

Molten Salts Discussion Group

Newsletter January 2008

Christmas Research Meeting 2007

The MSDG Christmas Meeting was held on Monday 17 December at the University of Nottingham London Office. The 36 participants were entertained by 10 oral presentations and 3 posters. The day concluded with the traditional wine and cheese party and the opportunity to review the events of recent times and to look forward to 2008.

Oral presentations

Novel processes for the pharmaceutical industry using ionic liquids and carbon dioxide as solvents

M.C.Kroon, L.J.Florusse, A.Shariata, K.E.Gutkowski, J. vanSpronsen, R.A.Sheldon & G-J.Witkamp & Cor J.Peters - Invited paper

A new method of chemical processing was described which uses ionic liquids and supercritical carbon dioxide as combined reaction and separation media. The carbon dioxide pressure controls the miscibility of the reactants, products, catalyst and the ionic liquid. A homogeneous liquid phase is reached at high carbon dioxide pressures which promotes fast reactions. At lower carbon dioxide pressures two phases are formed, the vapour phase contains the product and carbon dioxide while the catalyst remains in the ionic liquid phase. Compared to conventional processing, the new process not only uses less energy but also does not require the use of volatile organic solvents.

Molten salts, ceramic metal halide lamps & sustainable development

S.A.Mucklejohn

The contributions of ceramic metal halide lamps to sustainable development were quantified by a model which estimated the energy savings and the corresponding reductions of CO₂ emissions since the introduction of these products in the mid-1990's. The model is based on the energy usage of ceramic metal halide lamps compared to the energy used for equivalent systems with other light sources (a combination of incandescent lamps, halogen lamps and quartz metal halide lamps).

Adsorption studies on liquid surfaces in ultra-high vacuum: D₂O on 1-octyl-3-methylimidazolium using XPS

R.G.Jones

This report is the first description of a study of an adsorbate on an ionic liquid surface. The adsorption and desorption of D₂O on [OMOM]BF₄ were monitored by X-ray photoelectron spectroscopy (XPS). At 175K multilayers were deposited on the glassy ionic liquid surface and then thermally desorbed. After desorption of multilayers of D₂O, a monolayer D₂O remained adsorbed to the glassy ionic liquid and subsequently on the ionic liquid surface after melting. Some of the practical problems encountered in handling ionic liquids in UHV systems were described in detail.

Electro-deoxidation of iron(III) oxide in molten sodium hydroxide

A.Cox & D.J.Fray

The incentive for this study comes from the need to reduce CO₂ emissions from heavy industry. As an example, in 2000 iron ore smelting in the US produced approximately 2.6 x 10⁶ tonne of CO₂. Iron(III) oxide pellets were electrolytically reduced to iron in molten sodium hydroxide at 530°C and recovered to produce iron sponge containing no carbon nor sulfur with between 3 and 7 per cent oxygen. The product is suitable for re-melting, most of the residual oxygen forming a slag that can be tapped off. An inert nickel electrode was employed with the result that the only by-product was oxygen. The maximum current efficiency achieved was 88 per cent and the electrolytic energy consumption was 3.2 kWh.kg⁻¹. Although this technology is not intended to replace the conventional blast furnace smelting of iron ore, it may be attractive to niche markets.

Cathodic refining of metals using molten salts

D.J.Fray

Conventional refining of many metals usually entails addition of a reactive element to remove the undesirable impurity. The addition combines with the impurity to form a second phase that needs to be

removed from the system. A process that removes the undesired impurity without formation of another phase would be a better approach. This can be achieved by making the molten metal the cathode in a bath of a molten salt of a very electropositive element such as calcium or magnesium, depending upon the impurity to be removed. Recent work has concentrated on copper, tin, aluminium and glass forming alloys. One of the disadvantages of this method however, is the long refining times due to large volumes of molten metal and long diffusion distances. This can be overcome by a novel recessed electrode cell where the metal is distributed as droplets in the cell ensuring that the metal is well mixed ensuring high mass transfer and short diffusion distances.

EMITFSI - An ionic liquid for lithium batteries

Y.Wakizaka & J.Owen

EMITFSI (1-ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)-imide) was examined as an electrolyte for rechargeable lithium batteries. EMITFSI has several attractions for this application, it is cheap, easy to handle and has a relatively low viscosity. Both the conductivity and the lithium ion diffusion coefficient in LiTFSI/EMITFSI were found to decrease with an increase in lithium salt concentration. The transference number for lithium ions was found to be proportional to the concentration of lithium salt and higher than that of LiBF₄/EMIBF₄ at the same temperature and concentration of lithium salt. More than 100 mAh.g⁻¹ was retained as discharge capacity for 850 cycles using an optimised cell configuration.

The impact of defect chemistry on the reduction of TiO₂ and mixed metal oxides to form alloys of Ti via the FFC-Cambridge process

R.Bhagat, K.Rao, M.Jackson, D.Inman & R.Dashwood

Examination of the defect chemistry of intermediate compounds formed during the FFC-Cambridge process has allowed a re-interpretation of linear sweep voltammetry (LSV) results obtained on TiO₂ thin films. The reduction events observed on these voltammograms have been identified as TiO₂ to Ti₃O₅ (C4), Ti₃O₅ to Ti₂O₃ (C3), Ti₂O₃ to TiO (C2) and TiO to Ti (C1). LSV's conducted on TiO₂ thin films show significant discrepancies between theoretical values of charge passed per reaction event and those observed experimentally. A possible explanation is that during the initial stages of a sweep, two layers of Ti₃O₅ and Ti₂O₃ form, shielding the remaining TiO₂ thin film which leads to a significant amount of TiO₂ remaining unreduced. This is primarily due to the Ti₃O₅ and Ti₂O₃ having structures which do not accommodate sufficient oxygen vacancies to allow good conduction of O²⁻ ions. This leads to cathodic peaks that are smaller than expected when considering the quantity of material that is supposedly reduced. Additionally, it is believed that instead of acting as a blocking layer, CaTiO₃ acts as a solid electrolyte and there is evidence that reduction can continue under a continuous CaTiO₃ layer. The new theory can be used to explain some of the phenomena seen in TiO₂ pellet reduction and Ti alloy production from mixed metal oxides.

Nucleophilic substitutions in ionic liquids

G.Ranieri, J.Hallett & T.Welton

The kinetics of reactions of cationic sulfonium electrophiles with three amine nucleophiles (n-butylamine, di-n-butylamine, tri-n-butylamine) and a chloride ion were studied in several molecular solvents and ionic liquids. The solvent effects on these reactions were examined using a linear solvation energy relationship based on the Kamlet-Taft solvent scales (with parameters α , β , π^*). These correlations established that in reactions involving at least one neutral species, a single set of solvent descriptors can be used to build a comprehensive model encompassing both ionic liquids and molecular solvents. These models show that hydrogen bonding provides the dominant effects in determining the rate of reaction. In the fully ionic systems, however ionic liquids show an ionizing effect. This is radically different from molecular solvents which promote the formation of supramolecular aggregates yielding non-linear kinetic behaviour.

Production of NiTi via the FFC-Cambridge process

B.Jackson, D.Dye, M.Jackson, D.Inman & R.Dashwood

NiTi, or 'shape memory', alloys have many important applications but currently are very expensive to produce. The FFC-Cambridge process is a potential route to lower cost production of NiTi alloys as it avoids the costly melting and re-melting of the conventional manufacturing routes by directly producing homogeneous NiTi foam from an equiatomic mixture of NiO and TiO₂ via direct electro-deoxidation in molten CaCl₂. Constant voltage electrolysis of pressed and sintered NiO-TiO₂ pellets was carried out at -3.1 V (v standard chlorine electrode) for times from 10 minutes to 24 hours. Detailed analyses of the products showed that NiTiO₃ is reduced to NiTi via the successive formation of Ni, CaTiO₃, Ni₃Ti and

Ni₂Ti₄O. The findings are in agreement with the reduction route predicted from the predominance diagram for the Ca-Ni-Ti-O-Cl system.

The SILP (Supported Ionic Liquid Phase) concept - Recent developments within catalysts and reversible gas absorption

A.Riisager, H.Hamma, R.W.Berg & R.Fehrmann

An overview of SILP showed its growing importance in industrial applications as well as its potential for new applications. SILP is used in sulfuric acid production, hydroformylation and methanol carbonylation. Recent developments include reduction of NO_x<g> to N₂<g> and the reversible absorption of SO₂<g> where the characteristics of the ionic liquid are tuned to give the highest gas absorbance.

Poster presentations (Abstracts reproduced in full)

Study of the electrodeposition of transuranic elements in molten fluoride media

A.Huguet, S.Bourg, J.Lacquement, V.Ghetta & J.Fouletier

Pyrochemistry is regarded as a promising alternative technique for the reprocessing of some advanced nuclear spent fuels for which the current hydrometallurgical processes might not be compatible. A R&D program has been launched within the Nuclear Energy Division of the CEA to assess the potentialities of pyrochemical technologies towards the quantitative actinides recovery.

Today, electrolytic processes are mainly developed in molten chloride media with very few works in molten fluoride whereas thermodynamical predictions are more favourable in molten fluoride. The aim of this work is then to evaluate the performance of an electrolytic process for the An-Ln separation in molten fluorides versus chlorides.

The attempts of electrodeposition would be performed onto liquid bismuth. The main advantage of using a liquid metal cathode is that corrosion reactions observed on solid inert electrodes can be avoided due to alloy formation: besides the reduction potentials on molten electrodes are shifted positively. Furthermore, this work represents a breakthrough in the electrorefining methods so far as the electrolysis would be carried out onto a dropping bismuth electrode. The concept inspired from polarographic techniques, presents the advantage to lead to reproducible phenomena, due to the constant renewal of the drops.

The first step of the work would consist in designing and manufacturing a small electrolyser adapted to molten fluorides media. The cathodic system would then be firstly tested in chloride media in order to define the parameters for a quantitative electrolysis.

Once these parameters are optimised, the cell would be validated in the laboratory to predict the efficiency of an An-Ln separation in a LiF-CaF₂ eutectic mixture

Corrosion in molten salt reactors and a simple laboratory solution

D.Jewell & G.Z.Chen

Molten salts are ideal reaction media for a number of important processes, offering many properties that are extremely useful and often unique within their respective fields of application. Consequently, molten salt technology finds use in steel and non-ferrous metal refining and heat treatment, production of non-ferrous metals including Na, Li, K, Mg, Ca, Al, and Ti, processing of spent nuclear fuels and Molten Salt Oxidation (MSO) of coal or chemical weapons etc. Unfortunately, molten salts also present serious drawbacks that limit or prevent their use in a wider range of applications. Since most molten salts are highly corrosive [1-4] and their use often requires high temperatures (>350°C), the materials of construction for reactor vessels and containment systems require exotic alloys (e.g. Inconel) and/or refractory ceramics (e.g. Al₂O₃) to prevent catastrophic failure. Even when these expensive materials are employed, loss of containment from thermal or mechanical shock or attack by salt vapour can cause rapid and severe corrosion, especially at welded sections.

In this work, corrosion of metal based reaction by high temperature molten salt has been observed frequently which can cause serious delays to ongoing research and cost for repair or replacement. To combat this problem a simple laboratory solution is presented which successfully increases the longevity of reactor vessels.

- [1] F.J.Kohl *et al.*, *J. Electrochem. Soc.*, 126, 1054-1061 (1979)
- [2] M.Spiegel, P.Biedenkopf & H.J.Grabke, *Corrosion Science*, 39, 1193-1210 (1997)
- [3] F.Colom & A.Bodalo, *Corrosion Science*, 12, 731-738 (1972)
- [4] W.H.Smyrl & M.J.Blanckburn, *Corrosion*, 31, 370-375 (1975)

Investigation of the reduction electrochemistry of titanium oxides in molten calcium chloride using a cavity electrode and bulk pellet reduction

K.Rao, R.Bhagat, D.Inman & R.Dashwood

The reduction of rutile (TiO₂) in molten calcium chloride by the FFC-Cambridge process has been shown to proceed sequentially from TiO₂ to Ti₃O₅ to Ti₂O₃ to TiO and finally to Ti using thermally grown thin films [1,2]. Bulk reductions of pellets of TiO₂ have also been carried out by other research groups to identify the reduction pathway for this process, which was found to always involve the formation of CaTiO₃ and CaTi₂O₄. Linear sweep voltammetry has been conducted on TiO₂, Ti₃O₅, Ti₂O₃, TiO and CaTiO₃ powders placed inside a metallic cavity electrode [3]. Using each of the lower oxides has helped to isolate the immediate electrochemical reduction step from any previous electrochemical or chemical events. The voltammetry work has confirmed the stepwise reduction of TiO₂ to Ti as predicted by thermodynamic predominance diagrams for the Ca-Ti-O-Cl system [4]. In addition, each of the lower oxides investigated in the cavity electrode work was subjected to a sequence of partial and full reductions and the resultant phases identified using SEM and X-ray diffraction. There are significant variations in the reduction pathway of the same lower oxide powder from that seen in the cavity electrode and those in the bulk reductions of 1 g pellets. It was found that the main differences are seen in the additional phases formed, such as CaTiO₃ and CaTi₂O₄ in the bulk pellet reductions.

- [1] G.Z.Chen, D.J.Fray & T.W.Farthing, *Nature*, 407, 361-364 (2000)
- [2] K.Dring, R.Dashwood & D.Inman, *J. Electrochem. Soc.*, 152, 104-113 (2005)
- [3] G.Qiu, M.Ma, D.Wang, X.Jin, X.Hu & G.Z.Chen, *J. Electrochem. Soc.*, 152, E328-E336 (2005)
- [4] K.Dring, R.Dashwood & D.Inman, *J. Electrochem. Soc.*, 152, D184-D190 (2005)

The chairman closed the meeting by thanking the staff of the University of Nottingham London Office for their hospitality and cooperation.

Annual General Meeting 2007

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 2008 annual subscription to the MSDG for RSC members is £2.00.

Forthcoming conferences

International conference on ionic liquids for electrochemical devices, ILED-2008

16 to 19 June 2008, Rome, Italy

Information from: sonia.cirinna@uniroma1.it

MSDG Summer Meeting 2008

The MSDG Summer Meeting will be held at the University of Nottingham, 15 to 17 July (2 nights).

20th International conference on chemical thermodynamics

03 to 08 August 2008, Warsaw, Poland

See: www.icct2008.org/

EUCHEM 2008

The EUCHEM conference on molten salts and ionic liquids will be held in Copenhagen 24 to 29 August 2008. See: www.euchem2008.dk

Joint international meeting: The Electrochemical Society & The Electrochemical Society of Japan Molten salts & ionic liquids 16

12 to 17 October 2008, Honolulu, Hawaii

See: www.electrochem.org/meetings

Joint symposium on molten salts

19 to 23 October 2008, Kobe, Japan

See: <http://msc.electrochem.jp/ms8/>

VIII International conference on molten slags, fluxes & salts

18 to 21 January 2009, Santiago, Chile

See: www.molten2009.com/joomla/

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.

Bursaries for EUCHEM 2008

The MSDG invites applications for bursaries towards the costs of attending the EUCHEM 2008 Conference on Molten Salts and Ionic Liquids. Applications must be submitted to Robert Watson (E-mail: Robert.Watson@awe.co.uk) no later than 01 March 2008 and should include a budget showing estimated costs. Individual bursaries are unlikely to exceed 300 GBP. Preference will be given to those applicants who are submitting abstracts to the conference.

It is the intention of the MSDG committee to inform applicants of the outcome by 17 March so that successful applicants can take advantage of the early-bird registration fee and low cost flights.

Bursaries will be paid against receipts for expenses incurred, e.g. acknowledgement of conference registration, confirmation of flights, hotel bills.

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, 12 February 2008.

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