

Molten Salt Discussion Group

2013 Summer Research Meeting

&

50th Anniversary Celebration

Programme & Abstracts

9 - 11 July 2013
Fitzwilliam College, Cambridge

Programme

Tuesday 9th July

12:00 - 12:30 Arrival and Registration

12:30 – 13:50 Lunch

13:50 – 14:00 Chairman's welcome

14:00 – 15:30 Technical Session 1 (Chairperson : Dr Carsten Schwandt)

14:00 – 14:30 Shan Jin, Linpo Yu and **George Z Chen**

Department of Materials Science and Metallurgy, University of Cambridge, UK. **An electro-supramolecular study of the dielectric property of ionic liquids**

14:30 – 15:00 **Qian Xu**, Xue Kang, Shuang Li, Ximei Yang, Qiushi Song

School of Materials and Metallurgy, Northeastern University, Shenyang, 11004, China
Electrochemical Synthesis of AB₅-type RE-Ni Based Alloys via FFC Cambridge Process

15:00 – 15:30 I. Chojnacka¹, B. Salamon¹, B. Pilarek¹, L. Rycerz¹, J. Kapala¹, S. Gadzuric², W. Gong³, **M. Gaune-Escard**⁴

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Lanthanide-alkali metal halide systems: characterization, phase diagram calculation and prediction of phase diagram topology

15:30 – 16:00 Tea/coffee break

16:00 – 17:30 Technical Session 2 (Chairperson : Dr Robert Watson)

16:00 – 16:30 **S.A.Mucklejohn**¹, J.Porritt² and S.Tulej²

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Molten salts, ionic liquids, energy efficiency and the need for behaviour change

16:30 – 17:00 **M. T. Clough**,^a P. A. Hunt,^a and T. Welton^a
^a Department of Chemistry, Imperial College, London, SW7 2AZ, United Kingdom
Understanding the Decomposition of Ionic Liquids: A Combined Experimental and Theoretical Approach

17:00 – 17:30 **Doug Inman**
Visiting Professor, University College, London, and Emeritus Professor and Senior Research Fellow, Imperial College, London.
The MSDG at 50; a life story!

17:30 – 18:00 Celebration cake and tea.

19:00 – 20:30 Dinner

Wednesday 10th July

08:00 – 09:00 Breakfast (for residential attendees only)

09:30 – 11:00 Technical Session 3 (Chairperson : Professor Geir Martin Haarberg)

09:30 – 10:00 **D. Hu**, A. J. Stevenson and G. Z. Chen
Department of Chemical and Environmental Engineering, and energy and Sustainability Research Division, Faculty of Engineering, University of Nottingham, Nottingham, NG72RD, UK. Contact E-mail: George.Chen@nottingham.ac.uk
Selective Electrochemical Reduction and Anodic Dissolution of Ni from CeO₂-NiO in Molten CaCl₂ via the FFC-Cambridge Process

10:00 – 10:30 **V. Tomkute**¹, A. Solheim², E. Olsen¹
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² SINTEF Materials and Chemistry, P.O. Box 4760 Sluppen, NO-7465 Trondheim, Norway. viktorija.tomkute@umb.no
Carbon Capture by CaO in Molten Halide Salts

10:30 – 11:00 **Andrew Abbott**
Chemistry Department, University of Leicester, Leicester, LE1 7RH.
Ionic Liquids – Non-crystalline Ball Gazing

11:00 – 11:30 Tea/coffee break

11:30 – 12:15 Flash Posters Session (Chairperson : Dr Stuart Mucklejohn)

11:30 – 11:35 **Dr Igor N. Skryptun**, Iaroslav Fedorov and Sergiy Korobko
National Academy of Science, Kiev, Ukraine
The thermodynamic properties of solution metal oxides in molten alkali

11:35 – 11:40 R A Pierce ¹, T Caldwell ², T Paget ², **R Watson** ²
¹ Savannah River National Laboratory
² AWE plc, Aldermaston, Reading, UK. RG7 4PR
Carbonate oxidation and salt distillation of PuCl₃-NaCl-KCl

11:40 – 11:45 **Linpo Yu** and George Z. Chen*
Department of Chemical and Environmental Engineering, and Energy and Sustainability
Research Division, Faculty of Engineering, University of Nottingham, Nottingham NG7
2RD, UK. * Email: george.chen@nottingham.ac.uk
High Energy Capacity Supercapacitors Based on Ionic Liquids Electrolytes

11:45 – 11:50 **Happiness V. Ijije**, Ossama Al-juboori and George Z. Chen*
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Research Division, Faculty of Engineering, University of Nottingham, Nottingham NG7
2RD, UK. * Email: george.chen@nottingham.ac.uk
Influence of Process Variables on the Electrolytic Conversion of CO₂ to Carbon

11:50 – 12:15 Free Poster discussion.

12:15 – 12:45 Open Discussion - Ionic liquids (Discussion Leader - Professor Andy Abbott)

12:45 – 13:30 Lunch

13:30 – 14:00 MSDG Committee Meeting

14:10 – 18:00 Bus to Duxford and return

19:00 – 19:30 Pimm's

19:30- 21:00 Banquet

Thursday 11th July

08:00 – 09:00 Breakfast (for residential attendees only)

09:30 – 11:00 Technical Session 4 (Chairperson : Dr John Slattery)

09:30 – 10:00 **H. Zhang** and I. Farnan

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Investigation of the microstructure and dynamics of LiCl/KCl molten salts by in-situ NMR spectroscopy

10:00 – 10:30 **Geir Martin Haarberg**¹, Bo Qin¹, and Ana Maria Martinez²

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²SINTEF Materials and Chemistry, NO-7465 Trondheim, Norway

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Electrodeposition of Lead, Tin and Indium from Chloride Melts

10:30 – 11:00 **Tim Paget**

AWE plc, Aldermaston, Reading, UK. RG7 4PR

Actinide Molten Salt Processing -The Next 50 years?

11:00 – 11:30 Tea/coffee

11:30 – 12:00 **Derek J. Fray**,

Department of Materials Science and Metallurgy, University of Cambridge.

Future opportunities for molten salts

12:00 – 12:45 Open discussion - high temperature molten salts (Discussion Leader - Professor George Chen)

12:45 – 14:00 Lunch

14:00 Meeting close.

Authors' Abstracts

Abstracts presented on the following pages are compiled by the MSDG for distribution amongst attendees of the 2013 MSDG Summer Research Meeting and are based on the submitted versions from the authors who are responsible for issues related with the scientific correctness and copyright. An abridged version is available at the MSDG's website.

LECTURES

An electro-supramolecular study of the dielectric property of ionic liquids

Shan Jin,^{a,b,c} Linpo Yu^{a,b} and George Z. Chen^{a,b,*}

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Room temperature ionic liquids (RTILs) attract considerable attention because they are finding more and more applications in both industrial and scientific fields, as electrolytes, solvents, extraction media, co-catalysts etc.^{1,2} Therefore, various physical and chemical properties have been studied. Particularly, the dielectric properties, typically represented by the dielectric constant, ϵ , are crucially important and useful to understand and utilise the dissolution power of RTILs. The ϵ value of a non-conducting medium can often be measured using a capacitor device. This method is however not applicable to an RTIL.¹ To probe the dielectric properties of ionic liquids, we have designed an electro-supramolecular approach (Figure 1), taking advantage of the through-space electrostatic interaction between the redox centre and the complexed cation in a ferrocene crown ether molecule (Fc and Na⁺ ion in Figure 1).³ The study was carried out in an ionic liquid, (BMIM)PF₆, a molecular solvent (acetonitrile) and their mixtures. Cyclic voltammetric findings indicated that the ϵ value of (BMIM)PF₆ (67±1) was markedly higher than that assessed from dielectric spectroscopy ($\epsilon = 11.4$).⁴ Mixing the RTIL with acetonitrile ($\epsilon = 37.5$) led ϵ to decrease, as shown in Figure 1, in an interesting non-linear manner. The rationale is worthy of discussion.

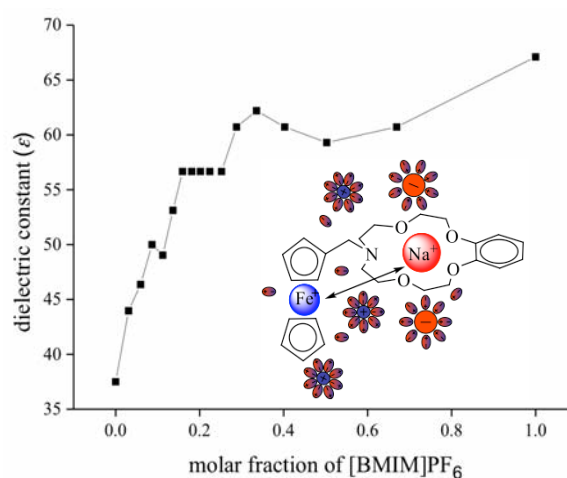


Figure 1. Electro-supramolecular analysis of ϵ , the dielectric constant, as a function of x , the mole fraction of [BMIM]PF₆ in its mixture with acetonitrile at 25 °C.

Acknowledgement

This work was partly supported by each of the NSFC (20803027 and 21173094), Season Long Cleantech Limited (Beijing), and the EPSRC (EP/J000582/1).

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Electrochemical Synthesis of AB₅-type RE-Ni Based Alloys via FFC Cambridge Process

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Abstract

The FFC Cambridge process is a method by which the metal oxides can be electrochemically deoxidized in the molten salts to form metals and alloys. Its essential advantage exists in the production of low cost alloys and intermetallics directly from the mixed oxide precursors. This paper is a review of our results on electrochemical synthesis of RENi_{1-x}M_x (RE=La, Ce and mischmetal; M=Cu and Al) in the LiCl-KCl molten salt at about 650 °C by the FFC process. The crystal structures and morphologies of the alloys prepared can be changed by the modification of their particular components and post heat treatment.

References

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Lanthanide-alkali metal halide systems: characterization, phase diagram calculation and prediction of phase diagram topology

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The lanthanide trihalides have been the subject of investigations for many years. The physicochemical properties of the compounds they form, for instance with the alkali halides, can be examined and correlated in a way which is unique since the lanthanides regularly vary along the series they form in the periodic table.

Lanthanide metal halides as also the systems they form with alkali metal halides were recently the subject of focused and renewed interest. While the lanthanide fluorides or chlorides and related systems have been investigated in the past in relation with different applications, mostly nuclear in the 1950s and 1960s, very little existed until recently on their bromide and iodide counterparts. The rare earth bromides and iodides are attractive components for doses in high-intensity discharge lamps and new highly efficient light sources with energy saving features. Photoluminescence and photo-stimulated luminescence of lanthanide-doped bromide materials induced recently active research targeted to commercial X-ray storage phosphors, while laser activity has been achieved very recently in lanthanide-doped bromide host crystals. The properties of many of the rare earth halides, however, are poorly characterized. The bromides have received even less attention in the scientific literature than the chlorides and iodides. Comprehensive thermochemical parameters for the lanthanide tribromides are not available in any of the standard compilations of thermodynamic properties.

This presentation is a part of the large program focused on thermodynamic properties, structure and electrical conductivity of lanthanide halides and lanthanide halide-alkali metal halide systems. It reports the phase diagrams and electrical conductivity of the TbBr₃-MBr binary systems (M = alkali metal). Accordingly, intensive efforts are being made at an international level both in R&D aspects and also in database development.

The thermodynamic properties (temperature and enthalpy of phase transition, heat capacity of solid and liquid phases) and the phase diagrams of mixtures were experimentally investigated by Differential Scanning Calorimetry (DSC). The liquid-liquid enthalpy of mixing was measured by high temperature microcalorimetry.

The electrical conductivity of liquid mixtures was measured down to temperatures below solidification over the whole composition range.

Assessment and optimization were performed using the CALPHAD method over the whole temperature/composition range. Specific modeling and optimization procedure were used for the thermodynamic description of the liquid phase.

All existing LnX₃-MX phase diagrams (Ln=lanthanide, M=alkali metal, X=halide) have been analyzed for the purpose of evidencing a possible relation between the phase diagrams topology and physicochemical properties of the system components. The ionic radii (r_i) and/or charges (e_i) as also their combination, called "ionic potential" $IP = e_i/r_i$, where $e_i = Z_i\varepsilon$ (Z_i = valency, ε = elementary charge), were found to be important parameters in this respect.

Molten salts, ionic liquids, energy efficiency and the need for behaviour change

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Many research projects involving the use of molten salts and ionic liquids are based on the concept of reducing the environmental impact of industrial processes. Numerous excellent examples of such projects have featured in meetings of the Molten Salts Discussion Group over the past 50 years. These industrial processes range from the small scale, such as the use of molten salts in discharge lamps (mg quantities), through to the use of ionic liquids in flue gas cleaning (kg scale) and nuclear fuel reprocessing (tonne scale). Energy efficiency is a recurring theme in these projects as more efficient processes should result in lower environmental impacts and lower costs. However, basing the future on improvements in energy efficiency alone is unlikely to provide a truly sustainable platform for industry, commerce and the natural environment to co-exist.

Energy efficiency has long been considered an essential tool to tackle rising global energy consumption and the associated climate change impacts. However, estimates of possible energy savings through energy efficiency frequently fail to acknowledge the impact of possible 'rebound effects' that accompany the introduction of energy efficient technologies.

In the mid-nineteenth century, William Stanley Jevons [1] put forward the idea that economically justified energy efficiency improvements will increase, rather than reduce energy consumption, based on observations relating to coal use and steam engines. This notion is now known as the 'Jevons Paradox': as engines became more efficient at pumping flood water out of mines, greater production of lower-cost coal was enabled, thus making it more affordable for steam engines to consume coal for many other uses. One such important use was in pumping air into blast furnaces, increasing temperatures and lowering the amount of coal required to make iron, thus lowering the cost of iron. 'Lower-cost iron, in turn, reduced the cost of steam engines, creating a positive feedback cycle. It also contributed to the development of railways, which lowered the cost of transporting coal and iron, thereby increasing demand for both' [2]. The Jevons Paradox is now more generally referred to as The Rebound Effect.

Three types of price-induced rebound effects are recognized: Direct rebound effect - where increased efficiency results in its increased consumption because it is cheaper; Indirect rebound effect - where savings from efficiency cost reductions enable more income to be spent on other products & services; Economy-wide rebound effect - where more efficiency drives economic productivity overall, resulting in more economic growth and consumption at a macroeconomic level. Direct and indirect rebound effects may be illustrated by the installation of an energy efficient domestic boiler which lowers heating bills in a household. That household may choose to increase the thermostat temperature (a direct rebound effect) or it may use the savings to buy energy consuming appliances (an indirect effect). This work is based on a comprehensive study of The Rebound Effect in lighting [3].

Countering the impacts of rebound effects will require attitude & behaviour changes by individuals, policy makers, governments, politicians and regulatory bodies.

References

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Understanding the Decomposition of Ionic Liquids: A Combined Experimental and Theoretical Approach

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The applications of ionic liquids have become very far-reaching: as solvents and catalysts, as electrolytes in battery technology, and recently in the extraction of useful materials from biomass. Recent research has indicated that ionic liquids with the acetate anion give improved result in biomass extraction experiments (1). However, the thermal properties of this and similar ionic liquids remain poorly characterized. Despite exhibiting very low vapour pressures at room temperature, ionic liquids are known to volatilize at higher temperatures (2), as well as decomposing into volatile neutral species (3). An understanding of the safe operating temperatures, the nature of decomposition products, and the underlying chemical decomposition mechanisms is therefore crucially important for the use of ionic liquids in large-scale industry.

The thermal stability of a large series of dialkylimidazolium carboxylate ionic liquids has been investigated using a broad range of experimental and computational techniques. The emphasis has been towards determining the long-term thermal stability of the ionic liquids, and understanding the kinetics and chemical mechanisms of degradation.

References

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The MSDG at 50; a life story!

Doug Inman

Visiting Professor, University College, London, and Emeritus Professor and Senior Research Fellow, Imperial College, London.

A founding father will give his personal view of highlights in the history of the Group

Selective Electrochemical Reduction and Anodic Dissolution of Ni from CeO₂-NiO in Molten CaCl₂ via the FFC-Cambridge Process

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A safe, reliable, economic and sustainable nuclear energy supply is a real requirement to stop the controversy regarding the commercialisation of the Gen III+ and Gen IV reactor systems. The application of closed loop nuclear energy cycle is essential to achieve this target, which requires the development of a specific spent fuel reprocessing technology.

The REFINE (A coordinated materials programme for the sustainable **RE**duction of spent **Fuel** vital In a closed loop **Nuclear Energy** cycle) programme is funded by the EPSRC to create a coordinated UK research programme to deliver the materials science required for sustainable molten salt enabled spent fuel reprocessing in a closed loop nuclear energy cycle [1]. The research group based at the University of Nottingham is focusing on exploiting the pivotal FFC-Cambridge Process [2] for the partial direct electrochemical reduction of metal oxide in molten CaCl₂, aiming to improve actinide and fission product separation in the electrorefiner. This provides the feed material for the electrorefiner, where actinide separation from fission products occurs *via* selective anodic dissolution.

Some preliminary investigation results have been obtained using methods such as Cyclic Voltammetry (CV) and potentiostatic electrolysis on metal oxide mixture of CeO₂ and NiO (a molar ratio of CeNi₂) in molten CaCl₂. CeO₂ was adopted here as an electrochemical surrogate of PuO₂, as their electrochemical and some physical properties are similar. NiO was mixed with CeO₂ to test the feasibility of selective reduction and anodic dissolution of Ni from the mixture because NiO possesses well separated reduction and re-oxidation potentials from that of CeO₂. According to CV investigations, the potentials for reduction of NiO and re-oxidation of the Ni metal were detected, which were then utilised during the potentiostatic electrolysis to separate Ni from the original mixture of CeO₂ and NiO. Based on SEM and EDX analysis results, atomic content of Ni was reduced by more than three times after the selective electrochemical reduction and anodic dissolution processes (see **Figure 1**).

Future works will be focusing on using ZrO₂ as an electrochemical surrogate of UO₂ to replace NiO, and changing the composition of metal oxide mixture to a more closed ratio to that of real spent fuel.

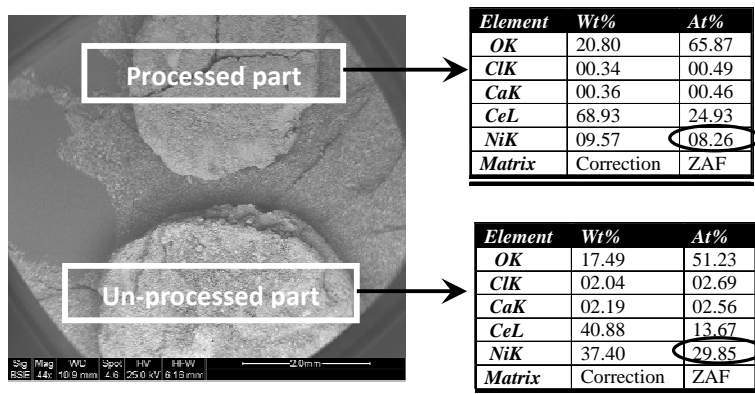


Figure 1. SEM and EDX analysis results showing the selective removal of Ni from CeO₂-NiO *via* the combination process of electrochemical partial reduction and anodic dissolution.

Acknowledgement: This work is sponsored by the EPSRC (EP/J000582/1).

References

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Carbon Capture by CaO in Molten Halide Salts

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Modifications/synthesis techniques of CaO-based sorbents for CO₂-capture have given materials with enhanced CO₂ capture capacity, thermal stability, and mechanical strength; but still, no strategies have showed complete elimination of degradation related to attrition and sintering [1, 2]. The application of molten salt technology where the sorbent dissolution/dispersion may enable improved reactivity of the sorbent with CO₂ due to rapid gas-liquid interactions in the molten salt [3]. Therefore, the separation of CO₂ from simulated flue gas by commercially available CaO dissolved or partly dissolved in CaF₂/NaF and CaF₂/CaCl₂ melt was evaluated. Initially, thermal analysis of the NaF/CaF₂, CaO/NaF/CaF₂ and Na₂CO₃/NaF/CaF₂ chemical systems was carried out at 560-1190 °C. Optimization of CO₂ absorption/desorption by CaO in NaF/CaF₂ and CaF₂/CaCl₂ chemical systems was carried out by studying the effects of the CaO concentration in the metal halide salts, the temperatures for the carbonation/decarbonation reactions, the gas flow rate and composition, and the sorbent cyclic capacity. The absorption/desorption processes in CaO/CaF₂/NaF were tested using FT-IR gas analysis, thermo-gravimetric analysis and X-ray diffraction. CO₂ capture was accomplished at 670-840 °C by bubbling CO₂ through the melt prepared of CaO dispersed in a eutectic NaF/CaF₂ and CaF₂/CaCl₂ mixtures. Extremely high sorbent carbonation efficiency was accomplished in CaO/NaF/CaF₂ melt, >99 % of the applied CO₂ was separated in the initial carbonation reaction stage (Figure 1). In addition, the results indicate that the high absorption efficiency in the fluoride melt is enabled by the exchange reaction given in Equation (1) below, as CO₂ is captured as Na₂CO₃ rather than CaCO₃. The thermal decomposition of the formed CaCO₃/Na₂CO₃ has been tested at temperatures ranging from 904 °C to 1180 °C, which resulted in near 100 % efficient desorption for all samples consisting of CaO, CaF₂ and CaCl₂. Furthermore, the formation of Na₂CO₃ in CaO/CaF₂/NaF system was confirmed by XRD analysis.

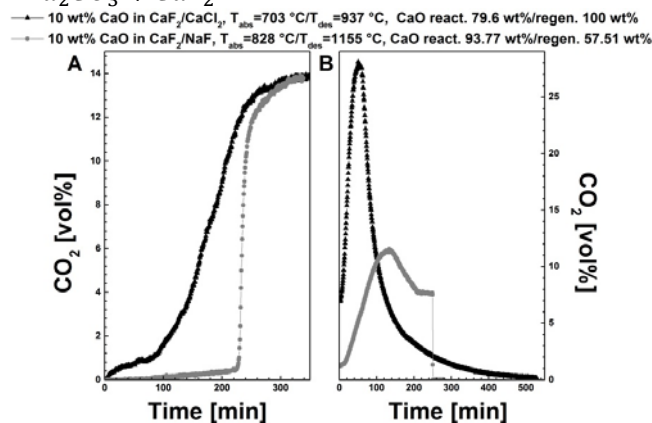
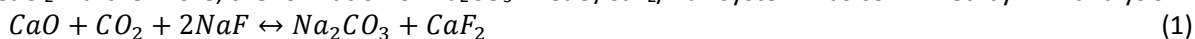


Figure 1. Effect of molten metal halide salts utilization as a solvent for CaO dissolution/dispersion in carbon capture process: A) CaO carbonation by bubbling 14vol% of CO₂ in N₂; and B) carbonates decomposition under pure N₂.

References

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Ionic Liquids – Non-crystalline Ball Gazing

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As the Molten Salt Discussion Group looks back over the past 50 years of the topic it can reflect on all of the advances made in high temperature systems over that period. It is however clear that over the last 20 years academic activity with low temperature salts has far exceed that of high temperature systems. Is this a flash in the pan or are these young upstart here to stay? In this presentation we look forward to some of the directions that low temperature systems may take over the next few decades and highlight some of the challenges that need to be overcome.

Investigation of the microstructure and dynamics of LiCl/KCl molten salts by in-situ NMR spectroscopy

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The LiCl/KCl molten salt system is used as a media in pyrochemical processing for separating actinide metals from spent nuclear fuel. In order to control the process efficiently, it is necessary to have a fundamental understanding of the effect of dissolved cations on the microstructure and the dynamics of the salts.

Due to the corrosiveness of molten LiCl, KCl and their mixtures, high temperature measurements are difficult and experimental data on their local structure and dynamic properties are quite rare. By numerical simulation, the local structure in molten LiCl was considered as an octahedron of 6 Cl⁻ surrounding one Li⁺, but with most of the octahedral having at least one vacant site [1]. Upon mixing with KCl, the Li-Cl distance decreased accompanied with the decrease of the Li coordination number, and vice versa for K-Cl [2]. This points to a change of the internal mobility of ions with composition. The change could not be explained by considering ionic motion independently, because there are significant interionic correlations. Particularly, the intermediate range chemical ordering of Li⁺ ion is considered as a general property of simple mixture of lithium halides with other alkali halides [3].

Recently, in-situ high temperature NMR has been used as an effective way to monitor the changes in microstructure and dynamics of fluoride salts at temperatures relevant to the pyrochemical process. For example, the local microstructure and self-diffusion coefficient of specific ions in molten LiF/KF system have been carried out successfully despite the severe technical challenges posted by their corrosiveness [4]. In this work the in-situ high temperature NMR is used to study atomic scale processes involved in molten LiCl/KCl salt systems. Using NMR spectroscopy, we are able to observe the chemical shift variation with composition, which informs us about the average local environment of ions (e.g. type and number of surrounding ions). Furthermore, the element specific motional correlation time of ions will be obtained, to understand the dynamic mechanism of ions in molten salt systems.

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Electrodeposition of Lead, Tin and Indium from Chloride Melts

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Computers and TV sets are frequently being replaced. The screens of such devices contain high amounts of metal compounds, and recycling for the metal value or for environmental reasons is increasingly important. Electrolysis in molten salts is an option to recover metals such as lead, tin and indium which are important constituents of CRT screens and ITO coatings.

Electrochemical studies were carried out to study the behaviour of dissolved Pb, Sn and In chlorides in molten LiCl-KCl at 450 °C.

Pb deposition from dilute solutions of PbCl₂ in molten LiCl-KCl is diffusion controlled. Li alloys are formed at low cathodic potentials. In (III) is reduced to In (I) before In is deposited. In (II) is not stable. Sn is deposited from Sn (II).

Future Opportunities for Molten Salts

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The world faces some interesting challenges in the future and these include better ways of generating and storing energy, green processing of materials and meeting the demand for food for an ever increasing population. This talk will cover possible ways in which molten salts can contribute to solving these challenges.

Only small fraction of the sun's energy falling on the earth is converted to electrical energy using solar panels¹. There are two reasons for this – the cost of the solar panels and their relatively low efficiency. For the foreseeable future, it is likely that silicon will be the prime material for solar cells but its production is very energy inefficient, coupled with an excessive production of CO₂ (60Kg CO₂/kg Si)². Electro-deoxidation of native silica in molten CaCl₂ – CaO melts is a possibility for producing PV silicon and coupling this with an electrochemical method of making black silicon, which reflects less light, may prove attractive³.

Nuclear energy is another source of CO₂ free energy and molten salts can play a part in nuclear energy either by forming an integral part of the nuclear reactor⁴ or recycling used oxide fuel rods⁵. Lithium-ion batteries are perhaps the most attractive and convenient way of storing energy but, ideally, the capacity needs to be increased and one way of doing this is to use an alternative anode material such lithium tin or silicon intermetallics but these materials decrepitate on use⁶. This can be overcome by filling carbon nanotubes with tin or silicon by an intercalation process in molten salts⁷. Liquid metal batteries⁸ and lithium air batteries⁹ can also use molten salts as the electrolyte.

As many metals occur as oxides in the earth's crust, reduction with carbon usually involves the production of CO₂; the reduction of Fe₂O₃ generates 5% of the world's annual production of CO₂ together with another 5% when crude iron is converted to steel. There are two possible ways of reducing this, one being capturing the CO₂, perhaps in a molten salt¹⁰ and the second is electrochemically reducing the oxide in a molten salt using an inert anode. Inert anodes will be described for molten oxide and CaCl₂ – CaO melts using metallic¹¹ and ceramic materials¹². These technologies might be used to generate oxygen from lunar regolith¹³.

There are significant areas of the earth's crust that are capable of sustaining agriculture but only if nutrients are added. The most common fertiliser is KCl which can only be commercially sourced from Canada or Russia at significant expense. In Brazil, there is a vast resource of low grade potassium silicate which can be simply converted into KCl by molten salt ion exchange using NaCl and CaCO₃. The development of this project leading to an investment of \$600m will be described.

These very diverse projects will demonstrate that the field of molten salts will be active for years to come offering innovative solutions to some of the world's problems.

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POSTERS

The thermodynamic properties of Solution Metal Oxides in Molten Alkali

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High Energy Capacity Supercapacitors Based on Ionic Liquids Electrolytes

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Nowadays, supercapacitor is playing a more and more important role in energy storage. However, the energy capacity of the conventional supercapacitor is much lower than its competitor, the rechargeable battery, on the basis of the same type of electrolyte. Several efforts have been made to improve the supercapacitors' energy capacity, such as using the design of asymmetric supercapacitor cell (different positive and negative electrode materials),¹ controlling the capacitance ratio of the positive and negative electrodes made from the same material,² and serially stacking the cells through bipolar electrodes.³ All these efforts are based on the aqueous electrolytes and there is a strong desire for changing aqueous to organic electrolytes to achieve a high working voltage. Here, ionic liquids have been chosen as the electrolytes of the supercapacitors.

Comparing to the aqueous electrolytes, ionic liquids have wide electrochemical windows, which means that a supercapacitor based on ionic liquid electrolyte can work in a higher voltage than the one based on aqueous electrolyte. Figure 1 illustrates the increasing working voltage in the CV of a symmetric supercapacitor made from two 40 mg activated carbon pellet in each electrode.

However, it is also noticeable that the CVs are significantly distorted from a rectangular shape that is expected for capacitive behaviour. This distortion was apparently due to the relatively higher resistance of ionic liquids, and calls for further efforts to understand the causes and develop new improvement strategies.

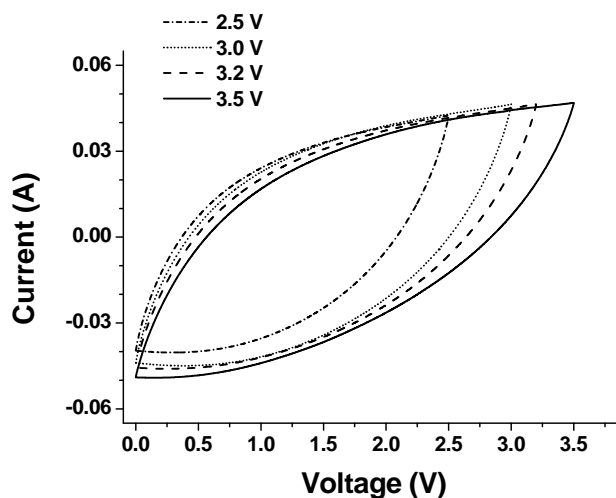


Figure 1. CVs of a symmetric supercapacitor made from two 40 mg activated carbon pellet (diameter: 13 mm). Scan rate: 20 mV/s. The separator: filter paper.

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Influence of Process Variables on the Electrolytic Conversion of CO₂ to Carbon

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Industrial use of carbon (e.g. power generation and house heating) utilizing fossil fuel produces significant amount of anthropogenic CO₂ which has an overall effect on the global atmospheric temperature. Technologies that can efficiently take away and reuse¹ large volumes of the CO₂ produced from emissions are needed. One way of handling captured CO₂ is by electrochemically engineering its reduction by molten salt technology into materials and fuels such as carbon and carbon monoxide. This process proceeds via an electro-deposition route which involves the cathodic reduction of carbonate ions to carbon in molten carbonate salt mixtures². Carbonate salts were chosen because of their good thermal and electrochemical stability which includes the capability of regenerating carbonate ions via the reaction of oxide ions with CO₂.

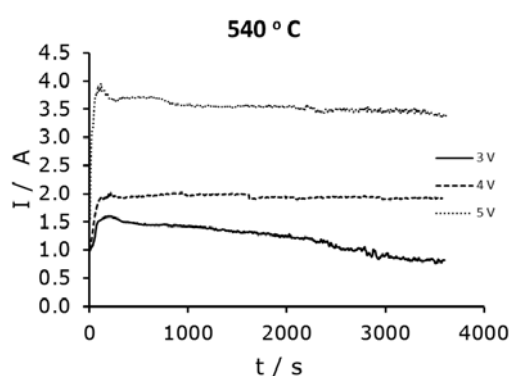


Figure 1-Current-time plots recorded during electrolysis in a molten Li₂CO₃-K₂CO₃ (62:38 mol %) at 540 ° C; Anode: 5 mm diameter mild steel; Cathode: 6 mm stainless steel; CO₂ flow rate: 200 mL/min

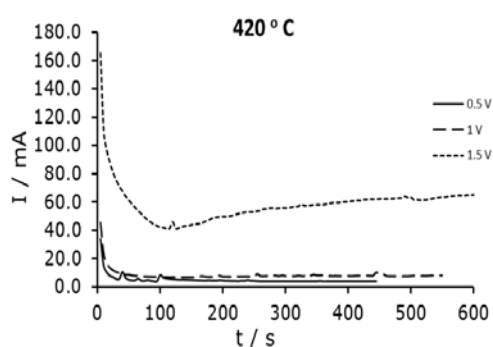


Figure 2 Current-time plots recorded during electrolysis in a molten Li₂CO₃-Na₂CO₃-K₂CO₃ (43.5:31.5:25 mol %) at 420 ° C; Anode and cathode: 5 mm steel; Cathode; CO₂ flow rate:

In this study, the effect of process variables such as molten salt composition, temperature, electrolysis voltage, gas composition on the overall conversion process was investigated. The results showed that by carrying out carbon deposition in different molten salt mixtures, different forms of carbon were obtained. Electrolysis voltage of 0.5 – 5 V was studied (Figures 1 and 2), high carbon deposition rates were obtained with increasing voltage (maximum value of 0.11 g cm⁻² h) and current efficiencies of over 70 % were achieved^{3,4}. Carbon deposition was carried out at temperatures as low as 420 ° C simply by changing the molten salt composition. Changing the gas composition also shows the feasibility of utilizing typical flue gas composition as the actual feed gas for the conversion process. Lastly the deposited carbon was used to construct supercapacitors (an energy storage device) and specific mass capacitance of up to 180 F/g was obtained in 1.5 M H₂SO₄ and 130 F/g in 3 M KCl.

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