

Molten Salt Discussion Group

2013 Christmas Research Meeting

Final Programme & Abstracts

16th December 2013
Burlington House, London

Authors' Abstracts

Abstracts presented on the following pages are compiled by the MSDG for distribution amongst attendees of the 2013 MSDG Christmas Research Meeting and are based on the submitted versions from the authors who are responsible for issues related to the scientific correctness and copyright. This booklet is also available at the MSDG's website.

MSDG Christmas Meeting 2013 Final Programme

08:30 Registration and poster-set-up

08:55 Welcome and Introduction from Professor Andrew Abbott

09:00 Invited Lecture

The Simple Molten Salt Reactor – Safe, cheap nuclear energy at last?

Ian Scott

Somerset House, Strand, London, WC2R 1LA

Contact E-mail: ian.scott@the-weinberg-foundation.org

09:40 Technical Sessions 1 Chair Professor Geir Martin Harberg

09:40 **Recent Developments in Metalysis Metal Powder Production and its Associated Processing**

Lucy Grainger, Ian Mellor, Kartik Rao, Greg Doughty

Metalysis Ltd.

10:05 **Can Ionic Liquids Provide an Alternative Pathway to Processing Lignocellulosic Materials to Biofuels?**

R. J. Gammons^{1,2}, J. M. Slattery¹, S. Shimuzu¹, N. C. Bruce² & S. J. McQueen-Mason²

¹Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK

²CNAP, Department of Biology, University of York, Heslington, York, YO10 5DD, UK

Contact E-mail: rjg501@york.ac.uk.

10:30 Morning coffee and Poster Session No. 1

11:00 Technical Sessions 2 Chair Professor George Chen

11:00 **Thermoelectric cells with molten carbonate electrolytes**

Geir Martin Harberg¹, Signe Kjelstrup², Marit Takla² and Xue Kang²

¹ Department of Materials Science and Engineering, Norwegian University of Science and Technology, NO-7491Trondheim, Norway

² Department of Chemistry, Norwegian University of Science and Technology, NO-7491Trondheim, Norway Contact E-mail: geir.martin.haarberg@ntnu.no

11:25 **A Fluidised Cathode Process for the Direct Electrochemical Reduction of Tungsten Oxide in a Molten LiCl-KCl Eutectic**

Rema Abdulaziz, L.D.Brown, D.Inman, S. Simons, P.R.Shearing & D.J.L.Brett

¹ Electrochemical Innovation Lab, Department of Chemical Engineering, University College London, Torrington Place, London, WC1E 7JE, United Kingdom. Contact E-mail: d.brett@ucl.ac.uk

11:50 **Uranium electroplating in molten lithium chloride-potassium chloride eutectic**

Leon D.Brown, R.Abdulaziz, S.Simons D.Inman, D.J.L.Bret, P.R.Shearing

Electrochemical Innovation Laboratory, Dept. Chemical Engineering, UCL, London, WC1E 7JE.

Contact E-mail: d.brett@ucl.ac.uk

12:15 **Chromium electrodeposition using a novel type IV deep eutectic solvent**

Azeez A. Al-Barzinjy^{1,2}, Andrew. P. Abbott¹ & Karl S. Ryder¹

¹ Department of Chemistry, University of Leicester, Leicester, LE1 7RH, UK

²Department of Physics, College of Education, University of Salahaddin, Hawler, Iraq

Contact E-mail: aa643@le.ac.uk

- 12:40 **What is at the outer ionic liquid/gas surface? A LEIS study**
Ignacio J. Villar-Garcia¹, Sarah Fearn¹, Gilbert De Gregorio², Nur Liyana Ismail², Alastair J. S. McIntosh², Kevin R. J. Lovelock²
¹ Department of Materials, Imperial College London. ² Department of Chemistry, Imperial College London. kevin.lovelock@imperial.ac.uk
- 13:05 Lunch, & Poster Session No. 2
- 14:00 Annual General Meeting of the MSDG.
- 14:30 Technical Session No. 3 Chair Dr Trevor Griffiths
- 14:30 **Funding a feasibility study for a pilot scale MSR**
Jasper Tomlinson and Trevor Griffiths
- 14:55 **Extraction of CO₂ from diluted flue gases – a new application for molten salts**
Espen Olsen¹, V. Tomkute¹ and A. Solheim²
¹Dep. Mathematical Sciences and Technology, Norwegian University of Life Sciences, Drøbakveien 31, N-1432 Ås, Norway, ²SINTEF Materials and Chemistry, Sem Sælands vei 2a, N-7439 Trondheim, Norway
espen.olsen@umb.no
- 15:20 **Probing the Complex Structure of Ionic Liquids using MD Simulations**
K. Shimizu^{1,2}, C. E. S. Bernardes¹, José N. Canongia Lopes^{1,2}
¹Centro de Química Estrutural, Instituto Superior Técnico, 1049 001 Lisboa, Portugal
²Instituto de Tecnologia Química e Biológica, Universidade Nova de Lisboa, 2780 901 Oeiras, Portugal
Contact E-mail: jnlopes@ist.utl.pt
- 15:45 Afternoon tea and Poster Session No. 3
- 16:15 Technical Session No. 4 Chair Dr Robert Watson
- 16:15 **Flue Gas Cleaning by Ionic Liquids**
Peter Thomassen, Andreas J. Kunov-Kruse, Susanne, L. Mossin, Helene Kolding, Søren Kegnæs, Anders Riisager, Rolf W. Berg and Rasmus Fehrmann
Centre for Catalysis and Sustainable Chemistry, Department of Chemistry, Technical University of Denmark Building 207, Kemitorvet, DK-2800 Kgs. Lyngby, Denmark
- 16:40 **50 Years ago in America: my time in Oak Ridge**
Trevor R. Griffiths
- 17:15 Wine and Cheese Reception
- 18:00 Close of Meeting.

LECTURES

The Simple Molten Salt Reactor – Safe, cheap nuclear energy at last?

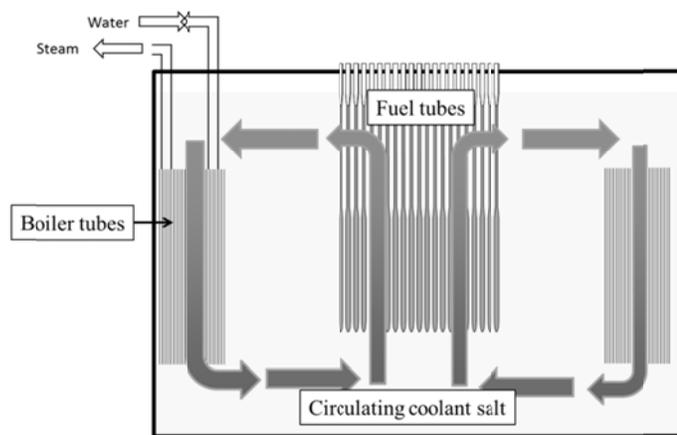
Ian R. Scott M.A., Ph.D.¹

¹ *Weinberg Foundation, Somerset House, Strand, London, WC2R 1LA*
Contact E-mail: ian.scott@the-weinberg-foundation.org

Nuclear energy has become prohibitively expensive. It is now clear that the cost of creating new nuclear power generation capacity, for all its security of supply and environmental advantages, will come at the cost of increased electricity prices for the consumer and industry. Molten salt nuclear reactors have been discussed for decades and have many advantages over current water moderated and cooled reactors. It has rarely been credibly suggested however that they would have a significant cost advantage. This is because the innate engineering complexity of high temperature, corrosive molten salts being pumped around complex plumbing would carry a large capital cost.

The Simple Molten Salt Reactor (Simple MSR) seeks to overcome this problem and has the potential to reduce the cost of nuclear power to the point where it is competitive with the cheapest fossil fuel power sources.

At the heart of the reactor is a very simple concept, that the molten fissile fuel salt should not be pumped but instead be contained in simple static fuel tubes immersed in a large pool of a second, coolant, molten salt. Conventional thinking has been that the low thermal conductivity of molten salts ($\sim 1\text{W/m}^{\circ}\text{K}$) made it essential to pump the molten salt fast enough to create turbulent flow in the heat exchangers. However we have established that natural convection in suitably shaped fuel tubes can allow sufficient convective heat transfer for realistic power density levels to be achieved.



The result is a reactor design which is “walk away” passively safe, with fission products and fissile fuel in chemically stable and non-volatile forms so airborne release of radioactivity cannot occur even after catastrophic failure of every containment system. The absence of pumps, valves, heat exchangers, reprocessing loops, helium sparging, emergency drain tanks and other expensive components of conventional molten salt reactor designs makes it likely that capital costs for the reactor would radically lower than for convention nuclear plants.

The result is a reactor design which is “walk away” passively safe, with fission products and fissile fuel in chemically stable and non-volatile forms so airborne release of radioactivity cannot occur even after catastrophic failure of every containment system. The absence of pumps, valves, heat exchangers, reprocessing loops, helium sparging, emergency drain tanks and other expensive components of conventional molten salt reactor designs makes it likely that capital costs for the reactor would radically lower than for convention nuclear plants.

Molten salt thermo-hydraulics, chemistry and corrosion are central to our attempt to establish the viability of the reactor concept and the input of this expert molten salt community in challenging and perhaps helping to examine these aspects is earnestly sought.

Recent Developments in Metalysis Metal Powder Production and its Associated Processing

Lucy Grainger, Ian Mellor, Kartik Rao, Greg Doughty

Part of Metalysis's focus over recent years has been on the development of both its Tantalum and Titanium powder products, in conjunction with exploring potential applications for these. A combination of both traditional and newer alternative powder metallurgy techniques have been investigated, in relation to the downstream processing of Metalysis products.

The presentation will discuss the progress that has been made both in terms of the production and subsequent consolidation of Titanium and Tantalum metal powders at Metalysis over that last 12 months.

Can Ionic Liquids Provide an Alternative Pathway to Processing Lignocellulosic Materials to Biofuels?

R. J. Gammons^{1,2}, J. M. Slattery¹, S. Shimuzu¹, N. C. Bruce² & S. J. McQueen-Mason²

¹Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK

²CNAP, Department of Biology, University of York, Heslington, York, YO10 5DD, UK

Contact E-mail: rjg501@york.ac.uk (for contact author only)

Research into the use of ionic liquids as 'green solvents' is becoming ever more important. Current literature has shown the application of certain ionic liquids, based on the imidazolium cation in particular, to be suitable for solubilising lignocellulosic material.^[1,2] These natural polymers are very useful as green feedstocks and using ionic liquids as solvents to pre-treat lignocellulosic material could prove very valuable for the biofuel industry and could also provide added value chemicals from a renewable source.^[3,4] We are interested in developing a better understanding of the dissolution and processing of plant biomass in ionic liquids. Our work so far has been focussed on the use of both aprotic and protic ionic liquids for the dissolution and processing of a variety of different plant biomass. Experimental investigations into the nature of ionic liquid effects on the lignocellulosic material is underway, using techniques including powder XRD and electron microscopy. Detailed work using enzyme hydrolysis to explore the amount of sugars released after ionic liquid pre-processing shows some very promising initial results. An attempt to use high throughput robots to screen and optimise current processes is also ongoing.

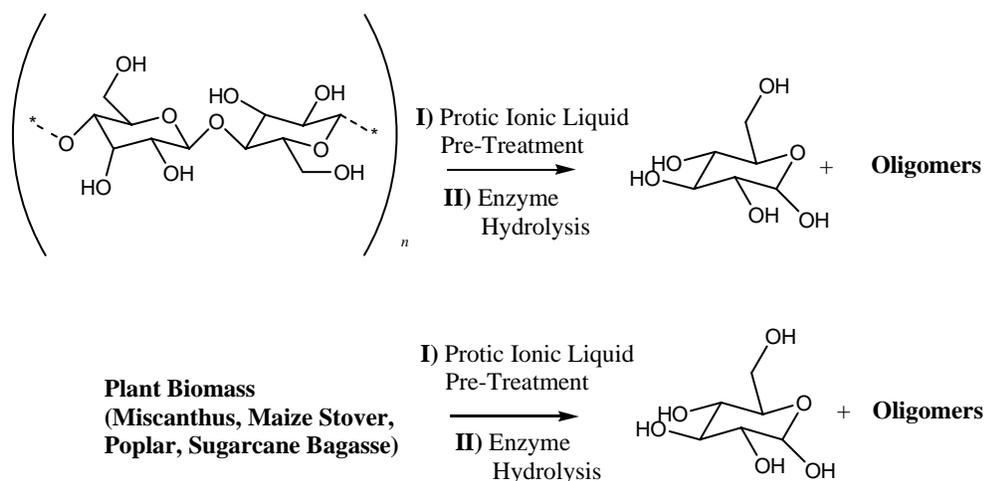


Figure 1: Scheme of cellulose/biomass to potential products

References

1. N. Sun, H. Rodriguez, M. Rahman, R. D. Rogers, (2011), *Chem. Comm.*, **47**, 1405-1421
2. R. P. Swatloski, S. K. Spear, J. D. Holbrey, R. D. Rogers, *JACS*, 2002, **124**, 4974-4975
3. S. Zhu, Y. Wu, Q. Chen, Z. Yu, *Green Chem*, 2006, **8**, 325-327
4. J. Vitz, T. Erdmenger, C. Haensch, U. S. Schubert, (2009), *Green Chem.*, **11**, 417-424

Thermoelectric cells with molten carbonate electrolytes

Geir Martin Harberg¹, Signe Kjelstrup², Marit Takla² and Xue Kang²

¹ *Department of Materials Science and Engineering, Norwegian University of Science and Technology, NO-7491Trondheim, Norway*

² *Department of Chemistry, Norwegian University of Science and Technology, NO-7491Trondheim, Norway*
Contact E-mail: geir.martin.haarberg@ntnu.no

Thermoelectric energy converters are units that directly convert a heat flux into electricity and may therefore be used for recovery of waste heat. State-of-the art thermoelectric convertors are currently using semiconductors. The technology is well known, but under development. It is likely that the technology based on semiconductors has an upper limit for power production, as the type of charge carriers is limited to electrons or positive holes.

By replacing semiconductors with electrochemical cells, it may be possible to increase the power production and conversion efficiency. The power production depends on the temperature difference and the thermoelectric power (the Seebeck coefficient), which is related to the entropy change of the electrode reactions. A challenge will be to establish an electrochemical cell with two electrodes at different temperatures in a real industrial environment.

Preliminary experiments were carried out in molten $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$ at temperatures from 550 - 850 °C. Reversible electrodes with respect to carbonate ions were established by using mixtures of O_2 and CO_2 . Solid MgO particles were added to the molten electrolyte in order to improve the conditions for obtaining reliable electrode potential measurements. Two identical electrodes were located at different temperatures for determining Seebeck coefficients based on potential measurements. Seebeck coefficients of the order of 1 mV/K were obtained.

A Fluidised Cathode Process for the Direct Electrochemical Reduction of Tungsten Oxide in a Molten LiCl-KCl Eutectic

R. Abdulaziz¹, L.D.Brown¹, D.Inman¹, S. Simons¹, P.R.Shearing¹ & D.J.L.Brett¹

¹ Electrochemical Innovation Lab, Department of Chemical Engineering, University College London, Torrington Place, London, WC1E 7JE, United Kingdom
Contact E-mail: d.brett@ucl.ac.uk

The direct electrochemical reduction of metal oxides has been evinced by the FFC Cambridge [1] process. Subsequently, it has been applied to a number of refractory metals and their alloys. The ‘fluidised cathode’ process is a new technique to perform electrochemical reductions on metal oxides. Its dynamic nature could eliminate some of the issues associated with the FFC Cambridge process, and increase the efficiency of metal productions via the electrochemical route.

The fluidised cathode process employs metal oxide particles as the cathode. These particles are suspended in the salt electrolyte and agitated via a suitable method (e.g. stirring, gas bubbling). They are reduced when they come into contact with a metal current collector. To avoid the reoxidation of the reduced metal particles, the anode is separated in its own compartment, which allows for the flow of electrolyte but not for the metal particles to reach the counter electrode. Figure 1 (a) is a schematic of the fluidised cathode process.

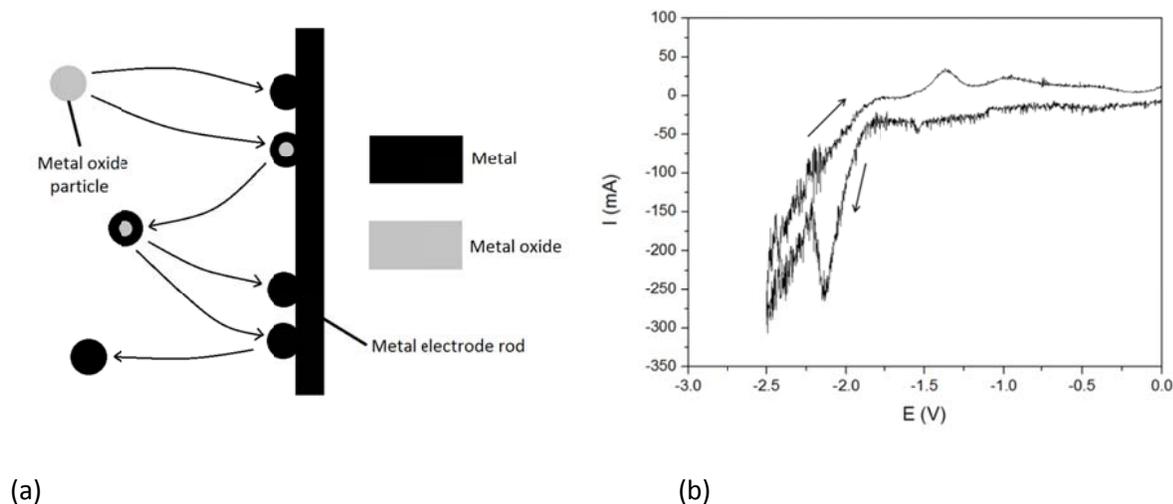


Fig.1: (a) Schematic of a fluidised cathode process in molten salt; (b) cyclic voltammogram of WO_3 fluidised cathode in LiCl-KCl eutectic at 450 °C, scan rate: 50 mV s^{-1} , reference electrode: Ag/Ag^+ .

To illustrate the process, WO_3 particles were reduced to W in a LiCl-KCl eutectic, however the process is applicable to the range of metals’ and molten salts’ systems. A chronoamperogram of the reduction of WO_3 fluidised cathode is presented in Figure 1 (b).

References

[1] G.Z.Chen, D.J.Fray & T.W.Farthing, *Nature*, **407**, p.361-364 (2000).

Uranium electroplating in molten lithium chloride-potassium chloride eutectic

Leon D. Brown^a, R. Abdulaziz^a, S. Simons^a, D. Inman^a, D. J. L. Brett^a, P. R. Shearing^a

^aElectrochemical Innovation Laboratory, Dept. Chemical Engineering, UCL, London, WC1E 7JE

Abstract

Nuclear reprocessing is vital to close the nuclear fuel cycle; current reprocessing techniques such as the PUREX process operate using a liquid-liquid extraction process and produce weapons grade product streams. In order to help maintain a proliferation resistant reprocessing strategy, molten salt electroreduction and electrorefining can be adopted instead of liquid-liquid extraction processes. In this work, the authors have studied the electrochemical plating of uranium onto grade 316 stainless steel. Previous studies have highlighted the dendritic nature of electrochemically plated uranium deposits [1-3]. However, the authors have adopted a pulse technique that led to smooth, adherent films of chromium on stainless steel [4]. Lead chloride is added to the lithium chloride-potassium chloride eutectic melt; lead is displaced by metallic uranium once the latter is introduced into the melt. This provides the electrolyte with sufficient U^{3+} ions to allow for a sufficiently high limiting current to maintain primary electrodeposition. The electrode potentials have also been compared with previously published data [5]. Lastly, the films have been characterised both chemically and structurally using energy dispersive x-ray spectroscopy and scanning electron microscopy respectively. In future, these films will be used as precursor materials for molten salt electroreduction experiments.

References

- [1] D. Inman, G. J. Hills, L. Young, J. O'M. Bockris, Electrode reactions in molten salts: the uranium + uranium trichloride system, *Trans. Faraday Soc.*, 1959, 55, 1904-1914.
- [2] T. Koyama, M. Iizuka, Y. Shoji, R. Fujita, H. Tanaka, T. Kobayashi, M. Tokiwai, An Experimental Study of Molten Salt Electrorefining of Uranium Using Solid Iron Cathode and Liquid Cadmium Cathode for Development of Pyrometallurgical Reprocessing, *Journal of Nuclear Science and Technology*, 34 (1997) 384-393.
- [3] J.J. Laidler, Pyrochemical recovery of actinides, in, Argonne National Lab., Declassified Report, IL (United States), 1993.
- [4] T. Vargas, D. Inman, Controlled Nucleation and Growth in Chromium Electroplating from Molten LiCl-KCl, *Journal of Applied Electrochemistry*, 17 (1987) 270-282.
- [5] D. Inman, J.O.M. Bockris, The reversible electrode potential of the system U/UCl_3 in molten chloride solvents, *Canadian Journal of Chemistry*, 39 (1961) 1161-1163.

Chromium electrodeposition using a novel type IV deep eutectic solvent

Azeez A. Al-Barzinjy^{1,2}, Andrew. P. Abbott¹ & Karl S. Ryder¹

¹ *Department of Chemistry, University of Leicester, Leicester, LE1 7RH, UK*

² *Department of Physics, College of Education, University of Salahaddin, Hawler, Iraq*

Contact E-mail: aa643@le.ac.uk

Chromium plays an important role in a number of fields of modern industries, for example as a protective material in automotive and planes as well as for decorative purposes. A novel Deep Eutectic Solvent (DES) can be formed between $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and urea (Fig. 1). A eutectic was formed from variety compositions, and the phase diagram behaviour of the system was studied. It has been well recognised that, in general, DES suffer from low fluidities and low conductivities which has restricted their use as an electrolyte for electrodeposition process, especially for large scale applications. The physical properties of these systems have been characterised and it was noted that their viscosities were lower and the conductivities were found to be larger than for other reported DES systems.^{1,2} Generally it was shown that these liquids are simple to synthesize and they help to avoid the use of Cr(VI) and its compounds, which are toxic and classified as carcinogenic.³ These systems are excellent candidates for electrochemical applications, such as hard chrome electrodeposition, as determined by EDAX and hardness testing.



Fig 1: The new DES and its

two solid components.

References

[1] A. P. Abbott, J. C. Barron, K. S. Ryder and D. Wilson, *Chem. Eur. J.* 2007, 13, 6495-6501.

[2] A. P. Abbott, G. Capper, D. L. Davies and R. K. Rasheed, *Chem. Eur. J.*, 2004, 10, 3769-3774.

[3] C. T. J. Low, R. G. A. Wills and F. C. Walsh, *Surface and Coatings Technology*, 2006, 201, 371-383.

What is at the outer ionic liquid/gas surface? A LEIS study

Ignacio J. Villar-Garcia¹, Sarah Fearn¹, Gilbert De Gregorio², Nur Liyana Ismail², Alastair J. S. McIntosh², Kevin R. J. Lovelock²

¹ Department of Materials, Imperial College London. ² Department of Chemistry, Imperial College London. kevin.lovelock@imperial.ac.uk

Traditionally, liquid surface structure has been probed indirectly using surface tension. Generally, element specific, model independent techniques require ultrahigh vacuum (UHV) conditions, which lead to evaporation of most liquids. Ionic liquids have sufficiently low vapour pressures at room temperature that they can be studied under UHV conditions (system pressure $<10^{-9}$ mbar).^{1,2} The ionic liquid/gas surface underpins applications such as gas storage, gas separation, nanoparticle synthesis and supported ionic liquid phase catalysis.³ For all of these applications, one needs to know which elements of the ionic liquid-based system are located at the outer surface. Low energy ion scattering (LEIS) is one of the most surface

sensitive techniques available for studying surfaces. We have used LEIS to identify the elements present at the outer ionic liquid/gas surface of a wide range of ionic liquids; systematically varying both the cation and the anion charged headgroups, and also their alkyl chain lengths (where feasible). Most surprisingly, we have found that the nitrogen atoms on the imidazolium ring are not “visible” at the outer surface; in addition, the nitrogen atom in the nitrogen-containing anion $[\text{Tf}_2\text{N}]^-$ is also not observed at the outer

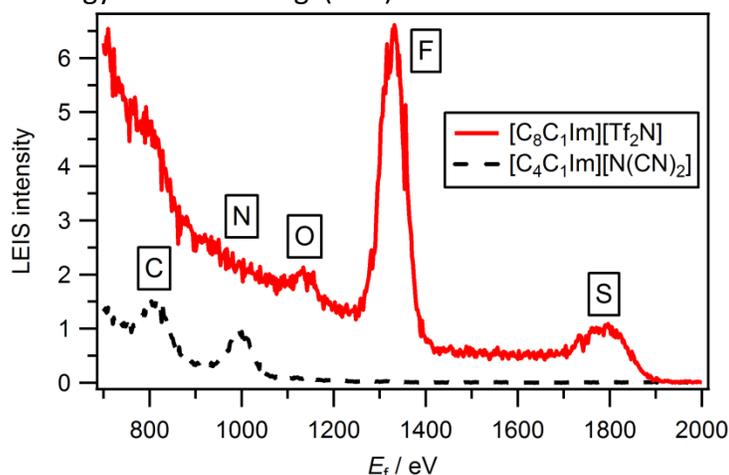


Figure 1. Low energy ion scattering (LEIS) spectra for $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ and $[\text{C}_4\text{C}_1\text{Im}][\text{N}(\text{CN})_2]$, recorded using He^+ at 3 keV, detected at a scattering angle of 145° .

surface (Figure 1). However, for both $[\text{N}(\text{CN})_2]^-$ and $[\text{SCN}]^-$ -containing ionic liquids, nitrogen is clearly observed at the outer surface (Figure 1). In addition, we have also used LEIS to study the orientation of a variety of anions at the ionic liquid/gas surface.

1. K. R. J. Lovelock, *et al.*, *Chem. Rev.*, 2010, **110**, 5158-5190.
2. K. R. J. Lovelock, *et al.*, in *Ionic Liquids UnCOILed: Critical Expert Overviews*, eds. K. R. Seddon and N. V. Plechkova, Wiley, 2012, pp. 251-282.
3. K. R. J. Lovelock, *Phys. Chem. Chem. Phys.*, 2012, **14**, 5071-5089.

Funding a feasibility study for a pilot scale MSR

Jasper Tomlinson

185 New Kent Rd SE1 4AG

(44) 207 357 9457 / 07785551068

Abstract:

This presentation describes the steps that have led up to an opportunity for a micro-enterprise, Energy Process Developments Ltd, to set up in the UK in order to undertake a feasibility study for a pilot-scale nuclear molten salt reactor. The task essentially is to choose between various options best suited to demonstrating - for the public, for decision makers, and for all interested parties - a working pilot-scale reactor. This reactor can subsequently be scaled up to an industrial proto-type that will lead the way to a new industry-standard reactor for nuclear power. The ultimate fuel of choice will be thorium, both for its radio-chemical advantages, and for its long-term sustainability.

Extraction of CO₂ from diluted flue gases – a new application for molten salts

E. Olsen¹, V. Tomkute¹ and A. Solheim²

¹Dep. Mathematical Sciences and Technology, Norwegian University of Life Sciences, Drøbakveien 31, N-1432 Ås, Norway

²SINTEF Materials and Chemistry, Sem Sælands vei 2a, N-7439 Trondheim, Norway

espen.olsen@umb.no

Capture and storage of anthropogenically emitted fossil carbon has been identified as a key technology to avoid damaging, irreversible heating of the earth beyond 2°C. Currently available 1. Generation systems based on absorption by diluted amine solutions are associated with costs too high to reach widespread impact. 2. Generation systems based on high temperature solid state Ca- or carbonate looping (Eq. 1) are being extensively studied due to the potential for lower energy consumption and overall lower costs. We have developed a method where the active substances are present as (partially) dissolved in molten halide salts¹. This enables fast gas-liquid interaction with rapid kinetics between the CO₂ in the gas to be cleaned and the active, absorbing substances. Very high absorption efficiency and excellent cyclability has been achieved in a laboratory scale reactor with a N₂ based simulated flue gas with CO₂ content from 1 – 20 vol%. The method shows promise for extracting CO₂ from a wide range of gas mixtures. By employing NaF in the molten salt, the content of CO₂ in the gas after absorption can be reduced to levels below 100ppm.

(1)

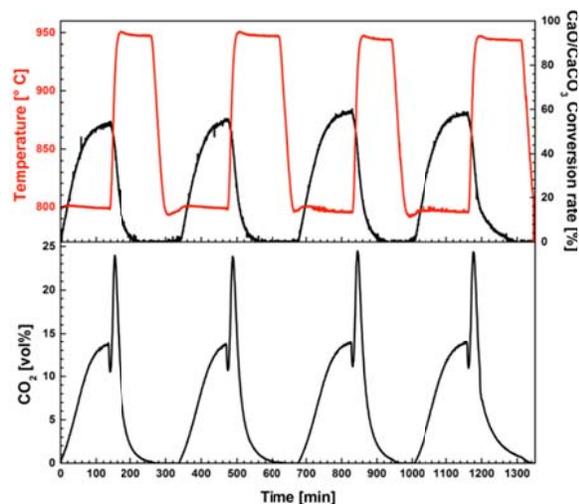


Figure 1: Absorption and release of CO₂ from 14wt% CO₂+N₂ in CaCl₂ containing 5wt% CaO. The top panel showing the temperature during thermal cycling and the conversion rate. The bottom panel showing the content of CO₂ in the gas emitted¹.

¹ E. Olsen, V. Tomkute, "Carbon Capture in Molten Salts", Energy Science and Engineering, 1, 3, 144-150. DOI: 10.1002/ese3.24

Probing the Complex Structure of Ionic Liquids using MD Simulations

K. Shimizu^{1,2}, C. E. S. Bernardes¹, J. N. Canongia Lopes^{1,2}

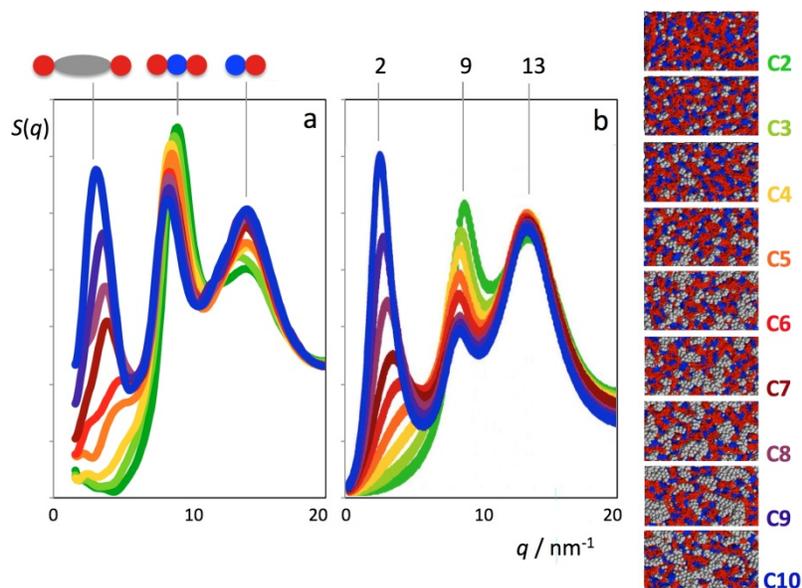
¹Centro de Química Estrutural, Instituto Superior Técnico, 1049 001 Lisboa, Portugal

²Instituto de Tecnologia Química e Biológica, Universidade Nova de Lisboa, 2780 901 Oeiras, Portugal

Contact E-mail: jnlopes@ist.utl.pt

Ionic liquids (ILs) are fluids characterized by an intricate interplay between electrostatic, van der Waals and hydrogen-bond interactions. Such a balance hinders the formation of long-range crystalline structures around room temperature but nevertheless imposes a sort of mesoscopic ordering in the fluid phase. As such, ILs are recognized as nano-segregated fluids, composed of a polar network that is permeated by more or less extensive non-polar domains. This feature of ILs has major consequences for their macroscopic properties, namely, their solvation towards different types of molecular compounds.

In this contribution we will show several examples of such interplay and illustrate the enormous variety of structural effects that can emerge when the nature of the ionic liquids or of their mixtures with molecular compounds is changed. We will explore the meso-structures that can be found in ionic liquids ranging from the original “red-and-green” representations, the interactions of ionic liquids with molecular species or solid substrates (ILs as charge templates), the influence of the ubiquitous alkyl side chains (per-fluorinated, functionalized, symmetrical) in the morphology of the resulting structures, or even the complex relationship between the charged parts of the ions that lead to polar networks with distinct structural features.



References

- [1] K. Shimizu, M.F. Costa Gomes, A.A.H. Pádua, L.P.N. Rebelo & J.N. Canongia Lopes, *Journal of Molecular Structure: TheoChem*, **946**, p.70-76 (2010).
- [2] K. Shimizu, A. Pensado, P. Malfreyt, A.A.H. Pádua & J.N. Canongia Lopes, *Faraday Discussions*, **154**, p.155–169 (2012).

Flue Gas Cleaning by Ionic Liquids

Peter Thomassen, Andreas J. Kunov-Kruse, Susanne, L. Mossin, Helene Kolding, Søren Kegnæs, Anders Riisager, Rolf W. Berg and Rasmus Fehrmann

Centre for Catalysis and Sustainable Chemistry, Department of Chemistry, Technical University of Denmark, Building 207, Kemitorvet, DK-2800 Kgs. Lyngby, Denmark

Introduction

Emission of acidic gases such as NO_x , SO_x and CO_x from, e.g. energy production by fossil fuels in power plants, ships and other industrial sources is a major concern in relation to atmospheric pollution and climate changes. Therefore, these gases have to be effectively removed from flue gases. Presently this is mainly achieved by relatively energy intensive and resource demanding technologies via selective catalytic reduction (SCR) of NO_x with ammonia, by gypsum formation after SO_2 wet-scrubbing while organic amines are being used as absorbents in CO_2 scrubbers. This leads to concern about, e.g. intensive energy requirements for desorption, corrosion of steel pipes and pumps, CO_2 absorption capacity and thermal decomposition of the amine. In this work, we demonstrate how ionic liquids (ILs) can be tuned by design to perform as selective, high-capacity absorbents of environmentally problematic flue gases like, e.g. SO_2 , NO , NO_2 and CO_2 .

Results and Discussion

Reversible absorption has been obtained for several different ILs at different temperatures and flue gas compositions. Furthermore, different porous, high surface area carriers like meso-porous silica and titania have been applied as supports for the ionic liquids to obtain Supported Ionic Liquid-Phase (SILP) absorber materials, Figure 1.

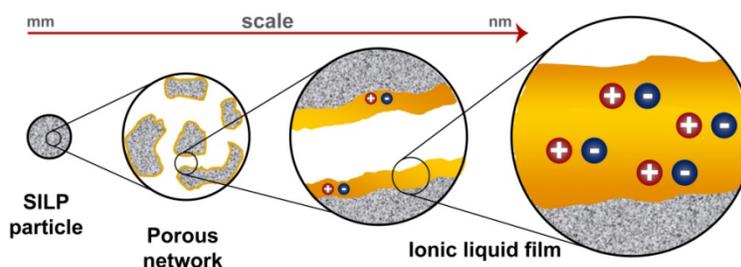


Figure 1. Principle of SILP materials.

These materials benefit from low mass transport resistance of the often highly viscous ionic liquids by the distribution of the liquid as a thin film (or small droplets) on the high surface highly porous carrier material which enable fast absorption/desorption rates of the particular gas exposed to the SILP absorber.

The results show that CO_2 , NO , NO_2 and SO_2 can be reversibly and selectively absorbed using different ILs, and SILP absorbers are promising materials for industrial flue gas cleaning. Absorption/desorption dynamics can be tuned by temperature, pressure, gas concentrations and the properties of the porous carrier.

The mechanism of absorption seems to be remarkably different depending on the gas and the type of ionic liquid chosen for the absorption process. Thus CO_2 seems to be absorbed by our applied amino acid based ionic liquids in the form of covalent bonded carbamate species stabilized by internal hydrogen bonding. SO_2 is absorbed by strong coordination to Lewis basic anions like chloride in our selected ionic liquid, while NO is transformed by a catalytic process assisted by strong Lewis bases, present in the ionic liquid, to nitric acid (Figure 2) eventually changing the ionic liquid anion to nitrate by evaporation of the protonated original anion of the selected ionic liquid.

In addition physical absorption of the gases contributes more or less to the total absorption capacity of the ILs where the chemically-like absorption mechanisms described above, however, seem to dominate.

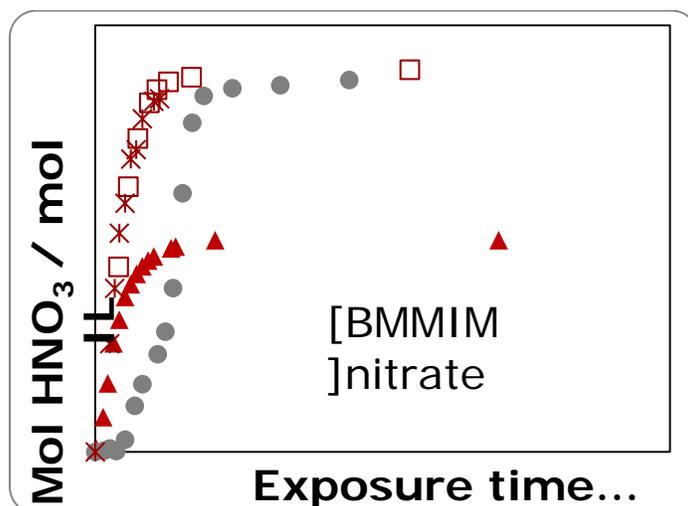


Figure 2. NO absorption capacity at room temperature given as produced HNO_3 in various ionic liquids vs. time. (Gas composition: 7% NO , 2% H_2O , 7% O_2 , balance N_2).

Significance

The absorption/desorption process may be performed by shaping the SILP absorber material in honey comb structures as the traditional SCR de NO_x catalyst used in power plants today, leading to optimized gas diffusion and low pressure drop of the passing flue gas. Installed as a traditional rotating heat exchanger it will facilitate desorption by elevation of the

temperature in a smaller side channel and make it possible to desorb the gases in concentrated form. In the case of CO₂ this gas may be disposed by pumping it to underground exhausted gas or oil pockets while SO₂ might be further processed to commercial grade sulfuric acid in the traditional catalytic oxidation process forming SO₃ by oxidation with air. Finally, NO is already converted to nitric acid of commercial grade by the absorption process and the acid may therefore be desorbed by heating and condensed easily again and stored for further handling e.g. via unloading by ships in a convenient harbor.

References

S.B. Rasmussen, J. Huang, A. Riisager, H. Hamma, J. Rogez, J. Winnick, P. Wasserscheid, R. Fehrmann, *ECS Trans.* **2007**, 3, 49-59.

J. Huang, A. Riisager, R.W. Berg, R. Fehrmann, *J. Mol. Catal. A: Chem.* **2008**, 279, 170-176.

A. Riisager, A.J. Kunov-Kruse, S. Mossin, R. Fehrmann, Absorption and Oxidation of NO in Ionic Liquids, WO2013079597.

R. Fehrmann, A. Riisager, Enhanced deNO_x by combination of IL preoxidation catalyst and downstream SCR catalyst, Patent pending 2013.

S. Mossin, P. Thomassen, A.T. Madsen, A. Riisager, R. Fehrmann, Combined oxidation and absorption of NO_x by an ionic liquid tandem process, Patent pending 2013.

50 Years ago in America: my time in Oak Ridge

Trevor R Griffiths

In the summer of 1962 I arrived in Tennessee to take up my first post-doctoral appointment for a year at the Oak Ridge National Lab, returning for the summer of 1968. They had a lot of equipment “firsts” including their design of a spectrophotometer capable of measuring the spectra of molten salts $>1000^{\circ}\text{C}$ and ORACLE (Oak Ridge Automatic and Computing Engine), an early computer that used valves, (ECC93), and Algol 60. Programs were being developed such as a floating point feature to handle decimal points in calculations.

Many of the molten salt “greats” were there, Max Bredig, Pedro Smith, Jack Young, etc., probably around a hundred molten salt chemists. Publications and regular reports output was continuous.

The thorium molten fluoride reactor was being completed and operated and there was great hope for its adoption as a smaller version of the water-cooled ones.

Cameras were not allowed in ORNL and some corridors were guarded by security with guns to keep “aliens” out. Thus this film, originally recorded on Standard Eight film, now slightly faded, includes scenes of a flight over the Oak Ridge lab and the surrounding area, and what can be done evenings and weekends, after our daily 7.30 to 5pm stint, plus scenes of the Tennessee area and the delights of a week’s holiday in Florida. Some ORNL literature of the time will be on display afterwards.

POSTERS

Stiction, stick-slip and quantized friction across ionic liquid thin films

Alexander M. Smith¹, Kevin R. J. Lovelock², Nitya Nand Gosvami³, Tom Welton², and Susan Perkin¹

¹Department of Chemistry, University of Oxford, UK

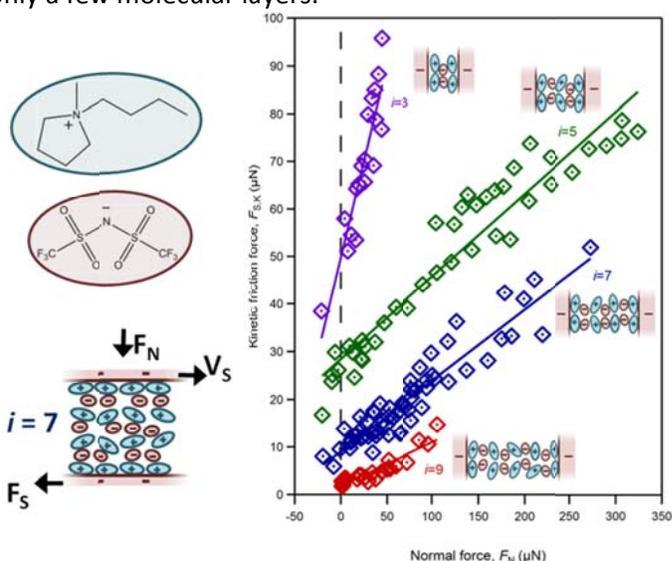
²Department of Chemistry, Imperial College London, UK

³Department of Mechanical Engineering and Applied Mechanics, University of Pennsylvania, USA

Contact E-mail: alexander.smith@chem.ox.ac.uk

Ionic liquids combine remarkable physical properties and as a result are attracting great interest as precision lubricants. Ionic liquids form intricate layered structures at surfaces due to a delicate interplay between electrostatic, van der Waals and solvophobic interactions [1,2], yet despite their burgeoning interest it is not clear how this nanostructure relates to their lubrication properties.

Using a Surface Force Balance, we measured the friction force between atomically smooth and negatively charged mica surfaces across ionic liquid films of controlled thickness at the molecular level [3]. Here we report that the friction force is a multi-valued function of load and is quantized with respect to the number of confined ion layers; thus there is no single friction-load relationship for a particular liquid. The friction coefficients differ for each number of ion layers due to their varying cation/anion composition with distance from the surfaces. High resolution friction traces reveal stiction spikes at the onset of sliding, with shearing of the film progressing by means of stick-slip cycles for low shear velocities. These results are of direct relevance to the development of ionic liquid lubricants for specialised applications, such as their use in nano-scale devices where lubrication must be achieved in only a few molecular layers.



Friction forces between mica sheets across films of $[\text{C}_4\text{C}_1\text{Pyrr}][\text{NTf}_2]$, demonstrating the discrete or quantized nature of the friction. Inset diagrams indicate the liquid structure for each regime.

References

- [1] S. Perkin, *Phys. Chem. Chem. Phys.*, **14**, p.5052-5062 (2012).
- [2] A. M. Smith, K. R. J. Lovelock, N. N. Gosvami, P. Licence, A. Dolan, T. Welton, and S. Perkin, *J. Phys. Chem. Lett.*, **4**, p.378-382 (2013).
- [3] A. M. Smith, K. R. J. Lovelock, N. N. Gosvami, T. Welton, and S. Perkin, *Phys. Chem. Chem. Phys.*, **15**, p.15317-15320 (2013).

Nanostructural organization in protic ionic liquids probed by molecular dynamics simulations

A. A. Freitas¹, K. Shimizu¹ and J. N. Canongia Lopes¹

¹Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais 1, Lisbon, 1049-001, Portugal

Contact E-mail: adilsondefreitas@ist.utl.pt

The notion that the structure of ionic liquids (ILs) is complex and can exhibit nanoscale segregation started to be investigated almost ten years ago using molecular modeling studies.[1] Evidence relating the structure of ILs to their macroscopic properties has also been interpreted in terms of the underlying nanoscale segregation.[2] One of the central guidelines in most of these investigations has been the use of homologous series of ionic liquids — where the alkyl side chain attached to one of the ionic species is slowly increased — to explore in a systematic way the effect of the ratio between polar and non-polar ionic moieties on the IL structure. In this context, the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide series, $[C_nC1im][Ntf_2]$, has been one of the preferred choices for both experimental and theoretical studies.[3]

In this work, we have decided to extend our previous simulation studies on the nanostructuration in ILs to protic ionic liquids, namely butylammonium octanoate $[N_{4HHH}][C_7oac]$, shown in Figure 1. Computer simulations of this protic ionic liquid revealed a type of microphase separation between polar and nonpolar domains that is distinct in nature from those observed for other families of ionic liquids.

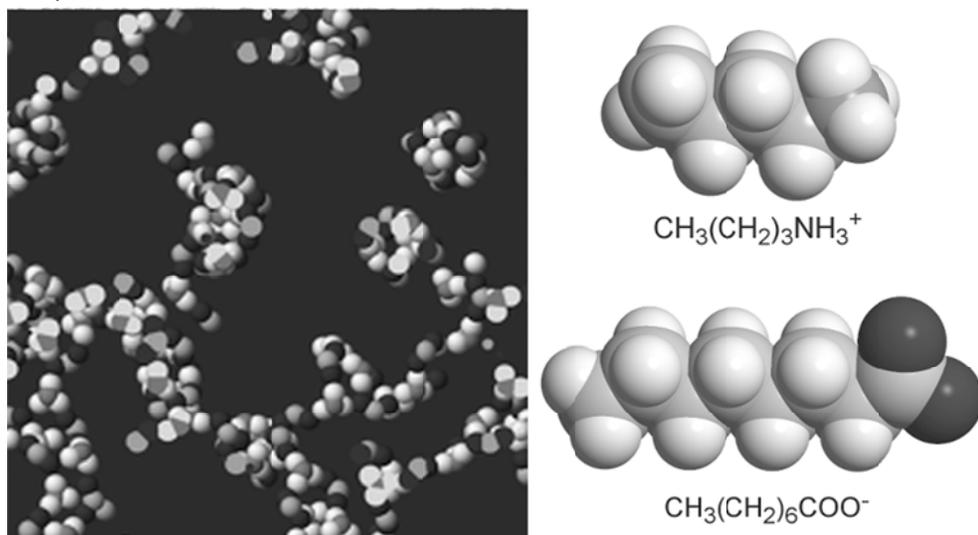


Figure 1. Snapshot of the simulation run for the ionic liquid $[N_{4HHH}][C_7oac]$, formed by $CH_3(CH_2)_3NH_3^+$ and $CH_3(CH_2)_6COO^-$ ion pairs. The non-polar domain is depicted as a continuous background and the atoms of the polar network are represented as small spheres.

References

- [1] J.N.C.Lopes, M.F.Costa Gomes & A.A.H.Pádua, *J. Phys. Chem. B*, **110**, p.16816-16818 (2006).
- [2] A.A.H.Pádua, M.F.Costa Gomes & J.N.C.Lopes, *Acc. Chem. Res.*, **40**, p.1087-1096 (2007).
- [3] K.Shimizu, A.A.H.Pádua & J.N.C.Lopes, *J. Phys. Chem. B*, **114**, p.15635-15641 (2010).

Electrochemical behaviour of ferrocene in the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate, EMIMBF₄, at 298K

M. Vega¹, E. Barrado¹, Y. Castrillejo¹, R.A.S. Couto², M.B. Quinaz² & J.L.F.C. Lima²

¹ Department of Analytical Chemistry, University of Valladolid, Campus Miguel Delibes, Paseo de Belén 7, Valladolid, 47011, Spain

² Department of Chemical Science, Laboratory of Applied Chemistry, Faculty of Pharmacy, University of Porto, Portugal

Contact E-mail: solvega@qa.uva.es

Electrochemical oxidation of ferrocene at platinum and glassy carbon electrodes in the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate, EMIMBF₄, has been studied by cyclic voltammetry (CV), convolutive potential sweep voltammetry (CPSV), chronopotentiometry (CP) and chronoamperometry (CA).

On both electrodes, the electro-oxidation of Fc to Fc⁺ takes place in a quasi-reversible electrochemical mode. The intrinsic rate constant of charge transfer, k^0 , and the charge transfer coefficient, α , have been calculated for the first time in the mentioned ionic liquid, by simulation of the cyclic voltammograms, logarithmic analysis of the convoluted curves and from the steady-state current potential curves by applying the Gauss–Newton non-linear squared method. The diffusion coefficient of Fc has been also calculated by CV, CPSV, CP and CA. ANOVA has shown that with a 95% confidence level, there are no significant differences between the diffusion coefficients obtained with both electrodes by the different techniques, being the mean value $(3.1 \pm 0.5) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$.

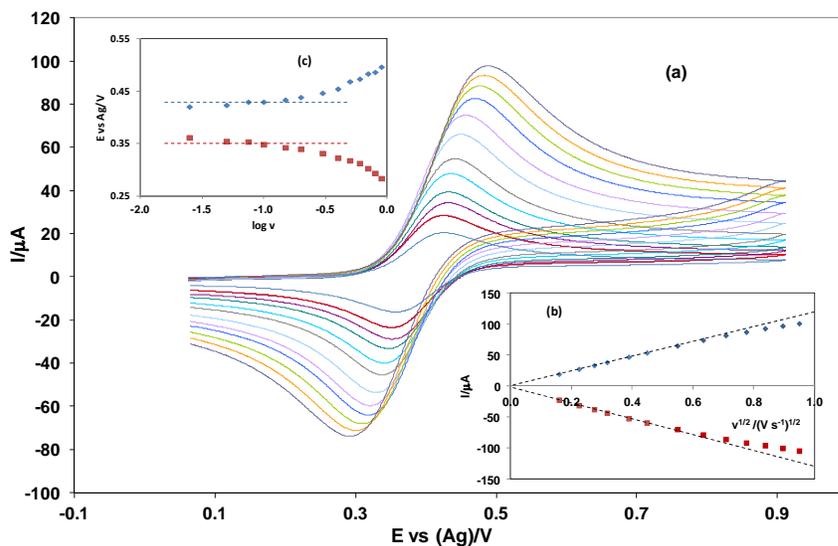


Figure 1.- (a) CVs obtained with a Fc solution on a Pt electrode ($S = 0.127 \text{ cm}^2$). Sweep rates: 25; 50; 75; 100; 150; 200; 300; 400; 500; 600; 700 and 800 mV s^{-1} . (b) Variation of the cathodic and anodic peak currents with the square root of the sweep rate. (c) Variation of the cathodic and anodic peak potentials with the logarithm of the sweep rate.

Acknowledgements. This work was supported by the Ministerio de Ciencia e Innovación (Spain) Project CTQ2010-19912.

Nano-segregation in ionic liquids: scorpions and vanishing chains

K.Shimizu^{1,2}, C.E.S.Bernardes¹, A.Triolo³ & J.N.C.Lopes^{1,2}

¹ Centro de Química Estrutural, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisbon, Portugal

² Instituto de Tecnologia Química e Biológica, Universidade Nova de Lisboa, Av. República, 2780-157 Oeiras, Portugal

³ Istituto di Struttura della Materia, Consiglio Nazionale delle Ricerche, Area della Ricerca di Tor Vergata, Via del Fosso del Cavaliere 100, I-00133 Rome, Italy

Contact E-mail: karina.shimizu@tecnico.ulisboa.pt

The present study analyses the large structural differences, first observed using X-ray diffraction [1], between 1-alkyl-3-methylimidazolium-based ionic liquids, $[C_n\text{mim}][\text{Ntf}_2]$ ($n = 3, 6, 9$), and their counterparts with ether-substituted alkyl side chains, $[(C_1OC_1)_{(n/3)}\text{mim}][\text{Ntf}_2]$ ($n = 3, 6, 9$). The MD simulations—obtained using a non-polarizable atomistic force-field to model the ionic liquids under discussion—demonstrate that the suppression of the nanostructured nature in the ionic liquids with ether chains is persistent along the entire series and it is not due to any modification of the polar network of the ionic liquid but rather due to the different morphologies of the non-polar regions that surround it [2]. The modification of the non-polar regions—shift from bulky segregated domains in $[C_n\text{mim}][\text{Ntf}_2]$ to thin enveloping ones in $[(C_1OC_1)_{(n/3)}\text{mim}][\text{Ntf}_2]$ —are caused by the inability of the oxygen-substituted alkyl side chains to pack effectively side by side, the existence of kinks along the chain that lead eventually to intra-molecular, scorpion-like interactions between the chains and the imidazolium ring, and by their stronger interactions with the cations of the polar network via the lone electron pairs of the ether oxygen atoms.

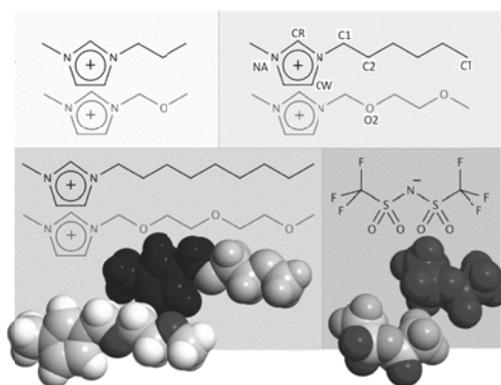


Figure 1. Structural formulas of the $[C_n\text{mim}][\text{Ntf}_2]$ and $[(C_1OC_1)_{(n/3)}\text{mim}][\text{Ntf}_2]$ ionic liquids. Spacefilled atomistic representations of a selected ion pair, $[(C_1OC_1)_2\text{mim}][\text{Ntf}_2]$, with grayscale colors (foreground) and black and gray coded (background) to highlight the polar and nonpolar parts of the ions (black=anion and imidazolium ring; gray=alkyl/alkylether chain).

References

- [1] A.Triolo, O.Russina, R.Caminiti, H.Shirota, H.Y.Lee, C.S.Santos, N.S.Murthy & E.W.Castner, *Chem. Commun.*, **48**, p.4959-4961 (2012).
- [2] K.Shimizu, C.E.S.Bernardes, A.Triolo, J.N.C.Lopes, *Phys. Chem. Chem. Phys.*, **15**, p.16256-16262 (2013).

Oxoacidity behaviour of Tb(III) and electrochemical formation of Tb-Ni alloys in the eutectic LiCl-KCl. Y.Castrillejo¹, R. Fernández¹, M. Vega¹, R. Gómez¹ & E. Barrado¹

¹Department of Analytical Chemistry, University of Valladolid, Campus Miguel Delibes, Paseo de Belén 7, Valladolid, 47011, Spain Contact E-mail: ycastril@qa.uva.es

Rare earth (RE) metals and their alloys are increasing in importance, particularly in the fields of magnetism, energy and high technology. The use of molten salts as reaction media provides a unique opportunity for the electrowinning and electrorefining of high purity RE metals, as well as for the electrochemical synthesis of their alloys. Another important issue concerning REs and molten salts is pyrochemical reprocessing of nuclear fuel. The transmutation of the more hazardous radionuclides in the nuclear waste into less hazardous or shorter lived elements would significantly reduce the volume and the required storage time for the waste, and can be done only after separation of minor actinides (Ans) from other fission products, specially lanthanides (Lns). This separation process can be carried out in molten salt media, whose properties allow high actinide content, shorter cooling times and inherent proliferation resistance.

Ans-REs separation in molten chlorides contemplates a two-step process: (i) selective extraction of Ans and (ii) extraction of (REs) for decontamination of the salt. Our studies are devoted to the acquisition of fundamental data of REs to allow the design and assessment of reprocessing processes involving: (i) electrolytic extraction using inert (e.g. W and Mo) and reactive (e.g. Cd, Bi, Ni or Al) cathodes [1] and (ii) selective dissolution/precipitation of rare earth oxides [2].

In the present work, the electrochemical formation of Tb-Ni alloys was investigated at 723K in the eutectic LiCl-KCl. On a reactive Ni electrode, the electrochemical system Tb(III)/Tb(0) was observed at less cathodic potential values that on an inert W electrode, this potential shift is caused by the decrease of Tb activity in the metal phase due to the formation of Tb-Ni intermetallic compounds. Analysis of the samples after electrolysis by X-ray diffraction and SEM with EDX, allowed the identification of different intermetallic compounds.

The identification of the Tb-O compounds that are stables in the melt as well as the determination of their solubility products were carried out by potentiometric titration using an yttria stabilised zirconia membrane electrode (YSZME). The results indicated the stability of TbOCl and Tb₂O₃. The best chlorinating conditions have been extracted from the comparison of the E - pO^{2-} diagram corresponding to the Tb-O compounds and that of some chlorinating mixtures.

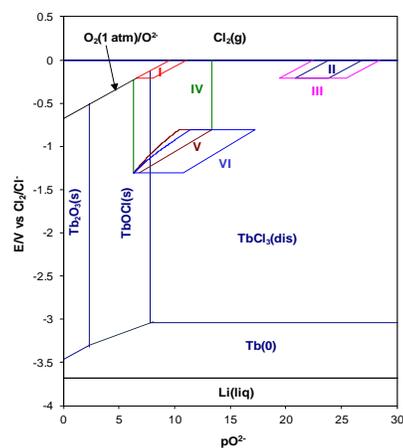


Figure 1.- E - pO^{2-} diagram of Tb-O compounds The chlorinating mixtures are; (I) Cl_2+O_2 , (II) Cl_2+C , (III) Cl_2+CO , (IV) $HCl+ H_2O$, (V) $HCl+H_2+ H_2O$, (VI) $HCl+H_2+CO$.

Acknowledgements. This work was supported by the Ministerio de Ciencia e Innovación (Spain) Project CTQ2010-19912.

References

- [1] Y. Castrillejo, R. Bermejo, A.M. Martínez, E. Barrado & P. Díaz, *J. Nucl. Mater.* **360**, p. 32-42 (2007).
- [2] Y. Castrillejo, M.R. Bermejo, E. Barrado, A.M. Martínez & P. Díaz, *J. Electroanal. Chem* **545**, p.141-157 (2003).

Seebeck coefficients of cells with molten eutectic Li/K carbonate electrolytes with MgO

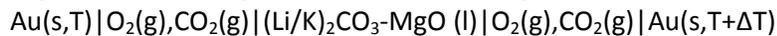
X.Kang^{1,2}, M.Takla¹, O.Burheim¹, G.M.Haarberg¹ & S.Kjelstrup^{1*}

¹ Department of Chemistry, Norwegian University of Science and Technology, Trondheim, 7034, Norway

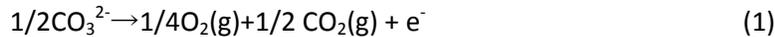
² School of Resources and Materials, Northeastern University at Qinhuangdao, Tai Shan Lu 143, Economy and Technological Development Zone, Qinhuangdao, Hebei, 066004 China

Contact E-mail: signe.kjelstrup@ntnu.no

The process industry, in particular the metallurgical one, dissipate a lot of thermal energy. Thermoelectric energy generators can be used to recover energy wasted in this manner, but these generators are hampered by low conversion efficiencies. There is therefore a large effort world-wide to improve on their performance. So far semiconductors are used as main materials in an effort to improve the figure of merit; meaning to increase the Seebeck coefficient, reduce the thermal conductivity and the electric resistivity of the device. While Seebeck coefficients for semiconductors are order of magnitude 200 $\mu\text{V}/\text{K}$, some electrochemical cells give larger values, due to contributions from the chemical reaction at the electrode. Our work is to start seeking for appropriate electrochemical systems in terms of molten salts. We report recent results using the eutectic mixture of $(\text{Li}/\text{K})_2\text{CO}_3$ with added MgO, in a cell with gas electrodes, following Jakobsen and Broers [1] as follows:



The left-hand side electrode reaction is:



The theory of irreversible thermodynamics is indispensable for a description of the conversion of thermal energy to electric energy [1-2]. We develop the relevant description elsewhere. Here we report measured Seebeck coefficients in the 500-850 $^\circ\text{C}$ range for different gas mixture. Values around 1.2 mV/K were obtained at 550 $^\circ\text{C}$ rising to 1.4 mV/K at 850 $^\circ\text{C}$, values 6 times larger than those typical for semiconductors. The variation in the Seebeck coefficient with temperature was very small. $0.635\mu\text{V}/\text{K}^2$. The variation in the value at 550 $^\circ\text{C}$ with gas composition gave the predicted theoretical slope with -0.086mV, and the experimental slope with -0.116mV.

We therefore propose that electrochemical cells with molten salts and gas electrodes are investigated as candidates for thermoelectric energy conversion.

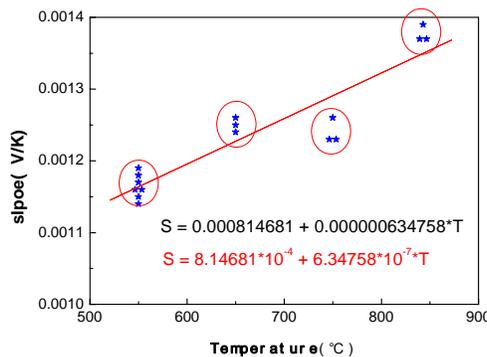


Fig.1 Seebeck coefficients of Cell I as a function of temperature

References

[1] T.Jacobsen, G.H.J.Boroers, *J. Electrochem.Soc.*, **124**, p.207-214 (1977)

[2] S. Kjelstrup, D. Bedeaux, *Non-equilibrium thermodynamics of heterogeneous systems*, World Scientific, Singapore, 2008

NOTES

