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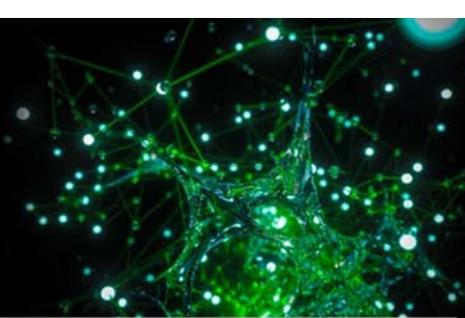
QUEEN'S UNIVERSITY
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QUILL25-MSILDG: Applications of Ionic Fluids

Book of Abstracts

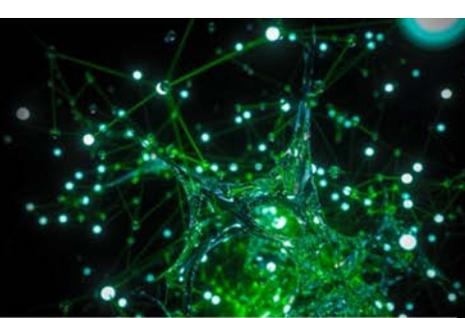
Celebrating 25 years of the QUILL Research Centre
in conjunction with the 2024 MSILDG Summer
Research Meeting



QUILL25-MSILDG: Applications of Ionic Fluids
Monday 2nd – Tuesday 3rd September 2024
Programme

Monday 2nd September – Venue: Canada Room/Council Chamber, Lanyon Building, QUB

- 09.45 – 10.20 Tea/Coffee
- 10.20 – 10.40 Welcome and Sponsor talks
- 10.40 – 11.20 **Anton Paar Keynote** - Margarida Costa Gomes (École Normale Supérieure de Lyon) *Three Approaches to Choose an Ionic Solvent – Revisited*
- 11.20 – 11.40 Haresh Manyar (QUILL) *Glycerol Derived Fuel Additives: From Process Optimisation to Technoeconomic Feasibility*
- 11.40 – 12.00 Safwan Salam (Petronas) *COSMO-RS-Based Screening of Ionic Liquids and Deep Eutectic Solvents for Efficient Direct Air Capture*
- 12.00 – 12.20 Shuoshuo Zhang (University of St Andrews) *Molten Lithium Carbonate Corrosion on SiC Heating Elements: Insights and Investigation on Protective Coatings*
- 12.20 – 13.20 Lunch (Great Hall)
- 13.20 – 13.40 Flash talks
- 13.40 – 14.20 **Keynote** – David Mecerreyes (POLYMAT University of the Basque Country) *From Poly(Ionic Liquids) to PolyDES and New Applications for Ionic Polymers*
- 14.20 – 14.40 Andreas Taubert (University of Potsdam) *Having Fun With Zwitterions: From Hydrogels to Ionic Liquid Crystals*
- 14.40 – 15.00 Emma McCrea (QUILL) *Methanolysis of Polyethylene Terephthalate (PET) Using Protic Ionic Liquids*
- 15.00 – 15.30 Tea/Coffee
- 15.30 – 15.50 Aloisia King (QUILL) *Manipulating Cation Lewis Acidity to Create Functional Ionic Liquid Systems*
- 15.50– 16.10 Lars Rehmann (University of Western Ontario) *Ionic Liquid Mediated Recovery from Lipids from Oleaginous Microorganisms*
- 16.10 – 16.30 Leila Moura (QUILL) *Impact of the Presence of Cyano Groups in the Solubility of Ethane and Ethylene in Ionic Liquids*
- 16.30 – 18.00 Poster Session (South Dining Hall)
- 19.30 – 22.00 Reception & Dinner (Naughton Gallery & Great Hall)
- 21.00 – 21.30 After-dinner talk – Prof Paul Davey *History of QUILL*



Tuesday 3rd September – Venue: Canada Room/Council Chamber, Lanyon Building, QUB

- 09.00 – 09.40** **Keynote** – **Agi Brandt-Talbot (Imperial College London)** *Applications of Ionic Liquids in Biorefining*
- 09.40 – 10.00** **Matt Panzer (Tufts University)** *Who's in Charge? Polyzwitterion Scaffolds for Ionogel Electrolytes*
- 10.00 – 10.20** **Ruwaida Asyikin Abu Talip (Universiti Teknologi PETRONAS)** *Effect of Deuteration Towards Physical, Chemical and Electrochemical Properties of BMIM Triflate Ionic Liquids*
- 10.20 – 10.50** **Tea/Coffee**
- 10.50 – 11.10** **Sanskrita Madhukailya (QUILL)** *Controlling LCST Phase Behaviour Via Structured Design of Ionic Liquids*
- 11.10 – 11.30** **Christian Balischewski (University of Potsdam)** *Elucidating the Iron-Based Ionic Liquid [C₄py][FeCl₄]: Structural Insights and Potential for Nonaqueous Redox Flow Batteries*
- 11.30 – 11.50** **Luis Branco (Universidade Nova de Lisboa)** *Ionic Liquids for Pharmaceutical and Therapeutic Applications*
- 11.50 – 12.10** **Haris Amir (QUILL)** *The Synthesis and Characterisation of Borate Anions for Functional Applications*
- 12.10 – 12.30** **Alberto Puga (Universitat Rovira i Virgili)** *How Wet Was My Liquid! Carboxylate Hydrates For CO₂ Capture*
- 12.30 – 13.30** **Lunch** (Great Hall)
- 13.30 – 13.50** **Eduards Bakis (University of Latvia)** *Designing Ionic Liquids as Charge Transfer Complexes*
- 13.50 – 14.10** **Giovanni Pireddu (NAAREA)** *Classical Molecular Dynamics Simulations of Molten Actinide Chlorides*
- 14.10 – 14.30** **Hector Rodriguez (Universidade de Santiago de Compostela)** *Ionic Liquids and Salt-Containing Eutectic Solvents for the Valorisation of Waste from Food Processing Industries: A Couple of Examples*
- 14.30 – 14.50** **Jose (Pepe) Palomar (Universidad Autónoma de Madrid)** *Carbon Capture and Conversion Thermodynamics: How to Promote Process Efficiency?*
- 14.50 – 15.20** **Tea/Coffee**
- 15.20 – 15.40** **Jean Le Bideau (Nantes Université)** *Enhanced Li⁺, Mg²⁺ and Zn²⁺ Diffusion at the Polymer-Ionic Liquid Interface within Ionogel*
- 15.40 – 16.00** **Bamidele (Dele) Akinwolemiwa (University of Nottingham)** *Design Considerations for Dissolved Na-ion in Ionic Liquid for Supercapatteries*
- 16.00 – 16.20** **Coby J Clarke (University of Nottingham)** *Linking Molecular Scale Interactions to Macroscopic Properties in Metal Ionogels*
- 16.20 – 17.00** **Fray Lecture** - **Andy Abbott (University of Leicester)** *Past and Future Applications of Deep Eutectic Solvents*
- 17.00** **Presentation prizes**

QUILL25-MSILDG: Applications of Ionic Fluids

List of Research Presentations

Monday 2 nd September	
Presenter	Title of Presentation
Margarida Costa Gomes (École Normale Supérieure de Lyon)	Three Approaches to Choose an Ionic Solvent – Revisited
Haresh Manyar (QUILL)	Glycerol Derived Fuel Additives: From Process Optimisation to Technoeconomic Feasibility
Safwan Salam (Petronas)	COSMO-RS-Based Screening of Ionic Liquids and Deep Eutectic Solvents for Efficient Direct Air Capture
Shuoshuo Zhang (University of St Andrews)	Molten Lithium Carbonate Corrosion on SiC Heating Elements: Insights and Investigation on Protective Coatings
David Mecerreyes (POLYMAT University of the Basque Country)	From Poly(Ionic Liquid)s to PolyDES and New Applications for Ionic Polymers
Andreas Taubert (University of Potsdam)	Having Fun With Zwitterions: From Hydrogels to Ionic Liquid Crystals
Emma McCrea (QUILL)	Methanolysis of Polyethylene Terephthalate (PET) Using Protic Ionic Liquids
Aloisia King (QUILL)	Manipulating Cation Lewis Acidity to Create Functional Ionic Liquid Systems
Lars Rehmann (University of Western Ontario)	Ionic Liquid Mediated Recovery from Lipids from Oleaginous Microorganisms
Leila Moura (QUILL)	Impact of the Presence of Cyano Groups in the Solubility of Ethane and Ethylene in Ionic Liquids

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Coby J Clarke (University of Nottingham)	Linking Molecular Scale Interactions to Macroscopic Properties in Metal Ionogels
Andy Abbott (University of Leicester)	Past and Future Applications of Deep Eutectic Solvents

Three Approaches to Choose an Ionic Solvent – Revisited

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Abstract

Ionic liquids, composed of large, flexible, and asymmetric ions with delocalized electrostatic charges, represent a vast and varied family of liquids, each with distinct chemical structures and interactions. This intrinsic diversity leads to remarkable properties, making them highly attractive as solvents or absorbers. However, the rational design of an ionic liquid tailored to specific properties remains a significant challenge.

This presentation revisits three crucial considerations in the selection of ionic solvents: (1) Favorable solute-solvent interactions, whether physical or chemical, are essential in determining solubility and selectivity. (2) The microscopic structure of the solvent directly influences the entropy of solvation, thereby dictating the absorption mechanisms. (3) The difficulty of achieving efficient mass transport underscores the importance of using mixtures of ions or balancing chemistry with free volume to optimize performance.

Recent advancements in ionic media design are presented to illustrate how these factors can be leveraged to create ionic solvents tailored for selective absorption.

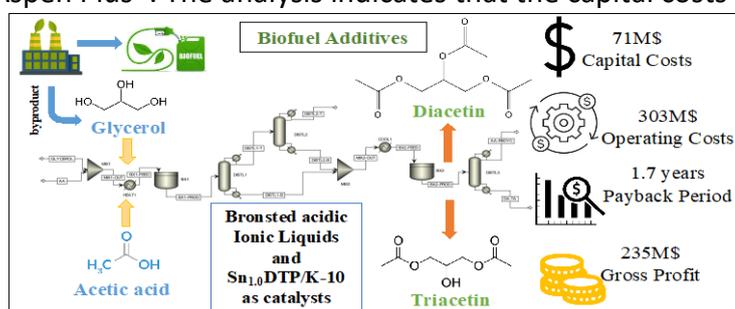
Glycerol Derived Fuel Additives: From Process Optimisation to Technoeconomic Feasibility

John Keogh, Manish Tiwari, Callum Jeffrey, Krutarth Pandit and Haresh Manyar*

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Abstract

With increasing energy demand, decreasing fossil fuel reserves, and climate emergency it is imperative to develop renewable biofuels and fuel additives. One of the potential alternatives is the bio-refinery concept, where biodiesel serves as a replacement of fossil fuels. However, bio-diesel production is associated with formation of up to 10wt% of waste glycerol as a liability. To enhance economic viability of biorefineries, it is essential to add value to glycerol, for instance, glycerol esterification using renewable acetic acid. Glycerol esters have a wide range of applications, both di- and tri-acetins are effective as fuel additives, improving the combustion and fuel economy of the biodiesel, whilst also decreasing harmful emissions. Typically, esterification process requires stoichiometric use of mineral acids or AlCl_3 as catalyst. With increased importance placed on green chemistry, catalysts need to be safe, non-corrosive and recyclable. In this work, it has been shown that low-cost and commercially available Bronsted acidic ionic liquids are efficient and reusable liquid acid catalysts for esterification. In particular, using $[\text{H-NMP}][\text{HSO}_4]$ as catalyst, the glycerol esterification was accomplished with 99% conversion of glycerol within 30 minutes, with 97.6% yield of di- and triacetin fuel additives [1]. For optimisation of the glycerol esterification process, the Design of Experiments (DoE) approach was applied, taking into account the variables such as speed of agitation, reaction temperature, glycerol:acetic acid mole ratio and catalyst loading. Herein, we also compared the efficacy of Bronsted acidic ionic liquids as catalysts with solid acid catalyst, such as tin exchanged tungstophosphoric acid (DTP) supported on montmorillonite K-10. Partially, exchanging the H^+ ion of DTP with Sn ($x = 1$) increased the acidity of the catalyst and showed an increase in the catalytic activity. Different process parameters were optimised, and a suitable kinetic model was fitted. Langmuir-Hinshelwood (L-H) dual-site model was able to describe the experimental data with high agreement between the experimental and calculated results [2]. Furthermore, we have studied the economic feasibility of a facility producing di- and tri-acetins by a two-stage process using 100,000 tonnes of glycerol per year using Aspen Plus[®]. The analysis indicates that the capital costs are 71 M\$ while the operating costs are 303 M\$/year. The gross profit is 60.5 M\$/year while the NPV of the project is 235 M\$ with a payback period of 1.7 years. Sensitivity analysis has indicated that the product price has the most impact on the NPV [3].



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COSMO-RS-Based Screening of Ionic Liquids and Deep Eutectic Solvents for Efficient Direct Air Capture

Siti Nur Alwani Shafie ^a, Nur Insyirah Zulkifli ^a, Siti Musliha Mat Ghani ^a, Nik Abdul Hadi Md Nordin ^{a*}, Mohd Dzul Hakim Wirzal ^a, Khairiraihanna Johari ^a, Safwan Abdul Salam ^b, Farahdila Kadir Khan ^{b*}, Shazleen Saadon ^b

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Abstract

Direct Air Capture (DAC) technology has emerged as a viable solution to directly capture non-point source CO₂ and enable its secure storage or utilization with adsorption as one of the potential technologies to be employed. Various efforts have been made to improve the adsorption capacity of the adsorbent by performing modification, specifically using amine and/or silane functionalization. This work explores alternative solvents to be used for the adsorbent modification, namely ionic liquids (ILs) and deep eutectic solvents (DESs) due to their low volatility, tunable properties, and specific interactions with CO₂. Comprehensive screening of 1402 species of IL and DES is performed using COSMO-RS by evaluating their interaction with CO₂, N₂ and O₂. From the results of CO₂ interaction, IL with cation from the Imidazolium group with longer alkyl chains (e.g. [1-Ethyl-2,3-methyl-imidazolium], [1-Propyl-2,3-methyl-imidazolium]) and anion from the Imide/amide and halogenide groups show the highest CO₂ interaction. For DES, Choline chloride-based, Lidocaine-based and Decanoic acid-based DES shows the highest affinity towards CO₂. From the N₂ and O₂ interaction, IL with shorter alkyl chain cation with anion from the Borate and Halogenide groups shows the lowest affinity towards N₂ and O₂. Meanwhile, DES Urea-based and Choline chloride-based DES exhibit the lowest N₂ and O₂ interaction. Therefore, it is suggested that Imidazolium-based cation with acetate-based anions ILs and Choline chloride-based DES will be the sustainable and effective material for atmospheric CO₂ capture.

References

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- [3] Liu, X.Y., Huang, Y., Zhao, Y. S., Gani, R., Zhang, X. P., Zhang, S. J., *Ionic Liquid Design and Process Simulation for Decarbonization of Shale Gas*. Ind. Eng. Chem. Res, 2016. **55**: p. 5931-5944.
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Molten Lithium Carbonate Corrosion on SiC Heating Elements: Insights and Investigation on Protective Coatings

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Abstract

The synthesis of lithium battery materials involves the use of muffle furnaces operating with SiC type heating elements. Usually, the industrial SiC heating element is protected by passive oxidation forming a protective silica film on the surface of the element. However, this strategy is not suitable for heating elements that operate in a Li-rich environment due to lithium silicates formation.

First, we characterised the oxidation of the SiC in air. Then, in the presence of lithia. After basic characterisation of the SiC rod and its oxidation in air, its reaction products in the presence of Li were studied. SiC rods were reacted with Li_2CO_3 , a likely source of lithium, by three increasingly aggressive methods: vapour-phase, wetting and full-immersion, particularly at the temperature just above the Li_2CO_3 melting point, to deliver accelerated ageing. The characterisation was achieved via an integrative data analysis through the coordination of Raman, XRD, and Energy dispersive X-ray analysis (EDX) techniques.

We found that molten Li_2CO_3 reacts with the originally protective silica surface layer forming three main lithium silicates ($\text{Li}_x\text{Si}_y\text{O}_{x/2+2y}$). The degradation of surface silica into non-adherent lithium silicates leads to spallation, which exposes fresh SiC for further oxidation and a speeding-up of the SiC oxidation process. Both processes eventually lead to a complete structural failure of the SiC rod.

After acquiring a basic understanding on SiC degradation upon lithiation, we tested four affordable and readily available high-viscosity silicate salts as coating materials, all which were found effective in lithiation protection. The coating protects SiC in two aspects. First, it works as a barrier for SiC oxidation. Second, it pre-infiltrates SiC before lithiation and fills all gaps in the SiC rod. Due to the high viscosity, the coating can block or slow down Li from infiltrating further into the inner structure of the rod by slowing down the formation of lower melting point glasses. This effectively increases the lifetime of SiC heating element.

From Poly(Ionic Liquid)s to PolyDES and New Applications for Ionic Polymers

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Abstract

In this lecture, we will review our recent activities in the synthesis, characterization and applications of new ionic polymers. First, several examples on the synthesis of poly(ionic liquid)s will be shown. The application of those poly(ionic liquid)s in batteries will be explained showing examples of its use as polymer electrolytes in lithium and sodium batteries as well as polymer binders in high voltage cathodes.¹

Second, a novel family of multifunctional deep eutectic monomers based on polyphenols and the corresponding polymers will be discussed. Phenolic chemistry allows modulating molecular interactions tuning the ionic polymer properties from soft adhesive to tough materials. Pyrogallol and hydrocaffeic acid-derived ionic polymers showed outstanding adhesiveness. Additionally, phenolic polymeric deep eutectic solvents (polyDES) featured metal complexation ability, anticorrosion properties and fast processability by digital light 3D printing for bioelectronic applications.²

References

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Having Fun With Zwitterions: From Hydrogels to Ionic Liquid Crystals

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Abstract

Besides many other things, zwitterions can be used to make ionic liquids, ionic liquid crystals, or ionogels. The intriguing aspect of many of these zwitterion-based (soft) material is that already the zwitterions themselves have interesting properties like rather high thermal stabilities. These properties can then further be altered and expended by making ionic liquids from these zwitterions. The group has been researching zwitterion-based materials for roughly a decade [1-5] and the presentation will introduce some of the basic concepts, molecular building blocks, and materials that have been developed. The focus of the presentation will be on a large group of zwitterions, their phase behavior, and their ion transport properties. Moreover, we will show how these zwitterions can be transformed into ionic liquid crystals with a rather high thermal stability, interesting proton transport properties, and again interesting liquid crystallin phases. Some of the zwitterions are also able to enhance the performance of enzymes or are able to stabilize rather reactive media, which would otherwise decompose relatively rapidly. Figure 1 shows the general reaction towards some of our zwitterions, a photograph of zwitterion-based hydrogels, and the texture of a zwitterion-based ionic liquid crystal recently made in the laboratory.

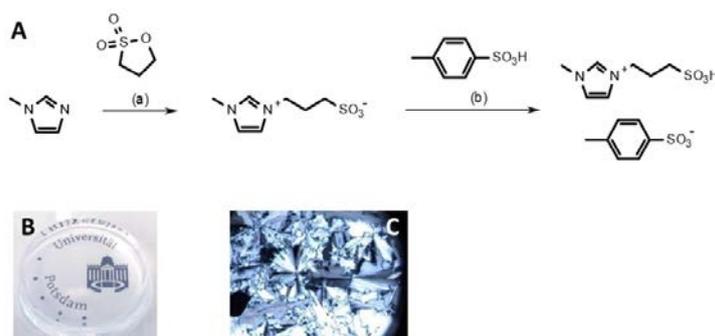


Figure 1 A) Reaction towards some of our zwitterions and ionic liquids [1], B) photograph of zwitterion-based hydrogels [4,5], C) and the texture of a zwitterion-based ionic liquid crystal.

Acknowledgements: The author thanks A. Lange, S. Shehaj, Dr. T. Mai, Dr. R.B.J. Ihlenburg, Dr. E. Delahaye, Dr. C. Günter, Dr. K. Zehbe, S. Mies, and A. Nitschke for their efforts and hard work in generating all the wonderful data that will be presented at the conference. Funding by the University of Potsdam, the Deutsche Forschungsgemeinschaft DFG, and the Deutsche Akademische Austauschdienst DAAD is gratefully acknowledged.

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Methanolysis of Polyethylene Terephthalate (PET) Using Protic Ionic Liquids

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Abstract

The deployment of innovative technologies is crucial for addressing the environmental challenges posed by plastic waste, particularly polyethylene terephthalate (PET). A promising approach involves the use of ionic liquids, developed by our group, to catalyse the depolymerisation of PET into dimethyl terephthalate (DMT) via methanolysis.¹ By incorporating a microwave reactor, this process is further enhanced, offering faster reaction times and improved efficiency. However, the separation of the resulting products, particularly the isolation of high-purity DMT from the reaction mixture, presents significant challenges that must be overcome to fully realise the potential of this method. This approach not only underscores the need for sustainable recycling solutions but also highlights the transformative potential of combining ionic liquids and microwave technology in advancing the circular economy.

This study aims to investigate the efficiency of ionic liquids as catalysts in the microwave-assisted depolymerisation of PET to produce DMT. Additionally, it assesses the environmental and economic feasibility of scaling up this ionic liquid-based, microwave-enhanced process for industrial recycling, while also addressing the challenges associated with separating DMT from the reaction mixture. By systematically exploring reaction parameters, including temperature, pressure and ionic liquid composition, the study seeks to optimise depolymerisation efficiency. The goal is to maximise DMT yield and conversion, while minimising energy consumption and refining separation techniques to ensure high-purity product recovery.

References

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Manipulating Cation Lewis Acidity to Create Functional Ionic Liquid Systems

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Abstract

Lewis acidity in ILs is most commonly associated with 'acidic' halometallate anions [1], or with recently emerging acidic cations, including borocations and solvate ILs (group I/II metal-complex cations).

An area of opportunity is for deploying the capability of either LA cations or anions in ILs to generate new Frustrated Lewis acid/base pairs (FLP) in an ionic liquid form that are capable of activating small molecules such as hydrogen. We have previously demonstrated that IL environments can extend the life-times of FLP encounter complexes to the NMR timescale [2] and reasoned that the FLP based on dilute solutions of *N*-alkylacridinium salts as LA and lutidine (2,6-dimethylpyridine) as base described by Ingleson and co-workers [3] could be transformed through variation of cation *N*-alkyl substitution and selection of appropriate anions. Moreover, with judicious selection of anions, both the FLP and products from heterolytic splitting and capture of hydrogen (as H⁺/H⁻), namely *H*-lutidinium cations and dihydro-*N*-alkylacridine could be maintained in an IL form (Figure 1). Such a system would be an intrinsic ionic liquid frustrated Lewis pair (IL-FLP) with the potential to control activation of small molecules (H₂/CO₂ etc) by manipulating the phase equilibrium.

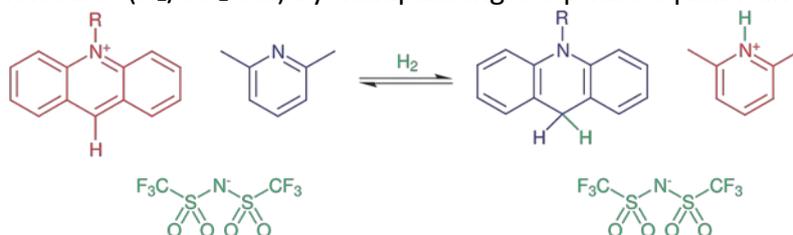


Figure 1 - On heterolytic activation of H₂ to H⁺/H⁻, the IL *N*-alkylacridinium bistriflylimide/lutidine FLP (*left*) is transformed into the corresponding IL *H*-lutidinium bistriflylimide/*N*-alkyl-9,10-dihydroacridine pair (*right*).

Here, we report the first studies of *N*-alkylacridinium bistriflylimide/lutidine systems as solvent-free ionic liquid FLP catalysts.

References

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Ionic Liquid Mediated Recovery of Lipids from Oleaginous Microorganisms

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Abstract

Various microalgae and yeast strains can produce high amounts of lipids. Initial applications of single cell lipids were sought in the fuels industry as a potential 'carbon neutral' feedstock for biodiesel. Current interest has shifted to the food and nutraceutical industry as algal lipids can be comparable to traditional lipid sources like meat and dairy. Of particular interest are strains with a high proportion of polyunsaturated fatty acids (PUFAs), particularly docosahexaenoic acid (DHA), for its health benefits. Cultivation of large quantities of microalgae (phototrophic or heterotrophic) and oleaginous yeast for the purpose of lipid production results in a wet feedstock from which the desired lipid fraction has to be recovered. Pre-treatment such as cell disruption followed by extraction is required to access the intercellular lipids. These steps are technically and economically challenging, even for high value products such as DHAs. Various ionic liquids can be used to fractionate the biomass and to disrupt the cell wall in a single step. This paper discusses the selection of ionic liquids for the fractionation and lipid extraction from *Rhodospiridium diobovatum* (yeast) [1], *Chlorella vulgaris* [2] and *Thraustochytrium sp* (algae) [3]. The cell-disruption was further enhanced through the use of a pulsed electric field during the IL pretreatment resulting in shortened processing time.

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Impact of the Presence of Cyano Groups in the Solubility of Ethane and Ethylene in Ionic Liquids

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Abstract

Light hydrocarbon separations are considered one of the 7 chemical separations to change the world. [1] Ionic liquids (ILs) have been studied as mass-transfer agents to promote the low-energy separation of these gases, contrasting with the current cryogenic distillation process. [2] So far it was found that the solubility of ethane, ethylene, propane and propylene in the ionic liquids tested are controlled by non-specific interactions, even for ionic liquids containing side-chain functionalisations designed to optimize the interactions with one of the hydrocarbons to be separated. This means that there is an inverse relationship between the molecular weight of the IL and the solubility of the gasses. However, the presence of cyano groups in the cation and anion of an ionic liquid seems to lead to the highest separation selectivities towards the unsaturated gas found in ionic liquids.

To further understand and harness this potential separation effect, we determined the ethane and ethylene solubility on a series of ionic liquids containing cyano functionalities in both the cation and anion of ionic liquids, using an isochoric saturation method. Molecular dynamics (MD) simulations of the systems were also performed and revealed and gave further insights into the molecular solvation mechanisms. [3, 4].

We have found that the presence of the cyano group has a small positive effect on the gas separation selectivity of ethylene over ethane, due to a slightly preferential weak interaction with the unsaturated gas, but that the solvation of both gases in all ionic liquids tested is still mostly entropically driven.

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Application of Ionic Liquids in Biorefining

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Abstract

Ionic liquids are versatile solvents that have shown promise in several applications, including biorefining. Defossilising the chemical industry is increasingly important as society transitions from fossil resource dependence to responsible utilisation of renewable and circular raw materials. Biomass is already an important feedstock materials and chemicals; however, better and new processes must be developed to fully exploit the potential and provide the diverse range of products and services that we are accustomed to or aspire to.

Ionic liquids can play a role in biorefining due to their strong interactions with biopolymers such as polysaccharides and lignin. In this talk, the journey of developing a wood fractionation process using low-cost ionic liquids [1] is followed from the lab to pilot scale and how the research has inspired additional sustainable ionic liquid applications, in particular, lignin carbon fibre spinning.[2] To develop relevant processes, cost-effectiveness and sustainability benefits need to be demonstrated in addition to performance, so insights from Life Cycle Impact Assessment and Techno-Economic Modelling are also presented.

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Who's in Charge? Polyzwitterion Scaffolds for Ionogel Electrolytes

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Abstract

Electrolytes consisting of ionic liquids (ILs) and dissolved alkali metal salts (such as lithium bis(trifluoromethylsulfonyl)imide, LiTFSI) can provide many beneficial properties for the realization of safer batteries, including: low volatility, nonflammability, high alkali metal cation conductivity, and a wide electrochemical stability window. By incorporating a 3D, volume-spanning solid network inside the IL phase, one can create a freestanding ionogel, which also adds a leakproof character to the list of intrinsic advantages of such materials. One particularly intriguing class of polymers that our group has been exploring in recent years for this application is polyzwitterions, (co)polymers containing one or more repeat units that feature zwitterionic (ZI) functional groups, which introduce even more charged moieties into already highly ion-dense systems.¹⁻³

Possessing notably high dipole moments, ZI side groups can endow polyzwitterion scaffolds with an ability to exert significant Coulombic interactions upon the various ionic species present within an ionic liquid-based electrolyte. Depending on the specific chemical details of the ZI motif (*e.g.* sulfobetaine vs. phosphorylcholine vs. carboxybetaine) and the selected IL environment, competing electrostatic interactions between the zwitterions and ionic species present may determine both ionogel mechanical behavior and the details of selective ion transport. For example, polymer networks synthesized using the ZI monomer 2-methacryloyloxyethyl phosphorylcholine (MPC) via *in situ* free radical polymerization within LiTFSI or NaTFSI-containing IL (1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide) solutions yield highly stable, noncovalent crosslinks that are Coulombic in nature and enabled by the spontaneous assembly of lithium or sodium alkali metal cations with MPC monomers. Experimental observations suggest that such noncovalent crosslinks can be highly robust, persisting even above 200 °C. Ongoing studies seek to further demonstrate that polyzwitterion-supported ionogels hold significant promise for realizing future batteries that operate safely under extreme environmental conditions.

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Effect of Deuteration Towards Physical, Chemical and Electrochemical Properties of BMIM Triflate Ionic Liquids

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Abstract

The deuterated compound has been extensively studied in the past 20 years ago signifying their relevance and importance in a wide range of fields [1-3]. The deuteration process where the hydrogen is exchanged with deuterium allows to alter the properties of the compound making them to have superior properties than the non-deuterated one. The deuteration of ionic liquids (ILs), a niche field of interest, has been reported to alter certain characteristics of the ILs. A strong isotope effect of deuterated triethylammonium methanesulfonate was demonstrated, which mainly affects the hydrogen bonding and the structural rearrangement of the ILs [3]. In another study, the deuterated 1-butyl-3-methylimidazolium triflate was reported to exhibit high viscosity and high density as compared to the non-deuterated one [1]. In this study, the synthesis of deuterated 1-butyl-3-methylimidazolium triflate (BMIM triflate) of the methyl group and its characterization are reported. To understand further the effect of the deuteration on the compound, the viscosity, density, ionic conductivity, and electrochemical window of the synthesized deuterated BMIM triflate were compared with non-deuterated BMIM triflate. Furthermore, using the computational method, COSMO-RS, the extent of how the deuteration affects the interaction energies viz. coulombic, hydrogen-bonding, and van der Waals interactions were also explored. This paper aims to enrich the understanding on the effect of deuteration towards the properties of the ILs. This will open the possibility for this special class of ionic liquids to be applied to more applications.

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Controlling LCST Phase Behaviour Via Structured Design of Ionic Liquids

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Abstract

The tetrabutylphosphonium 5-phenyl tetrazolate/water system ($[P_{4444}][Ph-Tet]/H_2O$), 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 both cation and anion modification can control the phase behaviour of the ionic liquid/aqueous systems changing the hydrophobicity (water content) of the IL-rich phase and reducing the cloud point temperatures 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 variable temperature is also investigated.

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Elucidating the Iron-Based Ionic Liquid [C₄py][FeCl₄]: Structural Insights and Potential for Nonaqueous Redox Flow Batteries

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Abstract

Nowadays, Ionic liquids (ILs) are gaining increasing interest in the fields of energy storage and energy production/conversion. In this study, we describe a low-melting organic-inorganic crystalline ionic liquid compound, *N*-butyl pyridinium tetrachlorido ferrate (III). The material can easily be synthesized using a one-pot approach in an ionic liquid medium. XPS and single-crystal X-ray diffraction confirm that the basic inorganic block is [FeCl₄]⁻, which is counterbalanced by an *N*-butyl pyridinium cation. The structure was further analysed and compared to previously studied transition metal based tetrahalido metallate ILs.^{[1][2]} The compound exhibits a melting point of 37.6 °C by differential scanning calorimetry, which is among the lowest values for a pyridinium-based metal containing ionic liquid. The material shows promising electrochemical behaviour at room temperature in both aqueous and non-aqueous solvents, and at elevated temperatures in its pure liquid state. In fact, a promising pseudo-reversible redox process was analysed and given its appreciable solubility in both water and acetonitrile, the compound can act as a redox active species in a supporting electrolyte for redox flow battery applications. As iron-based materials are gaining rapid interest in this area, an RFB prototype setting using two half cells was assembled using the compound in charge-discharge-cycling experiments.^[3] These classes of low melting ionic solids with long-range order and interesting electrochemical applications are potential candidates for a range of potential green energy storage and harvesting systems.

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Ionic Liquids for Pharmaceutical and Therapeutic Applications

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Abstract

Over the past few decades, Ionic Liquids (ILs) have been extensively studied across various fields of chemical and biological research, including pharmaceutical sciences, due to their highly tunable physical and chemical properties. In pharmaceuticals, ILs have been explored as green solvents for the preparation, purification, and crystallization of active pharmaceutical ingredients (APIs) [1]. Additionally, combining ionizable APIs with biocompatible organic counter-ions has demonstrated significant potential in enhancing the bioavailability of poorly water- and/or lipid-soluble drugs. This approach also helps reduce or eliminate polymorphism, leading to more effective drug formulations [1]. In recent years, our research team has reported on pharmaceutical ionic systems (ionic liquids and organic salts; API-OSILs) based on anti-inflammatory, antibiotic, anti-tumoral, and anti-tuberculostatic agents, showing notable advantages over the original APIs [2-5]. Despite these advancements, pharmaceutical ionic systems continue to prove effective as drug delivery systems, improving bioavailability (solubility, permeability) and addressing polymorphism.

Here, we present our latest developments in API-OSILs, including the synthesis and characterization of novel silica nanoparticles combined with pharmaceutical ionic systems. These innovative nanomaterials show promise for treating bacterial infections [6]. This methodology can be expanded to encompass a wider range of antibiotics and various ionic liquid precursors, making it an attractive alternative for producing novel pharmaceutical ingredients immobilized on nanoparticles, with a strong focus on combating bacterial resistance.

Acknowledgements:

This work was supported by the InsectERA – Novo sector bioindustrial Project (n^oC644917393-00000032), co-financed by PRR - Recovery and Resilience Plan of the European Union (Next Generation EU). The authors also thank the support from FCT/MCTES (UIDB/50006/2020, LA/P/0008/2020 and UIDP/50006/2020 of the Associate Laboratory for Green Chemistry – LAQV).

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The Synthesis and Characterisation of Borate Anions for Functional Applications

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Abstract

Ionic liquids containing borate anions have a long history; from tetraalkylborates¹ through tetrafluoroborates² to orthoborate anions,³ and most recently a range of functionalised cyanoborate systems.⁴ Here we describe studies exploring expansion of the range of available orthoborate anions suitable for forming ionic liquids through transformation from tetra-oxo (B{OOOO}) into mixed oxygen/nitrogen (B{OONN}) and ultimately to tetraamine (B{NNNN}) coordination environments.

In collaboration with Deakin university, a range of borates (figure 1) have been used as electrolytes in sodium cells, to investigate the formation of a solid electrolyte interphase (SEI). The conductivity of trihexyltetradecylphosphonium [P₆₆₆₁₄]⁺ based ionic liquids were recorded as well as diffusion NMR by using pulse field gradient (PFG) and echo based NMR experiments. In collaboration with POLYMAT (University of the Basque country) water soluble PDADMA borates were synthesised and investigated as binders for NMC cathodes in Li-ion batteries.

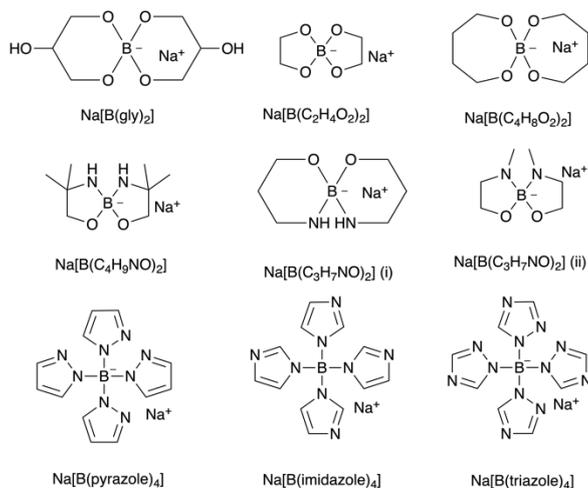


Figure 1 - Structure of the sodium salts of the B{OOOO}, B{OONN} and B{NNNN} borate anions under investigation.

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How Wet Was My Liquid! Carboxylate Hydrates for CO₂ Capture

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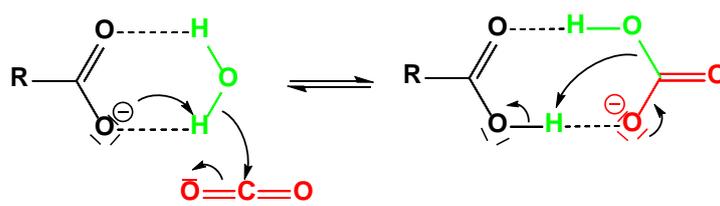
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Abstract

Examples of alternative non-volatile amine-free CO₂ chemisorbents that can be regenerated at moderate temperatures are scarce. Among these, ionic liquids (ILs) can be produced by judiciously combining anions of adequate basicity with low-acidity cations. A family of anions that fulfil the former requisite is that of carboxylates. Recent investigations have shown that, in the presence of small amounts of water, being the optimum around the 1:1 H₂O/IL molar ratio, carboxylate ionic liquid hydrates exhibit surprisingly high CO₂ solubilities. The major mechanistic route enabling chemical sorption in these systems involves formation of hydrogencarbonate as the trapped species (Scheme below).



We will present a systematic overview of the effect of water on both liquid properties and CO₂ solubilities of tetraalkylphosphonium and tetraalkylammonium carboxylate ionic liquids.^[1,2] Used as monohydrates, they exhibit highest capacities (3 mol L⁻¹, *i.e.* $\approx 0.9 \text{ mol}_{\text{CO}_2} \text{ mol}_{\text{IL}}^{-1}$, at 5 bar, 25 °C) at equimolar H₂O/IL ratios, approaching those of commercial aqueous amine sorbents. Importantly, the hydrated carboxylates studied can be readily regenerated to completion at temperatures as low as 60 °C, owing to their relatively low sorption enthalpies ($\approx 40 \text{ kJ mol}^{-1}$) and regeneration heats ($\approx 4.3 \text{ kJ g}(\text{CO}_2)^{-1}$). Finally, their application as solid-supported sorbents in fixed-bed capture-release mode will be presented.

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Designing Ionic Liquids as Charge Transfer Complexes

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Abstract

In line with the principles of green chemistry, chemical processes should prioritize safety and resource efficiency, including minimizing energy consumption. Energy-intensive chemical processes significantly contribute to CO₂ emissions in the production of fine chemicals. Harnessing light energy as a sustainable alternative for providing activation energy in chemical transformations offers great potential.

In this study, we investigate a class of highly conductive and fluid ionic liquids (ILs) that generate radicals upon light exposure in their neat state. We present evidence of radical formation in pyridinium tricyanomethanide ILs (**Fig. 1**) through ion pair charge transfer (CT), as confirmed by Electron Paramagnetic Resonance (EPR) and UV-Vis spectroscopy. The electron transfer energy can be tuned by targeted structural modifications of the IL cation, with verification provided by DFT modelling and cyclic voltammetry experiments.

This work paves the way for advancements in the applied photochemistry of ILs, a promising area of sustainable chemistry that has thus far received limited attention.

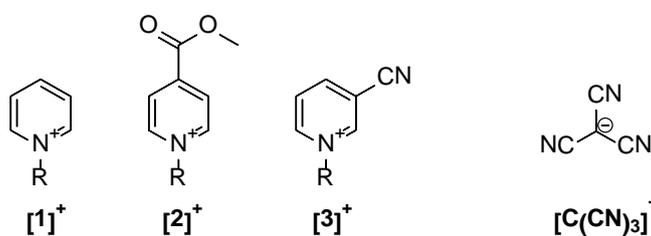


Figure 1 - Ionic liquid ion structures studied in this work

Classical Molecular Dynamics Simulations of Molten Actinide Chlorides

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Abstract

Next generation nuclear technologies can imply an extensive use of molten salts, including actinide halides, which constitute the nuclear fuel. Despite their importance, several practical challenges limit their experimental manipulations, resulting in knowledge gaps for their structural and thermophysical properties. Molecular dynamics simulations have the potential to bridge these gaps, as demonstrated in several previous works [1,2]. For example, in a recent work, we introduced and validated a new classical molecular model for plutonium-based molten chlorides [3].

In this work [4], we extend our approach to the development of new force fields for the actinide series, ranging from thorium to curium chlorides. We demonstrate the usage of our force fields to compute structural properties, density, heat capacity, and isothermal compressibility of pure actinide molten salts at various temperatures. We discuss our results in the context of already existing theoretical and experimental datasets. We find a general good agreement with other results and extend the predictions to systems not considered in previous works. Finally, we highlight the peculiarity of ThCl₄ compared to actinide trichlorides in terms of molecular and thermophysical properties.

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Ionic Liquids and Salt-Containing Eutectic Solvents for the Valorisation of Waste from Food Processing Industries: A Couple of Examples

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Abstract

The processing of fish and the production of juices and jams from citrus fruits are two representative examples of food processing industries that generate vast amounts of waste (approximately half of the mass of the raw material processed). The composition of this waste offers an opportunity for valorisation through the recovery of different byproducts of commercial interest. On the one hand, fish skin and scales can be the source of collagene, gelatine, fish protein hydrolysates, or hydroxyapatite, with applications in nutraceutical and pharmaceutical industries. Traditional techniques for their recovery involve the use of harsh chemicals and high temperatures, leading to potential degradation of amino acids and environmental concerns. On the other hand, the mechanical cold pressing of citrus fruit waste yields essential oils with varied applications as colourants, scents, and flavouring agents in food, beverages and pharamceuticals, and also as ingredients in a range of cosmetic and persynal hygiene products. Only a small percentage of the composition of these essential oils corresponds to the oxygenated compounds that are responsible for the favourable organoleptic characteristics, and more than 90% are non-active terpenic compounds that, in fact, can generate undesired compounds by oxidation and reduce the shelf-life of the essential oil. An effective deterpenation process, for example by liquid-liquid extraction, would lead to a more stable essential oil with a strong reduction in volume (implying strong reduction of storage requirements and transportation costs). Unfortunately, conventional solvents perform poorly from a thermodynamic perspective to carry out such deterpenation. Ionic liquids and other highly ionic fluids such as salt-containing eutectic solvents, with their unique solvation environment and a potentially negligible volatility, may be the basis for the development of alternative and more sustainable processes to (pre)treat fish processing waste in order to recover collagen-related products or natural hydroxyapatite, as well as to perform the deterpenation of citrus essential oils. In this presentation, an overview is given on the ongoing efforts of the authors towards these objectives.

Carbon Capture and Conversion Thermodynamics: How to Promote Process Efficiency?

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Abstract

Carbon capture and utilization (CCU) are main strategies to promote industrial decarbonization, with the goal to address the climate challenge of net-zero by 2050. Therefore, big efforts are being made by academic and industry for developing new efficient and cost-effective carbon capture (CC) technologies. It involves a wide range of industrial applications and CC systems, from the high CO₂ concentrated streams in low-carbon footprint energy production (H₂ production, pre-combustion, biogas upgrading) to relatively diluted (post-combustion) and highly diluted (direct air capture, DAC) carbon sources. The process performance of CC technologies is determined for several factors, highlights the CO₂ partial pressure of treated industrial streams, the sorbent material properties, the operating conditions, the process configuration and used utilities. Subsequent carbon utilization (CU) to produce added-value chemical products is also widely explored to decrease the carbon emission rates and promote carbon circular economy. This additional process must be optimized to reach neat CO₂ fixation in sustainable CCU applications. It implies the development of efficient catalyst and the design of reaction/separation process to produce commercial CO₂-based product at competitive cost and minimized environmental impacts. In the last years, Ionic Liquids (ILs) have become promising CO₂ chemical absorbent and CO₂ catalysts in the CO₂ cycloaddition to epoxides for cyclic carbonates production. Sequential CC and CU process designed using ILs as absorbent/catalyst were reported with lower energy consumption, process cost and environmental impacts than those based on benchmark industrial processes. Additionally, bifunctional ILs -able to chemically absorb and activate the CO₂ compound- were designed for new integrated CCU processes, allowing process intensification with corresponding decreasing of operating and capital costs. In this work several molecular simulations tools (density functional theory, COSMO-RS, molecular dynamics), combined with process simulations and life cycle assessment, will be applied to explore the thermodynamic limits of CCU strategies for cyclic carbonate production based on ILs, with the aim of overviewing the role of material properties and operating variables on CCU process performance, involving relevant industrial CC systems (pre-combustion, biogas, post-combustion, DAC) and different cyclic carbonate products (ethylene, propylene, hexylene, styrene, glycerol).

Enhanced Li^+ , Mg^{2+} and Zn^{2+} Diffusion at the Polymer–Ionic Liquid Interface within Ionogel

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Abstract

With the widespread use of batteries, their increased performance and safety is of growing importance. While looking for enhanced energy and power, as well as naturally abundant, eco-friendly and cheaper elements, one avenue for this is the enhancement of ion diffusion, particularly for efficient and safe solid-state-like electrolytes, and for different ions such as lithium (Li^+) and magnesium (Mg^{2+}), sodium (Na^+), zinc (Zn^{2+}).¹ Unravelling the origin of better cation diffusion in confined ionic liquids (ILs) in a polymer matrix (ionogels) was compared to that of the IL itself.² Ionic conductivity measured by EIS for ionogels (7.0 mS.cm^{-1} at 30°C) is very close to the conductivity of the non-confined IL (8.9 mS.cm^{-1} at 30°C), *i.e.* 1-ethyl-3-methylimidazolium bis(trifluorosulfonyl)imide (EMIM TFSI). An even better ionic conductivity was observed for confined EMIM TFSI with high concentrations (1M) of lithium or magnesium salt added. The improved macroscopic transport properties could be explained by the higher self-diffusion, measured by PFG NMR, of each ion at the liquid-to-solid interface induced by the confinement in poly(vinylidene fluoride) (PVDF) polymer matrix. Upon confinement, the strong breaking down of ion aggregates enables a better diffusion especially for TFSI anion and strongly polarizing cations (*e.g.* Li^+ , Mg^{2+}). The coordination number, obtained by in-depth Raman study, of these cations in the liquid phase confirmed that metal cations interact with the polymer matrix. Moreover, from the NMR study, it is a major result that the activation energy for diffusion is lowered (Fig. 1).²

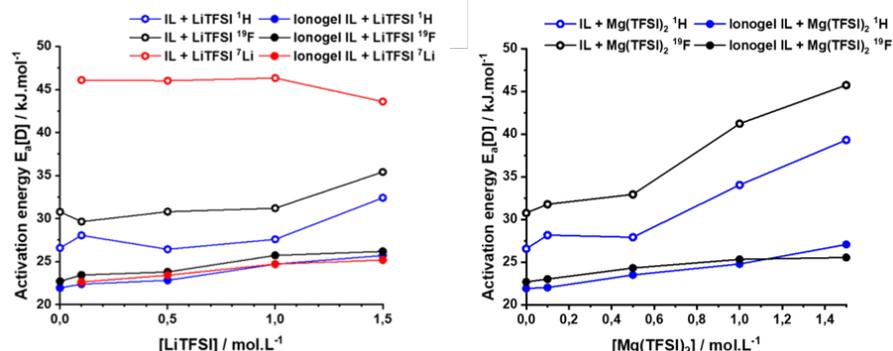


Figure 1 - Activation Energy for non-confined (open) and confined ILs (full) for Li^+ and Mg^{2+} systems, *resp.*

This enabled to assert that confining ILs improves the transport properties in the liquid phase of biphasic PVDF-based ionogels. Moreover, such decrease of activation energy has also been obtained with other ionogel (EO-based polymer, phosphonium-FSI-Li ILL).³ In addition, in order to deepen our understanding of these electrolytes, but also to be able to synthesize them optimally for a given application, we are currently modelling the molecular dynamics of the various ions (EMIM, TFSI, Li^+ , Na^+ , Mg^{2+} , Zn^{2+}) under different confinement conditions.⁴

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Design Considerations for Dissolved Na-Ion in Ionic Liquid for Supercapatteries

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Abstract

The redox mechanism of Na/Na⁺ dissolved in four different ionic liquids (ILs) with general formula XY, where X is either 1-methyl-1-propylpyrrolidinium [PYR_{1,3}] or 1-methyl-1-butylpyrrolidinium cations and Y is either (fluoromethanesulfonyl)imide [FSI] or bis(trifluoromethanesulfonyl)imide [TFSI] anions were investigated. The role of the substrates (platinum, copper, or glassy carbon) on the deposition/dissolution of Na/Na⁺ were also studied. It was observed that the interactions between the metal-ion and the anions, coupled with the type of substrates influence both the electrode potentials for the redox mechanism and the electrochemical stability of the ionic liquids. Electrochemical impedance spectroscopy was also used to further understand these interfacial mechanisms. This information was used to assess some important design considerations in the development of supercapatteries which exploits both battery and supercapacitor mechanisms towards optimal electrochemical energy storage. Furthermore, important findings from this research which may address some of the challenges of post-lithium-ion energy stores were presented.

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Acknowledgements

We are grateful to Rolls Royce (ongoing) and Innovate UK (past) for financial support.

Linking Molecular Scale Interactions to Macroscopic Properties in Metal Ionogels

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Abstract

Cross-linked molecular networks can be used to immobilise liquids to form free-standing gels. For ionic liquids, the resulting soft materials are named ionogels and their properties are very different to traditional gels such as hydrogels or organogels.¹ For example, ionogels are conductive and not susceptible to evaporation because ionic liquids are effectively involatile in atmospheric conditions. Hence, ionogels are good candidates for flexible electronics such as ionic skins, actuators, and sensors. In this talk, we show how mechanical and physical properties of poly(ethylene glycol) diacrylate (PEGDA) or 1,6-hexanediol diacrylate (HDDA) ionogels can be controlled through ionic liquid anions. We then expand on this concept to show how ionogel properties can be further manipulated by utilising metal containing ionic liquids, which gives multi-component systems with complex molecular interactions (e.g., cation-anion, anion-metal, metal-polymer).² Using a wide range of analytical techniques, we pry apart these systems to understand how interactions influence structure (using scattering, mechanical testing, and MD), transport properties (using impedance spectroscopy and NMR), and surface composition (using XPS and SIMS)(**Figure 1**). We complement this investigation with solution-based NMR experiments and thermal analysis to further show how metal ions interact with acrylate monomers. Altogether, this work provides a comprehensive overview of metal-IL-polymer interactions which will aid the development of new flexible electronics.

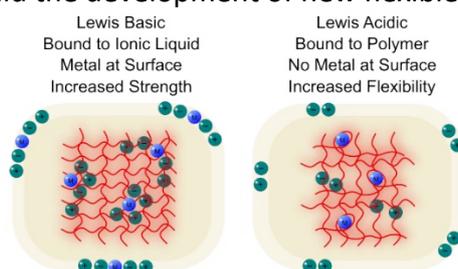


Figure 1 - The relationship between Lewis acidity/basicity of metals, the resulting interactions that occur, and the effect on the ionogel composition and properties.

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Past and Future Applications of Deep Eutectic Solvents

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Abstract

From very humble beginnings in 1999, the topic of deep eutectic solvents has come a long way with tens of thousands of papers now in the field. This presentation reviews the inventive process behind these fluids and some of the applications for which they have been used. It also questions many of the assumptions about the limitations of dense ionic fluids and points the direction in which future research could be focussed. Most importantly it questions whether there is a difference between ionic liquids, DESs and aqueous brine solutions.

QUILL25-MSILDG: Applications of Ionic Fluids

Monday 2nd September 2024

List of Posters

Monday 2 nd September	
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Zhong Zheng (Friedrich Schiller University)	Acetate-Based Ionic Liquids as Electrolytes for Energy-Storage Devices
Junzhe Quan (QUILL)	Forward Osmosis with Membrane Distillation Using Tetrabutylphosphonium Based LCST-Type Ionic Liquid as Osmotic Agent for Seawater Desalination
Haris Amir (QUILL)	The Synthesis and Characterisation of Borate Anions for Functional Applications
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Mark Briggs (QUILL)	1,2,3-Trimethoxypropane/Lithium and Sodium Bis(trifluoromethanesulfonyl)imide Solvate Ionic Liquids
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Jeremy Moses (QUILL)	Fabrication of Ionic-Liquid-Based Membranes for Electrochemical Devices
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Monday 2nd September

Presenter	Title of Poster
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Dylan McDonald (QUILL)	Preparation of Polymer Protic Ionic Liquids to be Used as Membranes in Proton Exchange Membrane Fuel Cells
Beth Murray (QUILL)	Aluminium Liquid Coordination Complexes (LCCs) as Electrolytes for Aluminium Batteries
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Lansen Lienuardy (QUILL)	Membranes for All-Iron, All-Soluble Flow Batteries
Oguzhan Cakir (QUILL)	Magneto-Structural Properties of Rare-Earth Magnets Synthesised Through Ionic Liquid Pathways
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Edwin Harvey (QUILL)	Compression-Moulded PMMA/Expanded Graphite Composites: A Scalable Approach for Manufacturing Redox Flow Battery Cell Architectures
Aodhán Dugan (QUILL)	Enhancing Vanadium Redox Flow Battery Performance with Hydrothermally Grown Polyoxometalate Nanoparticles on Graphite Felt
Michael Gamble (QUILL)	Enhanced Redox Flow Battery Performance by Nitrogen Doping of Graphite Felt Using Choline-Glycine Protic Ionic Liquid

Monday 2nd September

Presenter	Title of Poster
Beatrise Silava (University of Latvia)	Synthesis and Properties of 1-Methyl-3-(2,2,2-Trifluoroethyl) Imidazolium Ionic Liquids
Jose (Pepe) Palomar (Universidad Autónoma de Madrid)	Process Simulations on Ionic Liquid Application Developments: From Conceptual Design to Digital Twin Prototype
Juanjo Villora-Pico (QUILL)	Ionic Liquid Synthesis of Catalysts for Direct CO ₂ Hydrogenation to Short-Chain Hydrocarbons
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Andy Marr (QUILL)	Enzymes Entrapped in Ionic Liquid Gels
Dominic Burns (QUILL)	High Temperature Carbon Dioxide Capture via Carbonate-Bicarbonate Cycling
Yu Yu (Almath Crucibles Ltd)	Ionic-Conducting Ceramics for Molten Salt Applications
Yuhan Zhang (University of Nottingham)	Novel Molten Salt Electrolysis Process for Efficient Recovery of Titanium from Industrial Wastes (MERTi)

Flow Synthesis and Purification of Hydrophobic Ionic Liquids Using Commercial Devices

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Abstract

Flow chemistry, either in micro or mesofluidic reactors, is an innovative approach for intensified processes where reactions are carried out within a flowing stream of chemicals and solvents rather than in a more traditional batch system.[1] These technologies enable a precise control of reaction parameters in real time, such as temperature, pressure or reagent concentrations, often leading to an improvement of safety and efficiency for these easily scalable processes. By generating very efficient mass and heat transfers, flow chemistry not only permit a better control of experimental conditions and a very high reproducibility but can also lead to higher yields and reduced reaction times. [2] Such advantages make flow chemistry an interesting tool in many fields of chemistry such as pharmaceuticals, [3] biobased molecules [4] or material science [5] both in academy and in the industry. [6]

The canonical synthesis of ionic liquids, consisting in an amine quaternarisation by an alkyl halide followed by anion metathesis, can clearly benefit from the advantages of flow chemistry by greatly accelerating the kinetics of these processes. Following pioneering works on the synthesis of, for instance, ethylsulfate [7] or bromide [8] ionic liquids, we are proposing here a flow process for the synthesis of hydrophobic ionic liquids by concatenating the two reactions in one flow and using a commercial membrane separator for in-line purification.

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Acetate-Based Ionic Liquids as Electrolytes for Energy-Storage Devices

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Abstract

Ionic liquids (ILs) display good thermal stability, non-volatility, high conductivity, and a wide electrochemical window, and can be directly used as liquid electrolytes for supercapacitors.^[1, 2] This work presents the synthesis, characterization, and use of a series of aprotic and protic acetate-based ionic liquids (AclLs). These cheap ILs can be obtained through a simple synthesis (one or two steps) and display good transport and thermal properties. When used as electrolytes in electrical double-layer capacitors (EDLC) they allow the realization of devices with an operating voltage as high as 1.5V, which display very good cycling and float stability. The performance of these devices can be tuned by adjusting the water content of the IL. Interestingly, when high water content is present in the electrolyte, EDLCs containing AclLs can also be realized using aluminum current collectors.

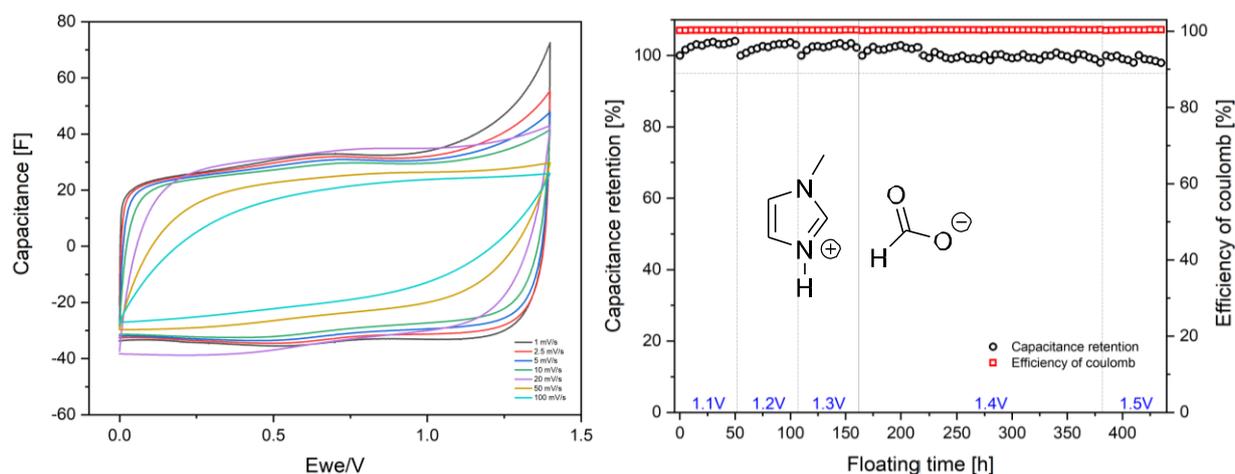


Figure 1 - 1-Methylimidazole acetate, Left: Cyclic voltammetry (scan rate of 1, 2.5, 5, 10, 25, 50, 100 mVs), Right: capacitance retention during float test carried out at stepwise increase operative voltage.

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Forward Osmosis with Membrane Distillation Using Tetrabutylphosphonium Based LCST-Type Ionic Liquid as Osmotic Agent for Seawater Desalination

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Abstract

Access to pure water is becoming a global challenge due to many environmental and societal reasons^[1]. Since traditional seawater desalination is highly energy intensive^[2] (either through multistage flash evaporation approaches or *via* reverse osmosis) there is a significant interest in developing desalination technologies with reduced energy demands. Forward Osmosis (FO) is one such example, however FO requires a high-performance draw fluid to extract water across a membrane and from which purified water can be subsequently recovered. This regeneration process represents the largest energy consumption component in FO processes, and the development of efficient draw fluids that can use low grade and environmentally friendly energy such as solar or waste heat for regeneration is a critical component of research^[3].

Ionic liquids that exhibit lower critical solution temperature (LCST) behavior have been proposed as potential thermally switchable draw fluids for water desalination^[4], these include tetrabutylphosphonium arylsulfonates ([P₄₄₄₄][tol-SO₃]^[5]) and tetrabutylphosphonium 2,4-dimethylbenzenesulfonate ([P₄₄₄₄][DMBS])^[4]. We have examined the performance of series of known, and new, tetrabutylphosphonium and tetrabutylammonium-based ionic liquids as draw fluids in a laboratory-scale FO cell. The prospects, and possible deficiencies, of these ionic liquids as FO osmotic agents have been evaluated in terms of capacity, osmotic pressure, and effects of ionic liquid and electrolyte composition on critical behaviour and are reported here.

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The Synthesis and Characterisation of Borate Anions for Functional Applications

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Abstract

Ionic liquids containing borate anions have a long history; from tetraalkylborates¹ through tetrafluoroborates² to orthoborate anions,³ and most recently a range of functionalised cyanoborate systems.⁴ Here we describe studies exploring expansion of the range of available orthoborate anions suitable for forming ionic liquids through transformation from tetra-oxo (B{OOOO}) into mixed oxygen/nitrogen (B{OONN}) and ultimately to tetraamine (B{NNNN}) coordination environments.

In collaboration with Deakin university, a range of borates (figure 1) have been used as electrolytes in sodium cells, to investigate the formation of a solid electrolyte interphase (SEI). The conductivity of trihexyltetradecylphosphonium [P₆₆₆₁₄]⁺ based ionic liquids were recorded as well as diffusion NMR by using pulse field gradient (PFG) and echo based NMR experiments. In collaboration with POLYMAT (University of the Basque country) water soluble PDADMA borates were synthesised and investigated as binders for NMC cathodes in Li-ion batteries.

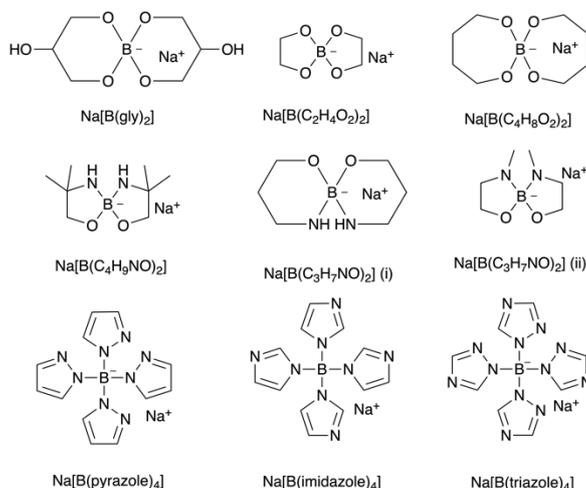


Figure 1 - Structure of the sodium salts of the B{OOOO}, B{OONN} and B{NNNN} borate anions under investigation.

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Manipulating Cation Lewis Acidity to Create Functional Ionic Liquid Systems

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Abstract

Lewis acidity in ILs is most commonly associated with 'acidic' halometallate anions [1], or with recently emerging acidic cations, including borocations and solvate ILs (group I/II metal-complex cations).

An area of opportunity is for deploying the capability of either LA cations or anions in ILs to generate new Frustrated Lewis acid/base pairs (FLP) in an ionic liquid form that are capable of activating small molecules such as hydrogen. We have previously demonstrated that IL environments can extend the life-times of FLP encounter complexes to the NMR timescale [2] and reasoned that the FLP based on dilute solutions of *N*-alkylacridinium salts as LA and lutidine (2,6-dimethylpyridine) as base described by Ingelsson and co-workers [3] could be transformed through variation of cation *N*-alkyl substitution and selection of appropriate anions. Moreover, with judicious selection of anions, both the FLP and products from heterolytic splitting and capture of hydrogen (as H^+/H^-), namely *H*-lutidinium cations and dihydro-*N*-alkylacridine could be maintained in an IL form (Figure 1). Such a system would be an intrinsic ionic liquid frustrated Lewis pair (IL-FLP) with the potential to control activation of small molecules (H_2/CO_2 etc) by manipulating the phase equilibrium.

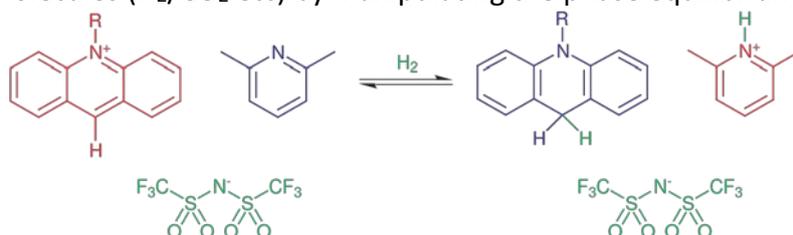


Figure 2 - On heterolytic activation of H_2 to H^+/H^- , the IL *N*-alkylacridinium bistriflylimide/lutidine FLP (left) is transformed into the corresponding IL *H*-lutidinium bistriflylimide/*N*-alkyl-9,10-dihydroacridine pair (right).

Here, we report the first studies of *N*-alkylacridinium bistriflylimide/lutidine systems as solvent-free ionic liquid FLP catalysts.

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1,2,3-Trimethoxypropane/Lithium and Sodium Bis(trifluoromethanesulfonyl)imide Solvate Ionic Liquids

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Abstract

1,2,3-trimethoxypropane (TMP) is a non-hazardous biosourced polyether that is coming under scrutiny as an alternative to glymes as solvents in lithium and sodium-air batteries [1] in addition to uses as solvents for catalysis and chemical transformations [2]. It has been reported to be both non-toxic [3] and biodegradable (in contrast to linear glymes that can induce reproductive toxicity) and (ii) derived from glycerol, a waste bio-resource (*cf* industrial glyme production from dimethylether and ethylene oxide).

The formation of solvate ionic liquids from Li[NTf₂] and Na[NTf₂] in TMP, analogous to the highly coordinated solvate ionic liquids from lithium salts in linear glymes [4] has been investigated by differential scanning calorimetry and the liquid coordination environments are under investigation using neutron scattering to determine the degree of cation-anion and cation-solvent association. TMP is a geometric isomer of diglyme (G2) but has the potential to coordinate to metal ions through both 5- and 6-membered rather than solely 5-membered chelates.

In this poster, the phase diagrams of Li[NTf₂]/TMP and Na[NTf₂]/TMP, determined by DSC, will be presented along with an ionic liquid catalysed methylation route to synthesis and isolation of 1,2,3-trimethoxypropane in good yield without the use of hazardous dimethylsulfate or bromomethane.

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Synthesis and Physicochemical Characterization of 1,3-Functionalized Imidazolium Ionic Liquids

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Abstract

Ionic liquids can be prepared from a variety of combinations of organic cations and anions that lead to fluids with distinct properties.¹ This work reports the development of a method for synthesizing, with high yields and at gram scale >5 g, new bis(trifluoromethanesulfonyl)imide imidazolium ionic liquids functionalized with ether groups. The structures of the obtained compounds were confirmed using ¹H and ¹³C NMR and mass spectrometry. The density and dynamic viscosity of the ionic liquids were determined using a vibrating U-tube densimeter and a falling ball viscometer, respectively. The new functionalized ionic liquids are up to 20% denser and 70% less viscous than the equivalent non-functionalised salts. The prepared ionic liquids aim to act as better solvents for Na⁺ ions and be used in electrochemical devices. The properties of the ionic liquids containing functionalized cations in positions 1,2- and 1,3- of the imidazolium cation were compared to understand the mechanisms of solvation of small cations in the liquid salts.

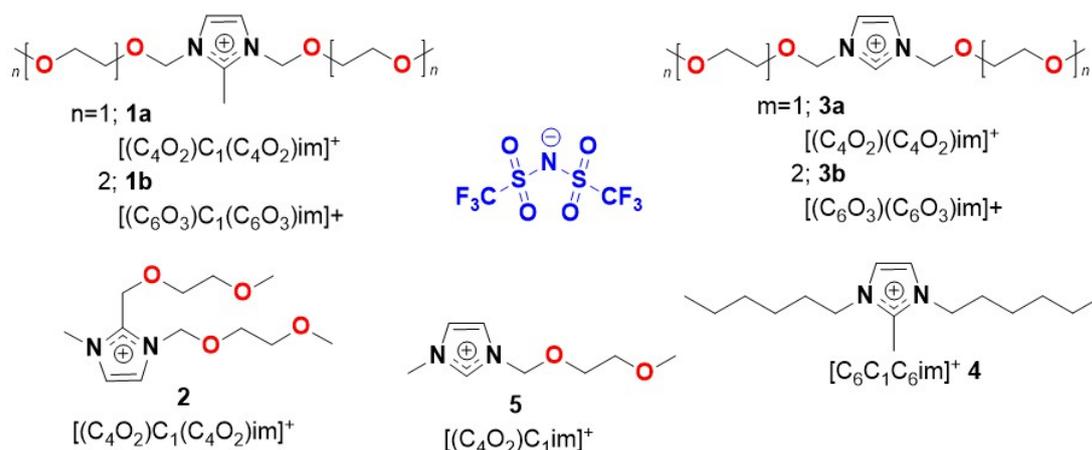


Figure 1 - The target compounds - bis(trifluoromethanesulfonyl)imide chemical structures.

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Analysis of the Redox Properties of Dissolved Metal Ions in Ionic Liquids for Supercapattery Applications

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Abstract

The electrochemical stability of ionic liquids (ILs) and interaction of dissolved metal ions which influences the diffusion and reversible deposition/dissolution of the metal ions, are linked to the constituents of the ILs [1,2]. These factors are important in the selection of ILs for supercapatteries which combines Nernstian and capacitive charge storage mechanisms at the negative and positive electrodes respectively [3]. To understand the redox mechanisms of dissolved metal ions in ILs for supercapatteries, this study investigates the electrochemical properties of ILs with general formula XY containing dissolved Li⁺, Na⁺, or Mg²⁺, where X is either 1-methyl-1-propylpyrrolidinium [PYR_{1,3}] or 1-methyl-1-butylpyrrolidinium cations and Y is either (fluoromethanesulfonyl)imide [FSI] or bis(trifluoromethanesulfonyl)imide [TFSI] anions. The cyclic voltammograms show that the redox mechanisms of the dissolved metal-ions are strongly dependent on their interaction with the anions. Furthermore, the rigorous studies of the pairing of ILs with these dissolved metal ions reveals some important design considerations in ongoing efforts to develop optimal supercapatteries.

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Acknowledgements

We are grateful to Rolls Royce (ongoing) and Innovate UK (past) for financial support.

Fabrication of Ionic-Liquid-Based Membranes for Electrochemical Devices

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Abstract

Climate change poses a significant threat to our planet, necessitating the development of sustainable and environmentally friendly energy solutions. Hydrogen, as a clean fuel, presents a promising alternative, particularly when utilized in fuel cells to produce electricity with water as the only byproduct. However, the widespread adoption of hydrogen fuel cells is hindered by the limitations of current membrane technology. Nafion[®], a widely used perfluorinated membrane, is not only costly and environmentally unfriendly but also limited to operating temperatures of 80 °C or below [1].

My work builds upon previous work by Rao *et al.* that explores the potential of ionic-liquid-based membranes as a viable alternative to Nafion[®] [2]. Ionic liquids (IL) are compounds composed of ions designed such that the compound exists in a liquid state below 100 °C. This research focuses on integrating a protic ionic liquid (PIL) with a polymerized ionic liquid (poly-IL) backbone to develop a novel composite membrane. The primary objective is to determine the optimal ratio of protic IL to poly-IL, aiming to enhance the performance and durability of the membrane while maintaining cost-effectiveness and environmental sustainability.

By investigating the properties and interactions of these innovative materials, this study seeks to contribute to the advancement of hydrogen fuel cell technology, potentially offering a more efficient and eco-friendly solution to the energy challenges posed by climate change.

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Boron Lewis Acids: A Study of Metal-Free Catalysts

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Abstract

Recently, there has been growing interest in main group catalysis, as an alternative to platinum group metals, with a particular focus on boron chemistry, a highly abundant element with a low environmental impact. Boron compounds are well known to act as Lewis acids and have shown to catalyse hydrogenation reactions.¹ However, despite being well known, analytical techniques available to study these compounds remain limited.

Lewis acidity is difficult to quantify due to dependency on the base and a variety of other factors such as sterics of substituents and distortion of geometry which makes it difficult to create a standard measurement scale.² Existing methods such as Gutmann method³ and FIA scale⁴, rely on a “probe” molecule to assess probe/acid interactions and depend on the hard/softness of the acid.

This work aims to isolate one of these components of Lewis acidity and measure the intrinsic Lewis acidity in the absence of the base using synchrotron-based X-ray spectroscopy techniques: X-ray absorption spectroscopy (XAS) and X-ray Raman spectroscopy (XRS), a novel technique which uses hard X-rays to measure light elements, which traditionally requires a vacuum and restricts sample environments.⁵

We have studied a range of boron Lewis acids using XAS and XRS and alongside simulations to measure the B K edge and therefore the $1s \rightarrow \text{LUMO}$ transition in the hopes to develop a new probe-free Lewis acid scale in the absence of the Lewis base. In the future, we hope to expand to acid/base pairings in frustrated Lewis pairs and pair this with neutron scattering studies to study the structure of these systems and eventually study operando hydrogenation reactions with FLP-SILP systems.

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Methanolysis of PET Using Ionic Liquid Catalyst

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Abstract

Waste PET (polyethylene terephthalate) is a growing concern, with single use PET bottles filling up oceans and causing a great environmental problem worldwide, due to its resistance to natural degradation. PET can be chemically recycled into its monomers, dimers or oligomers. This can be done by a range of processes, our focus is methanolysis to produce DMT (dimethyl terephthalate), hydrolysis to produce TPA (terephthalic acid), and glycolysis to produce BHET (bis(2-hydroxyethyl)-terephthalate). In this project, we are using a Brønsted acidic ionic liquid as a catalyst in different molar ratios, in the Anton Parr monowave reactor in different conditions, to determine the most efficient method of methanolysis.¹

Currently, mechanical recycling is the most common method used. This however presents the challenge of reduced molecular weights, causing weaker plastics which eventually end up being unfit for use and contributing to the environmental problems we are facing. Chemical recycling aims to restore the polymers back to their monomer, so that plastic use can be a closed loop process. Use of the microwave reactor allows for shorter reaction times, while also being energy efficient. Ionic liquids are suitable catalysts in this process compared to the current mechanical process due to their low cost, and minimal energy is required to make them.

Here we report our work on the degradation of PET, and what conditions are the most effective with highest percentage conversion and yields.

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Preparation of Polymer Protic Ionic Liquids to be Used as Membranes in Proton Exchange Membrane Fuel Cells

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Abstract

With the growing threat of climate change and global warming, finding cleaner ways of producing energy is imperative. One such way is to use a proton exchange membrane fuel cell to convert green hydrogen into electricity and only water as a byproduct. This is mostly accomplished using perfluorinated membranes such as Nafion[®]. The main challenge of using such a membrane is that the proton conductive properties of the membrane is tied to water uptake by the membrane, meaning the cell struggles to perform at temperatures above 100 °C. This, coupled with the unsustainability of perfluorinated membrane production that releases fluorinated pollutants, begs for an alternative solution. High-temperature proton exchange membranes are therefore being investigated due to their higher proton conductivity, without the drawbacks that are faced when using perfluorinated membranes in low-temperature proton exchange membrane fuel cells. Ionic Liquids have been proposed as one of the solutions due to their non-volatile nature and conductive properties. It was found that doping perfluorinated membranes or other polymer membranes with ionic liquids can lead to higher proton conductivity within operating PEMFCs, with the added benefit of higher operating temperatures due to the low volatility of ionic liquids. This avenue still requires the production of a suitable membrane that allows a great amount of uptake of the ionic liquid for this to work effectively at higher temperatures. The idea of having a polymer protic ionic liquid that can be cast into a membrane for PEMFCs was therefore investigated to effectively fulfil the dual roles of membrane and electrolyte. This will forgo the need to make a membrane and a complementary protic ionic liquid, mitigating the potential for loss of the liquid component. Diallylmethylamine was therefore investigated due to its polymerizable allyl groups and was reacted with a range of Brønsted acids to produce several monomeric protic ionic liquids. The protic ionic liquid monomers were subsequently polymerised and casted into membranes and tested for their thermal stability and proton conductivity.

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Aluminium Liquid Coordination Complexes (LCCs) as Electrolytes for Aluminium Batteries

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Abstract

Rechargeable batteries play a vital role in global energy management strategies. The EU recognizes energy storage solutions as a crucial component in enabling grid flexibility and facilitating the integration of renewable energy sources into the energy system. Presently, lithium-ion batteries are considered cutting-edge technology, however, they are plagued by high costs and flammability concerns.¹ Although offering several advantages, it is important to note that lithium has a low abundance on Earth, which contributes to its high cost and reduces the long-term sustainability of relying heavily on the metal.²

Aluminium (Group 13) appears to hold significant promise, as it is abundantly available on Earth, therefore cost-effective, offers safe handling, the capability to exchange three redox electrons per cation, and exhibits high gravimetric and volumetric capacity.³ While there has been significant research on electrolytes for lithium-ion batteries, limited attention has been given to finding suitable electrolytes for Al-batteries. However, ionic liquids (ILs) have emerged as promising candidates, offering high ionic conductivity, minimal volatility, very low flammability, and excellent chemical and electrochemical stability. They also present certain challenges, such as cost and corrosivity.⁴

At this juncture, we introduce liquid coordination complexes (LCCs) as analogues of ILs, that have been developed specifically to address the challenges encountered with ILs in various applications. LCCs supply the demand for cost-effective analogues of ILs that possess, high metal content, and adjustable environments around the metal centre, making them interesting candidates as electrolytes for Al-batteries.⁵ Here, we report on a crucial finding that doping LCCs with non-coordinating organic solvents (following the principles of 4th evolution of ionic liquids),⁶ modifies the performance of the electrolyte, potentially enhancing it in certain instances.

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Hybrid Fire Prevention / Mitigation System for Lithium-Ion Batteries in EVs

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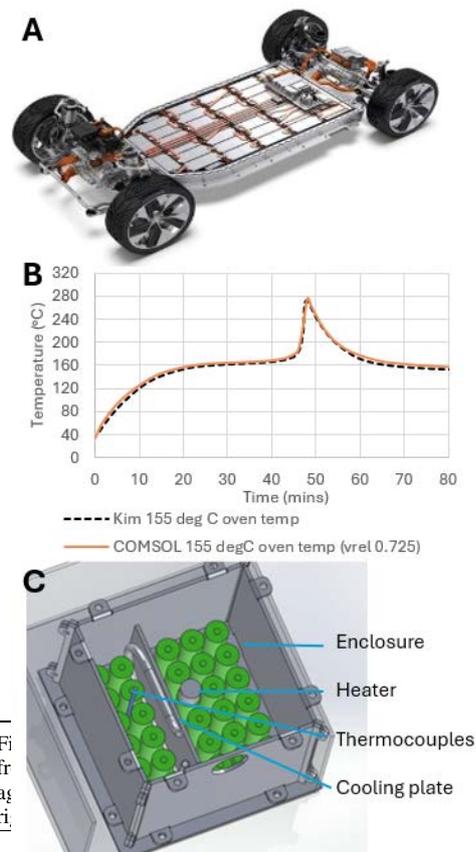
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Abstract

As many nations begin to implement plans to ban the sale of new internal combustion vehicles to tackle climate change, there is expected to be a steady rise in the uptake of hybrid and electric vehicles (EVs) (1). To aid in this transition there is a need for improvement in the safety of these vehicles. One of the main safety concerns is centred around the battery packs that are used in these vehicles. These packs are made up of cells that are electrically connected in series and parallel to create a pack that can meet the voltage, current and energy demands of an EV (Figure 1A). The pack can vary in size and construction, from around 30 kWh up to 100 kWh depending on the application of the vehicle.

The battery packs/cells operate optimally in a narrow temperature window (15-35 °C) and are sensitive to thermal deviations outside of it (2). If these cell temperature deviations are significantly away from optimum as can be caused by thermal, mechanical or electrical abuse, a dangerous thermal event can occur (3). In these events large amounts of heat can be generated, through Joule heating and thermal decomposition potentially resulting in an exothermic runaway reaction and even combustion of the cell contents. Under these circumstances the pack can enter thermal runaway, where the heat from one cell propagates to the neighbouring cells causing a runaway reaction culminating in the destruction of the pack and vehicle. Thermal runaway events like these pose a serious risk of property damage and more importantly to the safety of the occupants.

This poster presentation details the work carried out to date on a hybrid system, consisting of interstitial materials and liquid cooling to carry out both thermal management, alongside the ability to arrest thermal runaway propagation between cells. This includes the development of 2D and 3D COMSOL models which utilises chemical kinetics modelling to investigate the viability of the concept, including the validation of component models against literature (Figure 1B). As well as the steps taken to conduct physical validation of these models using a low power rig and a cell analogue (Figure 1C). These validation steps will allow the optimization of designs using these models and the development of guidelines for the development of systems that improve the safety of electrified vehicles.



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Electro-Photo Generation of Highly Reducing Radical Anions for CO₂ Activation

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Abstract

Electrophotochemistry is the combination of two popular fields of chemistry – electrochemistry and photochemistry. By utilising both the principles of light and electricity to study and control chemical reactions, it is an area of research that holds a lot of potential and has recently drawn a lot of attention. We hope that through using electrophotochemistry, we will be able to tackle the issue of global warming, by taking CO₂ and converting it into a more value-added product.

The first study for this project involved testing a range of electrophotocatalysts using cyclic voltammetry, and finding three properties: their redox potential, diffusion coefficient and their heterogeneous electron transfer constant. Looking at previous papers, we could see that there didn't seem to be much reproducibility between figures for the same catalyst in the same electrolyte from one paper to another, so we realised that there is a need to find these properties more accurately under a defined set of conditions to aid comparison.

To do this, we turn to rotational disc voltammetry. Using this method, and a different set of calculations, we are able to control more variables, such as resistance, baseline current, and diffusion effects. A series of experiments was then carried out on two families of commonly used mediators: TEMPO and its derivatives, and a selection of electrophotocatalysts. Using this new method the values were a lot closer to what we expected. We plan on using this method to categorise a range of different types of electrocatalysts, to provide a list with accurate electrochemical properties that can be used by myself and hopefully other electrochemists in the future.

To confirm the accuracy and validity of our results, we plan on using used DigiSim software to simulate CVs of each catalyst to be able to compare actual experimental results to simulations. So far, the simulations have good overlap with our experimental results, so we are confident that this method of finding these parameters is accurate.

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Membranes for All-Iron, All-Soluble Flow Batteries

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Abstract

The issue of climate change and the transition to renewable energy highlight the importance of long-duration energy storage (LDES). Yet, current energy storage technologies, such as lithium-ion batteries, are not viable for LDES due to scalability and safety issues.[1], [2] Flow batteries (FBs) present a promising alternative for LDES, owing to its unique feature of independent scaling of energy and power capacity through the use of liquid electrolytes stored in external tanks.[3] Vanadium is typically used as the main component of the electrolyte; however, the price volatility of vanadium restricts the widescale application of the all-vanadium FB. Iron-based FBs offer a more cost-effective solution due to their abundance, though their performance is still heavily dependent on the membrane used. Nafion[®] membranes are commonly used in FB technologies owing to their excellent properties but are also costly, hindering their widescale use.[4] Work in this project therefore focused on exploring the performance of alternative commercial membranes that have been tested with the all-vanadium FBs but not with iron FBs, which could potentially present a more optimal and cost-effective solution for all-iron, all-soluble FBs. Performance indicator testing was conducted to probe chemical stability, mechanical stability, thermal stability, as well as assess ionic conductivity, to identify the best candidate membrane for this promising FB chemistry.

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Magneto-Structural Properties of Rare-Earth Magnets Synthesised Through Ionic Liquid Pathways

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Abstract

Rare-earth magnets are crucial in various technological applications, from renewable energy to electronics. This study aims to synthesize and characterize novel rare-earth magnetic clusters using ionic liquid pathways, focusing on understanding and controlling their magneto-structural properties at the molecular level. Ionic liquids provide unique solvent environments that enable the creation of rare-earth magnetic clusters unattainable through conventional synthesis. These nanocluster magnets constitute an intermediate state of matter between discrete molecules and nanoparticles, with defined molecular structures capable of exhibiting cooperative magnetic phenomena. This research aims to exert synthetic control over magnetic materials at the molecular cluster level.

The cluster compounds studied feature three-dimensional acetate and oxalate frameworks housing arrays of rare-earth metal ions; their magnetic properties derive from the magnetic moments of the rare-earth ions coupled via oxygen bridges. Structural crystallographic analysis will reveal the coordination modes of rare-earth ions within the acetate and oxalate frameworks.^{1,2} Magnetic measurements demonstrate that minor structural modifications give rise to significant changes in magnetic exchange pathways. Tuning the magneto-structural characteristics of these cluster compounds may ultimately enable their development into molecular analogues of permanent magnets. This work aims to demonstrate the promise of ionic liquids as versatile solvent systems for discovering new magnetic materials with tailored nanostructures and properties.

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Comparative Study of Electrolyte in All-Iron Redox Flow Batteries: Enhancing Efficiency and Affordability for Sustainable Energy Storage Systems

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Abstract

Redox flow batteries are highly scalable solutions for grid-scale energy storage, offering the advantages of separating energy capacity from power output and long lifetime. Among these redox flow batteries, vanadium redox flow batteries have first reached commercial advancements. However, their further practical utilization is challenged by the rising cost and unstable supply chain of vanadium [1]. In the pursuit of sustainable energy storage systems with enhanced efficiency and affordability, All-Iron Redox Flow Batteries (AIFBs) are considered promising alternatives. One of the main challenges of conventional AIFBs is the concern about possible dendrite formation from repeated stripping and deposition processes on the Fe anode [2]. The optimization of electrolytes in AIFBs is focused on enhance overall performance and reduce dendrite formation. According to recent research progress, all-soluble AIFBs with iron-based organic complexes, such as Fe-gluconate and Fe-NTMPA2, have shown remarkable advantages such as high stability, high Coulombic/energy efficiency and low capital cost without forming precipitation [3], [4]. This poster presented recent advances in cost-effective and high-performance electrolytes utilized for all-soluble AIFBs.

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Controlling LCST Phase Behaviour Via Structured Design of Ionic Liquids

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Abstract

The tetrabutylphosphonium 5-phenyl tetrazolate/water system ($[P_{4444}][Ph-Tet]/H_2O$), 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 both cation and anion modification can control the phase behaviour of the ionic liquid/aqueous systems changing the hydrophobicity (water content) of the IL-rich phase and reducing the cloud point temperatures 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 variable temperature is also investigated.

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Hydrophobic Low Melting Mixtures for Biogas Upgrading

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Abstract

Biogas is a carbon neutral energy source produced from the anaerobic digestion of organic waste. Its major components are methane (CH₄) and carbon dioxide (CO₂) with other impurities present in smaller quantities such as volatile organic compounds (VOCs). Upgrading of biogas to biomethane can be carried by pressure and temperature swing adsorption, liquid scrubbing, membrane separation and cryogenic methods. However, in general these methods involve large facilities with multi-step, energy intensive processes that often incorporate hazardous materials [1]. Alternative low-energy purification processes would make biogas a significantly more attractive as an energy source of methane for small scale widespread application. Changing from multiple steps to a single technology for multiple contaminants would lead to a process that could be implemented on a much smaller geographical footprint ideal for smaller agricultural purposes.

Low melting mixtures (LMMs) offer alternatives to traditional biogas upgrade sorbents such as alkanolamines, however lower CO₂ capacities coupled with high viscosities of physisorbant LMMs has limited their application scope. Here we report the study of hydrophobic LMMs based on trioctylphosphine oxide (TOPO) [2,3] that couple lower viscosities and a high tolerance to environmental water with high CO₂ capacity. Measurements using headspace GC have also shown that these are effective solvents for the removal of several different classes of VOC commonly found in biogas which could enable them to be implemented as a "one pot" upgrading method.

Experiments carried out using both CO₂ and CH₄ have shown that these materials have comparable capacities and selectivities for CO₂ over CH₄ when compared to fluorinated ILs and industrial standards such as Genosorb 1753. Partition coefficients of VOCs in the same LMMs previously tested for gas sorption are also lower than that of many standard sorbents. These measured properties along with the relatively low viscosity make these materials seem like a viable new technology for biogas upgrading in the future.

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Protic ILs for CO₂ Capture

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Abstract

Carbon dioxide (CO₂) is a major contributor to climate change brought on by global warming. Governments across the globe are bringing forward directives to reduce anthropogenic CO₂ emissions.¹⁻⁴ A technical report on the application of amine scrubbers which are the current industrial standard used for CO₂ scrubbing in flue gas found major flaws in the implementation and operation.⁵ Therefore new technologies could be developed to overcome the current shortcomings of the present industrial capture system. Basic ionic liquids (ILs) can mimic amine scrubbers in their potential for CO₂ capture with a potentially higher (> 0.6 mol CO₂/mol amine) capture capacity and minimal degradability issues, making them well suited to work at high temperatures and low CO₂ partial pressures. They offer a competitive advantage for specific niche markets i.e. CO₂ capture from wet flue gas streams such as those originating from refinery or cement plants, notoriously hard-to-decarbonise sectors. In this context, we propose to study a range of protic ILs containing anions with a range of basicities for CO₂ absorption in industrially-relevant conditions, meaning at CO₂ absorption temperatures of ≈90 °C, desorption temperatures of ≈160 °C, low CO₂ partial pressures (40 – 80 mbar) and in the presence of water. This work represents the initial study and screening of two ILs: 1,8-diazabicyclo(5.4.0)undec-7-enium imidazolide ([DBUH][Im]) and its analogue 1,8-diazabicyclo(5.4.0)undec-7-enium 1,2,4-triazolide ([DBUH][Triz]) which have exhibited CO₂ uptake capacities of 0.88 mol CO₂/mol IL and 1.5 mol CO₂/mol IL respectively at 35 °C, which is higher than the industrial amine scrubber monoethanolamine (0.6 mol CO₂/mol amine) under the same conditions. Further to this we aim to gain insight into their CO₂ absorption mechanisms and uptake capacities across a range of pressure as well as their potential as industrial CO₂ absorbents by assessing their thermal stability.

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Compression-Moulded PMMA/Expanded Graphite Composites: A Scalable Approach for Manufacturing Redox Flow Battery Cell Architectures

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Abstract

Redox flow batteries (RFBs) are promising energy storage devices that utilise liquid electrolytes pumped through an electrochemical cell [1]. However, RFBs are still not widely commercialised, partly due to the low manufacturability of the cell architecture. For instance, flow fields are used to distribute electrolyte through the cell, yet these are difficult and time consuming to machine into graphite plates [2]. We present a method for fabricating cell architectures using a mouldable polymethyl methacrylate (PMMA)/expanded graphite composite material. The process employs computer numerical control (CNC)-manufactured moulds, offering a scalable alternative to traditional graphite machining. While the electrical conductivity of our moulded polymer composite (200 S/m) is lower than that of crystalline graphite (330 – 200,000 S/m) [3], it demonstrates enhanced electrochemical properties, as evidenced through cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) analyses. The PMMA/expanded graphite composite offers significant advantages over traditional graphite plates, including easier manufacturing, improved shapability, and potential cost reductions. By addressing this key bottleneck in RFB production, this work contributes to advancing the practical implementation and potential adoption of these promising energy storage devices in grid-scale applications.

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Enhancing Vanadium Redox Flow Battery Performance with Hydrothermally Grown Polyoxometalate Nanoparticles on Graphite Felt

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Abstract

This research explores the enhancement of vanadium redox flow batteries (VRFBs) through the modification of graphite felt (GF) electrodes with polyoxometalate (POM) nanoparticles. VRFBs show promise for stationary energy storage technologies due to their durability, relative safety, high round-trip efficiency and scalability. However, their high cost, partly due to low power density, hinders widespread industrial adoption. This study aims to address this challenge by improving electrode performance. This research aims to improve power density by modifying GF electrodes using POMs, known for their high redox activity, structural versatility, and ability to act as catalysts in various electrochemical processes.⁽¹⁾ In this study, commercial GF electrodes were decorated with tetrabutylammonium hexamolybdate (TBA-H) nanoparticles hydrothermally for 4 h @ 120°C. Scanning electron microscopy (SEM) confirmed the successful growth of nanoparticles on the GF fiber surface, while energy dispersive X-ray spectroscopy (EDS) characterised these as primarily molybdenum and oxygen-containing species. However, cross-sectional imaging revealed limited growth on inner fibers. Cyclic voltammetry (CV) was used to evaluate the electrochemical properties of the modified electrodes in both negative and positive electrolytes. While minimal change was observed in the positive electrolyte, the negative electrolyte showed a 142 % and 91 % increase in peak cathodic and peak anodic current densities, respectively. This suggests that TBA-H decorated GF could potentially enhance VRFB performance, particularly in the negative half-cell reaction. Future work will focus on achieving even distribution of POM species throughout the GF structure and investigating its impact on overall battery performance. This research contributes to ongoing efforts to improve VRFB technology, potentially leading to more cost-effective and efficient large-scale energy storage solutions.

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Enhanced Redox Flow Battery Performance by Nitrogen Doping of Graphite Felt Using Choline-Glycine Protic Ionic Liquid

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Abstract

In order to mitigate the intermittent nature of renewable energy sources like solar and wind, efficient energy storage systems like redox flow batteries (RFBs) need to be utilised [1]. In the vanadium redox flow battery (VRFB), which is the RFB with the greatest commercial application to date, different oxidation states of vanadium are utilised within a liquid electrolyte to drive the storage and generation of electrical energy [2]. However, the VRFB suffers from high fixed costs and low power density [2]. To address these problems, the electrocatalytic performance of the graphite felt electrodes (GF) need to be improved, as they contribute significantly to the overall efficiency of the battery [3]. An effective dopant for GF is nitrogen, due to its ability to enhance charge transfer and provide additional active sites for active species reaction [3]. This study aims to improve the electrocatalytic performance of GF through nitrogen doping using a novel, green protic ionic liquid (PIL) approach.

Specifically, in this study, the PIL choline-glycine ([Ch][Gly]) has been used for the first time to dope GF electrodes by creating nitrogen doped carbon surfaces. [Ch][Gly] has been chosen for GF modification because of its thermal stability and favorable chemical structure for nitrogen doped carbon (NDC) creation *via* pyrolysis [4,5,6]. In order to be able to accomplish this, the novel methodology used involved synthesizing and purifying [Ch][Gly], applying it to thermally activated GF and pyrolysing to create NDC. In order to confirm the synthesis and purification of [Ch][Gly], characterisation techniques such as Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) were employed. Scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), Raman spectroscopy and contact angle testing will be used to verify NDC decoration on GF.

Important results to date include the confirmation of the synthesis of [Ch][Gly] through the aforementioned techniques and it is predicted that the successful decoration of GF with NDC will be verified through the use of SEM, EDX, Raman spectroscopy and contact angle testing. Specifically, what is hoped to be observed is a doped electrode that is hydrophilic and has fibres that are visibly decorated with particles that contain nitrogen.

While the results obtained so far are limited, it is predicted that the creation of nitrogen doped surfaces on GF through the use of [Ch][Gly] can yield the significant improvements in the capacity and power density that are characteristic with the nitrogen doping activation technique [7, 8]. This will in turn help make the VRFB more competitive on the energy storage system marketplace by reducing its cost per kilowatt hour and increasing the power density [9]. Additionally, it should allow for the inherent advantages of the VRFB, like long lifecycle, deep discharge tolerance and flexibility to separately scale energy and power within its design to be more of a consideration whenever the VRFB is being compared with other energy storage solutions for applications with renewable energy technologies [10].

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Synthesis and Properties of 1-Methyl-3-(2,2,2-Trifluoroethyl) Imidazolium Ionic Liquids

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Abstract

Fluorination of ionic liquids (ILs) typically enhances their thermal stability, increases hydrophobicity, and alters key physicochemical properties such as viscosity, density, and phase behavior due to the unique electronegativity and steric effects of fluorine atoms.[1]

This work introduces a series of 1-methyl-3-(2,2,2-trifluoroethyl)imidazolium-based ionic liquids, featuring the anions bistrifluoromethylsulfonylimide (TFSI), bisfluorosulfonylimide (FSI), and triflate (OTf, **Fig. 1**). Unlike the extensively studied non-fluorinated imidazolium ILs, the small fluorinated cation used in this study has received limited attention, with no systematic investigations reported to date.

A combined synthetic work and property investigation of viscosity, density, and phase behavior reveals that these novel fluorinated ILs exhibit higher viscosity and increased density compared to their non-fluorinated 1-ethyl-3-methylimidazolium counterparts. These findings highlight the significant impact of the trifluoroethyl group on the physicochemical properties of ILs, offering new insights and potential applications in fields where enhanced viscosity and density of low-molecular weight ILs are required.



Figure 1 - Ionic liquid ion structures studied in this work

This work was supported by the donation of Mikrotikls LTD, which is administered by the University of Latvia Foundation.

This work was supported by the Fundação para a Ciência e Tecnologia (FCT) (funded by national funds through the FCT/MCTES (PIDDAC)) to CIQUP; Faculty of Science, University of Porto (Project UIDB/00081/2020); and IMS Institute of Molecular Sciences (LA/P/0056/2020). R.M.A.S. is grateful to FCT for the award of his PhD grant (U1/BD/153093/2022).

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Process Simulations on Ionic Liquid Application Developments: From Conceptual Design to Digital Twin Prototype

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Abstract

Ionic liquids (ILs) are promising alternative compounds that enable the development of technologies based on their unique properties as solvents or catalysts. These technologies require integrated product and process designs to select ILs with optimal process performances at an industrial scale to promote cost-effective and sustainable technologies. The digital era and multiscale research methodologies have changed the paradigm from experiment-oriented to hybrid experimental–computational developments guided by process engineering. This presentation overviews the relevant contributions of process simulations to advance IL-based technology developments by guiding experimental research efforts and enhancing industrial transferability [1]. Robust simulation methodologies, mostly based on predictive COSMO-SAC/RS and UNIFAC models in Aspen Plus software, were applied to analyze key IL applications: physical and chemical CO₂ capture, CO₂ conversion, gas separation, liquid–liquid extraction, extractive distillation, refrigeration cycles, and biorefinery. The contributions concern the IL selection criteria, operational unit design, equipment sizing, technoeconomic and environmental analyses, and process optimization to promote the competitiveness of the proposed IL-based technologies. Process simulation revealed that multiscale research strategies enable advancement in the technological development of IL applications by focusing research efforts to overcome the limitations and exploit the excellent properties of ILs. Digital twin prototype emerges as suitable scalability tool to quickly advance in technology readiness levels of industrial IL applications.

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Ionic Liquid Synthesis of Catalysts for Direct CO₂ Hydrogenation to Short-Chain Hydrocarbons

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Abstract

The direct conversion of carbon dioxide into lower olefins (C₂-C₄) is a highly desirable process. These lower olefins, such as ethylene, propylene, and butenes, are crucial components in the chemical industry and for Liquefied Petroleum Gas (LPG). The reaction proceeds via two main consecutive reactions: Reverse Water Gas Shift (RWGS) to produce CO followed by the further conversion of CO to hydrocarbons via the Fischer–Tropsch reaction. Recent studies highlight the cost-effectiveness and satisfactory performance of bimetallic catalysts, particularly Ru and Fe, to enhance olefin selectivity, with precise MNP synthesis as a crucial factor for performance control. This study introduces a novel approach for synthesizing iron-ruthenium bimetallic catalysts that utilizes ionic liquids as solvents, ensuring precise and uniform distribution of active metal phases. Advanced characterizations and extensive tests reveal that this method surpasses traditional colloid-based techniques, resulting in superior selectivity for target hydrocarbons.

H₂-TPR profiles of Fe₂O₃-RuO₂ catalysts prepared via different methods COL and IL, displayed two reduction peaks corresponding to the reduction of Fe₂O₃ to Fe₃O₄ (620K), of Fe₃O₄ to FeO (800 K) and further to FeO and Fe⁰(900 K) (Figure 1a). The addition of RuO₂ resulted in accelerated Fe species reduction and hydrogen spillover from Ru to Fe₂O₃. The Ionic liquid method exhibited the absence of a peak related to the reduction of Ru⁴⁺ to Ru⁰ (380 K). Varying Fe:Ru ratios in the Ionic liquid catalysts showed that the reduction peak diminishes when ruthenium's reduction takes precedence, indicating improved reducibility through increased cooperativity between Fe and Ru species. When comparing catalysts of the same composition prepared using both COL and IL methods, there was a notable five-fold increase in CO₂ conversion under 20 bar pressure. Furthermore, increasing the total metal loading from 1wt% to 4wt% significantly improved selectivity for CH₄ and C₂-C₅ hydrocarbons (Figure 1b).

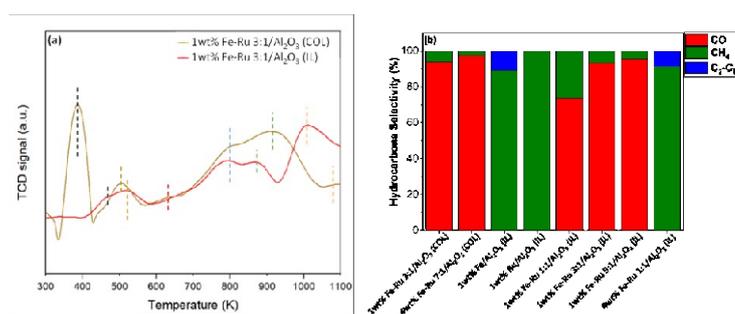


Figure 1. (a) H₂-TPR profiles of catalysts 1 wt% Fe-Ru 3:1/Al₂O₃ (COL and IL). (b) hydrocarbon selectivity at 20 bar (3:1 H₂/CO₂, 523 K)

In summary, this research effectively illustrates the improved synergy between bimetallic Fe-Ru species synthesized using the IL method, leading to superior performance and selectivity for short-chain hydrocarbons when compared to the conventional colloidal synthesis approach.

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Ionic Liquids Templated Synthesis of Cobalt-Substituted Mesoporous Aluminophosphates as Catalysts for Cyclohexane Oxidation

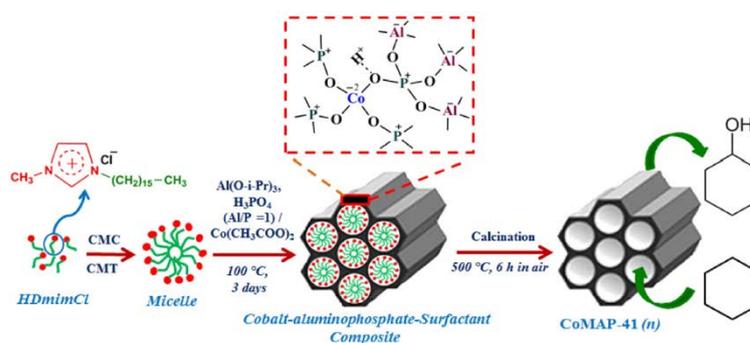
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Abstract

Aluminophosphates (AIPO) and metal-substituted aluminophosphates (MeAIPO) have attracted much attention due to their structural diversity and their applications as heterogeneous catalysts for cyclohexane oxidation, methanol conversion, and ethylene dimerization. However, there are very few reports of successful synthesis of stable hexagonal mesoporous AIPOs, as the AIPO mesostructure collapses upon removing the template due to lack of thermal stability. Therefore, there is a need for new surfactants and synthetic strategies to develop ordered mesoporous AIPOs. In this study, using ionic liquids as a structure-directing agent, we have successfully synthesized the ordered hexagonal mesoporous aluminophosphate and its cobalt-substituted analogue [1]. The resulting materials were systematically characterized by various analytical, and spectroscopic methods, confirming the presence of divalent cobalt in the tetrahedral framework. Further, the high surface area, pore volume, and thicker mesopore walls of these materials impart good thermal and hydrothermal stability.



Scheme 1 - The synthetic approach and the reactivity of CoMAP-41 for the chosen reaction.

Cobalt-substituted AIPOs were evaluated as catalysts for selective oxidation of cyclohexane to cyclohexanol using H_2O_2 as oxidant. Cyclohexanol has numerous industrial applications in the manufacture of paints, varnishes, and lacquers as a plasticizer and stabilizer, as well as in the preparation of nylon-10. The mesoporous catalysts showed excellent activity towards the oxidation of cyclohexane using hydrogen peroxide as an oxidant, with 98.5% conversion and 90.4% selectivity towards cyclohexanol. The catalyst is recyclable with a slight or no decrease in activity and exhibited the same combined selectivity of cyclohexanol and cyclohexanone as that of the fresh catalyst.

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Enzymes Entrapped in Ionic Liquid Gels

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Abstract

Nature provides great inspiration for living a more circular life, in better balance with our natural environment. Inspired by the cell, we created bioimimetic biocatalysts by entrapping enzymes [1] within ionic liquid gels [2]. What sets ionic liquids apart from other solvents and bulk liquids, is the ability to strategically alter key properties by changing the ions and functional groups. For example, reducing the hydrophilicity by including alkyl groups can lead to solvents that will dissolve polar molecules, yet are immiscible with water; and changing the functional groups on either ion can yield ionic liquids ranging from strongly basic to strongly acidic. An engineered ionic liquid environment can be created around a catalytic centre by entrapping chemocatalyst or biocatalyst with an ionic liquid within a gel.

Two very different gel systems containing enzymes are presented. The first is a supramolecular gel with a highly hydrophobic ionic liquid, for operating an enzymatic reaction in water. The second is polymeric gel containing a mixture of ionic liquid and water, a HydrIL, for operating an enzymatic reaction in an organic solvent.

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High Temperature Carbon Dioxide Capture via Carbonate-Bicarbonate Cycling

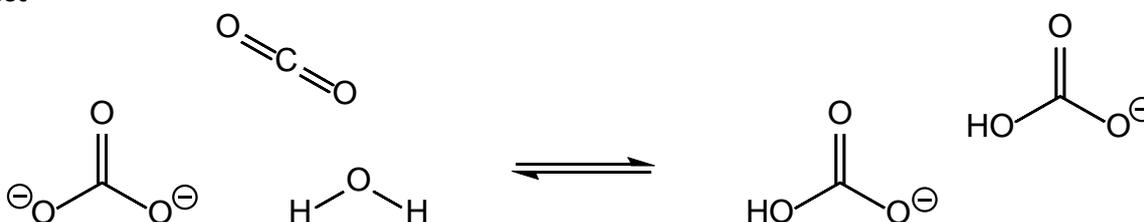
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Abstract



Ionic liquids (ILs) have been identified as potential materials for flue gas carbon capture for over two decades, however, drawbacks such as high material costs, stability and high viscosities limiting mass transfer among others have so far limited their deployment in real-world applications^[1]. Water in the gas stream can interfere with chemisorption processes, causing the formation of bicarbonate. In many cases, this is thought to be a dead end from which the starting material cannot be regenerated, a common approach now is to assume that drying the gas stream as a viable, and necessary step before carbon capture to prevent the formation of bicarbonate.

While researching superbase derived protic ILs for flue gas capture at Chevrons Richmond refinery in California, [DBUH][Im] was shown to absorb CO₂ in the presence of water via bicarbonate formation. At room temperature [DBUH][HCO₃] crystallised out of solution however, at 95°C the mixture was a low viscosity liquid capable of CO₂ capture with fast uptake kinetics. Further heating to 160°C then resulted in the decomposition of bicarbonate, releasing half of the absorbed CO₂ and forming an ionic liquid mixture containing divalent carbonate anions, capable of further CO₂ absorption cycles with a working capacity of *ca.* 50 g·kg⁻¹.

This system is far from optimised however it highlights the potential for reversible chemisorption of CO₂ in the presence of water. The process avoids drying the flue gas stream and reduces the temperature to which the gas must be cooled before absorption, the higher regeneration temperature is also achievable in a refinery due to the excess heat available from other refinery processes. The work done on this topic has been filed for patent at the US patent office^[2].

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Ionic-Conducting Ceramics for Molten Salt Applications

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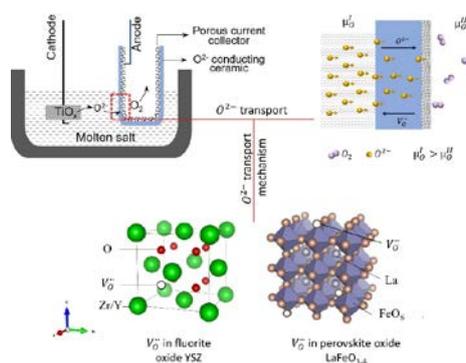
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Abstract

Molten inorganic salts serve as exceptional reaction media for a wide range of research and industrial applications, including electrolysis, thermal and nuclear processes, and electrochemical energy storage technologies. Ceramics with high chemical stability in molten salts and the ability to conduct specific ions are of significant interest for use as electrolyte/electrolyte separators in ion batteries or as inert anodes in electrolysis cells.^{1,2,3} Two prototypes of ion-conducting ceramics have been developed and characterised for Ti waste recycling via the FFC process and for sodium-activated carbon (Na-AC) molten salt supercapacities⁴, holding strong potential for commercialisation.



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Novel Molten Salt Electrolysis Process for Efficient Recovery of Titanium from Industrial Wastes (MERTi)

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Abstract

Titanium metal, which is named after the Titans of Greek mythology, has been commonly utilized in aerospace and marine industry due to its high strength-to-weight ratio and reliable corrosion resistivity. However, the premium pricing of titanium metal has limited its usage in terms of the increased global demand for lightweight materials. For aviation components, the buy-to-fly ratio could be as low as 20:1 and the titanium waste generated becomes brittle due to the oxygen contamination¹. Although these titanium waste could be recycled, the market value of these result materials (e.g., Ferro titanium) is not considerable (e.g., £ 1.00/kg)¹. Therefore, the recovery of Ti from titanium waste is investigated in this project utilizing molten salt electrolysis with inert anode, including various oxide ion and electronic conducting materials^{2,3}. Yttria-stabilized zirconia (YSZ) was sintered and pasted inside with NiO as anode, which shows considerable stability in both molten CaCl₂ and CaCl₂-NaCl at 900 °C after 3 hours' electrolysis. Titanium turnings were electrolysed in molten CaCl₂ but found to be immersed during the process, which is highly because of the high calcium oxide level remained inside molten salt. Consequently, further test was carried out in molten CaCl₂-NaCl (52:48 mol %) at 650 °C, with Ti turnings successfully deoxidized around 70% after 30 minutes electrolysis. The unexpected carbon contamination found from received samples also drops to 5 at% after the process. Future work will be emphasized on comparing the performance (e.g., Faradic efficiency) between commercial graphite and novel ceramic anode.supercapatteries.

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