

# Molten Salts Discussion Group

## Newsletter Autumn 2007

### Summer Research Meeting 2007

The MSDG Summer Research Meeting was held on Wednesday & Thursday 11-12 July at Fitzwilliam College, University of Cambridge where 34 participants enjoyed 12 oral presentations and 5 poster presentations. The recently established after dinner lecture provided another highly informative and entertaining evening with Andrew Abbott describing the creation and progress of Scionix, a spin out company from the University of Leicester.

### *Coordination chemistry and electrochemistry of tantalum in ionic liquids*

#### Olga Babushkina - Invited speaker

A variety of the novel pyrrolidinium based ionic liquids were prepared by combining salts of tantalum(V) ( $\text{TaCl}_5$ ,  $\text{K}_2\text{TaF}_7$ ,  $\text{TaF}_5$ ) with 1-butyl-1-methylpyrrolidinium ( $\text{Pyr}_{14}^+$ ) or 1-hexyl-1-methylpyrrolidinium ( $\text{Pyr}_{16}^+$ ) cations in combination with different anions, such as:  $\text{Cl}^-$ , trifluoromethanesulfonate ( $\text{TFMS}^-$ ), and bis(trifluoromethanesulfonyl) imide (TFMSI). Three different groups of ionic liquids were obtained and investigated. Chloride mixtures:  $(x)\text{Pyr}_{14}\text{Cl} \cdot (1-x)\text{TaCl}_5$  and  $(x)\text{Pyr}_{16}\text{Cl} \cdot (1-x)\text{TaCl}_5$  ( $x = 0.90-0.20$ ); Chloride-fluoride mixtures:  $(x)\text{Pyr}_{14}\text{Cl} \cdot (1-x)\text{K}_2\text{TaF}_7$  ( $x = 0.90-0.30$ ); Oxygen-containing chloride-fluoride mixtures:  $(x)\text{Pyr}_{14}\text{TFMS} \cdot (1-x)\text{TaCl}_5$  ( $x = 0.95-0.65$ ) and  $(x)\text{Pyr}_{14}\text{TFMSI} \cdot (1-x)\text{TaCl}_5$  ( $x = 0.95-0.30$ ). Raman spectra of the mixtures  $\text{Pyr}_{14}\text{Cl} \cdot \text{TaCl}_5$  and  $\text{Pyr}_{16}\text{Cl} \cdot \text{TaCl}_5$  at various molar ratios demonstrated that in mole fraction  $\text{Pyr}_{14}\text{Cl}$  &  $\text{Pyr}_{16}\text{Cl}$  in the range 0.90-0.45, Ta(V) exists as  $[\text{TaCl}_6]^-$  complex anions. At high concentrations of  $\text{TaCl}_5$  ( $x < 0.45$ ) the molecules of  $\text{Pyr}_{14}\text{Cl}$  &  $\text{Pyr}_{16}\text{Cl}$  are introduced in the crystal structure of  $\text{TaCl}_5$  and Raman spectra in this range are characterized by vibrational features of  $\text{Ta}_2\text{Cl}_{10}$  dimers.

### *Direct and mediated organic electrochemistry in ionic liquids*

#### Andrew Doherty

The direct electrochemical reduction of benzophenones in ionic liquids based on  $[\text{Bmim}]^+$  and  $[\text{Bmpyrd}]^+$  has been studied with and without the use of TEMPO as a recyclable catalyst. As well as being part of a catalytic cycle, TEMPO has the advantage of being very selective and does not contain Cr nor Mn. Diffusion coefficients in ionic liquids tend to be slow which makes them ideal for fundamental studies but of limited applicability for some commercial electrochemical processes. Despite the complex kinetics, a model for the disappearance of the TEMPO cation has been established.

### *Ionic liquids in vacuo: Recent progress - Imaging*

#### Peter Licence

Applying conventional surface science techniques to ionic liquids has shown liquid surface science to be an exciting new field. XPS studies produce excellent spectra which change significantly as the sample temperature is lowered, i.e. some ionic liquids show glass-like behaviour. Use of the recently installed surface analysis systems at the University of Nottingham Nanotechnology Centre has opened the way for some exciting new applications for ionic liquids in imaging.

### *Electrolytic metal extraction in liquid salts without $\text{CO}_2$ emission*

#### Guomin Li, Linpo Yu, Dihua Wang, Xianbo Jin & George Z Chen

There are three main interconnected elements that are responsible for the  $\text{CO}_2$  emissions in industrial electrolysis: oxide based feedstocks; high temperatures ( $>500^\circ\text{C}$ ); carbon-based anodes. Thus, if a process can avoid any one of the three elements, it may be considered a  $\text{CO}_2$ -free process. Much effort is being devoted by major industries to the development of non-carbon anodes. This study has used non-oxide feedstocks combined with low electrolysis temperatures:  $\text{MoS}_2$  was electrolysed in  $\text{CaCl}_2$  to Mo powder at the cathode and  $\text{S}_2$  at a graphite anode; solid  $\text{CuCl}$  was electrochemically reduced in an ionic liquid ( $[\text{Bmim}]\text{PF}_6$ ), leading to the formation of nano-particles of pure Cu.

### *Derivation of high temperature thermochemical data: Methods and examples*

#### G.Siddons, V.H.Ramos, S.A.Mucklejohn, J.C.Camacho, R.Devonshire & R.H.Davies

A review of the limitations of currently available data and methods highlighted an opportunity for quantum

chemistry calculations to play a major role in extending thermochemical data for species at high temperatures. Recent advances in computational methods to calculate molecular parameters & enthalpies of formation have led to reliable values being obtained for some species in less than 1 hour computing time. Initial calculations have been confined to gaseous species but this work will be extended to include condensed phases. This offers the possibility of deriving reliable thermochemical data for an enormous range of ionic liquids and molten salts.

#### *Salt sellers*

Andrew Abbott - After dinner speaker

The excitement, pitfalls, frustrations and opportunities arising from spin out companies were combined into a most entertaining and informative after dinner lecture. Scionix Limited is now a successful venture providing ionic liquids on a commercial scale and helping industries improve their processes. A key element in the company's progression has been working closely with local businesses.

*CEMOS (Catalyst Enhanced Molten Salt Oxidation) for complete and continuous pyrochemical reprocessing of spent nuclear fuel: An overview of a viable new technology for next generation nuclear reactors*

T.R.Griffiths & V.A.Volkovich

Future demand for electrical energy demand may not be satisfied without nuclear reactors, hence resolving the problem of spent nuclear fuel and radioactive waste is particularly important. After ten years work a potential complete pyrochemical reprocessing cycle, employing Catalyst Enhanced Molten Salt Oxidation, can now be envisaged. The reasons why the extensive molten salt oxidation experiments on nuclear fuel and waste in the 20th century were discontinued are now known to have arisen from a complete misunderstanding of the chemistry involved. Thus the full potential and advantages for a rapid and efficient separation and recycling technology described in this work were missed.

*Thermodynamical description of viscous flow in amorphous materials*

M.I.Ojovan, R.J.Hand & K.P.Travis

Assuming that viscous flow in amorphous materials is mediated by broken bonds (configurons) an universal equation of viscosity was derived:

$$\eta(T) = A_1 T (1 + A_2 \exp(B/RT))(1 + C \exp(D/RT))$$

where the coefficients  $A_2 = \exp(-S_m/R)$  and  $C = \exp(-S_d/R)$  are related to entropies of motion  $S_m$  & formation  $S_d$ , and  $B$  and  $D$  are enthalpies of motion and formation of configurons. Using this equation the viscosity of various amorphous systems such as  $\text{SiO}_2$ ,  $\text{GeO}_2$ ,  $\text{B}_2\text{O}_3$ , anorthite, diopside,  $(x)\text{Na}_2\text{O} \cdot (1-x)\text{SiO}_2$ ,  $(x)\text{PbO} \cdot (1-x)\text{SiO}_2$ , several soda-lime-silica glasses as well as some organic materials were examined. The equation provides an excellent description of the viscosity of these materials at all temperatures studied. The viscosity equation can be simplified to an Arrhenius-type in the limits of high and low temperatures. For many systems the equation can be simplified to a two-exponential form but for  $\text{B}_2\text{O}_3$  and soda-lime-silica glasses all parameters in the equation must be retained to obtain a correct description of viscosity. In the limit of very high temperatures, the activation energies of viscous flow of these materials tend to diminish; this behaviour is well described by the viscosity equation.

*Preparation of titanium by electrolysis of  $\text{Ti}_2\text{CO}$  solid solution in NaCl-KCl molten salt*

Shuqiang Jiao, Hongmin Zhu & Xuefan Gu

A consumable anode composed of a solid solution of titanium carbide and titanium monoxide ( $\text{Ti}_2\text{CO}$ ) can be prepared via carbothermic reduction of  $\text{TiO}_2$ . Upon electrolysis in a  $\{\text{NaCl-KCl}\}$  melt, the anode feeds  $\text{Ti}^{2+}$  into solution and carbon monoxide is generated. No excess carbon remains to contaminate the melt. On the cathode, high-purity titanium (>99.9 %) is produced. Results to date suggest anode and cathode current efficiencies of up to 93% and 89% respectively can be achieved, indicating that the method is potentially commercially viable.

*Electrochemical deoxidation of mixed metal oxides in molten calcium chloride to produce aluminium alloys*

Geir Martin Haarberg, Sigurdur Einarsson & Knut Arne Paulsen

Aluminium and aluminium alloys were prepared by electrodeoxidation of metal oxides in molten  $\text{CaCl}_2$  (95 mol%) –  $\text{NaCl}$  (4 mol%) –  $\text{CaO}$  (1 mol%) at 850°C. The experiments were run by applying a constant cathode potential versus a reference electrode ( $\text{Ag}/\text{AgCl}$ ). Aluminium of purity >95 wt% was obtained at

current efficiencies of about 5%. The main impurities were carbon and oxygen, the carbon originating from the graphite anode. Electrodeoxidation of mixed alumina and scandium oxide (2 wt%) led to the formation of intermetallic Al<sub>3</sub>Sc particles at current efficiencies of about 7%, which were characterised and analysed by SEM/EDS and XRD. Future work will concentrate on developing an inert anode and improving the current efficiency.

*The electrochemical deoxidation of mixed metal oxides to form low oxygen  $\beta$ -titanium alloys*

Rohit Bhagat, Martin Jackson, Richard Dashwood & Douglas Inman

Titanium alloys are widely used in medical applications, for instance Ti-Mo (15 wt%) has a modulus similar to that of bone and is hence used in joint replacement. Such alloys, with low oxygen contents, can be made by the FFC Cambridge process. The reduction pathways of several isomorphous  $\beta$ -Ti systems were investigated with a series of interrupted reductions on 1 g pellets of the appropriate mixed oxides. It was found that the various lower oxides formed during deoxidation can be beneficial to alloy homogenisation. Fundamental studies on Ti-Mo (15 wt%) were carried out using molybdenum micro-electrodes to identify the electrode potentials at which favourable lower oxides form, the aim being to optimise the deoxidation process and homogenisation of alloys.

*Investigation of the reduction electrochemistry of titanium oxides in molten calcium chloride using a cavity electrode*

Kartik Rao, K.Dring, D.Brett, D.Inman & R.Dashwood

Linear sweep voltammetry was carried out on TiO<sub>2</sub>, Ti<sub>3</sub>O<sub>5</sub>, Ti<sub>2</sub>O<sub>3</sub>, TiO & CaTiO<sub>3</sub> powders placed inside a metallic cavity electrode. Using each of the lower oxides helped to isolate the immediate electrochemical reduction step from any previous electrochemical or chemical events. The voltammetry work confirmed the stepwise reduction of TiO<sub>2</sub> to Ti as predicted by thermodynamic predominance diagram for the Ca-Ti-O-Cl system. It is found that a TiO precursor in such cavity electrodes reduces to Ti, without forming CaTiO<sub>3</sub>. The latter is an insulating intermediate phase whose formation is encouraged by the rising local oxide activity at the cathode surface during reduction. It has been suggested that TiO might be more suitable as a cathode precursor for the industrial production of titanium metal than TiO<sub>2</sub>. However, reductions of TiO on a larger scale have shown that the formation of a titanate phase cannot be easily avoided, with a significant volume fraction of 1 g pellets converting to CaTi<sub>2</sub>O<sub>4</sub> and CaTiO<sub>3</sub>.

**MSDG Christmas Meeting 2007 & Annual General Meeting**

The MSDG Christmas Meeting will be held at the University of Nottingham London Office on Monday 17 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.

**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](http://www.euchem2008.dk).

**Other meetings**

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)).

VIII International Conference on Molten Salts, Fluxes and Salts, Santiago, Chile, 18 to 21 January 2009 (see [www.molten2009.com/joomla/](http://www.molten2009.com/joomla/)).

**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)).