

Molten Salts Discussion Group

Newsletter Autumn 2006

Summer Research Meeting 2006

The MSDG Summer Research Meeting was held on Monday & Tuesday 10-11 July at Fitzwilliam College, University of Cambridge where 33 participants were entertained by 11 oral presentations and 4 poster presentations. The staff of Fitzwilliam College treated the participants and accompanying persons extremely well and provide a splendid banquet in advance of Frank Endres after dinner lecture. It seems the concept of an after dinner lecture has already become a popular feature of the MSDG Summer Meeting.

Oral presentations

Solar grade silicon by electrorefining in molten salts

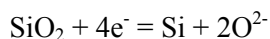
Geir Martin Haarberg, Ole Edvard Kongstein & Saima Sultana - Invited lecture

There is an increasing demand for high purity silicon to be used for the fabrication of solar cells. Looking to the next 50 years, solar energy will play an increasingly important role and this will require the production of large amounts of high purity silicon. There is a very strict limitation on the concentration of impurities in solar grade and electronics grade silicon, the requirements for boron and phosphorus are particularly severe. Electrorefining of metallurgical grade silicon to produce solar grade quality Si is an alternative approach which is potentially beneficial in terms of energy and cost. Preliminary studies were carried out in molten CaCl₂ (85 mol %), NaCl (5 mol %) and CaO (10 mol %) at 850°C. From cyclic voltammetry it was found that silicon could be anodically dissolved and cathodically deposited at potentials within the electrochemical window of the solvent electrolyte. Thin deposits of pure silicon were obtained during galvanostatic electrolysis experiments, although anodic passivation was observed when using metallurgical grade Si as anode. Future challenges will be connected to avoiding anode passivation and controlling the impurity levels of phosphorus and boron.

Electro-extraction of Si from SiO₂ in fused CaCl₂

Daniel Jewell, Xianbo Jin & George Chen

Experiments using a SiO₂/W micro-electrode showed that SiO₂ can be reduced easily in CaCl₂ at 850°C.

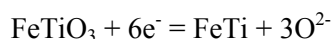


A model based on the concentration distribution of O²⁻ ions during potentiostatic electrolysis correctly predicted the changes in current with time. This includes an initial phase where the current increases rapidly and then decreases, reaching a steady state at long times.

Operation of lab scale electrolysis cells for the direct production of ferrotitanium from solid oxide precursors

Kevin Dring, Odd-Arne Lorentsen, Eirik Hagen & Christian Rosenkilde

The global market for ferrotitanium is currently in a period of sustained high demand. Production of ferrotitanium is believed to be more efficiently and cheaply accomplished via a novel electrochemical process. Norsk Titanium, in collaboration with Hydro Oil & Energy, has extensively investigated the direct electrochemical electrolysis for the production of ferrotitanium from its constituent oxides.



While immersed in a molten CaCl₂-based electrolyte, iron-titanium-oxygen compounds were cathodically polarized against a carbonaceous anode. The formation of ferrotitanium was found to proceed in a sequential manner, with the reduction of iron occurring during the early stages of the process. The lower oxides of titanium were observed, in conjunction with calcium titanate species at intermediate reduction times. The actual formation of ferrotitanium was only observed to occur at the final stages of electrolysis, when both iron and titanium containing sufficiently low oxygen were in physical contact. The loss of iron was observed during the reduction process and the use of graphitic anodes resulted in the undesirable formation of molten

carbonates, carbon scum on the surface of the electrolyte and carbide contamination of the cathode product. As a consequence of the latter effects, a significant reduction in current efficiency was observed.

Recent advances in the understanding of the structures of solid salt eutectics

David Kerridge

The factors that determine the structures of eutectic solids formed from binary mixtures have received little attention and are poorly understood. SEM and Raman mapping have proved to be valuable tools in characterising the structures of eutectic phases. There seems to be two types of structures, lamellar and conglomerate. Recently several systems have been studied including {NaNO₃ - NaNO₂}, {KNO₃ - KNO₂}, {NaNO₃ - KNO₃}, {KNO₃ - Ca(NO₃)₂}, {KCl - Na₂SO₄} and {KCl - K₂Cr₂O₇}. From studies conducted in the past few months on the {NaBr-NaNO₃} system, the tentative conclusion is that it is the temperature gradient rather than the melting temperature that is responsible for determining the structure (for identical cooling rates). Further analyses will be presented at future MSDG meetings.

Thermodynamic data for ionic liquids – needs and availability

Alan Dinsdale, Hugh Davies & Vlad Sokhan

Room temperature ionic liquids have much potential for use in industrial processes but there are very few data available to describe their thermochemical properties. The National Physical Laboratory has recently started a program to determine the thermochemical properties of some room temperature ionic liquids and of their mixtures. Experimental information in the literature concerning the thermodynamic properties of ionic liquids is essentially limited to melting temperatures and enthalpies of fusion. However, enthalpies of mixing between an ionic liquid and solutes are in very short supply. These data are key to the derivation of a full description of the thermodynamics of a system. In addition to reviewing published material, some systems will be the subject of experimental studies using differential scanning calorimetry and rotation reaction calorimetry. Selected systems will be studied by molecular dynamics simulation. An interesting aspect of modelling the interactions between ionic liquids is the choice of variables, high temperature systems are usually modelled using mole fractions but different parameters, e.g. volumes, might be more appropriate for ionic liquids.

Redox-active room temperature catalytic molten salts for hydrogen peroxide production

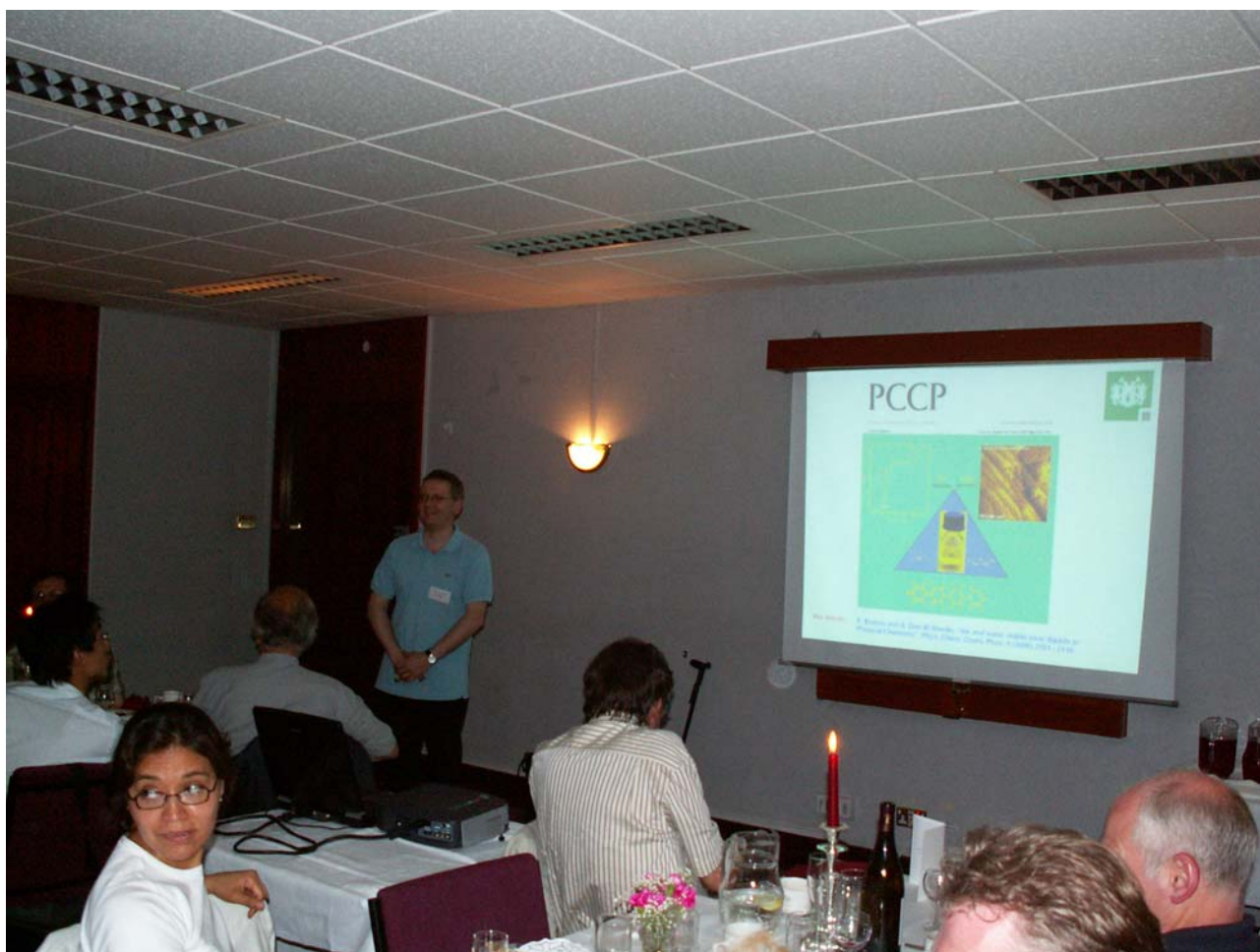
Kevin Murnaghan & Andrew Doherty

Production of hydrogen peroxide is a multi-billion dollar business with only a few large multi-national companies competing in the market. The favoured method of production is the auto-oxidation of an anthraquinone (AQ), usually in an alkylbenzene solvent using hydrogen and a solid supported catalyst such as 10% palladium on carbon. The reduced anthraquinone (AQH₂) readily reduces aqueous oxygen in a biphasic system to produce hydrogen peroxide. It has been shown recently that this process can be carried out in an ionic liquid, ([bmim]⁺ [BF₄]⁻, 3-butyl-1-methyl-imidazolium tetrafluoroborate). While this is a useful example of electrosynthesis in an ionic liquid, the possibility of functionalized ionic liquids specific to peroxide production remains the key goal, removing the need for a solvent and greatly improving the efficiency of the process, with the ionic liquid acting as both solvent and catalyst. A large number of molten salts (room temperature and high temperature) with anionic or cationic 9,10-anthraquinone and 1,4-naphthoquinone parts were prepared, exhibiting a range of physical properties. Some of these compounds proved to be promising and future synthetic strategies to produce suitable salts were reviewed.

Ionic liquids – the missing link to high temperature molten salts

Frank Endres - After dinner lecture

There are now more than 5000 peer reviewed publications on ionic liquids and the annual output of papers has risen strongly during the last 6 years. An overlooked property of ionic liquids is their ability to withstand temperatures above 250°C for many hours. Some ionic liquids can withstand temperatures of 400°C for short times, especially under an inert gas. This property makes ionic liquids interesting for chemical and electrochemical studies over a wide temperature range. For example, tantalum can be electrodeposited in an ionic liquid in thin crystalline layers of about 1 μm thickness at 200 to 250°C. The deposited layers protect shape memory Ni-Ti alloy from corrosion. At room temperature only non-stoichiometric subhalides are formed. Even at temperatures up to 100°C it is impossible to make the grey phase of selenium by electrochemical means in aqueous media. However, it is possible to produce the grey phase of selenium from an ionic liquid at temperatures between 120 and 150°C. Similarly, aluminium can be electrodeposited in microcrystalline and nanocrystalline form from ionic liquids in the temperature range 25 to 150°C.



The reduction of TiO₂ by the FFC process: Further fundamental electrochemical studies

Douglas Inman, Daniel Brett, Richard Dashwood & Kartik Rao

The reduction of titanium dioxide (TiO₂) in molten calcium chloride by the FFC process has been shown to proceed sequentially from TiO₂ to Ti₃O₅ to Ti₂O₃ to TiO and finally Ti. Each of these steps has been characterised using linear sweep voltammetry and through subsequent structural studies using x-ray diffraction (XRD) and secondary electron imaging (SEM) by Dring *et al.* It has been found that the current densities of the reactions TiO₂ to Ti₃O₅ (referred to as C4) and Ti₃O₅ to Ti₂O₃ (referred to as C3) are an order of magnitude lower than those of the subsequent cathodic reactions. Linear sweep voltammetry has been used to further elucidate reactions C4 and C3, mainly by examining the reverse scan behaviour with respect to differing hold times and scan rates. These studies, combined with some preliminary electrochemical impedance spectroscopy results, have led to a proposed mechanism for reactions taking place at the electrode/electrolyte interface. The presentation was followed by an extensive and lively discussion.

The electrochemical deoxidation of tungsten-titanium mixed metal oxides

Rohit Bhagat, Martin Jackson, Richard Dashwood & Douglas Inman

The electrodeoxidation of TiO₂ (also referred to as the FFC-Cambridge process) has been investigated to the point where the reduction pathway has been identified and process maps developed. Electrodeoxidation of mixed oxides has been employed to create titanium alloys incorporating elements that would not normally be alloyed with titanium, such as tungsten. When tungsten is in solid solution in titanium, it decreases the elastic modulus of the host and the properties of alloys can be tailored to match the elastic modulus of human bone for implants. Mixed metal oxide pellets were produced by mechanically mixing and compacting two or more metal oxides powders. The electrodeoxidation behaviour of these mixed oxide pellets was investigated using a series of partial reductions and predominance diagrams. These diagrams are constructed following the approach used by Littlewood for fused chloride systems. It is found that reduction is not a simple case of each metal oxide reducing individually to a pure element. Instead, during reduction the metal oxides interact to form compounds or solid solutions which give rise to a homogeneous structure.

*Spontaneous symmetry breaking at glass transition in amorphous materials*Michael Ojovan

The translation-rotation symmetry in the distribution of atoms and molecules is broken at crystallisation but remains unchanged at the liquid-glass transition, which retains the topological disorder of fluids. Glasses have a topologically disordered distribution of atoms and molecules but elastic properties of an isotropic solid. Moreover, the glass transition is considered as a second order transition in which a supercooled melt yields, on cooling, a glassy structure [IUPAC Compendium on Chemical Terminology (1997)]. The structural changes that occur in an amorphous material at the glass transition are very small. Therefore, the glass transition remains one of the most difficult problems of condensed matter. In contrast to atomic distribution, there is a symmetry breaking at the glass-liquid transition characterised by the reduction of the Hausdorff dimension of broken bonds distribution from the 3D Euclidean in the liquid state to the fractal $d_f=2.55\pm 0.05$ -dimensional in the glassy state. Similarly to Dienes' ratio, the glass transition temperature depends on thermodynamic parameters, e.g. enthalpy (H_d) and entropy (S_d), of broken bonds: $T_g \approx H_d/S_d$. Thermodynamic parameters of broken bonds can be calculated from viscosity-temperature relationships. Using amorphous SiO_2 and GeO_2 as reference network-forming materials, the calculated T_g values are in excellent agreement with experimentally measured calorimetric glass transition temperatures. Near T_g the heat capacity of amorphous materials has a universal power law behaviour: $C_p(T) \propto |T_g/(T-T_g)|^\alpha$ where the critical exponent $\alpha=0.59$.

*Cavity electrode: A novel experimental tool for investigation of oxide powders in molten salts*Guohong Qiu, Kai Jiang, Dihua Wang, Xianbo Jin, & George Chen

Novel cavity electrodes have been developed for the investigation of electrochemical properties of metal oxide powders in molten salts. They are simple to fabricate and are particularly well suited for cyclic voltammetry and chronoamperometry. Results from studying some typical oxides were presented, including NiO , Cr_2O_3 , TiO_2 and Tb_2O_3 and some mixed oxide powders. For conducting oxide powders, the cavity electrode exhibits voltammetric features similar to other electrode systems with the electrochemically active species being immobilised on the surface of an electrode. It was also shown that, in conjunction with a novel high temperature reference electrode, the cavity electrode is very useful in determining the mechanism of the electrodeoxidation of mixed oxide powders for making the respective alloys.

Posters - Abstracts reproduced in full*Glasses for nuclear waste immobilisation*

Olga Batyukhnova & Michael Ojovan

Vitrification of nuclear wastes is attractive because of its flexibility, the large number of elements which can be incorporated in the glass, its high corrosion durability and the reduced volume of the resulting wasteform. The high chemical resistance of glass allows it to remain stable in corrosive environments for millions of years. Several glasses are found in nature such as obsidians (volcanic glasses), fulgarites (formed by lightning strikes), tektites found on land in Australasia and associated microtektites from the bottom of the Indian Ocean, moldavites from central Europe, and Libyan Desert glass from western Egypt. Some of these glasses have been in the natural environment for about 300 million years with low alteration rates of only tenths of a nanometre per year. Both borosilicate and phosphate glasses are used to immobilise nuclear waste glasses, moreover in addition to relatively homogeneous glasses novel glass composite materials are used to immobilise problematic waste streams [1, 2]. The spectrum of wastes which are currently vitrified increases from high-level wastes [3] to low and intermediate wastes such as legacy wastes in Hanford, USA [4] and nuclear power plant operational wastes in Russia [5]. We give an overview of glasses used for nuclear waste immobilisation highlighting the waste loading limits, incorporation capabilities and properties of final vitrified waste products.

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A quartz Sealed Ag/AgCl reference electrode for high temperature molten salts

Pei Gao, Wei Xiao, Xianbo Jin, Dihua Wang, Xiaohong Hu & George Chen

High temperature molten salts play important roles in modern electrochemical research and industrial practices. Recently, in molten CaCl_2 at $\sim 900^\circ\text{C}$, it was reported that when a solid metal oxide, e.g. TiO_2 , was made into a cathode, regardless of the electronic conductivity, the oxide could be electrochemically reduced in the same melt directly to the metal [1]. The possibility of using this new electro-deoxidation method has been acclaimed for the economical and environmentally friendly production of many useful but currently expensive metals and semi-metals, typically Ti, Si, Nb and Cr, and their alloys [1-5]. However, in previous studies, except for some voltammetric observations from using a metal based pseudo-reference electrode coupled with a known electrode reaction as the internal reference [2], most results and analyses were linked with electrolysis in a two-electrode cell which only allowed the control of cell voltage or current. In this laboratory, a quartz sealed Ag/AgCl reference electrode was fabricated and studied in CaCl_2 based molten salts [6]. It performed satisfactorily in terms of reproducibility, reusability and stability in experiments that varied the temperature ($700^\circ\text{C} \sim 950^\circ\text{C}$) and service time (from hours to days). The electric resistance of the reference electrode decreased from $10^5 \Omega$ to $10^3 \Omega$ when increasing the molten salt temperature from 600°C to 950°C , following well Arrhenius' Law. The potential variation of the electrode upon changing the electrolyte composition (CaCl_2 , NaCl, KCl, and/or AgCl) suggested the selective conduction of Na^+ ions and possibly Ca^{2+} ions through the thin-wall of the sealed quartz tube. Prolonged use (2~3 days) of the reference electrode in the presence of both oxygen and molten chloride salt led to noticeable erosion of the quartz tube, particularly at the molten salt-quartz-gas triple phase boundary, which is attributable to the formation of calcium and/or sodium silicates under the influence of oxygen in the liquid and gas phases, respectively.

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A morphological study of the FFC chromium and titanium powders

George Chen & Derek Fray

Powder metallurgy (PM) depends, to a great degree, on the physical and chemical properties of the metal powders. Past industrial and laboratory practices in metal powder manufacturing have been focused on two processes: atomising and mechanical milling. Particle morphologies differ significantly between metal powders produced by the two methods. Spherical particles are usually produced by atomising but irregular broken particles are common from mechanical milling. Metal powders with other morphologies, particularly regular crystalline particles, are relatively new to the PM community. The FFC Cambridge Process promises the direct electrochemical reduction of solid metal oxide powders to metal and alloy powders in molten salts. It is simple in operation, low in energy consumption and, more importantly, versatile in product forms. Particularly, the FFC chromium and titanium powders are featured by their unique nodular and cubic particles, and may present new opportunities to the PM industry. In this presentation, the mechanism of electro-reduction of porous preforms of metal oxide powders in molten calcium chloride is discussed in terms of the formation of two typical FFC metal powder morphologies: titanium nodules and chromium cubes. Based on SEM observations in relation with electrolysis parameters, the two-dimensional nucleation and growth mechanism is assumed to be responsible for the metal particle formation process. Interruption of the preferential growth of the crystallites by oxygen and other influences present during electrolysis is

proposed to be an important determining factor for the formation of the two typical particle morphologies in the FFC metals.

References:

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(Author's note : This poster was previously presented at EuroMat 2005 in Prague, Sept. 2005)

Electrochemical studies of calcium in molten CaCl₂
A.Martin, J.Foulettier, M.Allibert & J-C.Poignet

MSDG Christmas Meeting 2006 & Annual General Meeting

The MSDG Christmas Meeting will be held on Monday 18 December at the University of Nottingham, London Office. 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.

MSDG Summer Meeting 2007

The MSDG Summer Meeting will be held 11 to 12 July 2007 at Fitzwilliam College, University of Cambridge.

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, 14 July 2006
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