



Christmas Research Meeting 2023

Programme and Abstracts

18th December 2023

Burlington House, London

The Molten Salts and Ionic Liquids Discussion Group have the pleasure of welcoming you to Burlington House, London for our annual Christmas meeting. We hope that you enjoy the meeting and your time in London.

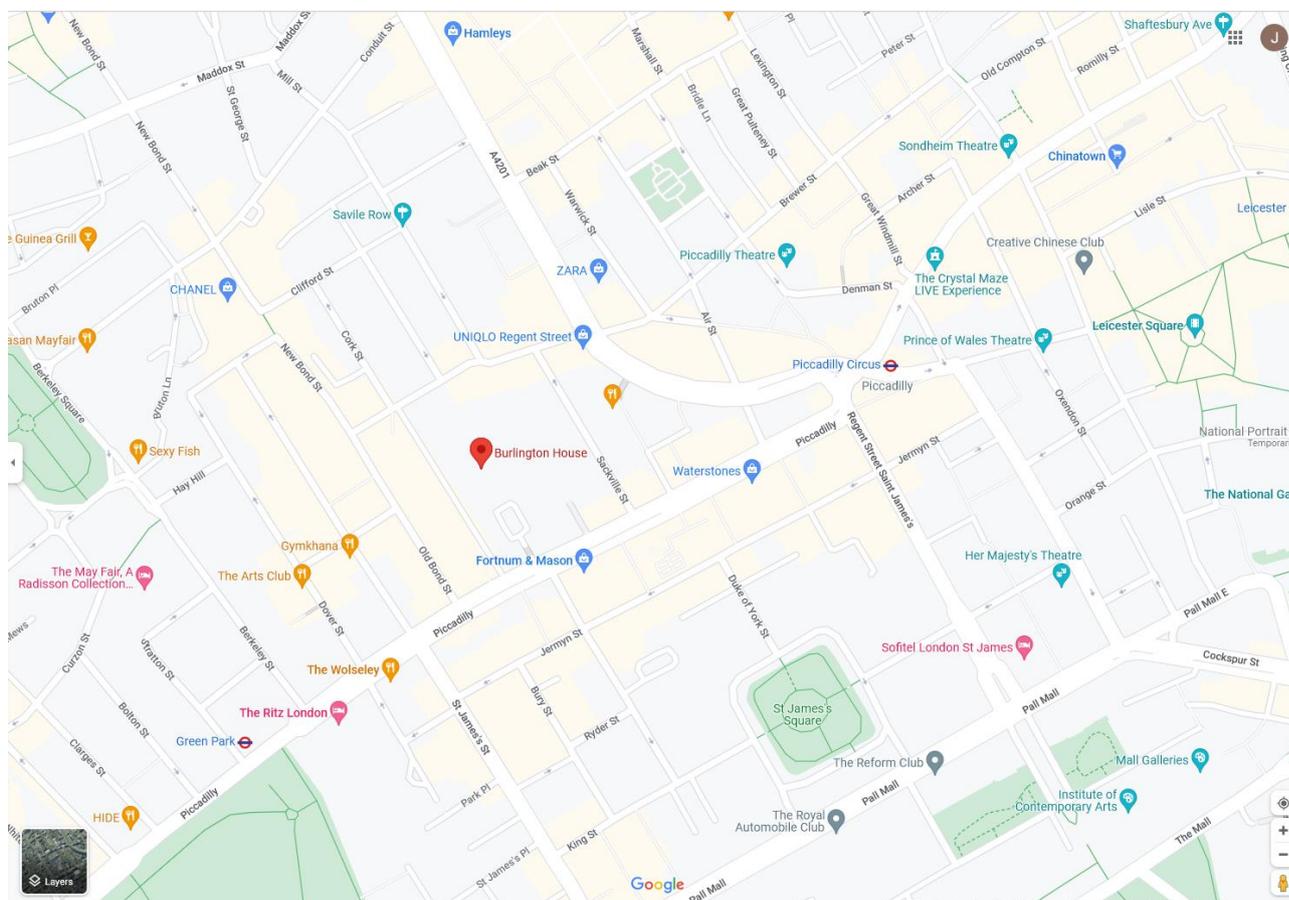
MSILDG Organising Committee

In-person Venue and Registration Information

The meeting will be held in the library of the Royal Society of Chemistry at Burlington House. Registration will open shortly before the main programme begins (see below for timings).

Getting to Burlington House

The venue website (<https://burlingtonhouse.org/>) has detailed instructions for how to reach the site, which is in the centre of London and easily accessible by public transport. A map of the local area is shown below.



Details for oral presenters

To maximise the number of speakers in the programme, contributed talks are limited to **15 minutes** + 5 minutes for questions. Please try to stick to this timing to allow everyone to speak. Online presenters, please join the meeting 5 minutes before the start of the session to test your connection.

Details for poster presenters

Poster boards will be available in the Council Room to display your poster for the duration of the meeting. There is no formal poster session, but there is plenty of time during the breaks and the reception for viewing and discussion.

Details for online attendees

For delegates attending the meeting online, we will be using the GoToMeeting platform. We have found this to be both functional and accessible for delegates from around the world. To join the meeting we recommend downloading the GoToMeeting app (<https://meet.goto.com/install>) in advance of the meeting to ensure that you are ready when the programme starts. Connection details are below:

MSILDG Christmas Meeting

Dec 18, 2023, 10:00 AM – 5:30 PM (Europe/London)

You can join the meeting from your computer, tablet or smartphone.

<https://meet.goto.com/306001381>

You can also dial in using your phone.

United Kingdom (Toll Free): 0 800 169 0432

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The Molten Salts and Ionic Liquids Discussion Group (MSILDG)

**Christmas meeting
18th December 2023
Burlington House, London**

Programme

09:00-10:00 Registration open

Session 1: 10:00-11:30

Session chair: *Dr Stuart Mucklejohn*

10:00-10:10 Welcome and Introduction

10:10-10:50 **Inman lecture:** Electrodeposition of Metals from Molten Salts: Effects of Metal Dissolution and Nucleation
Geir Martin Haarberg (Norwegian University of Science and Technology, Norway)

10:50-11:10 Contributed online talk: Atomic size controlling to synthesize single-atom materials in ionic liquids
Shujuan Wang (Shanghai University, PRC)

11:10-11:30 Contributed online talk: Separation of tungsten and cobalt by molten salt electrolysis of cemented carbide
Liwen Zhang (Beijing University of Technology, PRC)"

Coffee Break

Session 2: 11:50-12:50

Session chair: *Prof George Chen*

11:50-12:10 Contributed online talk: Liquid Alloy-Salt Catalytic System for Ammonia Synthesis
Xiaofei Guan (ShanghaiTech University, PRC)"

12:10-12:30 Contributed talk: Ni NPs in functionalized ionic liquids as chemoselective hydrogenation catalystst
Anders Riisager (Technical University of Denmark, Denmark)

12:30-12:50 Contributed talk: Spinning carbon fibres from low cost ionic liquids
Agi Brandt-Talbot (Imperial College, London, UK)

Lunch

During the lunch break the MSILDG will hold its **AGM** 13:20-14:00, open to all

Session 3: 14:00-15:40

Session chair: *Dr John Slattery*

- 14:00-14:40 Invited talk: Why are ionic liquid so viscous?
Tom Welton (Imperial College, London, UK)
- 14:40-15:00 Contributed talk: Structure-property relationships in new LCST ionic liquids
Sanskrita Madhukailya (QUILL, Queen's University, Belfast, UK)
- 15:00-15:20 Contributed talk: Hydroformylation of Ethylene by Supported Ionic Liquid-Phase (SILP) Catalysis
Rasmus Fehrmann (Technical University of Denmark)
- 15:20-15:40 Contributed talk: Phase Diagrams and the Materials Chemistry Group of the IOM3
Andy Watson (Hampton Thermodynamics and University of Birmingham)

Coffee Break

Session 4: 14:00-15:40

Session chair: *Dr Ian McPherson*

- 16:10-16:30 Contributed talk: Review on the Demonstration Progress of Electro-deoxidation Process in Molten Salt
Han Wang (University of Nottingham, UK)
- 16:30-16:50 Contributed talk: Molten salt electrochemistry assisted green synthesis of acetylene
Xianbo Jin (Wuhan University, PRC)
- 16:50-17:10 Contributed talk: Exploring the structure and properties of ionic liquid mixtures containing fluorinated and aliphatic components
John Slattery (University of York, UK)
- 17:10-17:30 Contributed talk: Electronic effect of the metal cation on the anion: implications for the reactivity of ionic liquids and concentrated electrolytes
Kevin Lovelock (University of Reading, UK)

Cheese and Wine Reception

Electrodeposition of Metals from Molten Salts

Effects of Metal Dissolution and Nucleation

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A large majority of elements of the periodic table is metals. Metal production is a large industry worldwide and many metals and alloys have excellent properties that make them indispensable for further development of the modern world. Metal production takes place by carbothermal reduction or using another reducing agent for iron and steel, silicon, manganese, ferro alloys, magnesium and titanium. However, electrolysis offers possibilities to reduce the carbon footprint significantly. Nickel, copper and zinc are being produced by aqueous electrowinning. Less noble metals may be produced by molten salt electrolysis. Aluminium is by far the most important metal produced by molten salt electrolysis, around 70 million tons being produced annually. Industrial processes have been developed for alkali metals, aluminium alloys and magnesium. Other attractive candidates for future development of molten salt electrowinning are titanium, silicon, rare earth elements especially within recycling of electronic waste. Metals are generally soluble in molten salts (1). In binary molten salt metal systems there is complete miscibility above a certain temperature. Dissolution of alkali metals in molten alkali halides gives rise to electronic conductivity due to the formation of mobile electrons. In other systems such as $\text{PbCl}_2\text{-Pb}$ and MgCl_2 subvalent ions (Pb_2^{2+} and Mg_2^{2+}) are formed. Such species can migrate in the electrolyte and become anodically oxidized. The main part of the loss in current efficiency for metal deposition processes in molten salts can be ascribed to the formation of dissolved metals. The back reaction between dissolved metals and anode product and the existence of electronic conductivity are important mechanisms, but also so-called metal fog often observed near the cathode during electrodeposition of metals from molten salts may be of importance. The fog consists of small droplets of metal formed by homogeneous nucleation from a supersaturated solution of dissolved metal (2). Figure 1 shows a cyclic voltammogram in molten NaCl-KCl with a glassy carbon working electrode. Reoxidation of deposited sodium is associated with a much lower charge than the deposition reaction. This is due to formation of dissolved sodium which diffuses away from the electrode.

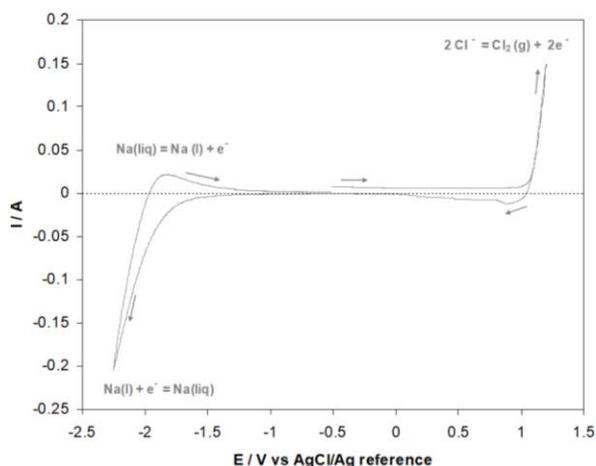


Figure 1. Cyclic voltammogram in molten eutectic NaCl-KCl at 850 °C with a glassy carbon working electrode, 200 mV/s.

References

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Atomic size controlling to synthesize single-atom materials in ionic liquids

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Abstract

Controlling the structure of nanomaterials at an atomic level has received considerable attention in recent years. However, the complexity of synthetic process faces great challenges in the delicate design and fine control of nano- and atomic-level materials. Ionic liquids (ILs) known as room-temperature molten salts, are particularly attractive materials for electrocatalysts construction and modification because of their electrochemical stability, high conductivity, and wide electrochemical window. We have achieved multi-scale size-control by combining ionic liquids with electrochemical technology, and can even finely control the construction of single atom materials. And single atom materials were applied to the field of water electrolysis, achieving excellent catalytic performance. Our works may provide a new insight into the accurate control of the single-atom electrodeposition kinetics in ILs, which has excellent promise to serve as a general strategy for the electrosynthesis of single atom materials for various applications.

Reference

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Separation of tungsten and cobalt by molten salt electrolysis of cemented carbide

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The molten salt electrolysis of tungsten and cobalt is to separate tungsten and cobalt from tungsten and cobalt by taking the cemented carbide as the soluble anode and using the molten salt electrolysis to make tungsten and cobalt dissolve in the form of ions and deposit at the cathode. This technology realizes the short process recycling of refractory tungsten secondary resources.

A systematic study was conducted on the anodic dissolution behavior of tungsten carbide and cobalt using electrochemical methods. Based on the difference in the dissolution/deposition potential of tungsten and cobalt, a two-step method was developed to separate tungsten and cobalt, obtaining tungsten powder with a particle size less than 200 nm and cobalt powder with a particle size less than 100 nm, the dissolution process of anode under different conditions was characterised and simulated, and the electrochemical dissolution law of tungsten and cobalt was summarised.

However, when the cobalt ion concentration is in a certain range, tungsten and cobalt are prone to co-deposition to generate Co_3W alloy which affects the purity of the product. Combined with the characteristics of W_2C impurities that are prone to appear in the cathode product, the tungsten and carbon are co-deposited to generate tungsten carbide through the addition of carbonate in the molten salt, or the use of the molten salt to capture CO_2 in the air. The final composite product of tungsten carbide powder and cobalt powder was obtained.

References

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Liquid Alloy-Salt Catalytic System for Ammonia Synthesis

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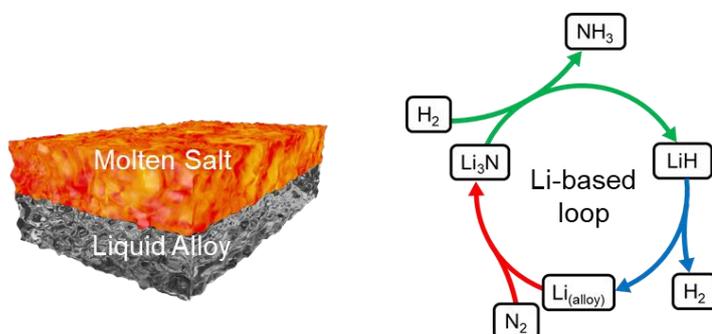
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Abstract Text / Images

The synthetic ammonia (NH_3) is widely used for the production of nitrogen fertilizer, a key to food security. In addition, NH_3 is an attractive energy carrier due to the high hydrogen content, high volumetric energy density, zero carbon, easy storage and transport. The current industrial NH_3 production still relies on the Haber-Bosch process which has high energy cost and CO_2 emission as well as the requirement for large-scale centralized operation.

In this presentation, I will discuss on the NH_3 synthesis from N_2 and H_2 with a novel lithium (Li)-based loop realized in a liquid catalytic system comprising a Li-based alloy at the bottom and a molten salt at the top. The Li-based loop consists of three reaction steps taking place simultaneously. The first step is the N_2 fixation by Li in the liquid Li-based alloy to form Li_3N , which floats up and dissolves into the molten salt. The second step is the Li_3N hydrogenation to form NH_3 and LiH in the molten salt. The third step is the regeneration of Li from the LiH . In such liquid alloy-salt catalytic system, the floating and dissolution of Li_3N enables the circumvention of the scaling relation exerted on Li. In addition, the reaction of H_2 with the Li_3N dissolved in the molten salt was much easier than with the solid Li_3N . The Li-based loop realized in such an integrated catalytic system offers a promising solution for distributed NH_3 production.



References

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Ni NPs in functionalized ionic liquids as chemoselective hydrogenation catalysts

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The decomposition of organometallic Ni⁰ complexes with stabilizing agents (organometallic approach) is an attractive method to obtain size-controlled Ni NPs in solution. The method allows fine control of the NPs growth, while offering a clean metal surface due to the absence of byproducts formed from the precursor complex. Moreover, the nature of the stabilizer can be tuned to affect the catalytic properties of the Ni NPs [1].

Ionic liquids (ILs) can function as both stabilizers and dispersion media for the synthesis of small and narrow-sized Ni NPs by the organometallic approach under mild conditions [2]. Such systems can also benefit from the use of functionalized ILs (FILs) that can interact with the metallic surface and create ligand effects during catalysis [3]. Controlled oxidation forming Ni-NiO NPs is another approach to modify the catalytic reactivity, as previously shown for solid NiO catalysts [4].

In this work, Ni NPs were synthesized in various ILs (Ni/ILs) and exploited as catalysts for the chemoselective reduction of 2-cyclohexen-1-one, as a representative of the group of α,β -unsaturated carbonyl compounds with industrial relevance. Interestingly, the Ni/ILs systems were found to be efficient catalysts for selective hydrogenation of the substrate to cyclohexanone using H₂, whereas the oxidized counterparts (Ni-NiO/ILs) were active and selective for catalytic transfer hydrogenation (CTH) to 2-cyclohexen-1-ol with 2-propanol as H-source and solvent, both under mild reaction conditions (Figure 1).

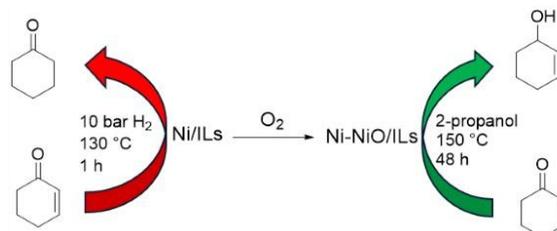


Figure 1: Chemoselective reduction of 2-cyclohexen-1-one with Ni/ILs and Ni-NiO/ILs.

References

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Acknowledgments

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Spinning carbon fibres from low-cost ionic liquids

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Lignins is an abundant biopolymer present in wood a promising precursor material for cheap renewable carbon fibres, however, cost-effective methods for producing lignin fibres that convert into high-quality carbon fibres are needed. Low-cost ionic liquids based on alkylammonium cations and hydrogen sulfate anions have been shown to have a high solubility for a variety of lignins. Based on this observation, we have developed a fibre spinning method that uses a low-cost ionic liquid (<\$1/kg) to produce fibres from industrial Kraft and ionosolv lignins. Lignin fibres are formed by spinning dopes consisting of the ionic liquid, water, a lignin and a fibre-forming additive into water to coagulate the dope into fibres. The fibres have >75% lignin content, resulting in the highest lignin content reported to date for wet-spun lignin fibres. Precursor fibres with lignin contents >80% have been converted into carbon fibres and characterised in detail. Technoeconomic estimates show that the ionic liquid solvent is 5 times cheaper than solvents used in the industrial carbon fibres process, opening up opportunities for a step-change in carbon fibre production cost.

Structure-property relationships in new LCST ionic liquids

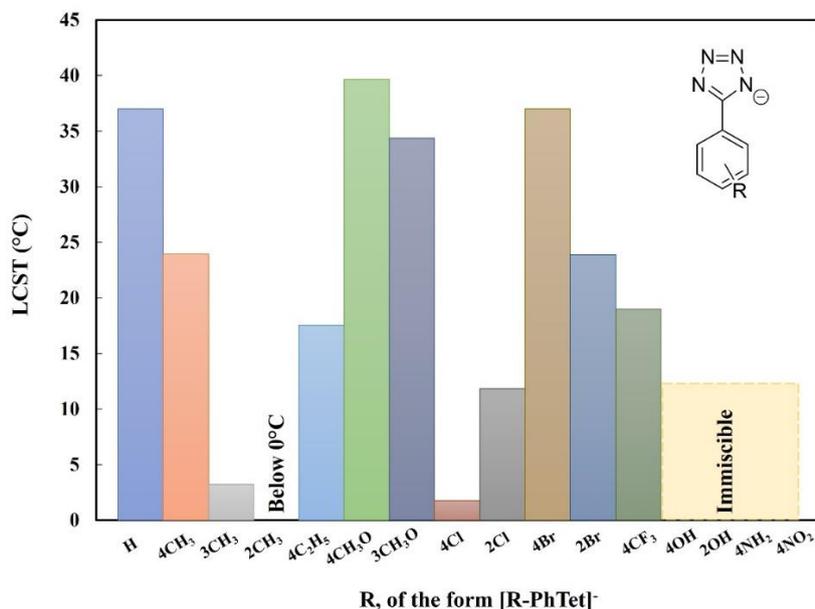
Sanskrita Madhukailya,^{1*} Leila Moura¹, John D Holbrey¹

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The tetrabutylphosphonium 5-phenyl tetrazolate/water system ($[\text{P}_{4444}][\text{Ph-Tet}]/\text{H}_2\text{O}$), containing the bioisosteric 5-phenyl-tetrazole analogue of benzoate, has previously been reported to exhibit LCST behaviour with water with a critical temperature of $\sim 40\text{ }^\circ\text{C}$ ¹. In line with other LCST forming tetrabutylphosphonium-based ionic liquids (for example with methylbenzenesulfonate anions²) there is potential to make use of these materials as draw fluids for low grade energy desalination or dewatering processes.

We have ongoing interest in investigating how both the critical temperatures and phase compositions can be influenced by the nature of substitution on the phenyl-ring of the anion along with moving from a range of monocationic phosphonium-based to dicationic phosphonium-based ionic liquid/water systems. We report how anion modification, by derivatization of 5-phenyltetrazolate anions with a range of small functional groups at the sites *ortho*, *para*, and *meta* to the tetrazolate, can control the phase behaviour of the ionic liquid/aqueous systems changing the hydrophobicity (water content) of the IL-rich phase and reducing the LCST from 40 to 10 °C (as shown in Fig. 1) to enable thermoresponsive draw-fluids for forward osmosis water purification. On that note, understanding the chemistry behind formation of LCST systems in the studied ionic liquid/water systems whilst changing different parameters like composition and salt concentration, in response to temperature is also investigated.



References

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Hydroformylation of Ethylene by Supported Ionic Liquid-Phase (SILP) Catalysis

Rasmus Fehrmann,^{1*} Minh Thang Le,² Eduardo J. Garcia-Suarez,^{1,3} Anders Riisager¹

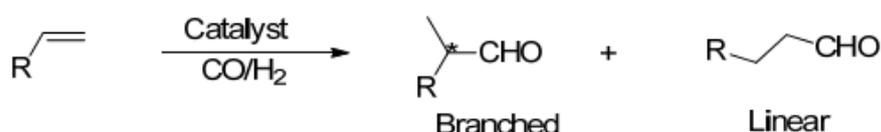
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Hydroformylation of olefins forms aldehydes which are valuable final products as well as intermediates in synthesizing bulk chemicals like alcohols, amines, and esters with a yearly world production of above 10 Mt. Industrial hydroformylation processes are essentially homogeneously catalyzed systems with an economic incitement for improvement by easy separation of products and reuse of catalysts, high reactivity and selectivity by using new catalysts, novel processes and alternative methodologies.



Typical reaction conditions: HRh(CO)(TPPTS)₃, 110-130 °C, 40-60 bar

One such potential candidate for an alternative catalyst is a Supported Ionic Liquid-Phase (SILP) catalyst comprising “heterogenized” homogeneous ionic liquid (IL) catalyst systems on a porous support. Such catalysts make it possible to apply the much-preferred fixed bed continuous flow process design, which overcomes the troublesome and energy demanding separation of the products from the reaction mixture obtained in the traditional homogenous batch process.

In our previous and very recent studies [1,2], we have prepared SILP catalysts containing immobilized Rh-complexes of TPPTS-Cs₃ in 1-butyl-3-methylimidazolium octylsulfate ([BMIM][n-C₈H₁₇OSO₃]) on SiO₂ support and investigated the influence of IL loading on the catalytic activity. The influence of other supports: SBA-15, MCM-41, Al₂O₃, ZrO₂ and TiO₂ has also been studied and the catalytic activity compared to the SiO₂ SILP catalyst. Finally, we will report on a comparison on the catalytic activity of the SiO₂ SILP catalyst by use of the ligand TPPTS-Cs₃ and the much cheaper TPPTS-Na₃ salt.

References

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Phase Diagrams and the Materials Chemistry Group of the IOM3

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The Materials Chemistry Group (MCG) is a new sub-group of the 'Materials Characterisation and Properties Group' of the Institute for Materials, Minerals and Mining. The MCG is essentially a continuation of the Materials Chemistry Committee (MCC), which was a technical committee of the IOM3 before a recent programme of restructuring of the technical communities.

The remit of the MCG is very much the same as the old MCC, having a focus on phase diagrams, thermodynamics and their application. There is an obvious synergy between the MCG and the MSILDG.

This presentation aims to outline the MCG and its activities, in particular, in relation to thermodynamic calculation of phase equilibria using experimental and *ab initio* data (DFT) and discusses how this may be of interest to members of the MSILDG.

Review on the Demonstration Progress of Electro-deoxidation Process in Molten Salt

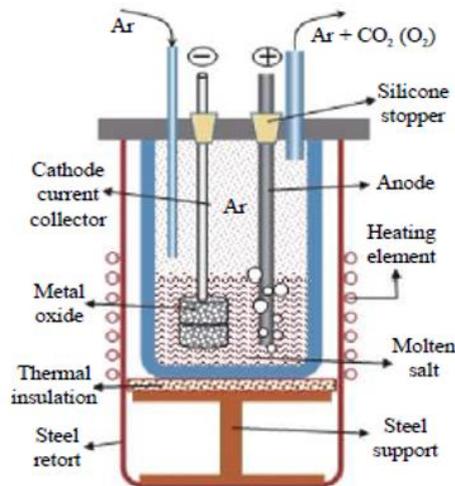
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In 1999, an international patent on what is now known widely as the Fray-Farthing-Chen (FFC) Cambridge Process was published and named after its founders. This process offers versatile opportunities for electrolytic extraction of metals and alloys directly from their solid compounds in molten salts. In the past two decades, it has been confirmed the scientific principle and technical feasibility and flexibility of the process for the extraction of almost all metals listed in the periodic table and their alloys from their respective oxide or sulphide precursors¹⁻⁴. Here, a brief review on the demonstration progress of this electro-deoxidation process is given, aims to summarise the achievement on the commercialisation progress and bring the challenges to both fundamental and industrial areas.



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Molten Salt Electrochemistry Assisted Green Synthesis of Acetylene

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The carbon-to-CaC₂ route holds promise in providing a sustainable elementary unit, C₂H₂, for the organic synthesis industry, but the traditional thermal reaction process suffers from low carbon efficiency, harmful gases contamination, high temperature operation and high-risk CO emission. The energy revolution, represented by renewable energy sources such as solar and wind power, has brought new opportunities for the green transformation of traditional chemical industries. Here we will present an electrolytic synthesis of solid CaC₂ from biochar in molten CaCl₂/KCl/CaO at 973 K, and the carbon utilization efficiency in the synthesis of acetylene using this electrochemical carbon-to-CaC₂ route can approach nearly 100%. The main electrode reactions are the solid convention of biochar to CaC₂ at the cathode and oxygen evolution at an inert anode. At the same time, as the traditional thermal forms CaS and Ca₃P₂ in the CaC₂ product, the electrolysis removes S and P from the solid cathode into the electrolyte, consequently nearly zero H₂S/PH₃ contamination would be found in the hydrolysed C₂H₂.

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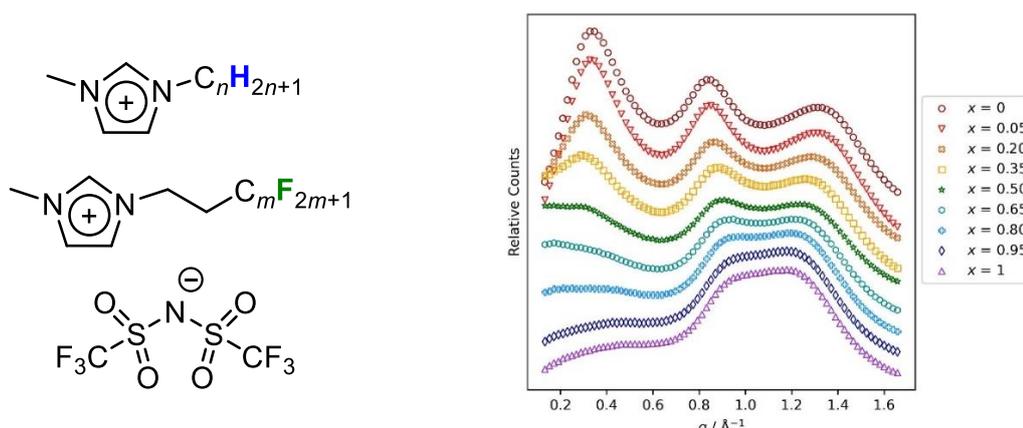
Exploring the structure and properties of ionic liquid mixtures containing fluorinated and aliphatic components

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Ionic liquids (ILs) have been tested in a range of applications, but their use as alternative solvents for synthesis and catalysis has been a key area of interest.^[1] ILs have been shown to self-organise in both the bulk liquid and at the gas-liquid interface.^[2] The ability to understand and control this organisation will allow us to tune the solvent micro-environment around solutes, the mass transport of gasses into/out of the liquid and other properties that will enable ILs to achieve their potential as designer solvents.



IL mixtures are of particular interest, as they offer the potential to access a wide range of liquid structure and properties by mixing a small number of pure ILs. Thus, the synthetic effort required to prepare ILs with desired properties is reduced. This talk will give an overview of our contributions, as part of a wider collaborative network, to the synthesis, characterisation and understanding of self-organised ILs.^[4] A particular focus will be on recent work on IL mixtures containing fluorinated and aliphatic components, which allow additional flexibility over the structure and properties of the liquids.

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Electronic effect of the metal cation on the anion: implications for the reactivity of ionic liquids and concentrated electrolytes

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Concentrated electrolytes, electrolytes where the concentration of the salt is far greater than the standard battery concentration of ~1 M, have been found to give far wider electrochemical potential windows, which is of great importance for battery development.^{1, 2} From DFT-based molecular dynamics (DFT-MD) calculations, it has been suggested that the observed wider windows arise from changes in the anion solvation environment and consequent differences in the liquid phase electronic structure.¹⁻³ However, there are no experimental measurements of the liquid phase electronic structure for concentrated electrolytes, meaning that these very tricky calculations have not been validated against experimental data.

The liquid phase electronic structure of ionic liquids (ILs) with large metal cation concentrations were characterised using a combination of X-ray photoelectron spectroscopy (XPS), synchrotron resonant XPS, X-ray absorption spectroscopy (XAS) and DFT calculations, along with the characterisation of the free anions in ILs with no metal cations present. ILs were used rather than concentrated electrolytes with neutral solvent molecules present, as ILs are non-volatile at room temperature, allowing the use of standard ultrahigh vacuum XPS apparatus to study them. Our measurements were performed on a combination of laboratory-based and synchrotron-based XPS apparatus, including beamline B07-B at Diamond Light Source. These large metal cation concentrations gave ILs where the amount of free anions and anions bound to a metal cation were similar. This approach allowed us to characterise the electronic effect of metal cation binding to anions. The metal cations studied include Li⁺, Zn²⁺ and Sn²⁺, which facilitated the probing of the importance of the metal cation formal oxidation state on the anion electronic structure. Our experimental results match very well to our calculations, validating the calculations and allowing further insight into the anion electronic structure. The anions studied include [NTf₂]⁻, [TfO]⁻, Br⁻ and Cl⁻; [NTf₂]⁻ is especially crucial for concentrated electrolytes. Our results are the first step towards experimentally characterising the full influence of salt concentration on electrolyte electronic structure and therefore electrolyte reactivity; we will discuss the implications of our results towards both concentrated electrolytes and ionic liquids.

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Molecular Dynamics Simulations of Lithium-ion Mobility in Concentrated Sulfolane-LiBF₄ Mixtures

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Conventional Lithium-ion batteries (LIBs) typically rely on volatile and flammable carbonate-based electrolytes, raising concerns regarding their thermal stability and toxicity. [1] Alternative approaches encompassing nonaqueous polyelectrolyte solutions, aqueous Li⁺-ion batteries, eutectic mixtures, superconcentrated or highly concentrated electrolyte (HCE) solutions have received increasing attention as strategies to overcome the safety and environmental issues regarding conventional LIBs. Focussing on HCE solutions, we used molecular dynamics (MD) simulations to explore the solvation behaviour of sulfolane-LiBF₄ mixtures going to [LiBF₄] up to 6 mol.L⁻¹ (**Fig. 1**). The relaxation dynamics of the contact ion pair and Li-sulfolane pair follows a Kohlrausch–Williams–Watts function. The initial stages of the ion pair relaxation in LiBF₄-sulfolane mixtures resemble that seen in glass-forming materials at much lower temperatures [2,3]. At high LiBF₄ content, the relaxation of the contact ion pair is dictated by long-range Coulomb interactions, while density fluctuations play an important role in relaxation of the Li⁺-sulfolane pair. As the salt concentration increases, the Li-ion transport changes from cage diffusion to hopping conduction, like the Grotthuss mechanism of proton transfer.

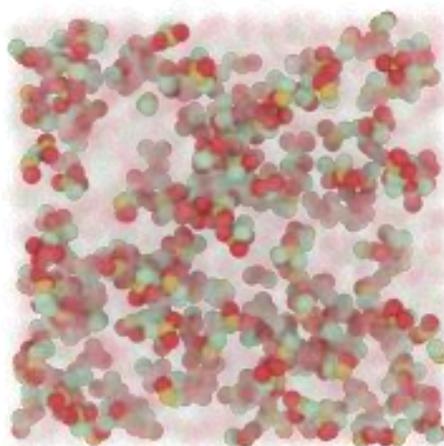


Fig. 1: MD simulation snapshot depicting the polar networks of the sulfolane/LiBF₄ mixture with molar fraction of sulfolane $\chi_{SL} = 0.68$. The highlighted Li⁺ ions are shared simultaneously by O atoms from sulfolane and F atoms from BF₄⁻. The colours grey, red, yellow, blue, light, and dark green represent C, O, S, Li, B and F atoms, respectively.

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In person Poster

Exploring the Interface between Metal Organic Frameworks and Ionic Liquids through Molecular Dynamics Simulations

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Type III porous liquids are a distinctive class of multiphase fluids constituted by porous solid hosts dispersed in size-excluded liquids. These materials have potential in processes such as gas storage, ion transport, energy storage, separation, and catalysis.[1] In this work the interactions on Type III porous liquids were characterized through classical Molecular Dynamics (MD) simulations. Specifically, the mobile phase was consisted of Ionic Liquids (ILs), while the solid substrate comprised Metal-Organic Frameworks (MOFs).

The ILs selected in this study were $[P_{6\ 6\ 6\ 14}][NTf_2]$, $[C_{14}C_{1im}][NTf_2]$, $[N_{14\ 1\ 1\ 2OH}][NTf_2]$ and $[C_{14}C_{1im}]Cl$ representing different possible arrangements of cations and anions interacting with MOFs (**Figure 1**). The MOF used was the crystalline structure of ZIF-8, characterized by its zeolitic imidazolate frameworks.

The MD analyses revealed that $[P_{6\ 6\ 6\ 14}][NTf_2]$, $[N_{14\ 1\ 1\ 2OH}][NTf_2]$ and $[C_{14}C_{1im}][NTf_2]$ were affected by the presence of the MOF, while $[C_{14}C_{1im}]Cl$ exhibited no deviation in comparison with its bulk phase results. Near to the ZIF-8 interface, the first three ionic liquids were arranged in a chessboard-like pattern formed by the cation headgroups and anions. However, this pattern is less defined for $[P_{6\ 6\ 6\ 14}][NTf_2]$, due to its more pronounced non-polar part attached to the cation moiety. In comparison to the $[NTf_2]$ -based ionic liquids, the behaviour of the polar part of $[C_{14}C_{1im}]Cl$ near the ZIF-8 surface shows a significant difference, influenced by the presence of the small Cl^- anions.

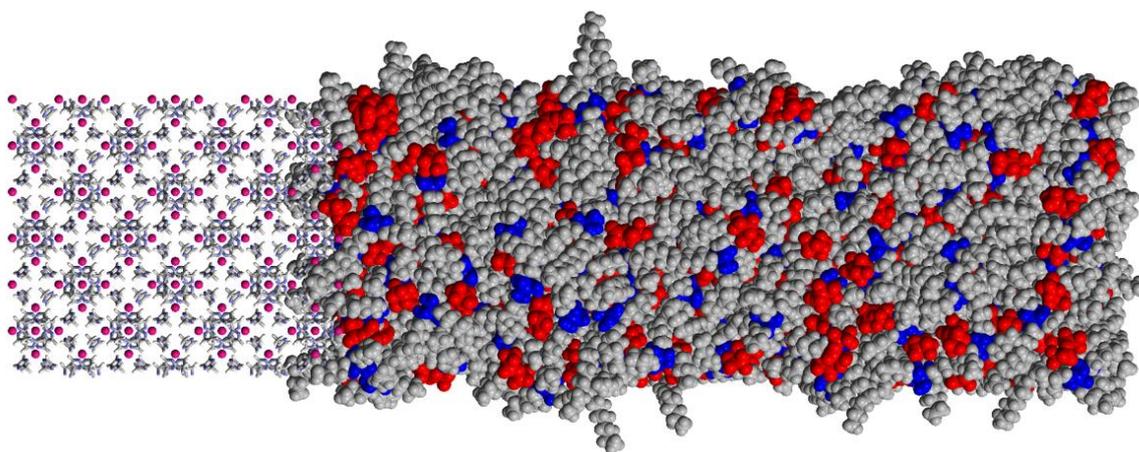


Figure 1: Snapshot of the ZIF-8/ $[P_{6\ 6\ 6\ 14}][NTf_2]$ system simulated at 350 K.

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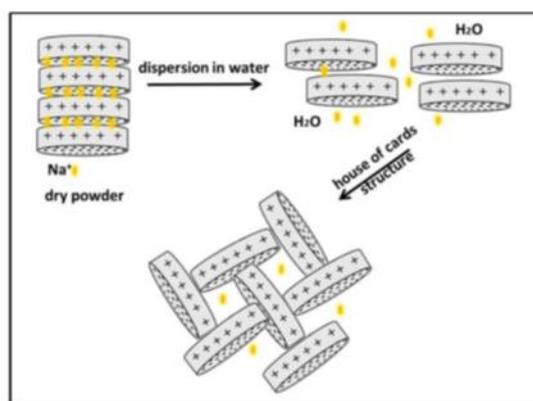
Impact of Cation Valence on Gelation and Viscoelastic Properties of Laponite Hydrogels

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Hydrogels have many properties which make them suitable for biomedical applications¹. These properties can be modified by the integration of inorganic ordered systems, in particular clays, into the gels. The most considerably used fillers are the lamellar structured clay minerals, because of both their abundance in nature and also because of their ready synthesis in a mineralogical pure form. The examples of these synthetic clays are laponite².



One example of a widely used synthetic clay is laponite ($\text{Na}+0.7[(\text{Si}8\text{Mg}5.5\text{Li}0.3)\text{O}20(\text{OH})4]-0.7$) which forms thixotropic hydrogels.³ We have done a multi-analytical study of two grades of laponite (RD - XLG) clay hydrogels has been established and initial studies performed on such hydrogels to investigate their structures after incorporating cations by using sundry technique (SEM ,EDX and BET).In addition, some aspects of their physical behavior such as rheological and gelation times.

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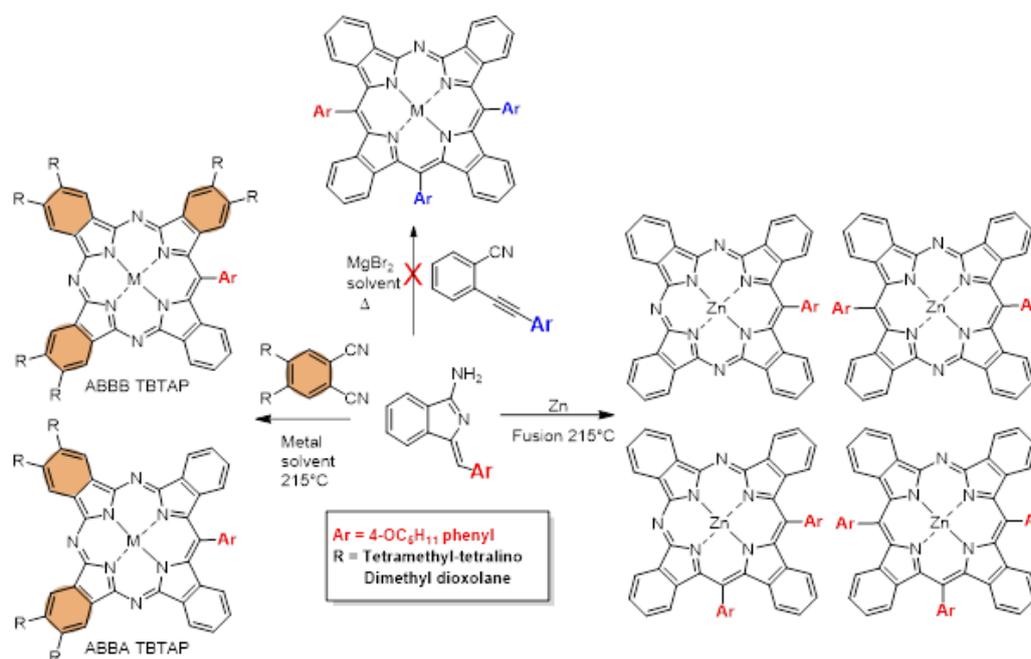
New Syntheses of tetrabenzoporphyrin hybrids

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The work described in this poster is concerned with the investigation of synthetic pathways toward tetrabenzoporphyrin/phthalocyanine hybrid macrocycles, specifically tetrabenzomonoazaporphyrins (TBMAs) or other less-nitrogenous hybrids. The initial investigation was conceived to modify the latest synthetic procedure developed in the Cammidge group whereby utilisation of a less nitrogenous precursor (alkynylbenzotrile, 1 x N) replaced phthalonitrile (2 x N) as co-macrocyclisation partner with an aminoisoindoline.¹ Unfortunately, no hybrids were formed, and a six-membered ring intermediate was obtained. We switched to investigate Linstead's conditions of fusion in the presence of zinc metal at high temperature on our proposed reactants (alkynylbenzotrile with aminoisoindoline) and, interestingly, formation of ZnTBTAP, cisTBDAP, transTBDAP and traces of ZnTBMAs were observed.² However, the formation of these hybrids proved to be a result of macrocyclisation of one reactant only "the aminoisoindoline". With discovery of this result, then, we further explored the latest Cammidge procedure to synthesise TBTAPs by employing substituted phthalonitriles ("B") with aminoisoindolines ("A"), in this case using zinc and different metals to track the origin of each unit in the final TBTAPs. ABBB TBTAPs were selectively obtained in high yield when zinc metal was utilised while a mixture of ABBB and ABBA TBTAPs were obtained when different metals were employed.³



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Physical properties study of Laponite – Cellulose derivatives Composite Hydrogels

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Hydrogels derived from cellulose have a vital role in improving agricultural sector to meet the rising demand for food. Introducing inorganic clay could improve the properties (such as chemical retention, structural integrity) of these hydrogels¹. Laponite RD clay has agricultural and horticultural benefits and a role in soil enhancement^{2 3}. This study aims to synthesize different composite hydrogels derived from the RD form of laponite and cellulose derivatives. A structural study was performed on composite hydrogels. These studies were performed using scanning electron microscopy (SEM), energy dispersive X-ray (EDX) and surface area measurements (BET gas adsorption) measurements. In addition, thermal analysis and rheological studies were conducted.

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Total Synthesis of new Environmentally Green Chiral iodoarene Lactate based Catalysts and their Recycle in Enantioselective Oxidation Reactions

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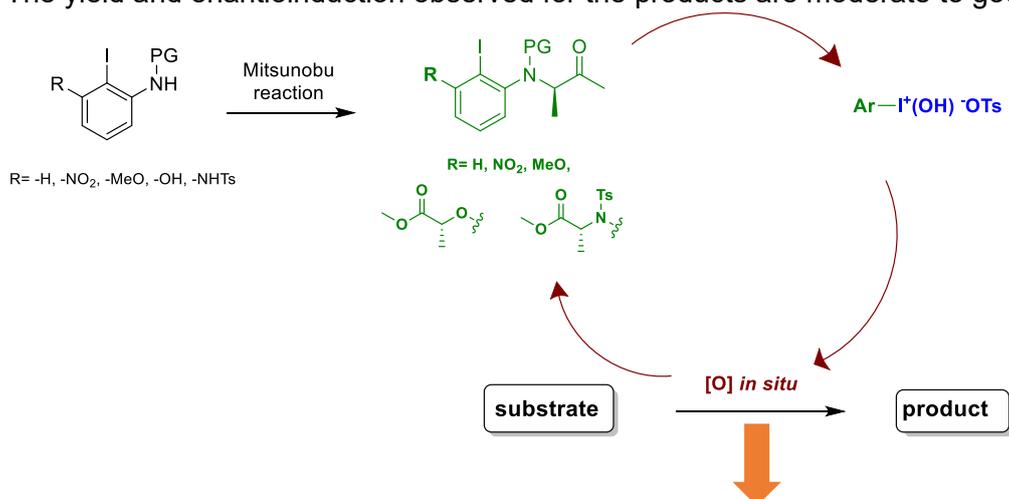
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Abstract:

In modern synthesis, reagents and catalysts for oxidation reaction should be chemically and environmentally efficient.¹ Iodine as a main group element has become a green alternative to heavy transition metals in synthesis due to its low toxicity, ready availability and ease of handling.^{2,3} Due to a strong electrophilic iodine centre, chiral organoiodine catalysts have been explored extensively in stereoselective reactions.³

Thus, it is of great interest to design and synthesise new chiral iodoarenes catalysts for enantioselective reactions. We report their successful synthesis in good yields. The potential of the organoiodine catalysts was subsequently investigated in the α -oxytosylation of ketones, in the oxidative rearrangement of alkenes and in the lactonization of carboxylic acids. The yield and enantioinduction observed for the products are moderate to good.



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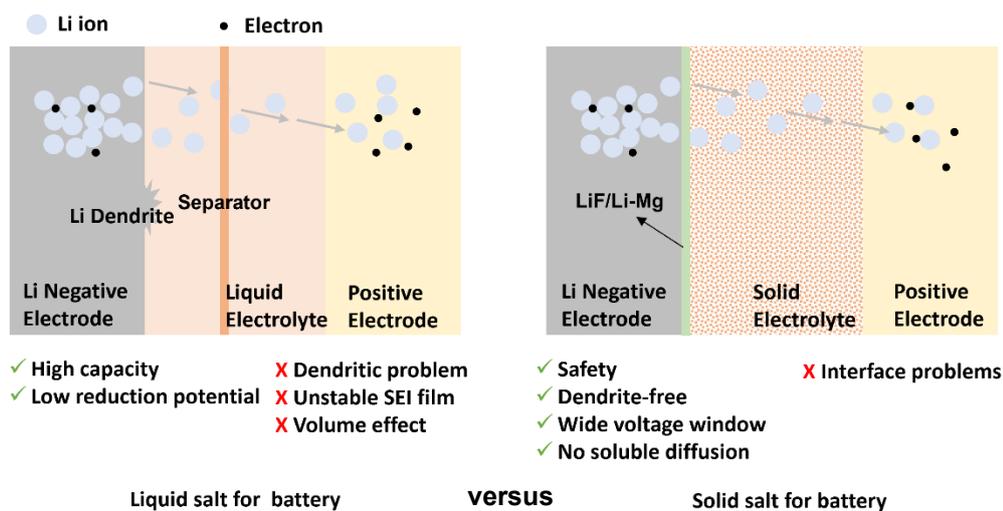
Solid salt of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ for Li-metal batteries

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The next iterative step to increasing the energy density of lithium (Li) batteries is to use a Li metal negative electrode¹⁻³. Li dendrites, however, can short-circuit the battery with a liquid salt electrolyte during dis-/charging, resulting in serious safety issues⁴. Solid salt of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ is a promising candidate for all solid-state Li batteries because of its high mechanical stability and Li-ion conductivity. The high mechanical stability could hinder the growth of Li dendrites to a certain extent⁵, but the poor contact, severe parasitic reaction between the Li metal and $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ still deter practical applications. In this work, a LiF/Li-Mg hybrid layer is formed in situ by sputtering MgF_2 on the Li surface. The Li-Mg alloy layer with good Li-ion conductivity could lead to uniform Li deposition whilst the LiF layer with high interface energy against Li could hinder the penetration of Li dendrites. As a result, the cell with LiF/Li-Mg shows excellent performance, providing an effective approach to a stable interface between the Li metal negative electrode and solid salt of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$.



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