

# Molten Salts Discussion Group

## Newsletter Autumn 2008

### Summer Research Meeting 2008

The MSDG Summer Research Meeting was held Tuesday to Thursday 15 - 17 July at the University of Nottingham where more than 50 participants enjoyed 17 oral presentations, 5 poster presentations and a highly entertaining and informative after dinner lecture.

Following a delightful meal served in Hugh Stewart Hall, Douglas Inman reviewed two important events for the Group - the 45th anniversary and the election of the chairman, Derek Fray, to a Fellow of the Royal Society.

The meeting concluded with a visit to, and guided tour of, Ratcliffe-on-Soar power station where 18 of the meeting participants were the guests of E.ON.

The MSDG is organising a 2 day symposium on molten salts and ionic liquids as part of the 42nd IUPAC Congress in Glasgow 02 to 07 August 2009. The MSDG committee invite all members to join them in Glasgow where there will be opportunities to meet researchers from many other fields. The keynote speakers will be: Frank Endres (Technische Universität Clausthal); Hongmin Zhu (University of Science & Technology Beijing); Tom Welton (Imperial College); Vladimir Volkovitch (Ural State Technical University).

Details about the IUPAC Congress can be found at <http://www.iupac2009.org>

### *The multiple phases and faces of room temperature ionic liquids*

J.N.C.Lopes & L.P.Rebelo - Invited paper

The discovery that ionic liquids can be distilled at low pressures and high temperatures has changed the perception that ionic liquids do not have a significant gas phase. However, characterising the liquid - vapour equilibrium remains a major challenge. Molecular dynamics (MD) have shown ionic liquids can be represented as nano-segregated fluids with polar and non-polar domains. Congruent melting inclusion compounds can be formed by binary mixtures of ionic liquids with aromatic compounds, one such example is [C<sub>2</sub>mim][NTf<sub>2</sub>] with C<sub>6</sub>H<sub>6</sub>. MD studies have been used to illustrate the interactions between the aromatic molecule and the cation and anion of the ionic liquid.

### *High temperature ionic liquids in mesoporous membranes for the separation of CO<sub>2</sub>-H<sub>2</sub> gas mixture*

C.Peters

This research is funded by the Global Climate & Energy Project (GCEP) which promotes high risk - high reward concepts that would have dramatic impacts. The industrial scale production of hydrogen generates huge amounts of CO<sub>2</sub> and the separation of H<sub>2</sub> from CO<sub>2</sub> is very expensive. Thus, this process was accepted as a suitable topic for study. The use of ionic liquids supported on porous membranes has been explored as a new approach to separating H<sub>2</sub> and CO<sub>2</sub>, one example is [Emim][NTf<sub>2</sub>] supported on  $\gamma$ -alumina. Extensive measurements for the solubility of H<sub>2</sub> and CO<sub>2</sub> in this system have been carried out over large ranges of temperature and pressure.

### *A comparison of the behaviour in molten sulfate of oxidised and carburised type 304 austenitic steel over 2000 hours and the quantitative analysis of corrosion products in the melt by a novel treatment of their absorption spectra*

T.R.Griffiths & N.J.Phillips

The elegant use of mathematical smoothing techniques has confirmed that a great deal of information can be extracted from electronic absorption spectra. In this case, these techniques were used to examine the products from the corrosion of steel coupons by thin films of sulfates at 650°C and compared to results from inductively coupled plasma - atomic emission spectroscopy (ICP-EAS). These experiments were part of a study of the hot corrosion of type 304 austenitic steels by flue gases in the boilers of coal fired power stations.

*Ionic liquids in chemical and electrochemical systems*J.Salminen, M.H.Barker, J.Newman & J.Prausnitz

The properties needed for ionic liquids to be used in lithium-ion batteries were reviewed with particular emphasis on the need to avoid unwanted reactions which can lead to early failure and enormous costs for battery manufacturers. The absorption of water into the ionic liquid from the atmosphere was a recurring problem and highlighted the desirability of developing ionic liquids which absorb very little moisture. Some preliminary results from toxicity studies were also presented.

*Tin filled carbon nanotubes for lithium-ion batteries*R.DasGupta & D.J.Fray

Lithium-ion batteries are attracting much interest for use in electric vehicles. A route to increasing the capacity of these batteries is to change the anode from graphite, which has a theoretical capacity of 372mAh/g, to tin, which has a theoretical capacity of 992mAh/g. However, the volume changes associated with tin during cycling destroys the electrode structure. A potential solution to this problem is to use tin-filled carbon nanotubes. Tin-filled carbon nanotubes and nanoparticles were produced in an electrochemical process in LiCl - SnCl<sub>2</sub> at 775°C with a graphite anode and cathode. The nanotubes had diameters in the range 75 - 80 nm, some of which were filled with tin. Coin cells with anodes made from these materials are ready for testing.

*Solubility of calcium in CaCl<sub>2</sub>-CaO*R.F.Watson & S.Shaw

The solubility of calcium in CaCl<sub>2</sub>-CaO is of interest to the reduction of metal oxides with calcium, the regeneration of calcium from CaCl<sub>2</sub>-CaO and the electrochemical reduction of metal oxides. The solubility of calcium in CaO at 1073K was measured in alumina crucibles and the results combined with previously published reports for the CaCl<sub>2</sub>-CaO and Ca-CaCl<sub>2</sub> systems to model the behaviour of the Ca-CaCl<sub>2</sub>-CaO ternary system.

*The use of inexpensive ionic liquids for metal deposition*M.H.Barker, J.Salminen, T.Moisio, T.Vainikka & K.Kontturi

The need for inexpensive materials in industrial processes was illustrated by considering commercial scale copper plating where a tankhouse might employ 2000m<sup>3</sup> of solvents. Voltammetry measurements for a wide range of metals were carried out in the low cost ionic liquids Reline 203 and Oxaline 100. Electrodeposition tests were also conducted in these ionic liquids - copper, platinum and palladium plating were successful but experiments with aluminium, tantalum, titanium and magnesium proved more challenging.

*How polar are ionic liquids ?*J.P.Hallet & T.Welton

Ionic liquids are generally considered to be very polar solvents but attempts to quantify the polarity of ionic liquids have to date yielded a confusing mixture of results. However, use of the Kamlet-Taft scales whereby polarity is expressed in terms of dipolarity ( $\pi^*$ ), hydrogen bond accepting ability ( $\beta$ ) and hydrogen bond donating ability ( $\alpha$ ) brings clarification. Similarly, rates of nucleophilic substitution reactions in ionic liquids can be expressed by the Linear Solvation Energy Relationship based on the Kamlet-Taft parameters. The results from this approach are useful for predicting nucleophilic interactions at metal centres involved in catalytic processes.

*Impact of different composition cathode on electro-deoxidization process*Du Jihong, Xi Zhengping, Li Qingyu & Tang Yong

Electro-deoxidization processes tend to be slow and reaction rates need to be improved if such processes are to be used successfully in industrial environments. The activities of cathode assemblies for the production of Ti and Zr from the electro-deoxidization of the corresponding oxides can be increased by the addition of CaO or CaCO<sub>3</sub> to the oxide powders prior to sintering. Experimental results showed that the sintered doped cathodes have higher porosity, different particle size distribution and different microstructures for the calcium titanates when compared to those cathodes without dopants. These changes resulted in significantly faster rates of electro-deoxidization.

*Kinetic measurements in room temperature ionic liquids using the scanning electrochemical microscope (SECM)*

D.Walsh, A.W.Taylor, Fulian Qiu, Jingping Hu & P.Licence

Scanning electrochemical microscopy (SECM) is a scanning probe technique that employs the faradaic reaction occurring between an ultra-microelectrode tip (radius typically  $<15\mu\text{m}$ ) and the substrate as the analytical signal. The technique was developed in 1989 and has proved to be extremely useful in probing heterogeneous kinetics at the electrode - electrolyte interface and numerous redox systems have been studied in a variety of electrolytes. By employing very slow scan rates it has been possible to use SECM to obtain steady state voltammograms in ionic liquids for the first time. The SECM feedback approach curves obtained using this system agreed with the curves generated from conventional SECM theory. By positioning the SECM tip within a few hundred nanometres of a Pt substrate, it was possible to probe the heterogeneous electron transfer kinetics across the electrode - RTIL interface.

*Molten salt assisted in-situ formation of titanium carbide coatings on graphite flakes*

Xiaoguang Liu & Shaowei Zhang

To improve surface properties and rheological behaviour of graphite flakes for refractory applications, TiC coatings were prepared in-situ using a low temperature molten salt technique. Titanium metal powders and graphite flakes were combined with various amounts of low melting salts sintered at 650 to 950°C for 4 to 12h. Examination of the products confirmed that nano-sized TiC coatings had been formed on graphite flakes at temperatures as low as 850°C. These coated flakes retain the morphology of the uncoated flakes, indicating that the molten salt synthesis process was dominated by the “template-growth” mechanism. The reaction rate was determined by a combination of temperature, reaction time, salt type, salt assembly and salt-to-reactant ratio. The much improved water-wettability and rheological behaviour indicated that TiC-coated graphite could be the basis for high temperature graphite-based lubricants and carbon-containing refractory castables.

*Derivation of thermochemical parameters for SnXX' (X, X' = Cl, Br, I)*

G.Siddons, H.D.B.Jenkins, S.A.Mucklejohn & R.Devonshire

The procedures followed to determine a consistent data set of thermodynamic parameters to describe the Sn(II) halides (Cl, Br, I) were described. The work is to support the lighting industry where researchers need to predict the vapour pressures and species present as a function of temperature, pressure and composition. Errors were found in published databases for SnBr<sub>2</sub> – this highlighted the need to go back to the original data. As obtaining experimental data is difficult the available literature data were assessed, otherwise computational or estimation methods were used.

*An XPS study of ionic liquid based solutions*

I.Villar-Garcia, E.F.Smith, R.G.Jones & P.Licence

During XPS studies charging of the ionic liquid surface can lead to a gradual drift of the XPS peak positions. Internal references such as the aliphatic carbons on the ionic liquid side chain (if present) or added silver micro particles can be used to correct the spectrum. Ionic liquids based on an alkyl – methyl imidazolium cation were studied with a range of anions. The N binding energy was found to vary with the anion, however the alkyl group had no effect. When a dissolved Pd(II) catalyst was studied the liquid was observed to change from yellow to black over time corresponding to the formation of Pd(0). In the XPS spectrum this could be seen as an increase in the Pd(0) and decrease in the Pd(II) peaks with time. For Rh-catalysts the Rh binding energy was found to vary with the ligand used.

*COST Action MP0602: High temperature lead-free solders (HISOLD)*

S.A.Mucklejohn

This EU funded COST action is seeking to find lead-free replacement solders with operational temperatures in the range 250 – 350°C. A range of possible systems has been identified; appropriate macro scale and small scale physical properties need to be identified and studied to demonstrate their suitability. A fruitful discussion highlighted the new materials need to be environmentally friendly, easily recyclable (for instance the presence of Bi could be a problem for the Cu industry), have suitable fluxes identified and be suitable for both low & high voltage applications (such as hybrid cars).

*Free radical polymerisation in ionic liquids*

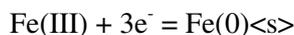
P.N.Gooden, K.J.Thurecht, D.J.Irvine &amp; P.Licence

Free-radical polymerisation of methyl methacrylate (MMA) in [Emim] [EtSO<sub>4</sub>] has been carried out successfully and shown to be suitable for large scale production with easy separation and recovery of the ionic liquid. The traditional methods of molecular mass capping using dodecylmercaptan as a chain transfer agent significantly reduces the molecular mass of the polymer but to a lesser extent than in analogous reactions in xylene. Similarly, the adverse effect of elevated temperatures upon reactions of this type is much less significant for polymerisations conducted in ionic liquids than those in organic solvents. Almost quantitative yields can be obtained for polymerisation at temperatures up to 120°C in ionic liquids while almost no polymer is observed with an organic solvent due to rapid initiator termination.

*Electrochemical behaviour of Fe(III) in molten NaCl-FeCl<sub>3</sub>*

G.M.Haarberg &amp; M.Keppert

The electrowinning of iron is one approach being considered under the ULCOS initiative (Ultra Low CO<sub>2</sub> Steelmaking). The electrochemical behaviour of dissolved Fe(III) species and the electrodeposition of iron in molten NaCl containing small amounts of FeCl<sub>3</sub> were studied at 890°C by linear sweep cyclic voltammetry and potential step chronoamperometry. Tungsten wire was used for the working electrode and the cathode. The results showed that iron was deposited in one step by the reduction of Fe(III) species. The rate of reaction was diffusion controlled.

*Electroactive ionic liquids*

A.W.Taylor, Fulian Qiu &amp; P.Licence

Functionalised ionic liquids containing a ferrocene moiety were studied electrochemically in a high vacuum system designed to minimise the adverse effects of dissolved water and oxygen. Typical conditions were 5mM concentration, 0.58 mm diameter Pt working electrodes, pressure less than  $1 \times 10^{-5}$  mmHg. A series of novel ferrocenium ionic liquids were synthesised, including 1-ferroceniummethyl-3-methylimidazolium di{bis(trifluoromethanesulfonyl)imide}, in the search for a suitable redox reference substance for use in non-aqueous solutions.

Posters - Abstracts reproduced in full*Electrolytic production of Uranium metal from U<sub>3</sub>O<sub>8</sub> in the Advanced Spent Fuel Conditioning process*

Sang Mun Jeong, Jin-Mok Hur, Byung Heung Park, Chung-Seok Seo, Hansoo Lee &amp; Seong-Won Park

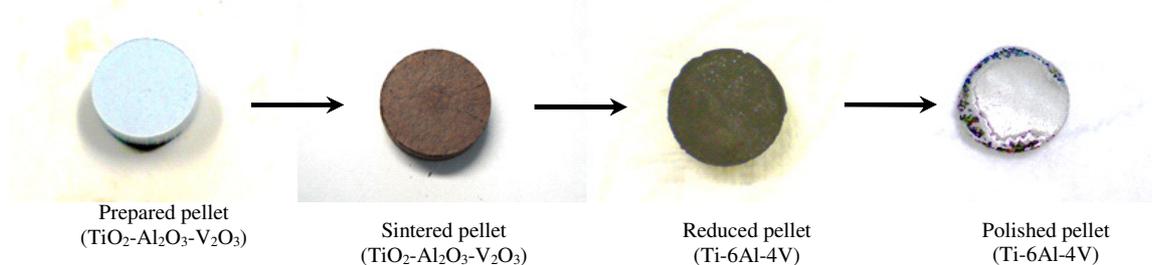
The Korea Atomic Energy Research Institute (KAERI) has developed the Advanced Spent Fuel Conditioning Process (ACP) based on a pyrochemical process.<sup>1-3</sup> The aim of the ACP is to reduce the volume, the radiotoxicity and the heat load of the spent oxide fuels (SFs) discharged from the current fleet of commercial PWRs, and eventually to create a facile form of a metallic ingot for a disposal. An electrolytic reduction process has been developed as a key unit of the ACP which consists of several steps including a voloxidation, an electrolytic reduction, a waste salt treatment and so on. In the ACP concept, the spent oxide fuel, which is voloxidized in advance, is converted to a metallic form by an electrochemical method in a LiCl-Li<sub>2</sub>O molten salt, and then the waste salt is transported to be prepared as an ingot form. In this work, the effect of a scale-up on the electrolytic reduction of uranium oxides has been studied by using different scale reactors. Also, the behaviour of alkali metal (AM) and alkali earth metal (AEM) has been investigated by adding their oxides into the cathode basket. The electrochemical reduction has been carried out by using an integrated cathode consisting of the current collector, metal oxide powder and a porous magnesia diaphragm. The anode was platinum rods on which the reaction was simply the discharge of the oxygen anion to oxygen gas.

1. S. M. Jeong, J.-M. Hur, S. S. Hong, D. S. Kang, M. S. Jeong, C.-S. Seo, J.-S. Yoon & S.-W. Park, An Electrolytic Reduction of Uranium Oxides in the Advanced Spent Fuel Conditioning Process, *Nucl. Technol.*, **162**, 184-191 (2008).
2. S. M. Jeong, S.-B. Park, S.-S. Hong, S.-C. Seo & S.-W. Park, Electrolytic Production of Metallic Uranium from U<sub>3</sub>O<sub>8</sub> in a 20 kg Batch Scale Reactor' *J. Radioanal. Nucl. Chem.*, **268**, 349-356 (2006).
3. J.-M. Hur, S.-H. Cho, I. K. Choi, S. M. Jeong & C.-S. Seo, Preparation and Melting of U from U<sub>3</sub>O<sub>8</sub>, *J. Alloys & Compounds*, **452**, 23-26 (2008).

### Direct electrochemical production of Ti-6Al-4V alloys from mixed oxide preforms

Di Hu, Daniel Jewell & 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 (strength-to-mass ratio), which is even maintained at elevated temperatures (up to approximately 400°C), fracture resistant characteristics, and exceptional corrosion resistance.<sup>1</sup> The Ti-6Al-4V alloy is desirable for critical and demanding applications such as aerospace frames, military equipment and armour, engine components, petroleum refining, chemical and electrochemical processes, and marine applications.<sup>1,2</sup> In addition, the use of advanced game-improving materials has made titanium alloys attain near-mythical status in the sporting goods industry. As the most commonly used titanium alloy, Ti-6Al-4V accounts for over 45% of total titanium sponge production, currently estimated at 63,900t/annum.<sup>3</sup> Despite the increased usage and production of Ti-6Al-4V, as well as many other titanium alloys, it is still much more expensive (>35\$/kg)<sup>3</sup> when compared to many other metals (Al 2.6\$/kg, Fe 0.4\$/kg)<sup>3</sup> because of its high melting point (>1600°C), complexity of extraction, and problems during fabrication and machining.<sup>1</sup> During the last decade, many attempts have been made for the cost reduction of titanium alloys, especially Ti-6Al-4V, to utilize their high specific strength and excellent corrosion resistance.<sup>4</sup> The FFC-Cambridge Process, which has the potential to directly produce titanium alloys, is one of the rising novel titanium extraction methods as an alternative to the conventional Kroll process.<sup>5, 6</sup> In this work, the precursors of mixed oxides (TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-V<sub>2</sub>O<sub>3</sub>) were directly reduced to Ti-6Al-4V pellets using the FFC-Cambridge Process. The reduced pellet and the mixed oxides feedstock were characterized using spectroscopic and microscopic methods.



1. E. O. Ezugwu & Z. M. Wang, *J. Mater. Process. Technol.*, **68**, 262 (1997).
2. K. Klug, *et al.*, *JOM.*, **56**, 35 (2004).
3. U.S. Geological Survey, <http://minerals.usgs.gov/minerals/pubs/commodity/> [2008-04-30]
4. M. Jackson & K. Dring, *J. Mater. Sci. Technol.*, **22**, 881 (2006).
5. G. Z. Chen & D. J. Fray, Unpublished results, University of Cambridge (1999).
6. G. Z. Chen, D. J. Fray & T. W. Farthing, *Nature*, **407**, 361 (2000).

### Vapour phase of ionic liquids

Alexey Deyko, Kevin R.J. Lovelock, Jo-Anne Corfield, Peter Licence & Robert G. Jones

The heats of vaporisation using the temperature programmed desorption (TPD) method for the following ionic liquids: [C<sub>4</sub>Py][BF<sub>4</sub>], [C<sub>4</sub>C<sub>1</sub>Pyrr][PF<sub>3</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>], [C<sub>4</sub>C<sub>1</sub>Pyrr][N(CN)<sub>2</sub>], [C<sub>6</sub>Py][Tf<sub>2</sub>N], [C<sub>4</sub>C<sub>1</sub>Im][FeCl<sub>4</sub>] and [C<sub>2</sub>C<sub>1</sub>Im][SCN]. The method is based on linear heating of the sample in the line of sight of cryopumped mass spectrometer. All experiments were conducted in a UHV chamber with a standard sample holder. It was shown, that all studied ionic liquids evaporate as isolated neutral ion pairs. A mechanism for fragmentation and kinetics of desorption were suggested. Figure shows examples of the TPD curves (signal versus temperature) for different ionic liquids. To calculate the E<sub>a</sub>, a simple Arrhenius equation was used.

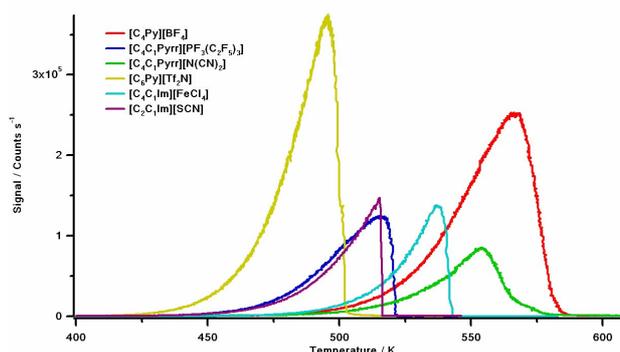


Figure 1. Summary of TPD results for studied ionic liquids

1. J. Dupont & A.Z. Suarez, *Phys. Chem., Chem. Phys.*, **8**, 2441-2452 (2006).
2. J.P. Armstrong, C. Hurst, R.G. Jones, P. Licence, K.R.J. Lovelock, C.J. Satterley & I.J. Villar-Garcia, *Phys. Chem. Chem. Phys.*, **9**, 982-990 (2007).
3. R. Gomes de Azevedo, J.M.S.S. Esperance, J. Szydłowski, Z.P. Visak, P.F. Pires, H.J.R. Guedes, & L.P.N. Rebelo, *J. Chem. Thermodyn.* **37**, 888 (2005).

#### NEXAFS of ionic liquids

Alexey Deyko, Kevin R. J. Lovelock, Ignacio J. Villar-Garcia, Alasdair Taylor, Vin Dhanak, Peter Licence & Robert G. Jones

Two ionic liquids ( $[\text{C}_4\text{C}_1\text{Im}][\text{BF}_4]$  and  $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ ) have been studied using NEXAFS technique. All experiments were done at Daresbury SRS. An attempt to study the orientation of molecules at the liquid surface was made. Figure shows an example of NEXAFS spectra for N 1s edge.

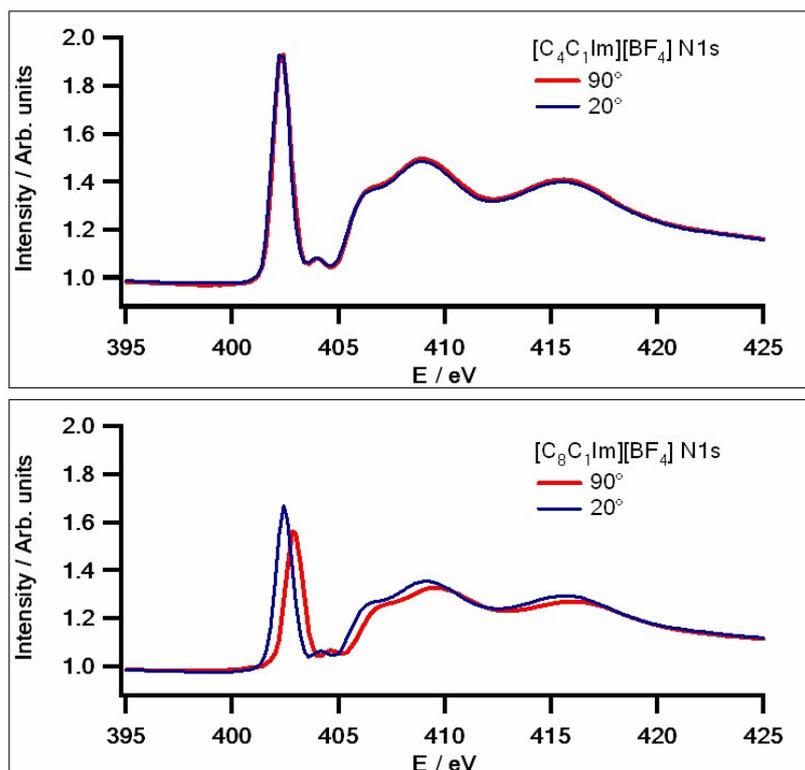


Figure 1. N1s spectra for  $[\text{C}_4\text{C}_1\text{Im}][\text{BF}_4]$  and  $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$

1. J. Dupont & A.Z. Suarez, *Phys. Chem. Chem. Phys.*, **8**, 2441-2452 (2006).
2. G. Hahner, *Chem. Soc. Rev.*, **35**, 1244-1255 (2005).
3. J.P. Armstrong, C. Hurst, R.G. Jones, P. Licence, K.R.J. Lovelock, J.C. Satterley & I.J. Villar-Garcia, *J. Phys. Chem. Chem. Phys.*, **9**, 982-990 (2007).

#### A morphological study of the FFC Chromium and Titanium powders

G. Z. Chen & D. J. Fray

Microscopic morphological features of the cubic chromium and nodular titanium powders prepared by electroreduction of the respective oxides in molten salts (the FFC Cambridge process) are compared with the preferential crystal growth mechanism. The analysis leads to an understanding of the determining forces for the formation of cubic particles in the chromium powders owing to preferential growth, but nodular particles in the titanium powder owing to interruption of the preferential growth by, particularly, oxygen atoms.

**MSDG Christmas Meeting 2008 & Annual General Meeting**

The MSDG Christmas Meeting will be held in London on Monday 15 December. The AGM will also be held at this venue on the same day. Further details of these meetings will be circulated by the Honorary Secretary.

**Forthcoming conferences****20th International conference on chemical thermodynamics**

Warsaw, 03 to 08 August 2008

See: [www.icct2008.org/](http://www.icct2008.org/)

**EUCHEM conference on molten salts and ionic liquids**

Copenhagen, 24 to 29 August 2008

See: [www.euchem2008.dk](http://www.euchem2008.dk)

**5th International Conference on Environmental Catalysis**

Belfast, UK, 31 August to 03 September 2008

See: [www.centacat.qub.ac.uk:5icec](http://www.centacat.qub.ac.uk:5icec)

**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](http://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/](http://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.

**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](mailto:djf25@cam.ac.uk)).