

Molten Salts Discussion Group

Newsletter September 2010

Summer Meeting and Research Workshop 2010

The MSDG returned to Fitzwilliam College, Cambridge for the 2010 Summer Meeting between 06 and 08 July. More than 35 participants gathered under very hot and sultry conditions. The conference opened with a workshop on research methods for molten salts and ionic liquids supported by the European Office of Aerospace Research and Development, Air Force Office of Scientific Research, United States Air Force Research Laboratory (www.london.af.mil). THE MSDG is extremely grateful for this support. The sponsorship enabled the workshop to be professionally recorded and it is hoped to make DVDs available to MSDG members later this year.

The workshop, which covered six topics, was complemented by 12 oral and 6 poster presentations. On Wednesday afternoon the participants paid a most enjoyable visit to Duxford Air Museum. This was followed by the conference banquet which concluded with the MSDG after dinner invited lecture. This year's speaker was Audrey Matthews from De Montfort University who gave a highly entertaining and informative description of the science of chocolate.

Workshop - Research Methods for Molten Salts and Ionic Liquids

Ionic liquids in chemicals synthesis

Tom Welton (Imperial College)

When using ionic liquids as solvents for chemical syntheses it is essential to work with ionic liquids that have high purity. Ionic liquids have very low vapour pressures and therefore cannot easily be purified by distillation. It is usual to purify ionic liquids by repeated recrystallisation before they are of sufficient purity for chemical synthesis. Fortunately, the colour of an ionic liquid is an extremely good indicator of the purity. When considering the replacement of conventional solvents with ionic liquids in industrial processes it is essential to ensure that the new approach has an economic benefit. Introductions of ionic liquids into industry, such as the BASF BASIL process, have only been successful when the processes have been both commercially and environmentally sustainable.

Spectroscopy

Trevor Griffiths (Redston Trevor Consulting Ltd)

The spectroscopy of materials at high temperatures present many practical difficulties, especially in the design of furnaces. Careful design & construction are essential to ensure temperature uniformity over the region of the optical ports which give access to the sample. The selection of materials for optical cells is another key factor, while fused silica is suitable for many molten salts it cannot be used for fluoride-containing mixtures. Sample preparation, handling and loading of sample cells have to be carried out under an inert atmosphere. This requires not only the right equipment but also training and practice, problems with static charge are often difficult to overcome unless the tricks of the trade have been assimilated. Sealing optical cells made from fused silica is a highly skilled operation and it often best left to a glassblower. The introduction of high quality fibre optics has had a major impact on high temperature spectroscopic studies, large distances from the sample cell to the spectrometer can now readily be tolerated. Small portable fibre optic spectrometers, such as those supplied by Ocean Optics, have effectively replaced the original bulky spectrometers

Environment, health and safety

Stuart Mucklejohn (Ceravision Limited)

An overview of health & safety regulations in the UK was followed by an introduction to some recently introduced EU directives which will have an impact on small on small companies wishing to produce and sell ionic liquids. The need to measure physical properties of ionic liquids was emphasised as these values are essential for inclusion in material safety datasheets. The importance of providing reliable information for potential customers and the public and avoiding 'greenwashing' were illustrated.

Calorimetry

Andy Watson (University of Leeds)

Calorimetry is the main experimental technique used for the determination of thermodynamic properties of materials. From the techniques that have been developed the following were used as examples that will be useful for studying ionic liquids. Iso-peribol calorimetry – The temperature change during a reaction is measured as a function of time, and with a suitable calibration, the heat effect can be determined. Isothermal calorimetry – no temperature change is measured but the heat effect is realised by the melting of ice in the calorimeter jacket. By measuring the amount of water produced, the amount of heat released can be determined. Adiabatic calorimetry – implies no loss of heat to the surroundings. In this example, this is simulated by varying the temperature of the surrounding vessel to match that of the temperature within the calorimeter itself. Used in the determination of heats of formation. Heat-flow calorimeters – heat changes are realised as an EMF generated in a thermopile between the calorimeter and surroundings owing to the Seebeck effect. A more sensitive version of this is the twin micro or Tian-Calvet calorimeter. Modifications to this have included automated sample delivery systems and gas-stirring for solution calorimetry. Used extensively for the determination of heats of formation and mixing of liquids. Differential Scanning Calorimetry (DSC) – used mainly for the determination of transformation temperatures and heat capacity measurements.

Electrochemistry

Carsten Schwandt (University of Cambridge)

Electrochemistry in molten salts on an industrial scale is used to produce Al and Mg. Further industrial applications are likely to emerge in the next few years such as the production of Ti from TiO₂ by the FFC-Cambridge process and the preparation of nano-materials. Molten salts have mobile anions and cations and have very high dielectric constants. After defining the fundamental quantities the presentation reviewed the commonly used electrochemical measurement techniques: chronoamperometry; cyclic voltammetry; impedance spectroscopy. Laboratory methods require high temperatures, inert atmospheres and refractory materials. Practical considerations were shown by displaying some equipment from the presenter's laboratory. The use of electrochemical studies to elucidate reaction pathways was illustrated by the presenter's work on the intermediates found in the electro-deoxidation of TiO₂ to Ti.

Thermodynamic data and modelling

Hugh Davies (National Physical Laboratory)

Despite having a reputation for being a difficult subject, thermodynamic calculations can now be carried out using a variety of commercially available software following a relatively short introduction and appropriate training. The need for reliable thermodynamic data was emphasised and an introduction to critical assessment provided. The modelling of interactions in binary systems was used to illustrate how binary phase diagrams are calculated. The behaviour of multicomponent systems are derived from a combination of the corresponding binary interactions.

Further details including free evaluation software downloads are available at www.npl.co.uk.mtdata and www.mtdata-software.com.

Papers

Titanium electrowinning from molten salts using a consumable oxycarbide anode

Ana Maria Martinez (Invited speaker)

The search for an alternative method to the Kroll process for the production of titanium sponge has been going on for more than 40 years. Research and development has been directed towards developing a continuous process to obtain high purity and low cost Ti powder or ingots for metallurgical applications. Several high temperature electrolytic processes in molten salts have been proposed, to date none of these have gone beyond pilot plant status. Recent studies at SINTEF involve a two stage process: carbothermal reduction of TiO₂ enriched titania slag to form titanium oxycarbide powder and electrolysis in a molten salt using a titanium oxycarbide consumable anode. Electrochemical studies show the stability of the various Ti species in the chosen electrolyte are crucial to the understanding of the dissolution mechanism of the anode and to optimise anode and cathode voltages during electrolysis.

Measurement of acidity/basicity in ionic liquids

Andrew Doherty, Eunan Marley, Rachid Barhdadi & Michel Troupel

Proton transfer frequently accompanies electron transfer during homogeneous redox reactions and during heterogeneous electron transfer at electrodes. Important examples for proton transfer are fuel cell, hydrogenation and the oxidation of alcohols. Since acidity or basicity of solutes influences the outcome of such reactions, estimation of dissociation (pK_a) is important. The acid/base strength of solutes is strongly related to the nature of the supporting media (e.g. dielectric constant, hydrogen bonding ability). A Pt/Pt-H₂ electrode for use in ionic liquids has been designed and constructed. The electrode was used to make [Bmpy][NTf₂] and [Bmim][NTf₂] and the values compared to those in acetonitrile. While strong acids behave as strong acids in the ionic liquids, bases were less basic in the ionic liquids than in acetonitrile. Further work is needed to interpret fully the results.

Pyrolysis of biomass in FLiNaK

Heidi Nygård & E.Olsen

Molten salt pyrolysis of biomass is a concept based on dispersion of biomass particles in a molten salt bath in the absence of oxygen. The inorganic salts used in the process have very high heat capacities and good thermal stability at high temperatures, qualities that promote flash pyrolysis which gives high yields of bio-oil. The catalytic properties of the salts are also thought to give rise to simpler product mixes compared to other pyrolysis methods. In addition, molten salts will retain noxious contaminants making it possible to use contaminated biomass as feedstock. The first set of experiments with rape seed and wood pellets proved successful with a 30% yield of bio oil. Future investigations will examine the effect of varying the temperature, changing the flow gas, using different molten salt systems and developing a continuous feeding system. The presentation was followed by a lively question and answer session.

Raman spectroscopy of niobium(V) in basic and acidic pyrrolidinium based ionic liquids

Olga Babushkina

The $x(\text{Pyr}_{14}\text{Cl}) - (1-x)\text{NbCl}_5$ system has been shown by Raman spectroscopy to contain a mixture of octahedral Nb species, NbCl_6^- (Nb(V)) and Nb_6^{2-} (Nb(IV)). At 20°C the balance is 75% Nb(V) plus 25% Nb(IV). At 70°C the corresponding values are 30% Nb(V) and 70% Nb(IV) over the composition range $x=0.85$ to 0.20. For mixtures of NbCl_5 in ionic liquids the form of the Nb species depends not only on temperature but also on the acidity/basicity of the ionic liquid. For electrochemical studies, such as the electrodeposition of Nb, the electrochemical window changes with the composition of the ionic liquid in the mixture.

3-layer electrorefining of silicon in a CaF₂-based electrolyte at 1723 K

Espen Olsen & S.Rolseth

There is a growing demand for solar grade silicon, purity 99.9999% (6N). Aluminium has been purified to 6N by 3-layer electrorefining (the Hoopes process) since the 1950's. This work investigated the suitability of 3-layer electrorefining for silicon. The laboratory scale reactor used a molten salt electrolyte of $\text{CaF}_2\text{-BaF}_2$, the upper layer being purified Si and the lowest layer Si/Cu. The cell was operated at 1450°C, current of ~40 A and a cell voltage of 1.5 to 2.0 V. The current efficiency was ~97%. Elements more electronegative than Si tended to accumulate in the electrolyte whereas elements less electronegative were retained in the Si/Cu alloy. Purified Si was collected at the top of the cell. The content of most transition metals and phosphorus was ~1 ppm by weight in the purified Si, Al and Cu contents were ~100 ppm. Boron was found not to be subject to this electrochemical purification. The key to success is the density differences of the 3 layers.

Materials chemistry in the UK

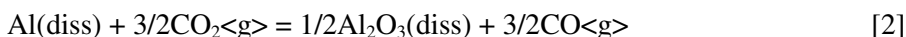
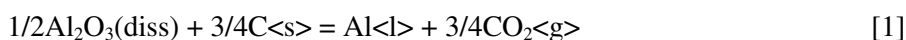
Andy Watson

After outlining the origins of the Materials Chemistry Committee (MCC) of the Institute of Materials, Minerals & Mining (IoM3), the role of the committee as the UK's representative to the Alloy Phase Diagram International Commission (APDIC) was detailed. A review of the experimental facilities for measuring thermodynamic properties in the UK has shown a disturbing decline, this has been accompanied by a loss of expertise. These changes are mirrored throughout most of Europe. However, it is clear that physicochemical properties of many ionic liquids will be needed in the near future if they are going to be used in industrial processes and this might lead to a resurgence in this field. The MCC chairman extended an invitation to ionic liquid researchers to join the committee.

Current efficiency measurements during aluminium deposition from cryolite-alumina melts

Geir Martin Haaberg, J.P.Armoo, H.Gudbrandsen, E.Skybakmoen, A.Solheim & T.E.Jentoftsen

Modern Hall-Heroult cells for the production of aluminium from alumina can operate with current efficiencies as high as 96%, even a small increase on this value would represent a significant cost saving to the industry. The corresponding energy consumption is ~14 kWh/kg Al in cells running at ~3000 kA. The annual production of primary aluminium was about 38 million tonnes in 2007. The back reaction [2] which takes place near the cathode surface is mainly responsible for the loss in current efficiency. The rate of reduction is controlled by the diffusion of dissolved Al through the diffusion layer, hence concentration of dissolved Al at the cathode - electrolyte interface and the diffusion layer thickness are important factors in the loss of current efficiency.



The impact of cathodic current density, electrolyte composition and phosphorus additions on the current efficiency were examined in a constant current electrolysis laboratory scale cell. The current efficiency was found to increase slightly with increasing cathodic current density. Increasing concentration of AlF_3 in the electrolyte gave higher current efficiency. Phosphorus additions, as expected, significantly reduced the current efficiency.

Quantitative X-ray synchrotron analysis of the FFC Cambridge Process

Rohit Bhagat, D.Dye, S.Raghunathan, D.Inman & R.Dashwood

The reduction sequence of TiO_2 to Ti in the electro-deoxidation process in molten CaCl_2 , the FFC-Cambridge process, has been the subject of much investigation and debate since the process was invented. To date most studies have been *ex-situ* but recently the opportunity to carry out *in-situ* studies with white beam synchrotron X-ray diffraction became available (in Grenoble). Using this technique, phases present during reduction could be identified with ~100 nm spatial resolution. TiO_2 becomes sub-stoichiometric very early in reduction facilitating the ionic conduction of oxygen ions, CaTiO_3 persists to nearly the end of the process and CaO forms just before the completion of the process. Another set of experiments are due to be conducted in late summer 2010.

Preparation of Nb-10Hf-1Ti alloy via the FFC-Cambridge process

Amr Abdelkader

The alloy Nb-10Hf-1Ti has important applications in the aerospace and nuclear industries. It is difficult and expensive to prepare by the traditional route of mixing, melting and re-melting the metals. This alloy, however, is an ideal candidate for preparation from the mixed oxides by the FFC-Cambridge process. The oxides have to be carefully treated by mixing and milling, carbon is added to the mixture to increase porosity. Several phases have been identified during the reduction including $\text{Ca}_2\text{Nb}_2\text{O}_7$, CaNb_2O_6 , $\text{Ca}_3\text{Nb}_2\text{O}_{8-x}$ and CaHfO_3 . After 4 h some metallic phases are formed, after 8 h Nb/Ti alloy phases can be identified. After 24 h reduction was complete with the ternary alloy being the only phase present.

Silicon surface texturing by electro-deoxidation of a thin silica layer in a molten salt

Eimutis Juzeliunas, A.Cox & D.J.Fray

Silicon with improved surface properties is urgently needed in many semiconductor and solar energy devices. A new method of silicon surface texturing has been developed which is based on thin silica layer electrochemical reduction in molten salts. A thermal silica layer grown on p-type silicon was potentiostatically reduced in molten CaCl_2 at 850°C. X-ray diffraction measurements confirmed the conversion of the amorphous silica layer into crystalline silicon. This new approach shows much promise for photovoltaic applications, for instance for the production of anti-reflection coatings in silicon solar cells.

Unique solvation behaviour of salts in ionic liquids

Matthew Liu, L.Crowhurst, J.Hallett & T.Welton

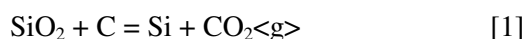
Kosower's Z scale, which is based on the charge transfer complex 1-ethyl-4-(methoxycarbonyl)pyridinium iodide, is used as a solvent polarity scale. The absorbance of the charge transfer band of the complex is a measure of the number of contact ion pairs in solution. Previous work at Imperial College has shown that ionic solutes do not associate in ionic liquids while it is well known that equilibria of free ions, ion pairs and

higher aggregates exist in molecular solvents. The behaviour of 1-ethyl-4-(methoxycarbonyl)pyridinium iodide dissolved in ionic and molecular solvents was studied using UV-visible spectroscopy and mathematical modelling. A double equilibrium model was required to represent ion association in molecular solvents. Ionic liquids formed ideal mixtures with the solute at low concentrations. The results showed that the charge transfer complex does not form any ion pairs in ionic liquids. These solutions have a non-discriminating ionic lattice structure. In molecular solvents, solvent separated ion pairs and contact ion pairs were formed.

Application of the SnO₂ inert anode for electrolysis of solid SiO₂ in CaCl₂-based molten salts

Han Wang & G.Z.Chen

The production of silicon by the carbothermic reduction of SiO₂ at 1700 - 1900°C generated approximately 17 million tonnes of CO₂ in 2009 from a global production of 5.4 million tonnes. There have been several reports of the preparation of silicon powders from the electro-deoxidation of SiO₂ in molten salts at 500 - 850°C. These studies used carbon anodes which results in the release of CO₂, with the net reaction [1].



With an inert, non-consumable anode, silicon can be produced without CO₂ emission from the electrochemical cell, [2]. However, this requires a higher voltage and the energy requirement to produce silicon is higher than with the carbon anode. Tin(IV) oxide, SnO₂, is a promising candidate for inert anodes and extensive studies have been carried out to compare corrosion, dissolution, electrical resistivity and actual performance in SiO₂ electro-deoxidation (CaCl₂-LiCl at 700°C) with SnO₂ and carbon anodes. The SnO₂ anode (fabricated from Stannex) had low electrical resistance and good dimensional stability. Some dissolution of the anode did occur and this increased at higher temperatures. The calculated energies for producing 1 kg of silicon from electro-deoxidation of SiO₂ with carbon or SnO₂ anodes are 13.0 kWh and 21.3 kWh respectively.

Posters (Summaries reproduced from the authors' abstracts)

Proton effects in the electrochemical behaviour of functionalised quinones in ionic liquids

Laura Diaconu & Andrew Doherty

The redox chemistry of quinones is important in a variety of applications which span from enzyme electrochemistry, redox catalysis through to bulk industrial processes. It is well known that their electrochemistry is pH-sensitive where, under protic conditions, quinone reduction results in the 2-electron/2-proton reduction to the hydroquinone form; whereas, under aprotic conditions, reduction occurs via two consecutive one-electron processes leading to the radical anion and di-anion, respectively. Since certain room temperature ionic liquids (RTILs) are effectively aprotic, these have become popular media for fundamental and applied electrochemical investigations where reactive intermediates are electrogenerated. Since the redox chemistry of quinones is of both fundamental and applied importance, the introduction of quinone functionality into RTILs' structure and their use as catalytic reaction media requires investigation. This communication showed the proton effects in the electrochemistry of anthra- and naphtha- quinone-functionalised RTILs in a molecular solvent (acetonitrile) and in the aprotic ionic liquid 1-butyl-1-methylpyrrolidinium bistriflimide ([Bmpy][NTf₂]). The electrochemistry of these quinone-functionalise redox active ionic liquids was also presented.

Tin oxide as anode in molten salts

Eirin Kvalheim, Geir Martin Haarberg & Ana Maria Martinez

During the last decades several processes for producing metals from reduction of metal oxides in molten chlorides have been proposed, such as the FFC process, production of various alloys and reprocessing of nuclear fuels. The two most commonly proposed chloride electrolytes are CaCl₂-NaCl and LiCl-KCl mixtures, while metal oxides are either added directly to the electrolyte or used as a pellet at the cathode. Common for these processes are the dissolution of oxide ions to the electrolyte and the oxidation of the oxide ions at the anode. The traditional anode material for electrowinning of metals from metal oxides in molten salts has been carbon, causing CO/CO₂ gas to be evolved. This is an environmental problem due to CO₂

being a greenhouse gas, and also consumes a lot of time and resources since the anodes has to be changed frequently. This is a major challenge in the production of primary aluminium metal and in other proposed molten salt electrolysis processes where a metal oxide is used as raw material. The aluminium industry has made an extensive research to find a suitable material for an oxygen evolving inert anode. Among the materials that have been tested are metals, ceramics and a mixture of metals and ceramics: cermets. Stainless steel based materials, SnO₂ and nickel ferrite-based materials seem to be the most promising ones. This work presented some results obtained when using tin(IV) oxide based materials in the molten eutectic LiCl-KCl mixture. With the development of several new processes for the production of metals from chloride melts, it is interesting to map the behaviour of the materials in this specific electrolyte. Commercial tin oxide from Dyson Industries Ltd was bought as 10 x 10 x 10 cm³ pieces and machined into 3 cm long rods with a diameter of 5 mm. Three different qualities; Stannex D, ELR and E, were tested. Cyclic voltammetry and electrolysis experiments were performed with the Stannex anodes. The electrolyte was the eutectic LiCl-KCl (59.5-40.5 mol %) with small additions of Li₂O (0-1.5 mol %). According to the literature, the solubility of Li₂O in the eutectic LiCl-KCl at 773 K is around 1.1 mol %. Cyclic voltammetry was performed at tungsten (W), glassy carbon (GC) and Stannex electrodes. In oxide free melt, the voltammograms showed evolution of chlorine gas at 1.0 V versus the Ag⁺/Ag reference electrode. At W and GC no preceding reactions could be seen, while at the Stannex electrodes a small peak could be seen at 0.35 V. When Li₂O was added, an additional peak appeared at potentials less anodic than chlorine gas evolution. This might be related to oxygen gas evolution. More thorough investigation of the anode reaction is necessary. 5 hour electrolysis was also carried out in the eutectic LiCl-KCl at 723 K, and the Stannex anodes showed a good performance. Further work will be done to examine the anode reactions in both LiCl-KCl and CaCl₂-NaCl electrolytes. Long time electrolysis will also be carried out.

The electro-carboxylation of benzophenone and 4-cyanophenone in Bmpy NTf₂

Eunan Marley & Andrew Doherty

The carboxylation of aromatic ketones has been subject of much interest in past, being an important step in the production of anti-inflammatory agents. The electro-carboxylation of compounds such as benzophenone has been studied in aprotic conventional solvents such as DMF. The additional aromatic group has been found to improve yield relative to compounds such as acetophenone, while the use of a sacrificial metal anode was found to further improve yield. The electro-carboxylation was found to involve a two-electron reduction process, with the carboxylation usually occurring at the carbon atom of the carbonyl group. In this communication, the electro-carboxylation of benzophenone, and its derivative 4-cyanobenzophenone, were investigated in the aprotic ionic liquid 1-butyl-1-methylpyrrolidinium bistriflimide ([Bmpy][NTf₂]), to confirm that reaction proceed as expected in the solvent. It was shown that the reactions proceed according to an ECE or DISP1 mechanism, which agrees with previously proposed mechanisms in conventional solvents.

Molecular dynamics simulation of the interface between the ionic liquid hydroxyethylimidazolium tetrafluoroborate and a glass surface

Karina Shimizu, A.A.H.Padua, L.P.N.Rebello & J.N.A.Canongia Lopes

It has been reported in different molecular simulation studies that ionic liquids exhibit medium-range ordering, that is, ionic liquids are micro-segregated media, composed of flexible polar networks permeated by non-polar domains. The so-called double dual nature of ionic liquids has also been demonstrated by different research studies carried out by the group at ITQB. In the present work, the interface between the ionic liquid hydroxy-ethylimidazolium tetrafluoroborate and a rigid glass surface was studied: we have investigated how a glass surface changes the nano-structure and charge distribution of the ionic liquids. Molecular Dynamics simulations were carried out for three different glasses and the same ionic liquid ([C₂OHmim][BF₄]). The glasses were silica, BK7 (a boro-silicate glass) and alumina. Figure 1 below depicts a snapshot of a simulation box containing 400 ion pairs of the ionic liquid and a silica glass. The results show that the ionic liquids position themselves according to the electric field of the glass. This means that the electric field of the ionic liquid near to glass surface is opposite to that of the electric field of the glass. Furthermore, at distances larger than 100 nm from the glass we have observed that the orienting effects induced by glass in the ionic liquid become negligible, i.e., at those distances the structure of the ionic liquid is similar to that of a bulk ionic liquid phase. However, charge fluctuations within the ionic liquid persist for longer distances.

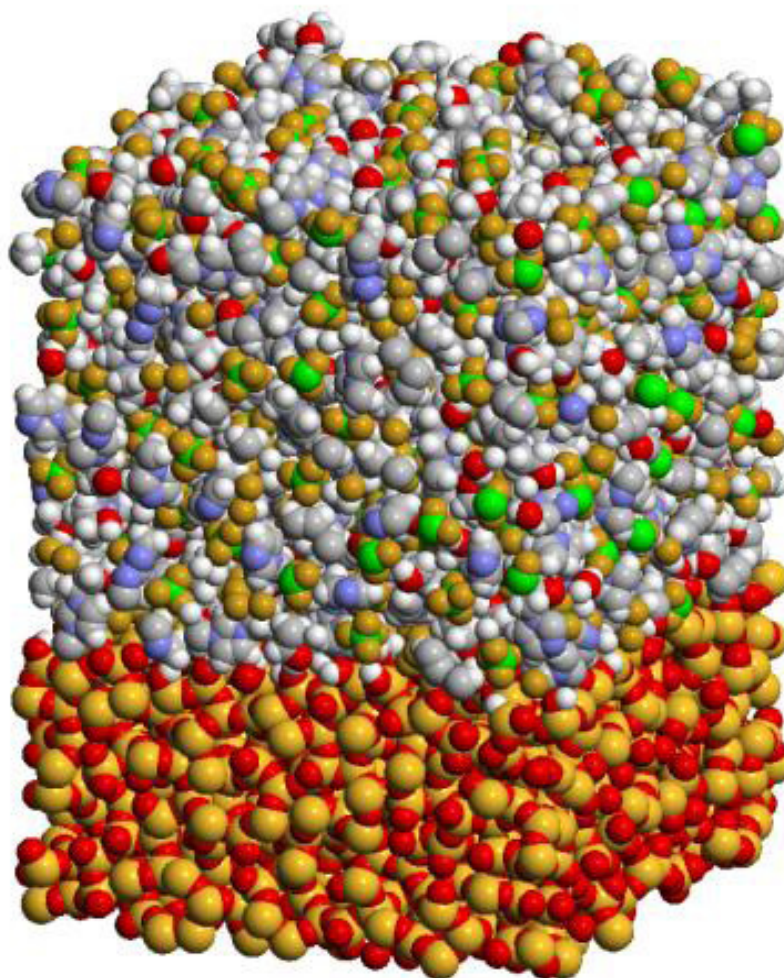


Figure 1.

Depolarized gas anodes for electrowinning of aluminium in cryolites

Saijun Xiao, T.Mokkelbost, O.Paulsen, G.M.Haarberg, A.P.Ratvik & H.Zhug

Consumable carbon anodes made from petroleum coke are used in the electrowinning of aluminium from dissolved Al_2O_3 with the release of the greenhouse gas CO_2 . Carbon anodes are also used in the FFC-Cambridge process, in which pure metal is produced by the direct reduction of solid metal oxides attached to the cathode. Dissolved oxide ions will be oxidized at the anode. Inert anodes of metals, ceramics or cermets have been suggested as they reduce CO_2 emissions significantly. However, inert oxygen evolving anodes require a higher anode potential than carbon, resulting in higher demand for expensive electrical power. An alternative approach is to substitute the consumable carbon anode with an oxidizable gas anode (e.g. H_2 and CH_4), resulting in a decrease in CO_2 emissions and, theoretically, the same requirement of electrical power as that for carbon anodes, while at the same time avoiding the periodic replacement of the carbon anode. The use of gas anodes has been reported in laboratory studies of electrolytic production of aluminium, using a porous carbon anode depolarized with CH_4 , H_2 and CO ; however, Stender found that CH_4 gas blocked the porous graphite anode. A magnetite anode was also tested with CO , which was not found to be oxidizable under the conditions used. When porous carbon was used as the gas anode, carbon oxidation competes with CH_4 oxidation, so, in principle, a porous non-oxidizable anode material such as SnO_2 and NiFe_2O_4 is to be preferred. Molten CaCl_2 - NaCl electrolytes containing dissolved Ag_2O was chosen as a surrogate for tests in the very corrosive cryolite electrolytes for aluminium electrolysis. Initial studies by the authors have shown that the cell voltage was decreased by 0.3 V and 0.5 V, when using Pt gas anode and porous SnO_2 -based material, respectively, with the introduction of H_2 in molten CaCl_2 - NaCl (70-30 mol %) containing CaO and AgCl at 953 K during constant current electrolysis. In this contribution the depolarization of Pt gas anode and porous SnO_2 -based anode was investigated with the introduction of H_2 and CH_4 in cryolite electrolytes for electrolytic production of aluminium.

Voltammetry of dynamic three-phase interlines: A case study on solid-state electro-reduction of SiO₂ to Si in molten CaCl₂

Wei Xiao, X.Jin, Y.Deng, D.Wang & G.Z.Chen

Solid state electro-reduction of SiO₂ to Si in molten CaCl₂ is being widely researched as a new silicon extraction process because of the importance of silicon solar cells. This poster presented the authors' recent study of the fundamental aspects of this new process by cyclic voltammetry using a silica sheathed tungsten disc (W-SiO₂) electrode in molten CaCl₂ at 900°C. The results (cyclic voltammograms) exhibited unusually increasing reduction current with decreasing the potential scan rate. When the cathodic limit was less negative than -1.00 V (vs. quartz sealed Ag/AgCl reference electrode), the reduction current was also smaller in the forward (negative) potential scan than that in the reversed (positive) scan. However, at a given reduction charge, the reduction current increased with the scan rate, following approximately a logarithmic law. These unique features have been elaborated according to the dynamic conductor (silicon) / insulator (silica) / electrolyte (molten salt) three phase interlines (3PIs) model. These novel findings should help the development of a direct electrolytic process for the clean, efficient and inexpensive production of high purity silicon.

Before Derek Fray closed the meeting George Chen invited members to join the 'Molten Salts' group in MyRSC as part of the Royal Society of Chemistry's website (you do not have to be a RSC member in order to join). See: <http://my.rsc.org/groups>. Once you are there, search for "molten" and you will see the MSDG page. You need to be a member of MyRSC to see this page. To join MyRSC, the webpage link is as follows. <http://my.rsc.org/home>.

Forthcoming conferences

2nd Asia Pacific conference on ionic liquids & green processes

07 - 10 September 2010, Dalian, China

See: <http://www.apcil.org/>

Discussion meeting on thermodynamics of alloys (TOFA 2010)

12 - 16 September 2010, Porto, Portugal

See: <http://www.fe.up.pt/~tofa2010/>

2nd International round table on titanium production in molten salts

19 - 22 September 2010, Tromsø - Trondheim, Norway

See: <http://www.registration.no/titanium.htm>

Nuclear materials 2010

04 to 07 October 2010, ZKM Karlsruhe, Germany

See: <http://www.nuclearmaterials2010.com/>

218th meeting of The Electrochemical Society - 17th International symposium on molten salts & ionic liquids

10 - 15 October 2010, Las Vegas, Nevada, USA

See: <http://www.electrochem.org>

22nd International CODATA conference

Scientific information for society: Scientific data & sustainable development

24 - 27 October 2010, Cape Town, South Africa

See: <http://www.codata2010.com>

MSDG Christmas Meeting

13 December 2010, Hatfield, London, UK

See: website to be announced

The 3rd Asian Conference on Molten Salts and Ionic Liquids
6 - 10 January 2011, Harbin, Heilongjiang, China
See: <http://acmsil.hrbeu.edu.cn/>

Molten salt technology, MS9
12 - 16 June 2011, Trondheim, Norway
See: <http://www.registration.no/ms9/index.html>

EUROMAT 2011 -- C51: Sustainable Processes in Ionic Liquids and Molten Salts for Materials
12 - 15 September 2011, Montpellier, France
See: <http://euromat2011.fems.eu/programme/topics-symposia/introductions/c51>

Fray International Symposium
27 Nov - 01 Dec 2011, Cancun, Mexico
www.flogen.com/FraySymposium.

Ninth International Conference on Molten Slags, Fluxes and Salts (MOLTEN12)
27 - 30 May 2012, Beijing, China
See: <http://hy.csm.org.cn/MOLTEN12/en/>

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, 15 Aug 2010; Revised 20 Aug 2010; 03 Sep 2010
News_0910.doc