Klaus was known to many members of the Molten Salts Discussion Group for his outstanding contributions to the high temperature chemistry of metal halides and metal oxides. His research was highly regarded, it was always topical and carried out with the greatest of care and precision. The resulting thermodynamic parameters derived from the experimental studies would therefore be reliable and of great importance to those working in similar fields. Klaus was particularly well known to us for his work on systems relating to high temperature lamp chemistry. He was always willing to share his results, discuss the interpretation and provide endless advice to those less experienced. He was also eager to discuss other researchers' results and the difficulties they had encountered. His willingness to offer advice on experimental procedures was greatly appreciated by all those working in high temperature chemistry, this included those with significant experience as well as those new to this type of work. His enthusiasm, dedication, friendly and welcoming presence will be greatly missed at scientific conferences.

The MSDG has sent a donation to the fund established in Klaus Hilpert's memory which will be used to help support young scientists.

Annual General Meeting 2006

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
Corresponding member	Rasmus Fehrmann
Honorary Auditor	Tony Wilson

Annual subscriptions

The 2007 annual subscription to the MSDG for RSC members is £2.00.

Dr.Hadi Abood - A message from David Kerridge

Hadi worked under my supervision on molten nitrate chemistry in the 1980s with intelligence and dedication, obtaining his PhD in 1985. Afterwards he returned to Iraq and communications deteriorated.

In 2005 he contacted me by E-mail with the news that he had again been able to take up a teaching post, this time at Al-Nahrain University, just outside Baghdad. We discussed what research he might be able to do with the limited facilities he had. Meanwhile a number of kind MSDG members had sent me reprints of their papers which I passed onto him, so as to bring him up to date with developments in molten salt chemistry. Hadi became fascinated with ionic liquids and indeed started three MSc students in this field. However the security situation has steadily deteriorated to an alarming extent, that academics are deliberately targeted and murdered by some gangs. Hadi has been increasingly concerned for himself and his family and is trying to live elsewhere temporarily.

The Council for Assisting Refugee Academics (CARA) in the UK has taken an interest in Hadi's case and might be able to finance a visit of a few months or even a year. However to stand any chance of getting a visa, he needs an invitation from a UK university. If anyone can help in any way, would they please contact me: dk@cornrose.fsnet.co.uk

Very many thanks - David Kerridge

MSDG Summer Meeting 2007

The MSDG Summer Meeting will be held in Fitzwilliam College, University of Cambridge on Wednesday & Thursday 11 - 12 July.

EUCHEM 2008

The EUCHEM conference on molten salts and ionic liquids will be held in Copenhagen 24 to 29 August 2008. The web site, www.euchem2008.kemi.dtu.dk, will be available from early 2007.

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).

S.A.Mucklejohn, Newsletter Editor, 17 January 2007. Revised 09 March 2007.

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