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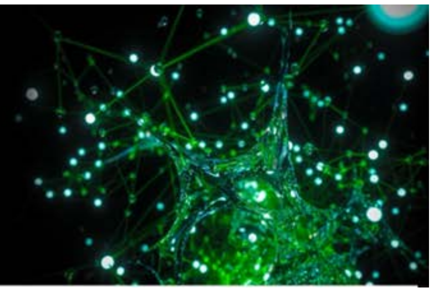


QUILL
Quarterly Reports

May - July 2023

CONFIDENTIAL (up to August 2026)

Contents

QUILL Quarterly Report

May 2023 – July 2023

Name:	Haris Amir		
Supervisor(s):	Professor John Holbrey		
Position:	PhD Student		
Start date:	10/01/2020	**Anticipated end date:**	09/2024
Funding body:	ESPRC/UKRI		

Design of New, Non-Coordinating, and Hydrophobic Anions for Functional Ionic Liquids

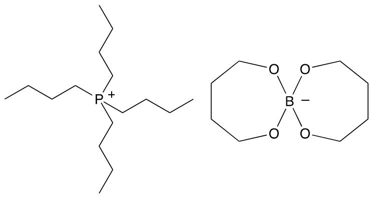
Background

New boron containing anions are of interest for the development of new ionic liquid anions with a wide range of potential applications including electro- and photo- chemistry, and for the separation and extraction of metals and waste. In this work, functional borate anions formed as complexes with O-, O/N-, and N- chelators for ionic liquid applications have been designed and investigated.

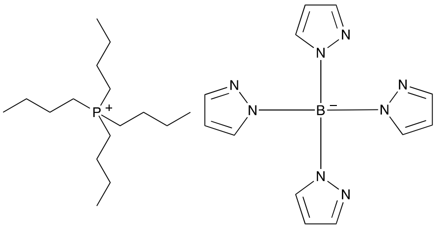
As discussed previously these borate salts were then paired with organic cations *via* ion exchange. The organic cations were trihexyltetradecylphosphonium and tetrabutylphosphonium. The latter mentioned was chosen to obtain molten salts due to the high symmetry of the cation and anion and obtain crystallography data to gain a better understanding of interactions occurring between the cation and anion in a crystal lattice. The following work was carried conducted during a visit to Deakin university, Institute for Frontier Materials (IFM) under the supervision of Professor Maria Forsyth and Dr. Mega Kar.

Organic ionic plastic crystals (OIPCs)

Once the tetrabutylphosphonium based ionic liquids were synthesised and characterised using several techniques, one of them being differential scanning calorimetry (DSC), it was found using this technique that two of the synthesised ionic liquids can be defined as OIPCs. OPICs consist of long-range ordered crystalline lattice, as temperature increases the material undergoes one or more solid-solid phase transitions.[1] This introduces crystallographic changes along with short-range disorder that arise form rotational motions of the molecule.[2] These solid-solid phase transitions often have a low entropy of fusion, and the plastic phase is entropically ‘liquid like’. This behaviour is favoured when used as an electrolyte material as it can reduce the surface contact issue between the electrolyte and electrode in case of volume expansion.[3] The two ionic liquids that exhibited OIPC behaviour is shown in figure 1.



$[P_{4444}][B(C_4H_8O_2)_2]$



$[P_{4444}][B(Pyrazole)_4]$

Figure 1 - Structure of $[P_{4444}]$ based OIPCs

The DSC (figure 2) show both exhibited one solid-solid phase transition before melting. The solid-solid phase transition for the OIPC [P4444][B($C_4H_8O_2$)$_2$] was shorter than compared to [P4444][B(Pyrazole)$_4$] before melting.

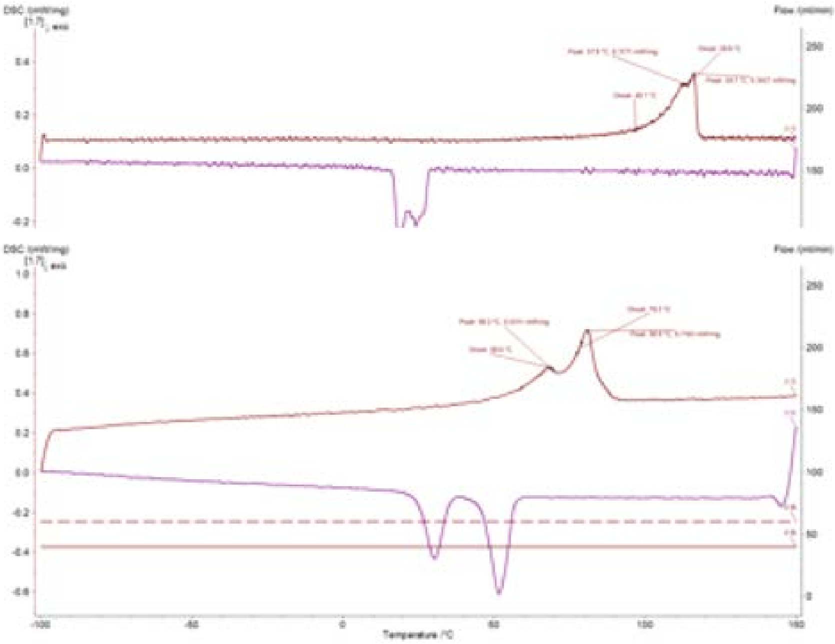


Figure 2 - DSC of [P4444][B($C_4H_8O_2$)$_2$] (top) and [P4444][B(Pyrazole)$_4$] (bottom)

To further understand these new OPICs, solid state NMR spectroscopy is carried out to investigate the dynamics of the cation and anion and to hopefully understand the ion chemistry. The NMR experiments were carried out with variable temperature (-30 to 60 ˚C) to see how the dynamics of the respective cation and anon changes, the spectra were analysed using a Gaussian peak shape.

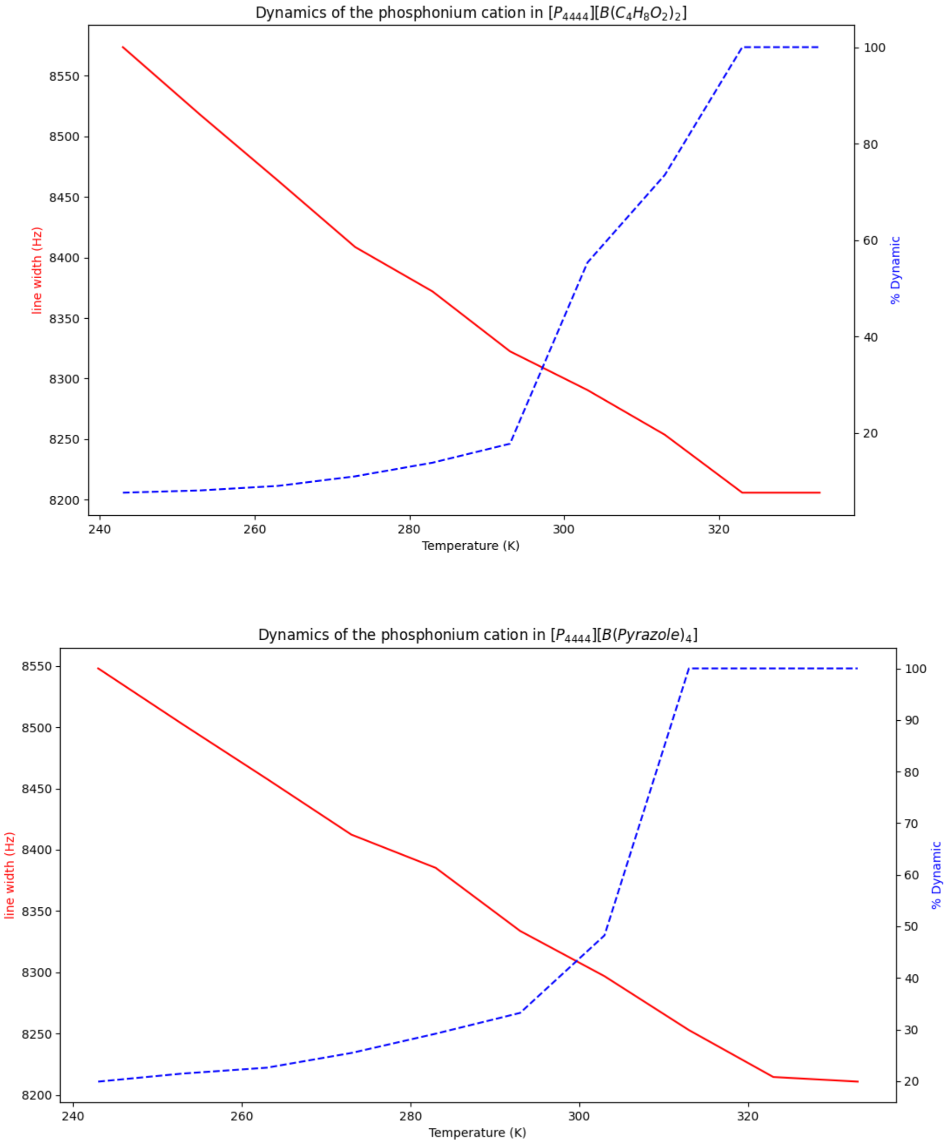


Figure 3 - The dynamics of the phosphonium cation in $[P4444][B(C_4H_8O_2)_2]$ (top) and $[P4444][B(Pyrazole)_4]$ (bottom)

The phosphonium cation in both OIPCs show that below room temperature the cation stays relatively static, but once taken above 30 ˚C the cation rapidly becomes fluid (dynamic) and when taken above the melting point of the OPICs the cation becomes 100 % dynamic.

When looking at the dynamics of the anions (figure 4) the anion stays relatively static suggesting that the bulky ligands around the boron centre restricts the fluidity of the borate anion. Measuring at temperatures above the melting point of the OPICs the anions still show dynamic of less than 40%. This suggests the cation plays a major role in the fluidity/dynamics for both OIPCs. Overall $[P4444][B(Pyrazole)_4]$ showed higher cation and anion dynamics when compared to $[P4444][B(C_4H_8O_2)_2]$. Future work for these OIPCs is to investigate the ionic conductivity, where the general trend for OPICs seems to be that higher dynamics tends to correlate to a better ionic conductivity.

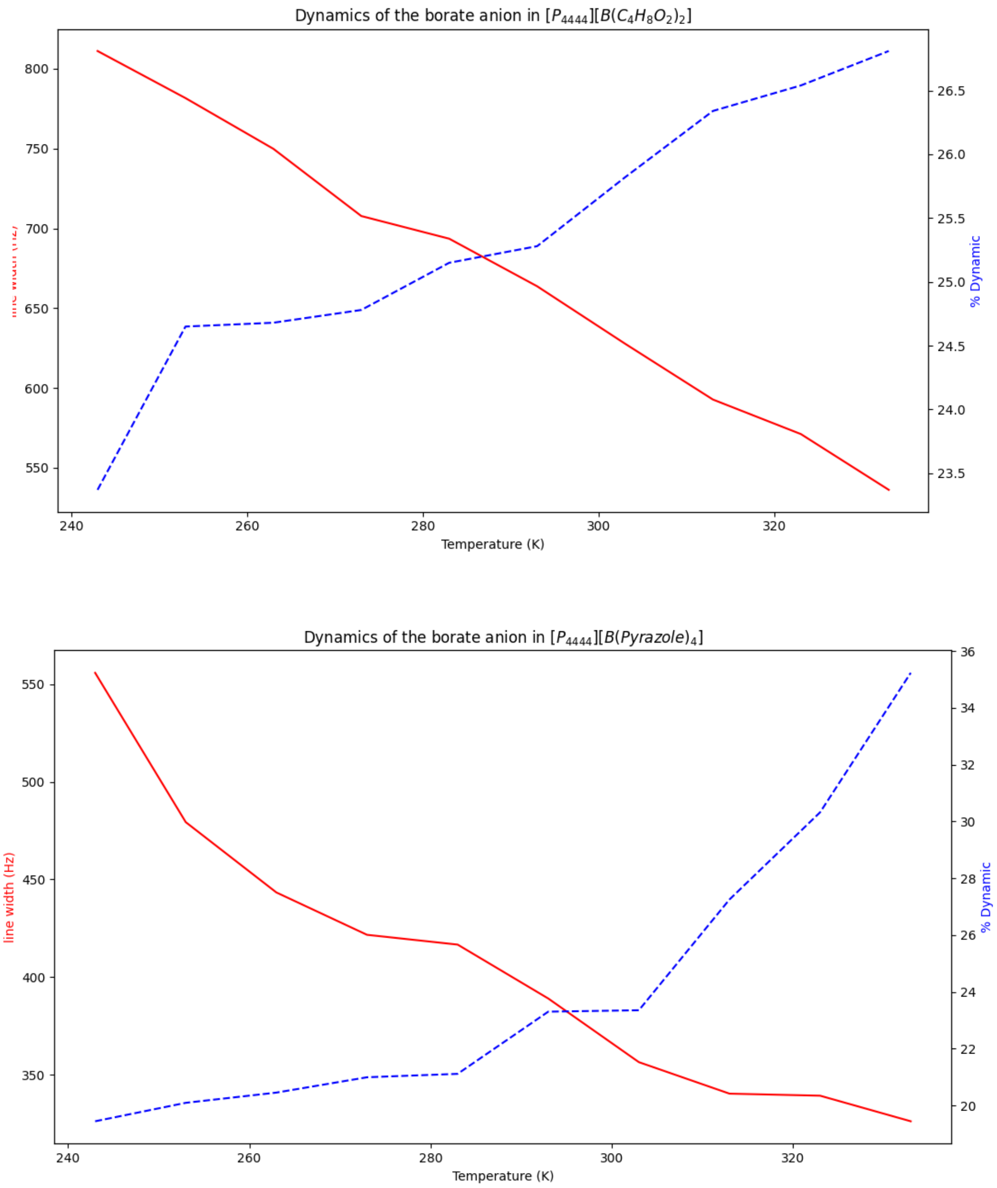


Figure 4 - The dynamics of the borate anion in [P4444][B($C_4H_8O_2$)$_2$] (top) and [P4444][B(Pyrazole)$_4$] (bottom)

References

1. S., Abeysooriya, *et al.*, 2022, Phys. Chem Chem Phys, 24, 4899–4909.
2. J. M. Pringle, *et al.*, J. Mater. Chem., 2010, 20, 2056–2062.
3. D. R. MacFarlane, *et al.*, J. Phys.: Condens. Matter, 2001, 13, 8257–8267.

QUILL Quarterly Report

May 2023 – July 2023

Name:	Dominic Burns		
Supervisor(s):	Prof John Holbrey, Prof Gosia Swadzba-Kwasny and Dr Hye-Kyung Timken		
Position:	PhD Student		
Start date:	1st October 2019	**Anticipated end date:**	30st September 2023
Funding body:	EPSRC		

Environmental Remediation Applications of Ionic Liquids Developing Ionic Liquid Technologies for Selective Aqueous and Gaseous Waste Management

Background

Lab work for the project is now finished, I am currently writing the thesis and two papers to supplement the work done for chapters 1 & 2 while a patent is currently being reviewed by Chevron for submission based on the work of chapter 3.

Chapters

1. Introduction
2. Hydrophobic Ionic Liquid Chlorides as Liquid Anion Exchangers
3. Synergized Ion Exchange
4. CO_2 Capture
5. Conclusions

Progress to date

Currently I am still writing the Introduction chapter as this must span the fields of; sulfate removal, ionic liquids used for ion extraction, anion receptor chemistry and ionic liquids for CO_2 capture so it is extensive. Data analysis and figures for my three science chapters is 90% finished however I will finish my introduction chapter first as this will help to form the narrative of where my work fits into the current body of published work.

Expected submission date

First draft to be completed by early October.

QUILL Quarterly Report

May 2023 – July 2023

Name:	Oguzhan Cakir		
Supervisor(s):	Professor Peter Nockemann		
Position:	PhD student		
Start date:	09/01/2023	**Anticipated end date:**	31/11/2026
Funding body:	Turkish Government (TENMAK)		

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

Background

Molecular nanoclusters constitute an intermediate state of matter between molecules and nanoparticles. The advantage of these materials is that, in contrast to conventional nanoparticles, they have a defined molecular structure that can exhibit cooperative spin-spin interactions, which might be used for magnetic high-density data-storage on a molecular level. We propose to investigate the synthesis of novel and interesting molecular cluster magnets using ionic liquid pathways; the aim is to achieve control over magnetic materials at cluster size with defined structures by using ground-breaking new synthetic methodologies.

Molecular cluster magnets provide a rich playground of different magnetic interactions in well-defined nanostructures, occupying the space between the quantum and classical world. Other interesting possibilities are clusters with antiferromagnetic or ferromagnetic intra-molecular couplings, which may exhibit bulk ferro- or ferrimagnetic interactions. Studying their physical properties contributes to our understanding of magnetic interactions in complex molecular structures. The use of ionic liquids allows for fundamentally different synthetic pathways resulting in compounds not accessible through conventional solvent-based synthesis.

Objective of this work

- Synthesise novel molecular cluster magnets with spin-cooperative behaviour using ionic liquid pathways
- Understand synthesis of molecular cluster magnets through ionic liquid pathways including the formation mechanism
- The magneto structural properties of both the liquid precursor and the solid-state molecular cluster magnets as a function of varying syntheses conditions.
- Use the understanding of formation mechanisms and magneto structural property relationships to inform the design of further molecular cluster magnets

Progress to date

The following post-graduate training programmes have been completed:

- "How to read critically and take good notes" by Fabiana McCracken at Queen's University.
-"Training on Pure and the Research Portal " by Rebecca Clarke at Queen's University.

- Academic writing courses by Rachael O'Neill at Queen’s University. (8 weeks)

A literature review was completed and presented to Prof Nockemann.

Structure of the literature review:

1. Ionic liquids
2. Ionic liquids for inorganic synthesis
3. Molecular magnets
4. Synthesis of Molecular Magnets
5. Ionic liquids for the synthesis of MMs
6. Magnetic Ionic Liquids (MILs)
7. Characterisation of MMs

Conclusions and future work

I succeeded with the initial review for my PhD project on the 21st of June.

I will start further experiments that we have planned. These experiments will be the first steps to synthesise boron-containing ionic liquids that are suitable as linkers in the synthesis of MMs. When these experimental studies are completed, a poster and presentation will be prepared for the next QUILL meeting and presented for feedback to the industrial advisory board.

QUILL Quarterly Report

May 2023 – July 2023

Name:	Andrew Forde		
Supervisor(s):	Dr Stephen Glover and Prof Peter Nockemann		
Position:	PhD student		
Start date:	03/06/2019	**Anticipated end date:**	30/12/2023
Funding body:	EPSRC		

Physics Informed Neural Networks for Battery Response Prediction

Currently in process of writing thesis titled "*Physics Informed Neural Networks for Battery Response Prediction*" as outlined below:

Thesis Outline

1. Introduction
2. Literature Review
3. PINNs for Electrical Li-ion Battery Modelling
4. PINNs for Cloud-Point Battery Thermal Modelling
5. PINNs Applications in Timestepping Battery Thermal Models
6. Application of PINNs in Coupled Electrochemical-Thermal Models
7. Discussion
8. Concluding Remarks
9. Appendices

QUILL Quarterly Report

May 2023 – July 2023

Name:	Edwin Harvey		
Supervisor(s):	Dr Oana Istrate, Prof Peter Nockemann and Dr Stephen Glover		
Position:	PhD Student		
Start date:	February 2022	**Anticipated end date:**	August 2025
Funding body:	Department for the Economy		

3D-Printable Redox Flow Battery Electrodes

Background

Redox flow batteries (RFBs) are promising candidates for grid-scale energy storage and stationary energy storage applications. They have a longer cycle life than lithium-ion and can use cheaper, safer, and more environmentally friendly electrolytes. Such systems are becoming more important as we rely more on intermittent renewable energy, such as wind and solar, as we move towards reaching net zero by 2050 (UK govt target).

The RFB design has not changed much since their inception in the 20th century (e.g. vanadium RFBs were invented in 1986 at the University of New South Wales, Australia). Electrodes are still typically made using carbon felt as these have good electrical conductivity, electrochemical activity, and are mechanically and chemically stable. However, using carbon felt as an electrode material limits cell design and is associated with a high interphase electrical resistance. Additionally, for flow-over electrode designs, flow channels must be machined into graphite plates which is complex and expensive. 3D-printable electrodes may offer a greater design freedom where, for example, flow channels can be printed as part of the design, and porous and solid elements can be combined.

Graphene nanocomposite materials may be able to replace graphite and carbon felt as an electrode material. Possible 3D-printing technologies for this material are fused deposition modelling (FDM), and stereolithography (SLA). FDM uses a heated thermoplastic filament which is extruded out of the printer nozzle, following a pre-calculated path to manufacture the part layer by layer. Graphene based nanocomposites have been printed using FDM but often suffer from agglomeration of graphene due to extruding conditions. SLA uses a liquid resin which is cured using UV light at the desired locations, also building the part layer by layer. SLA may offer improved graphene dispersion compared to FDM.

Objective of this work

To create a viable redox flow battery (RFB) electrode that has been manufactured through 3D-printing technology.

Progress to date

Initially, I spent time reading literature and planning my PhD by splitting it into work-packages that each last a few months. My first work-package is focused on manufacturing a 3D-printable RFB material utilising carbon nanofillers. After analysing the properties of various polymer matrices, I have decided to focus on acrylate-based monomers that can be polymerised in-situ with graphene. This is because various papers have shown this method to produce high electrical conductivity and excellent graphene dispersion.

During initial experimental work graphene oxide (GO) was synthesised using a modified Hummers' method. Following this, seven polymer/graphene nanocomposites were manufactured using SLA 3D-printing containing GO and graphene nanoplatelet (GNP) fillers. Nanofillers and nanocomposites were then characterised using FTIR, Raman spectroscopy, X-ray diffraction, tensile testing, and electrical testing. A literature study and experimental work were submitted as part of my differentiation which was completed in November 2022.

Since November 2022, I have been focused on manufacturing and modifying graphite powder and developing my characterisation skills. I have been undertaking an in-situ polymerisation method to produce high electrical conductivity nanocomposites which have the potential to be used as a 3D-printed electrode material.

Since February 2023, I have been focusing on a latex mixing method for producing graphite oxide nanocomposites. This has involved testing different mixing methods and adding salts to coagulate the particles into a nanocomposite.

Since May 2023, I have focused on refining the latex mixing method for the the production of mouldable graphene oxide composite materials. I have shaped the composite material and undertaken CV electrochemical measurements in a vanadium electrolyte which shows promising results. I've also been performing a full characterisation of the composite material (TGA, DSC, Raman, FTIR, etc.) and writing up the info for a paper submission.

Conclusions and future work

Currently focused on writing a paper with the working title: Mouldable graphene oxide composite as redox flow battery electrode material. Also looking at ways electrodes can be shaped such as through compression moulding and through 3D-printing such as FDM.

QUILL Quarterly Report

May – July 2023

Name:	Aloisia King		
Supervisor(s):	Prof John Holbrey and Prof Małgorzata Swadźba-Kwaśny		
Position:	PhD student		
Start date:	01 October 2021	**Anticipated end date:**	March 2025
Funding body:	EPSRC		

Intrinsic FLP Systems in Ionic Liquids

Background

Frustrated Lewis acid/base pairs (FLPs) are potential metal-free alternatives to platinum group metal catalysts and have been shown to activate hydrogen for hydrogenation chemistry [1]. Typical examples of FLPs that have been studied are combinations of a sterically hindered bulky phosphine Lewis base paired with a strongly electrophilic Lewis acidic susbstituted borane. While many of the advances in FLP chemistry have sought to exploit these bulky phosphine/borane pairs, less attention has been given to alternative acid/base pairs although examples with non-boron Lewis acid FLP components are known including N-alkylacridinium cations which have been show to exhibit FLPs chemistry when paired with lutidine (2,6-dimethylpyridine) as a base [2].

Objective of this work

The goal of this research is to develop organic FLPs (eliminating the need for group 13-based Lewis acids) within an intrinsic IL medium in which, ideally, the potential catalyst concentration in the liquid is maximised and enables reaction intensification creating greener, sustainable chemistry through facile synthesis and replacement of both conventional solvents and platinum group metal catalysts.

Progress to date

Four *N*-alkyl-acridinium salts and *N*-protonated heterocyclic ionic liquids as precursors for FLP studies have been successfully synthesised and characterised. *N*-Alkylacridinium *bis*{trifluoromethylsulfonyl}imide ([R-Ac][Tf_2N]) salts synthesised are highly soluble in H-lutidinium and H-picolinium *bis*{trifluoromethylsulfonyl}imide ([H-lut][Tf_2N] and [H-pic][Tf_2N]) ionic liquids. This contrasts with the reported poor [2] and limiting solubility of *N*-methylacridinium salts in organic solvents. The H_2 screening experiments, initiated previously are still under detailed investigation. Since the last report, I have carried out further detailed thermal analysis on the Intrinsically IL MethAc[NTf_2]/2,6-lutidine system and we are currently in the process of finalising these thermal diagrams *(Figure 1)*.

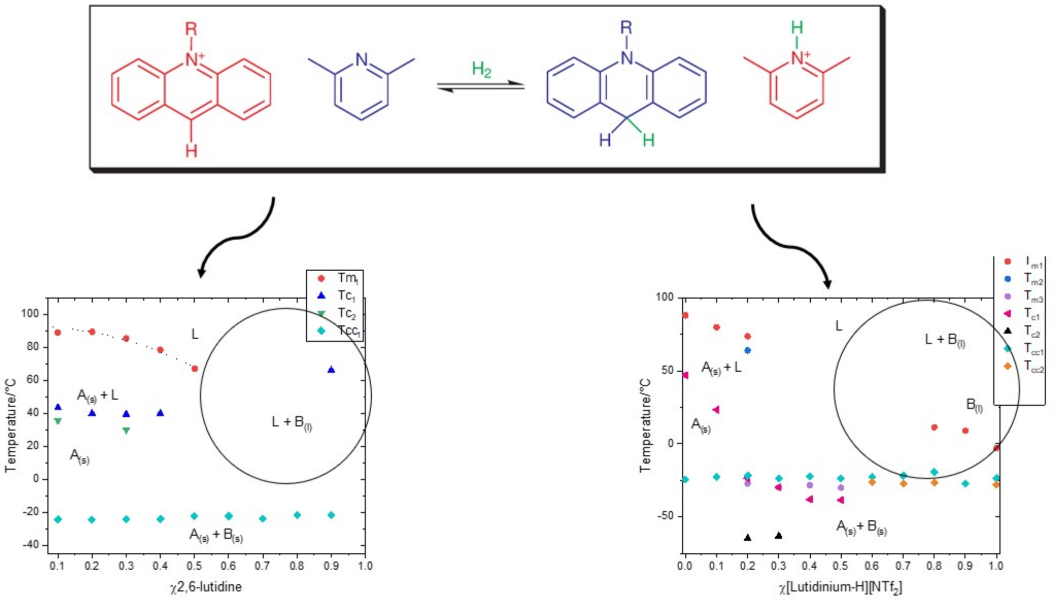
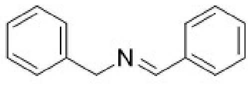
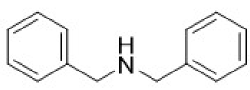
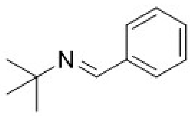
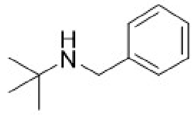
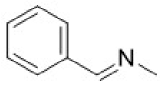
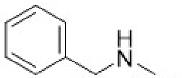


Figure 1 -Conceptual intrinsically IL FLP equilibrium and corresponding PD's exhibiting thermal behaviour for the entire compositional range; LHS PD(2,6-lutidine:Methylacridinium[NTf_2] preliminary phase diagram constructed from DSC data across the whole compositional range from $c_{2,6\text{-lutidine}}$ = 0.00-1.00. T_{m1} representative of melts associated with MethAc[NTf_2], T_{c1} representative of crystallization of MethAc[NTf_2], T_{c2} are second crystallizations associated with the MethAc[NTf_2] and finally T_{cc1} are cold crystallizations seen across the entire compositional range. All relevant data was included in the construction of this thermal diagram for completeness) and RHS PD ($c_{[\text{Lutidinium-H}][\text{NTf2}]}$ = 0.00-1.00. T_{m1}, T_{m2} and T_{m3} associated with melting points of pure and mixed component samples. T_{c1} and T_{c2} are indicative of the crystallization events that were observed in the pure component and the various compositional samples. T_{cc1} and T_{cc2} are the two cold crystallization events observed in the samples. All relevant thermal events were included on the phase diagram for completeness).

We plan to add phase boundary lines and finalise the important data points that have been included on the thermal diagrams in the near future. However, having conducting the DSC measurements at a reduced ramp rate of 2°C/ min, we have ultimately gathered a more accurate illustration of what is happening in the solid-liquid interface of the various compositional samples. Additionally, we have began the various substrate reactions with the "proof-of-concept" system and the results are in the process of being analysed. The substrates planned to be converted from aldimine to amines are included in Table 1.

Table 1 - Substrate and products of hydrogenation reactions

Substrate	Product
 N-benzylidenebenzylamine	 dibenzylamine
 N-benzylidene-tert-butylamine	 *N*-benzyl-2-methylpropan-2-amine
 N-benzylidenemethylamine	 *N*-methyl-1-phenylmethanamine

So far, we have carried out the reaction including entry 2 from the table above, but plan to carry out the other two reactions / analysis in the next month. These reactions are carried out with MethAc[NTf_2]/2,6-lutidine in a 1:1 composition at 60°C with 5% H_2 gas. However we also plan to carry out the same substrate reactions beginning with the hydrogenated products (RHS of equilibrium) to see if we can speed up reaction times of this strategically engineered system.

As well as the work mentioned above, ongoing investigations are being conducted to synthesise a range of 3,5-dicyanopyridine analogues. We anticipated that this set of molecules may be able to be used as alternative cations (within an FLP system), due to their similar hydride ion affinity to that of the dihydromethylacridinium molecule [3]. However, through recent discussions we have decided that this class of alkylated 3,5-dicyanopyridines should have a good, innate ability to act as IL based charge transfer materials, as previous work on cyanopyridinium IL work within the group was successful in establishing a new class of charge transfer materials [4]. However, this is proving difficult, as there is not much reported within the literature on these species. To date I have synthesized the 3,5-dicyanomethylpyridin-1-ium[NTf_2] and 3,5-dicyanoethylpyridin-1-ium[NTf_2] ILs successfully. Additionally, attempts have been made to synthesize the propyl, butyl and benzyl analogues of these ILs in multiple different ways, but I have not been capable just yet.

Conclusions and future work

I will continue to carry out our substrate reactions with the [Me-Ac][NTf_2]/2,6-lutidine IL system. Additionally, we hope to come up with a plan once we have carried out these reduction reactions to probe the fluorescent nature of the system, as we are not entirely sure if light has a role to play in the hydrogenation reactions of these species. Additionally, ongoing work is being undertaken in the exploration and the synthesis of the 3,5-dicyanopyridine ILs and I hope to make the propyl, butyl and benzyl analogues and probe the CTM nature of these species and their capabilities as cationic components of FLP systems.

References

1. D. W. Stephan and G. Erker, *Angew. Chem. Int. Ed.,* 2010, 49, 46–76.
2. E. R. Clark and M. J. Ingleson, *Angew. Chem., Int. Ed*., 2014, 53, 11306–11309.
3. Zhao H, Li Y, Zhu, X*ACS Omega.,* 2018, 3(10), 13598-13608.
4. C. Hardacre, J. D. Holbrey, C. L. Mullan, M. Nieuwenhuyzen, W. M. Reichert, K. R. Seddon and S. J. Teat, *New J. Chem.,* 2008, 1953-1967.

QUILL Quarterly Report

February 2023 – April 2023

Name:	Sanskrita Madhukailya		
Supervisor(s):	Professor John Holbrey and Dr Leila Moura		
Position:	PhD student		
Start date:	April 2021	**Anticipated end date:**	April 2024
Funding body:	TU-QUB-Joint PhD Scholarship		

LCST Behaviour in 5-Phenyltetrazolate Based Ionic Liquids

Background

In the previous report, deuteration of tetrabutylphosphonium bromide was attempted to prepare the D-ionic liquid for neutron scattering experiments. In addition to that, posters were presented at QUILL IAB and COIL-9 conference. Herein, a brief about some of the isothermal titration calorimetric experiments that were carried out in ENS de Lyon under Professor Margarida Costa Gomes, are reported. This was done with an intention to understand the thermodynamics of the LCST systems by quantifying the energies of hydration and comparing them to non-LCST behaviours.

Objective of this work

The ultimate objective of this research is to comprehend and elucidate the phase behaviour of certain ionic liquids known as the lower critical solubility temperature (LCST), with the purpose of establishing the boundaries and formulating a methodology for synthesizing such ionic liquids that possess the potential to function as draw solutes in the forward osmosis process for desalinating seawater. During this procedure, a series of ionic liquids containing the tetrazole moiety will be synthesized, assessed, and compared to the current ones, considering the selection of the anion or cation, which can influence the phase behaviours.

Progress to date

Experimental: The ionic liquids tetrabutylphosphonium 5-phenyltetrazolate, $[P_{4444}]$[PhTet] and tetrabutylphosphonium benzoate, $[P_{4444}]$[Bnz] were synthesised using reported methods and HPLC Plus grade water was supplied from Sigma-Aldrich. The chemical structures of the two ionic liquids studied in this work are represented in Figure 1.

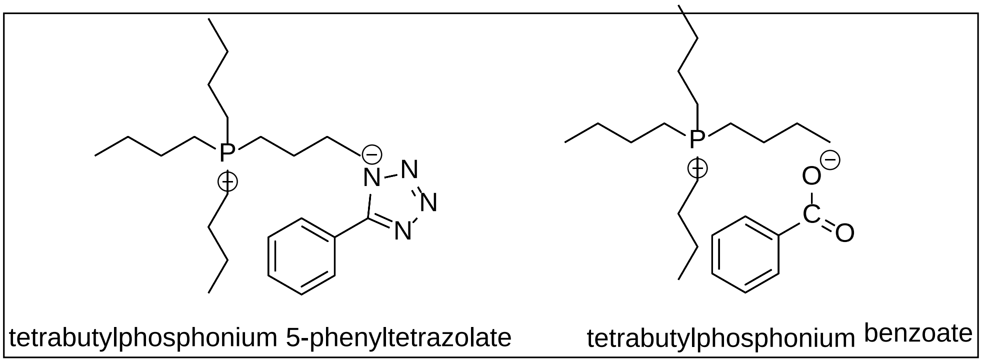


Figure 1 - The ionic liquids, [P_{4444}][PhTet] (left) and [P_{4444}][Bnz] (right), under study for isothermal titration calorimetry experiments.

Instrumentation: An isothermal titration calorimeter (TA instruments) equipped with a thermal activity monitor (TAM) III thermostat (TA Instruments) was used for measuring the mixing enthalpies (ΔH_{mix}) at atmospheric pressure and at 298.15 K. Two cells of 1ml were used: one of them containing the sample (working cell) and the other reference cell. During the titration experiments, small volumes (1 to 5 μl) of ionic liquid-water mixture or pure water, according to the conditions, of a known composition were injected (from a 250 μl syringe) into the working cell. To ensure an effective mixing, the liquid in the cell was stirred at 60 rpm. A motor-riven pump was used for the automatic injections (18-22 per experiment), each one during 30 to 90 s. Between them, an interval of 180 mins was established to allow baseline recovering.

After each injection, a peak corresponding to the heat effect of the mixing process was recorded. The area of the peak, Q, is proportional to the heat involved, and is the value required for the enthalpy of mixing calculations. The whole apparatus is connected to a computer by which we can program calibrations, injections and calculations of the heat involved in each addition.

Results and discussion: The area of the peak observed for each injection of the sample determines the Q per moles of the solute added. *Figure 2* represents an example of the integrated value of the heat released (Q in mJ) during the second injection of the sample, [P_{4444}][PhTet]/H_2O at 3.6953 x 10^{-6} moles of the ionic liquid in 8.30556 x 10^{-5} moles of water at 298.15 K.

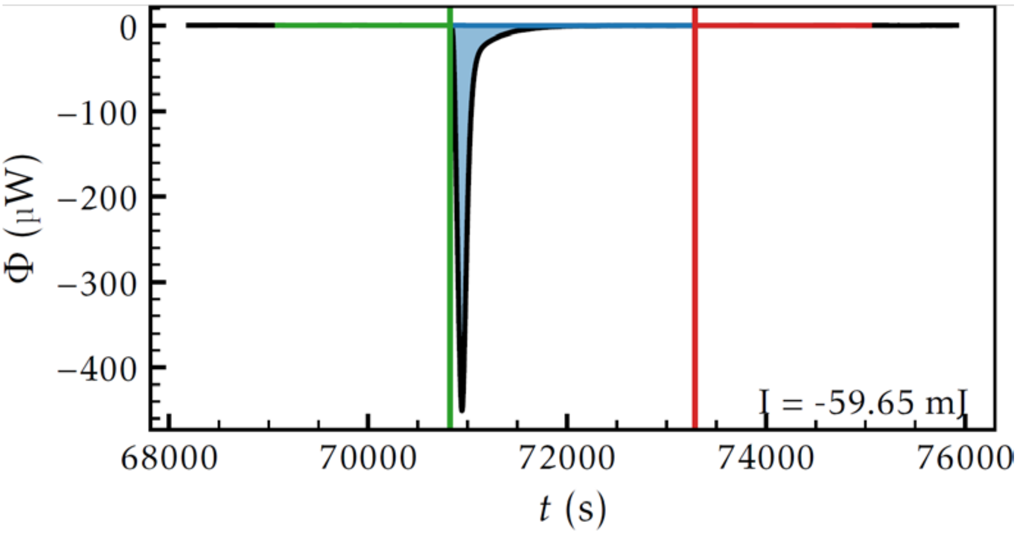


Figure 2 - Integrated value of the heat released on the second injection of the sample $[P_{4444}][PhTet]/H_2O$ (syringe), to H_2O (cell).

Different compositions of the mixtures of both the ILs with water were prepared and tested for their energies involved during the mixing process. It was observed that for the LCST ionic liquid, the heat involved somewhat remained the same for the different compositions studied, whereas, for the non-LCST IL, tetrabutylphosphonium benzoate, the heat involved changed drastically as the compositions were varied. (Data not included.)

Future work

1. Complete ITC experiments at 65°C and analyse results for a paper.
2. Complete deuteration of the cation for neutron scattering experiments, to be included in the paper.
3. Complete the thermophysical characterisation of the mono and dicationic ionic liquids for two other papers.

QUILL Quarterly Report

May 2023 – July 2023

Name:	David McAreavey		
Supervisor(s):	Dr Stephen Glover, Dr Oana Istrate and Prof Peter Nockemann		
Position:	PhD Student		
Start date:	1st October 2021	**Anticipated end date:**	31st March 2025
Funding body:	Department for the Economy		

Design and Development of an Effective and Interconnected Smart Fire Suppression System for Lithium-ion Batteries in Electric Vehicles

Background

As many countries around the world begin to implement their plans to ban the sale of new petrol and diesel vehicles in the coming decades, there is a clear shift occurring towards electrification of transportation. However, there are several challenges that should be addressed if mass adoption of these vehicles is to be successful. Chiefly among which are the needs to extend range and improve battery safety. Depending on the sources used it can be argued that EVs do have a good battery safety record and the number of electric vehicle fires that occur are relatively low. Tesla's 2020 vehicle safety report claims that one of their vehicles is almost ten times less likely to be involved in a vehicle fire, than the average vehicle on the road in America per mile driven, based on data from the national Fire Protection Association and US Department of Transportation. Contrary to this, in London in 2019 based on data from the London Fire Brigade the incident rate when adjusted for the number of EVs and IC vehicles on the road is more than twice as high for EVs. Regardless of the exact frequency, due to the nature of these thermal events they can often initiate thermal runaway, meaning that it is extremely difficult to extinguish as well as having the potential to burn both hotter and longer than a typical IC vehicle fire. The primary concern is of course for the safety of the occupants of the vehicle and the potential danger to their health. Additionally, an EV has the potential to ignite in scenarios where it may initially go unnoticed, usually if an IC vehicle ignites it will do so in use as this is when the highest temperatures are experienced. EVs on the other hand can ignite under circumstances such as when charging. This means that the thermal runaway process may go unnoticed for some time as well as likely being close to a home or garage, causing significant property damage.

An additional concern surrounding the adoption of EVs is the level of media attention that EV fires receive. Despite being relatively infrequent especially due to the low total market share, the negative publicity generated hinders the adoption of these vehicles. As well as causing the loss of resources that were originally carbon intensive to produce.

Objective of this work

The ultimate goal is to develop a fire suppression and thermal management system that can be realistically employed in a vehicle. This work may only achieve a step in this development for such a suppression system. It is vital to consider that such a system must be compatible with thermal management systems, as the implementation of a fire suppression system without an appropriate thermal management system essentially renders the vehicle useless. This means that a vehicle has the ability to keep the cells within its pack in the optimal temperature range, promoting longevity. As well as having a sufficient suppression system that is capable of preventing the propagation of thermal runaway between cells in the event of a fault or road traffic collision.

Progress to date

Since traveling to JSAE 2023 in Yokohama the decision was made to spend some time doing a thorough literature review to solidify the project direction, as well as hopefully produce a review paper that will also form the basis of the first chapter of my thesis.

To date a collection of approximately 50 papers that are specifically dedicated to the area of interstitial materials has been assembled and summarised. Additionally, a 6200 word first draft of the first couple of sections of a literature review have been written.

Discussions are ongoing around the possibility of physical testing being conducted at MIRA, as this would be a significant boost to the project.

Conclusions and future work

Further work on literature review will remain the primary focus alongside the development of a test plan.

QUILL Quarterly Report

February 2023 – April 2023

Name:	Sam McCalmont		
Supervisor(s):	Dr Leila Moura, Prof John Holbrey and Prof Margarida Costa Gomes		
Position:	PhD		
Start date:	Jan 2020	**Anticipated end date:**	July 2023
Funding body:	EPSRC Doctoral Training Partnership		

Chemisorbent Materials for Olefin and Paraffin Separation

Background

Separation of light olefins from their paraffin counterparts have been described as one of the seven chemical separations to change the world. Global annual production of light olefins exceeds 200 million tons, about 30 kg for each person on the planet. The current method for their separation is cryogenic distillation, one of the most energy-intensive processes in the industry. Alternative methods can focus on the olefin being selectively captured either through a physical interaction (physisorption) or chemical reaction (chemisorption).

One class of alternative sorbents are ionic liquids (ILs). However, so far, IL physisorbents have not demonstrated sufficient efficiency in either selectivity or capacity to compete with current technologies. Complexation of ethylene through its double bond with silver and copper ions has been used in the literature for chemical separation of olefins and paraffins. However, other components of raw gas feeds, such as acetylene, can react with the silver and become explosive. This has prevented the uptake of these materials into large scale processes.

Objective of this work

To develop and test new chemisorbent materials for the separation of light olefins and paraffins; to achieve high capacity combined with selectivity for the selected materials. To investigate, and rationalise, selectivity and capacities of chemisorbent based on measurement of gas solubility and partitioning from model industrial gas stream compositions and conditions.

Thesis title: Chemisorbent materials for olefin and paraffin separation

Submission date: To be decided

Thesis structure:

Chapter list:

1. Introduction + literature review
2. Gas solubility system

3. System and characterisation of materials
4. The use of phosphorus ionic liquids for ethylene and ethane separation
5. The use of cyanopyridinium ionic liquids for ethylene and ethane separation
6. The effect of the number of nitrile groups in the anion of the IL for ethylene and ethane separation
7. The influence of metals on the separation of ethylene and ethane in ionic liquids
8. Concluding remarks

QUILL Quarterly Report

May 2023 – July 2023

Name:	Anne McGrogan		
Supervisor(s):	Prof Gosia Swadźba-Kwaśny		
Position:	PhD		
Start date:	01/10/2019	**Anticipated end date:**	31/03/2023
Funding body:	EPSRC		

Thesis title: New Approaches to Studying Liquid Structure and Lewis Acidity

This report provides an overview of the thesis chapters.

List of chapters:

Chapter 1: Introduction
Chapter 2: The structure of protic ionic liquids based on sulfuric acid
Chapter 3: Structure of bistriflimide based ionic liquids
Chapter 4: Frustrated Lewis pairs in ionic liquids
Chapter 5: Boron Lewis acids

Expected submission date: 29/09/2023

QUILL Quarterly Report

May 2023 – July 2023

Name:	Beth Murray		
Supervisor(s):	Prof Małgorzata Swadźba-Kwaśny and Prof John Holbrey		
Position:	PhD		
Start date:	October 2022	**Anticipated end date:**	October 2025
Funding body:	Department of Economy		

Inorganic Chemistry of Group 13 Elements in Sustainable Uses

Background

Rechargeable batteries play a vital role in the energy management strategy of the European Union (EU). 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.[1] Secondary (rechargeable) batteries exhibit exceptional energy conversion efficiency, superior performance, reliability, and the ability to provide on-demand responses.[2] Presently, lithium-ion batteries are considered cutting-edge technology, however, they are plagued by high costs and flammability concerns. These batteries are widely prevalent in mobile electronic devices and are being increasingly utilized in transportation and grid applications.[1] Lithium-ion batteries offer several advantages, including high energy density, design flexibility, self-discharge, good cycle life, and low maintenance.[3] However, it is important to note that lithium has a low abundancy on Earth, which contributes to its high cost and reduces the long-term sustainability of relying heavily on the metal. Furthermore, as already mentioned elemental lithium is unstable and highly flammable.[4]

Metals from Groups 1 and 2 have been considered as substitutes for lithium (Li) in batteries, but aluminium (Al) from Group 13 appears to hold significant promise. It is abundantly available on Earth, making it a cost-effective option. Moreover, aluminium offers safe handling, the capability to exchange three redox electrons per cation, and exhibits high gravimetric and volumetric capacity.[5] One drawback of Al batteries is their limited commercialisation, primarily due to the absence of suitable electrolytes. Many attempts to commercialise Al batteries faced technical challenges, including difficulties in achieving reversible electroplating/stripping of aluminium, inadequate stability of Al-ion cells, and corrosion issues.[1] 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 a promising candidate. ILs are composed entirely of ions and often have a melting point below ambient temperature. They possess several desirable properties, including high ionic conductivity, minimal volatility, very low flammability, and excellent chemical and electrochemical stability.[3] Promising electrolytes were developed through the dissolution of aluminium salts, such as $AlCl_3$ or $Al(TFSI)_3$, in ionic liquids containing bis(trifluoromethanesulfonyl)imide ($[TFSI]^-$) or trifluoromethanesulfonate ($[OTf]^-$) anions.[6, 7] While electrolytes using ILs show promise, they also present certain challenges, such as cost. Despite the cost advantage of aluminium over lithium, the use of ionic liquids can introduce additional expenses. The organic cation, despite having a spectator role, contributes significantly to the overall cost. Secondly, one of the challenges associated with using ILs is their higher viscosity compared to organic solvents, which hampers the conductivity of Al(III). Another significant drawback is corrosion, especially in chloride-containing systems, which remains a critical issue. Lastly, there is a limited scope for optimisation when using ILs as electrolytes. The concentration of Al(III) is constrained by the solubility of the aluminium salt, and also by the potential negative effects that high salt concentration can have on the electrolyte, such as an increase in viscosity that can be detrimental to conductivity.

At this juncture, we introduce LCCs as novel 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 ionic liquids that possess, high metal content, and adjustable environments around the metal centre. These analogues are highly sought after for applications such as metal electrodeposition,[8] Lewis acid catalysis,[9] and as electrolytes for lithium-ion batteries.[10]

Objective of this work

The objective of this project was initially the synthesis of semiconductor nanoparticles using liquid coordination complexes (LCCs), however, the initial phase of my PhD work involved building on previous research conducted during my MChem project. In this study we employed hydrophobic deep eutectic solvents (DESs) for the extraction of gallium metal from zinc leachate solution, which is derived from the zinc manufacturing industry. Gallium's properties make it a vital component in various semiconductor applications, ranging from high-speed electronics to optoelectronics, and renewable energy technologies. Its unique characteristics enable the development of advanced devices with enhanced performance and efficiency.[11] This leads to the subsequent phase of my research which focuses on liquid coordination complexes for the synthesis of semiconductor nanoparticles. Like chlorometallate ionic liquids (ILs), liquid coordination complexes (LCCs) also possess high metal concentrations, which makes them favourable, convenient, and cost-effective alternatives for serving as single compound precursors in the synthesis of semiconductor nanoparticles. Lastly, the final segment of this work concentrates on the use of liquid coordination complexes based on aluminium as electrolytes in aluminium-ion batteries. This research is founded on the promising potential of aluminium in batteries, attributed to its high abundance on Earth, its capability to exchange three redox electrons per cation, as well as high gravimetric and volumetric capacity.[5]

Progress to date

I had the opportunity to visit Monash University in Melbourne, Australia for six weeks. During this time, I began work on developing aluminium LCCs as electrolytes for aluminium batteries in the Macfarlane research group.

In the initial stage of the research, the objective was to reproduce the literature data on the utilization of a urea-$AlCl_3$ LCC as an electrolyte in aluminium batteries. The LCC electrolyte had received considerable attention in previous publications, making it a suitable candidate for replication using a coin cell configuration. Coin cells were selected for this study due to their ability to operate with minimal electrolyte, allowing for symmetrical and full cell experiments to be conducted, although no literature had reported the use of a coin cell.

Figure 1 shows the preliminary results obtained from galvanostatic cycling test performed on symmetrical Al/Al cells, employing the urea-$AlCl_3$ electrolyte (χ_{AlCl_3} = 0.58). Unfortunately, initial findings showed a high overpotential of approximately 2 V, and cell shorting, which from further investigation proved to be that the Al discs needed to be polished before use, likely due to the presence of a residual oxide layer on the surface.[12]

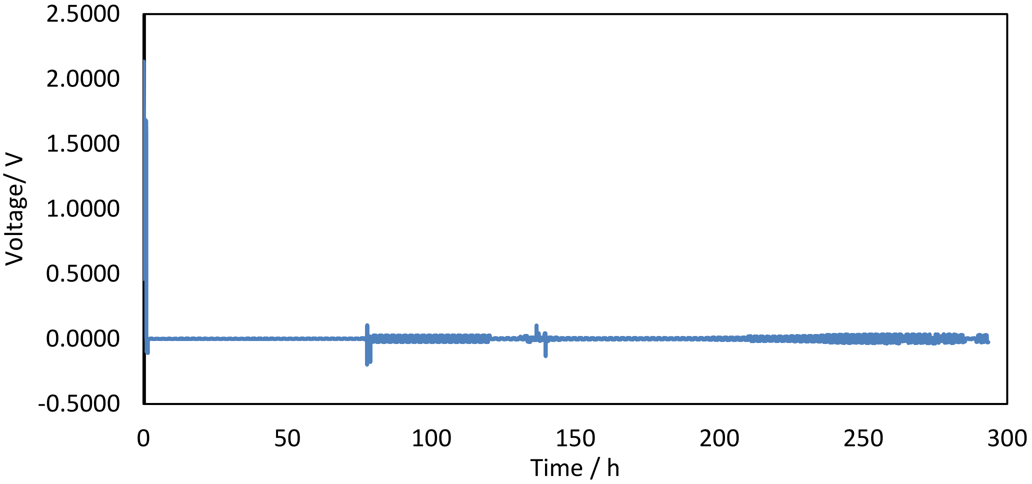


Figure 1 - Galvanostatic cycling of Al/Al symmetrical cell with urea-$AlCl_3$ electrolyte.

A polishing solution was prepared by combining sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4) and nitric acid (HNO_3) (further details in section 5.2.2). After polishing of the Al discs, the cycling results were comparable to literature,[5] showing a lower overpotential and stable cycling (Figure 2).

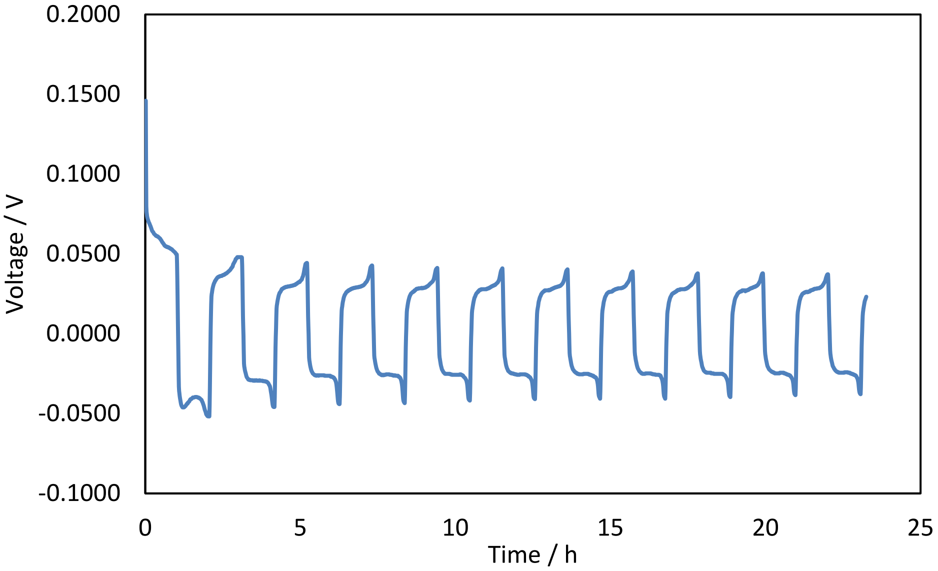


Figure 2 - Galvanostatic cycling of Al/Al symmetrical cell with urea-$AlCl_3$ electrolyte, after the Al electrodes were polished with acid.

The primary objective of this study was to synthesize various $AlCl_3$ LCCs and evaluate their performance as electrolytes. Once we established the viability of our setup by successfully replicating literature data, we proceeded to investigate the use of different ligands in conjunction with AlCl3. Trioctylphosphine oxide (TOPO), a large organophosphorus compound with long alkyl chains, was one of the ligands we investigated, as to my knowledge no previous literature had reported TOPO in an electrolyte for Al batteries. Figure 13 shows the galvanostatic Al/Al cycling obtained for the TOPO-$AlCl_3$ electrolyte in comparison to the control urea-$AlCl_3$ electrolyte. Despite the high overpotential observed during the cycling of the Al cell with the TOPO-AlCl3 electrolyte, it exhibited remarkable stability over several cycles. However, the question arose as to whether the size of TOPO might hinder its effectiveness as a charge carrier in an electrolyte.

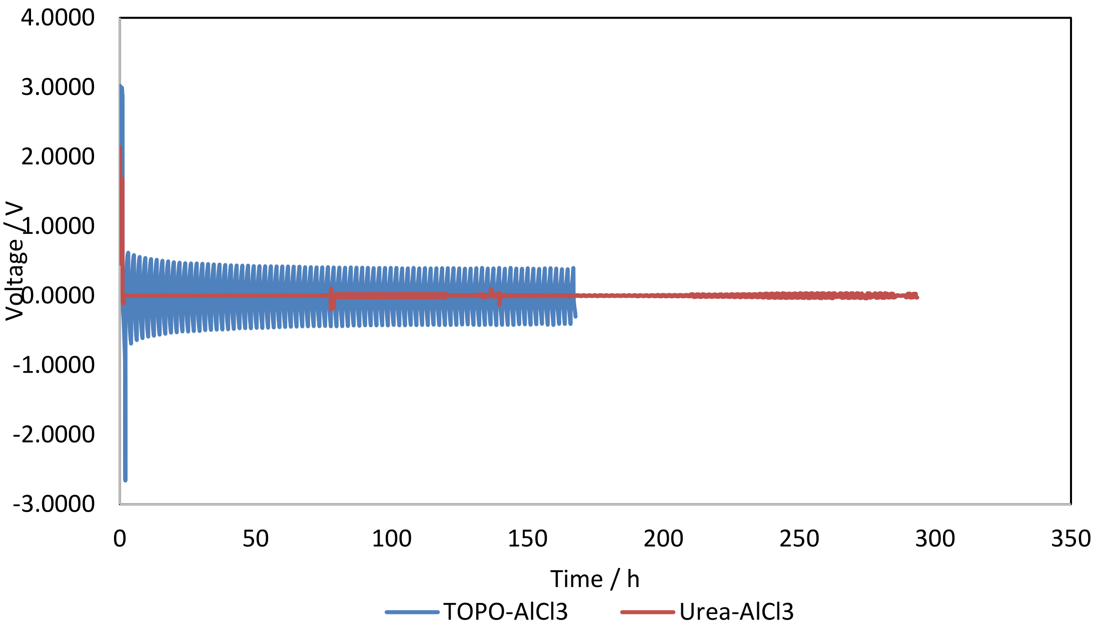


Figure 3 - Comparison of galvanostatic cycling of Al/Al symmetrical cell for TOPO-$AlCl_3$ electrolyte and urea-AlCl3

EMImCl-$AlCl_3$, a non-flammable IL that operates at room temperature, has gained significant attention as a favoured electrolyte for aluminium batteries. This IL exhibits notable attributes, including high ionic conductivity, exceptional thermal stability, chemical stability, and electrochemical stability.[13] In 2016, Sun *et al.* conducted a study investigating the impact of incorporating various common solvents, such as acetone, acetonitrile, tetrahydrofuran (THF), toluene, and dichloromethane (DCM), into the EMImCl-$AlCl_3$ IL. Cyclic voltammetry (CV) was employed as a screening method to assess the impact of solvents on the electrochemical activity of the solution. This technique was utilized to determine whether the interaction between the IL and a solvent induces significant changes in the electrochemical behaviour. interestingly, certain solvents like tetrahydrofuran (THF) and acetonitrile were found to negatively affect the performance of the electrolyte. In contrast, the addition of DCM and toluene not only sustained the deposition and stripping of aluminium effectively but also resulted in a notable improvement in current density. Specifically, the current density was enhanced by 13% with the addition of toluene and 10% with the addition of DCM, surpassing the performance achieved with the pure IL.[14] The urea-$AlCl_3$ is known to be a less effective electrolyte than EMImCl-$AlCl_3$, due to its higher viscosity and lower ionic conductivity.[15] In an attempt to explore similar effects observed in the EMImCl-AlCl3 system, we opted to incorporate DCM and toluene into the urea-AlCl3 LCC, to assess if such addition could enhance the performance of the electrolyte in any manner. Unfortunately results showed an equimolar blend of urea-AlCl3 and DCM led to a substantial increase in overpotential compared to the LCC electrolyte without DCM (Figure 3).

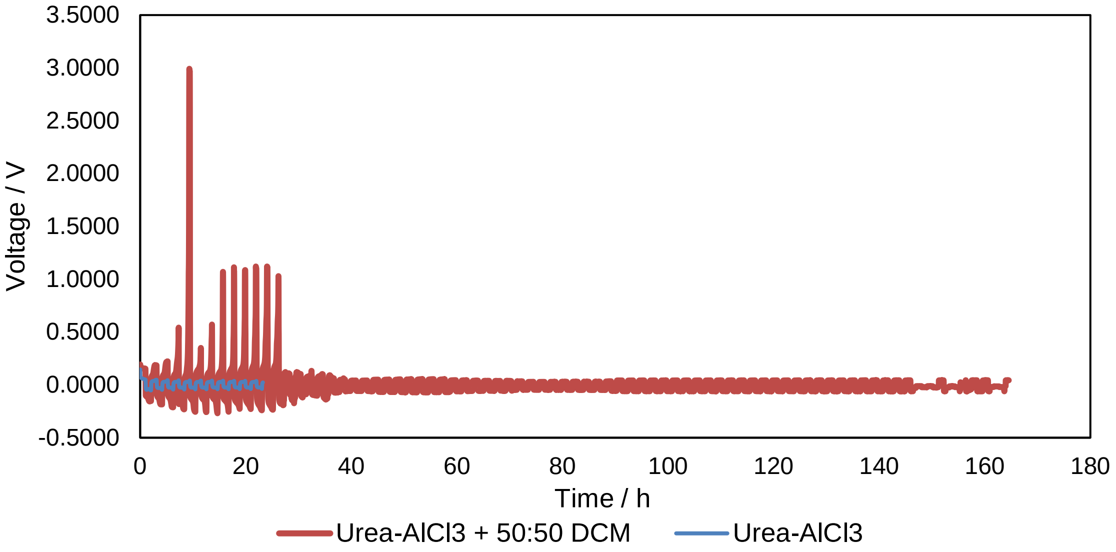


Figure 4 - Comparison of symmetrical Al/Al cycling with urea-$AlCl_3$ electrolyte and urea-$AlCl_3$ electrolyte with the addition of equimolar amounts of DCM.

The urea-$AlCl_3$ electrolyte was also studied with the addition of toluene (50% w/w) to explore the possibility of further enhancing the system. Symmetrical Al/Al cycling demonstrates promising outcomes, with the electrolyte performing well, particularly at higher current rates (Figure 4). This is a promising outcome, as to date no literature has reported on a urea-$AlCl_3$ electrolyte with the addition of toluene. While this initial progress is encouraging, further investigations are required to assess whether this system is a viable option for Al-ion batteries. These upcoming studies will encompass physical characterisations like viscosity, but the focus will primarily be on ionic conductivity. Additionally, I intend to experiment with different w/w% of toluene added to determine the optimal conditions.

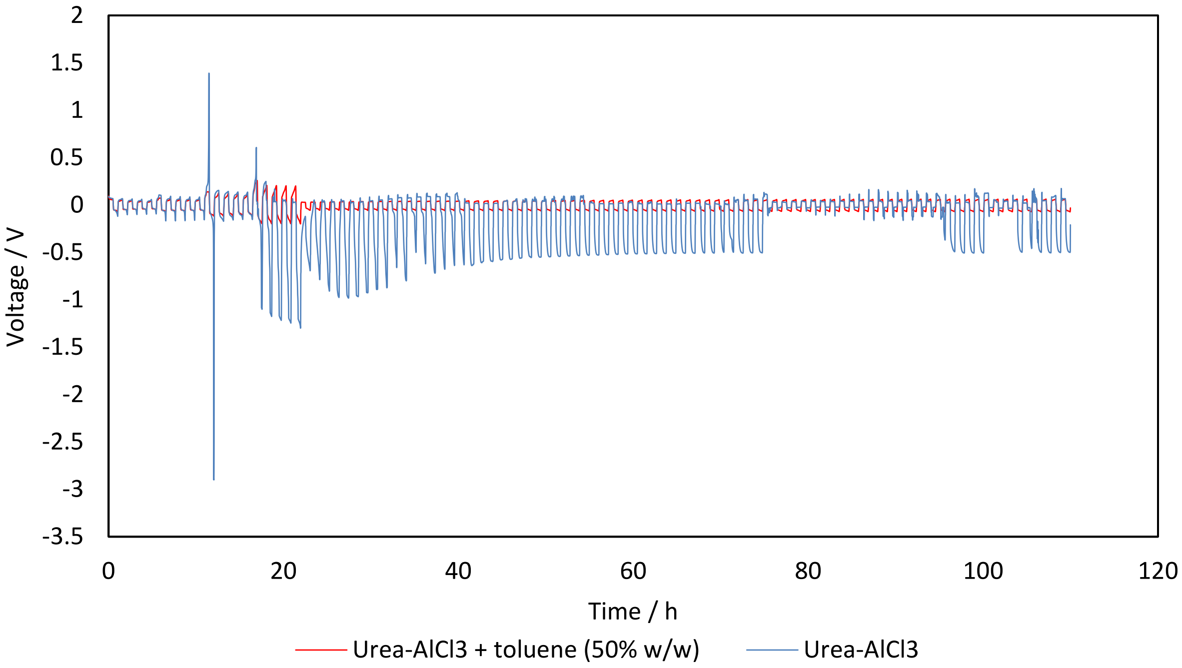


Figure 5 - Comparison of symmetrical Al/Al cycling with urea-$AlCl_3$ electrolyte and urea-$AlCl_3$ with the addition of toluene (50% w/w)..

As mentioned earlier, a coin cell configuration was utilized for all the studies due to the restricted supply of materials needed for preparing the electrolyte. This setup proved to be satisfactory for the Al/Al symmetrical cycling experiments. However, challenges arose when transitioning to a full cell configuration. A full cell configuration was made using a graphite cathode. The cyclic voltammetry (CV) results from the urea-$AlCl_3$ cell showed a trace similar to that reported in literature,[16] however, with an additional oxidation peak around 1.3 V (Figure?). To identify the nature of the additional peak, several coin cells with different independent variables were tested. One of these coin cells ran without a graphite electrode but only the carbon fiber paper support, and the peak was still observed. This result indicates that the graphite electrode was not the cause of this side reaction. Next, a coin cell experiment was conducted without the entire graphite cathode and support. In this test, the electrolyte was in direct contact with the stainless steel coin cell. Surprisingly, the oxidation peak remained present, implying that a side reaction might be occurring between the urea-AlCl3 electrolyte and the stainless steel coin cell. To conclusively confirm our speculation, a final test was conducted using a coin cell with an aluminium triflate ($Al(OTf)_3$) in diglyme electrolyte. This test showed no oxidation peak at 1.3 V, providing further evidence that the reaction occurs between the urea-AlCl3 electrolyte and the stainless steel coin cell. This is likely attributed to corrosion issues associated with chloride electrolytes,[17] as it interacts with the coin cell.

Conclusions and future work

The literature findings on the use of urea-AlCl3 ($\chi_{AlCl_3} = 0.58$) as an electrolyte for Al batteries were successfully reproduced using a coin cell configuration. Galvanostatic symmetrical cycling demonstrated stable performance once the aluminium electrodes were polished with an acid mixture to ensure the elimination of any residual oxide layer on their surfaces.

TOPO-$AlCl_3$ (χ_{AlCl_3} = 0.60) exhibited intriguing outcomes as an electrolyte, including high stability. However, its potential use as a battery electrolyte is likely hindered due to the size of the ligand, as it is not expected to function effectively as a charge carrier.

Continuing with the research on the urea-$AlCl_3$ electrolyte, additional investigations involved examining the impact of additives, such as DCM and toluene, on the electrolyte's performance. Unexpectedly, the addition of DCM had a detrimental effect on the galvanostatic symmetrical cycling, as results show high overpotentials. However, the addition of toluene yielded much more promising results, as the electrolyte performed well, showing good stability at much higher current rates.

This study has also revealed that coin cells are unsuitable for this research due to the corrosive nature of chloride electrolytes. The CV results indicated that an oxidation reaction was taking place between the urea-AlCl3 electrolyte and the stainless steel of the coin cell, necessitating the search for an alternative cell option.

A significant amount of future work remains to be conducted on this section of my project, in which I will collaborate with the Macfarlane group at Monash University. Some of the work we intend to carry out in the near future includes fine-tuning the amount of toluene added to the urea-AlCl3 LCC and comparing the results with the more extensively reported literature on EMImCl-AlCl3 electrolyte. Once we have established an optimised electrolyte composition, we will conduct rate capability tests to ensure that the cell can withstand higher current rates, up to 10 mA cm^{-2}. Additionally, long-term cycling tests will be performed at 1 mA cm^{-2} and 2.5 mA cm^{-2} to assess the cell's performance over extended periods. I also plan to perform characterisation studies on the optimum electrolyte composition, which will include measuring the viscosity of the electrolyte and the ionic conductivity. Furthermore, I intend to conduct speciation studies using techniques like ^{27}Al NMR and Raman spectroscopy to investigate the impact of adding toluene on the chemical species present in the electrolyte. These studies will provide valuable insights into the behaviour and composition of the electrolyte, which will aid in understanding its performance and properties.

As previously mentioned, finding a new cell configuration is necessary due to the corrosive nature of $AlCl_3$ in the electrolyte. My colleague at Monash University will be responsible for conducting this aspect of the work. This effort aims to identify a cell configuration that can withstand the corrosive effects of $AlCl_3$, ensuring the stability and longevity of the cell during the experiments. After addressing and resolving the cell configuration issue, we will proceed with conducting studies on graphite/aluminium full cell cycling. This step will involve testing the performance and cycling behaviour of the full cell, consisting of graphite as the cathode and aluminium as the anode, using the optimised electrolyte composition.

References

1. E. Commision, *COMMISSION STAFF WORKING DOCUMENT - Energy storage – the role of electricity*, 2017.
2. S. K. Das, S. Mahapatra and H. Lahan, *J. Mater. Chem.*, 2017, **5**, 6347-6367.
3. J. M. Tarascon and M. Armand, *Nature*, 2001, **414**, 359-367.

4. C. Julien, A. Mauger, A. Vijh and K. Zaghib, in *Lithium Batteries: Science and Technology*, eds. C. Julien, A. Mauger, A. Vijh and K. Zaghib, Springer International Publishing, Cham, 2016, pp. 29-68.
5. G. A. Elia, K. Marquardt, K. Hoeppner, S. Fantini, R. Lin, E. Knipping, W. Peters, J.-F. Drillet, S. Passerini and R. Hahn, *Adv. Mater.*, 2016, **28**, 7564-7579.
6. P. Eiden, Q. Liu, S. Zein El Abedin, F. Endres and I. Krossing, *Chem. Eur. J.*, 2009, **15**, 3426-3434.
7. N. M. Rocher, E. I. Izgorodina, T. Rüther, M. Forsyth, D. R. MacFarlane, T. Rodopoulos, M. D. Horne and A. M. Bond, *Chem. Eur. J.*, 2009, **15**, 3435-3447.
8. H. M. A. Abood, A. P. Abbott, A. D. Ballantyne and K. S. Ryder, *Chem. Commun.*, 2011, **47**, 3523-3525.
9. F. Coleman, G. Srinivasan and M. Swadźba-Kwaśny, *Angew. Chem. Int. Ed.*, 2013, **52**, 12582-12586.
10. K. Ueno, J.-W. Park, A. Yamazaki, T. Mandai, N. Tachikawa, K. Dokko and M. Watanabe, *The Journal of Physical Chemistry C*, 2013, **117**, 20509-20516.
11. R. R. Moskalyk, *Miner. Eng.*, 2003, **16**, 921-929.
12. Y. Zhao and T. VanderNoot, *Electrochim. Acta*, 1997, **42**, 1639-1643.
13. M. Armand, F. Endres, D. R. MacFarlane, H. Ohno and B. Scrosati, *Nature Materials*, 2009, **8**, 621-629.
14. X.-G. Sun, Y. Fang, X. Jiang, K. Yoshii, T. Tsuda and S. Dai, *Chem. Commun.*, 2016, **52**, 292-295.
15. M. Angell, C.-J. Pan, Y. Rong, C. Yuan, M.-C. Lin, B.-J. Hwang and H. Dai, *Proceedings of the National Academy of Sciences*, 2017, **114**, 834-839.
16. M. Angell, G. Zhu, M.-C. Lin, Y. Rong and H. Dai, *Adv. Funct. Mater.*, 2020, **30**, 1901928.
17. A. Bakkar and V. Neubert, *Electrochim. Acta*, 2013, **103**, 211-218.

QUILL Quarterly Report

November 2022 – January 2023

Name:	Liam O'Connor		
Supervisor(s):	Dr O Istrate and Prof B Chen		
Position:	PhD student		
Start date:	1st Oct 2020	**Anticipated end date:**	30th Sept 2023
Funding body:	Department for the Economy		

3D-Printed Polymer Graphene Nanocomposites for Biosensor Applications

Background

A polymer strain sensor works on the principle that the electrical conductivity is proportional to the mechanical strain applied. Thus far, literature has focused on the prosthetic using feedback from pressure sensors in the fingertip to give feedback to the user. One of the limitations of using this pressure sensor is that it can only distinguish objects within the surface area of the sensors, which is 15 mm2. A solution to the limitation of pressure sensors is to develop a strain-dependent electrically conducting material and coat the outer material of the prosthetic. An important feature of the material used to manufacture a prosthetic arm is that it needs to be 3D printable. 3D printing of the prosthetic arm is required because there is no standard size for a person's arm. The materials being investigated are thermoplastic polyurethane (TPU) because of its strong hysteresis response to mechanical strain, nylon-11 (PA11) because of its piezoelectric properties, and graphene nanoplatelets (GNP) because it is shown to increase the electrical conductivity of other piezoelectric polymers, such as polyvinylidene fluoride (PVDF) at 25 wt.% (weight per cent)

Objective of this work

The work aims to develop a strain-dependent electrically conducting material that can be used as a strain sensor and be FDM 3D printed. This will be done by determining the optimal graphene for the manufacturing of TPU/GNP filaments, determining the optimal graphene loading for the manufacturing of PA11/GNP filaments, determining the optimal graphene loading for the manufacturing of TPU/PA11/GNP filaments, and determining the optimal manufacturing layering for TPU/PA11/GNP filaments.

Progress to date

About 99% of the practical is done now focusing on the write up (Thesis outline is on next page)

Conclusions and future work

The TPU/PA11/GNP blend is ductile, like the TPU/GNP composite. It has an electrical percolation threshold like the PA11/GNP composite. PA11/GNP composite at 10wt. % showed an electric response to mechanical strain applied whereas the blended composite this was also shown in the 3D printed samples where the blended sample out preformed the dual printed sample

The next stage is to focus on the writing up of the thesis and publishing papers based around the work.

Thesis title - 3D-printed polymer graphene nanocomposites for biosensor applications

Chapter 1 – Introduction
Chapter 2 – Literature review
Chapter 3 – Experimental
Chapter 4 – The results from the graphene nanoplaletes (GNP) characterisation
Chapter 5 – Evaluate the influence of GNP loading on mechanical properties of TPU
Chapter 6 – Evaluate the influence of GNP loading on mechanical and electrical properties of PA11
Chapter 7 – Evaluate the influence of GNP loading on mechanical and electrical properties of TPU/PA11 polymer blend
Chapter 8 – Evaluate the influence of the manufacturing process on the mechanical and electrical properties of TPU/PA11/GNP nanocomposites

Expected submission date - 31/12/2023

QUILL Quarterly Report

May 2023 – July 2023

Name:	Scott Place		
Supervisor(s):	Dr Paul Kavanagh (Primary) and Dr Mark Muldoon (Secondary)		
Position:	PhD student		
Start date:	Oct 2019	**Anticipated end date:**	Oct 2023
Funding body:	EPSRC		

Molecular Electrocatalysts for Energy and Electrosynthesis Applications

Background

This project focuses on the nitroxide radical molecule, TEMPO, and its derivates, their electrokinetic properties, and their applications in energy storage, energy generation, and electrosynthetic applications. TEMPO-like molecules can be electrochemically oxidised at an electrode surface to an active oxoammonium form, which can then react with substrates in a chemical redox reaction, which regenerates them to their nitroxide (or hydroxide, when protons are present) form. These reactions follow the well-established EC’ (electrochemical-chemical) two-step reaction profile, studied extensively by Savéant and co-workers and Dempsey and co-workers, among others.

Electrolysis for organic synthesis is gaining popularity in the literature as a low-waste and simple procedure for converting a number of substrates to their corresponding products. TEMPO and its derivatives are an example of chemicals that can be used as electrocatalysts for oxidation reactions, where direct electrochemical oxidation of the substrate may be too energy intensive.

Objective of this work

The aim of this work is to use TEMPO and its derivatives as a case-study for the application of combined electroanalytical techniques for use in synthetic organic chemistry. Since electrochemistry and organic chemistry are typically divergent paths from an early stage in most chemist’s careers, there is a language-barrier of sorts between the two fields. Here we aim to show how electroanalytical techniques can be used to benchmark electrocatalyst performance, highlighting key considerations to take during the analysis.

Progress to date

In recent months, I completed optimisation and troubleshooting for an H-cell setup appropriate for benchmarking a suite of TEMPO-based electrocatalysts. I have completed three sets of electrosynthesis and analysed them for yields, conversions, and coulombic efficiencies to determine their performance. Additionally, I have begun work on using potentiometry may be used to optimise electrosynthesis reaction conditions and on how choice of membrane material in a divided cell may affect reaction yields and energy consumption.

Conclusions and future work

In the next few months, I will be working on finishing these studies and writing my thesis. The thesis will have the following results chapters:

1. Electrochemical characterisation of a commercially-available polymer-immobilised TEMPO derivative (PIPO)
2. Use of PIPO as an immobilised electrocatalyst for alcohol oxidation
3. Benchmarking of TEMPO-derivative molecular electrocatalysts for electrosynthesis applications
4. Investigation into the effect of membrane separators in divided electrosynthesis cells
5. Using potentiometry to quickly and rationally optimise reaction conditions for electrosynthesis

Expected submission date is the end of October.

QUILL Quarterly Report

May 2023 – July 2023

Name:	Junzhe Quan		
Supervisor(s):	Prof John Holbrey and Dr Leila Moura		
Position:	PhD student		
Start date:	01/10/2019	**Anticipated end date:**	01/10/2023
Funding body:	Self-funding		

Use Ionic liquids That Exhibit LCST (Lower Critical Solution Temperature) Behaviour as Draw Fluids for Water Treatment, Desalination and Separation

Background

New Ionic liquid materials have been recently developed that exhibit lower critical solubility temperature (LCST) behaviour with water. That is, they are miscible at a low temperature and split into two aqueous phases on heating beyond a critical temperature. Such materials have the potential to be used as draw fluids for forward osmosis (FO) water desalination using low grade energy to address the global challenge to provide clean, accessible drinking water to all the world's populations. In this research , new ionic liquids will be investigated as advanced fluids for forward osmosis water treatment. This offers opportunities to advance less energy intensive alternative to conventional reverse osmosis as a solution to the global challenge of providing potable water in regions of low availability.

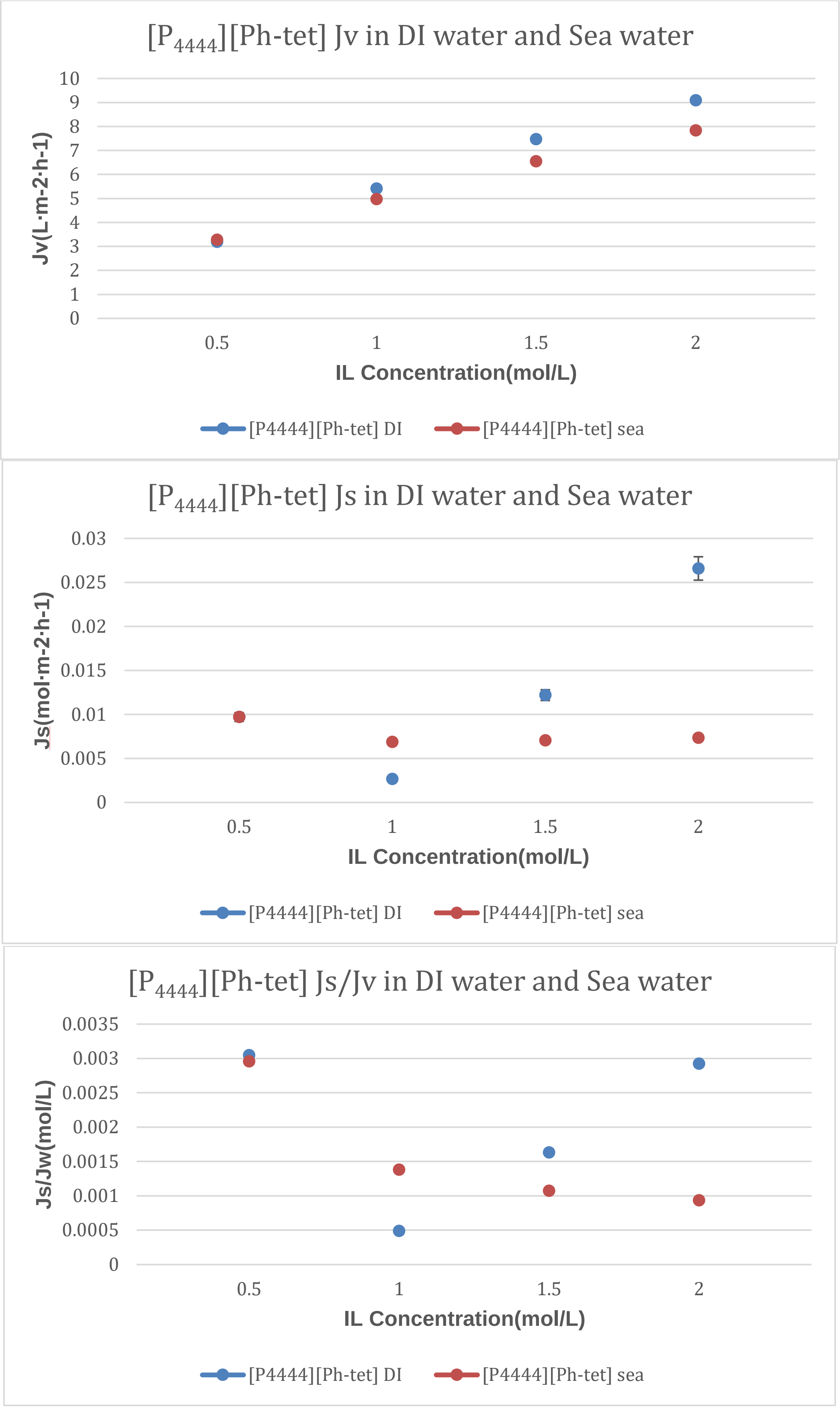
Objective of this work

My research program in the use of ionic liquids as potential draw fluids for FO water treatment includes:

1. Preparation of appropriate model tetrabutylphosphonium/ammonium ionic liquids.
2. Characterisation of aqueous/ionic liquid phase behaviour as a function of aqueous component salinity, pH, temperature and to draw structure-performance relationships with the ionic liquid cation/anion components.
3. Develop a FO membrane cell system to test and evaluate draw fluid characteristics and parameters of selected systems.
4. Optimize ionic liquid to use as draw fluid, developing a proof-of-concept ionic liquid-based FO desalination demonstrator for benchmarking.
5. Examine the applicability of these draw fluids to water-processing of a range of feeds and product streams (desalination, waste concentration, biomass dewatering).
6. Measure the energy consumption and compare with typical method of water treatment.

Progress to date

Based on the benchmark experiments done before, the capacity of our forward osmosis performance test system has been demonstrated. $[P_{4444}]$[Ph-tet]/water system has been tested on this system both in DI water and model sea water. The results are shown in figures below.



Data using [P_{4444}][Ph-tet] Jw, Js, Js/Jw both in DI water and model sea water (0.5M-2.0M IL concentration run with TFC membrane 15L/h flow rate, 298K)

Conclusions and future work

The findings reveal distinct trends in the behavior of the ionic liquid (IL) draw solute within two distinct feed solutions. Evidently, an escalation in concentration correlates with an augmentation in water flux, while a marginal discrepancy is observed between water flux in sea water and deionized (DI) water, with the former exhibiting a slightly lower flux. Notably, the solute flux in the reverse direction exhibits a unique pattern at the 0.5M concentration point, necessitating an in-depth exploration of the underlying factors influencing this phenomenon, including a comparative analysis with the 0.25M concentration point. Both concentrations demonstrate an upward trajectory; however, the augmentation in DI water outpaces that in sea water. This discrepancy underscores the influence of feed solution salinity on the reverse solute flux. Furthermore, the parameter Js/Jv underscores that the IL/water draw solute exhibits enhanced forward osmosis performance in seawater as opposed to DI water.

We will also focus on testing more LCST type IL materials to select and optimize the best one for various industrial applications. After testing these thermo-sensitive ILs, we will explore other types of draw solutes, such as switchable CO2-stimuli materials, and compare their performance to highlight the advantages of IL draw solutes.

QUILL Quarterly Report

January 2023-May 2023

Name:	John Young		
Supervisor(s):	Dr Leila Moura, Prof John Holbrey and Prof Sophie Fourmentin		
Position:	PhD student		
Start date:	2020	**Anticipated end date:**	2024
Funding body:	EPSRC		

Gas Separation Technologies

Background

Biogas is a renewable and carbon neutral energy source obtained through anaerobic digestion (AD) of organic waste. Biomethane is obtained through the upgrading of biogas produced from anaerobic digesters. It consists of mainly methane and carbon dioxide with many trace compounds including hydrogen sulfide, ammonia, silioxanes, terpenes and water vapour. Biomethane must be of a purity equal to or better than that of natural gas if it to be utilised for grid injection therefore a methane purity of above 96% must be achievable from any prospective technology. Carbon dioxide should make up 2.5-4% of the remaining volume with contaminants such as sulfur and siloxanes being limited to 10 mg/m^3 and 0.1 mg/m^3 respectively. The primary focus of this research is on carbon dioxide/methane separation as these are the two major components of biogas.

Currently biogas upgrading is multistep, with scrubbing used for carbon dioxide removal from the biogas stream to concentrate methane. This involves the use of liquid amines such as MEA (monoethanolamine) where carbon dioxide is captured through a chemisorption process. Regeneration of the amines requires high energy inputs in the form of steam at 100-150^{o}C to reform the initial liquid amine. Water scrubbing can also be used but this requires large amounts of water and leads to methane slip due to the lower selectivity of water compared with other technologies. Membranes offer another option for upgrading but these also suffer from a range of issues such a low throughput coupled with fouling and plasticisation. The degradation of membranes leads to issues both economically in the form of having to replace them but from an environmental standpoint it is unsustainable to continuously have to dispose of and manufacture replacement membranes. Cryogenic distillation offers a method of using nontoxic materials to produce high purity gas streams through the utilisation of low temperatures and high pressures which allows carbon dioxide to liquefy leaving a pure methane stream. However the energy cost associated with this method is massive which makes it less sustainable and exceedingly costly.

It is for these reasons that we seek to create novel materials which will be more efficient, more sustainable and economically viable for biogas upgrading. Initial work will consist of the use of deep eutectic solvents in conjunction with other materials to increase their upgrading capabilities.

Work to date

Gas screening methodology

Measurements to quantify the gas capacity and selectivity of both liquids and solids can be painstakingly slow and have a high associated cost. I have been developing a headspace GC (HS-GC) methodology to quickly screen liquid and solid sorbent materials for their gas capacity and separation ability. The screening can be performed at a range of pressures and temperatures, with a variety of pure gases and mixtures of gases. To do this I tested multiple combinations of HS-GC vials, stoppers and caps, resulting in the combination described in figure 1. The idea is to use the vials as mini equilibration vessels in which PVT based measurements can occur. These measurements are not expected to be as accurate as other methods, but we expect them to serve for screening purposes.

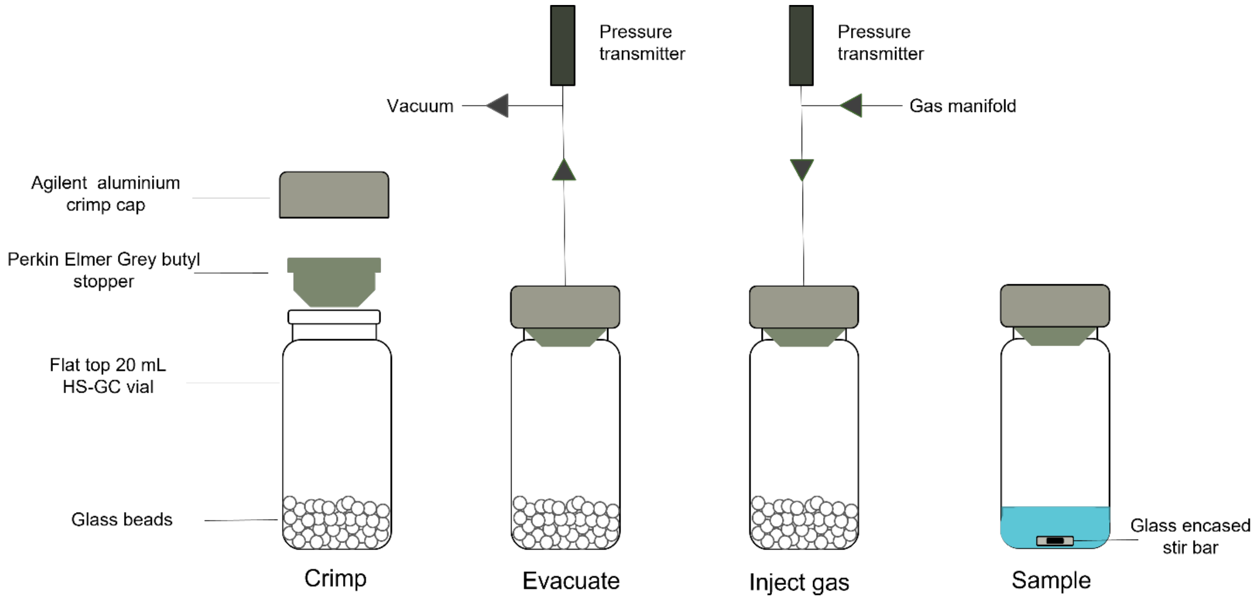


Figure 1 - Schematic of HS-GC vial preparation for calibration (glass beads) or for gas uptake measurements with sample (blue liquid)

By injecting a known "initial pressure" (quantity determined by PV calculations) of pure gas into an evacuated HS-GC vial we can compare the peak area associated with the injected gas from a calibration curve to the recorded peak area after equilibration with a known sorbent. The pressure difference in these two values equates to the gas uptake. An example can be seen below in figure 2 where a variety of CO_2 uptake isotherms of initial pressure against peak area shows that decreased peak areas can be seen in materials with a higher associated gas capacity. We have recently improved the method to allow for a triplicate of vials to be prepared in as little as 3 minutes by altering some experimental conditions.

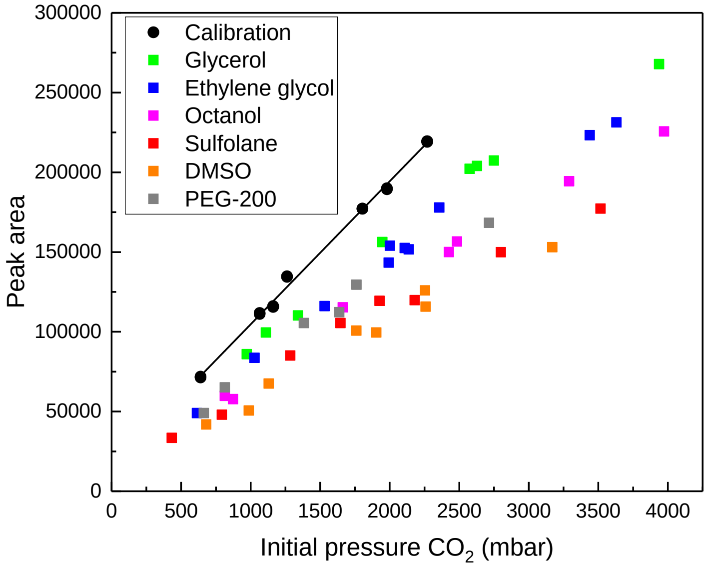


Figure 2 - Comparison of peak areas associated with different materials after equilibration with a known initial CO_2 pressure when compared to a calibration curve using glass beads[3–6]

This data was then converted to mole fraction as a function of equilibrated pressure and compared to literature data for the same materials (fig 3). It can be seen that the experimental gas capacities using this method are in good agreement with that of the literature data within the same pressure range.

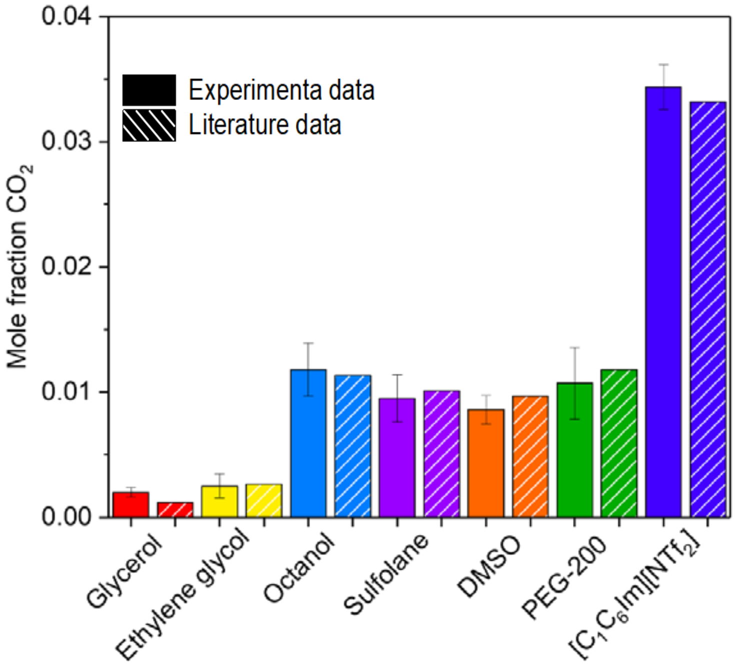


Figure 3 - Experimental uptake data of mole fraction of CO_2 obtained at 1 bar in this work (Solid colour) when compared with uptake data from literature sources (white stripes) showing good agreement with literature data[3–6]

The same experiments have also been carried out with high capacity materials such as zeolites, molecular sieves, porous liquids and chemisorbant solutions. All materials showed good agreement with that of the literature.

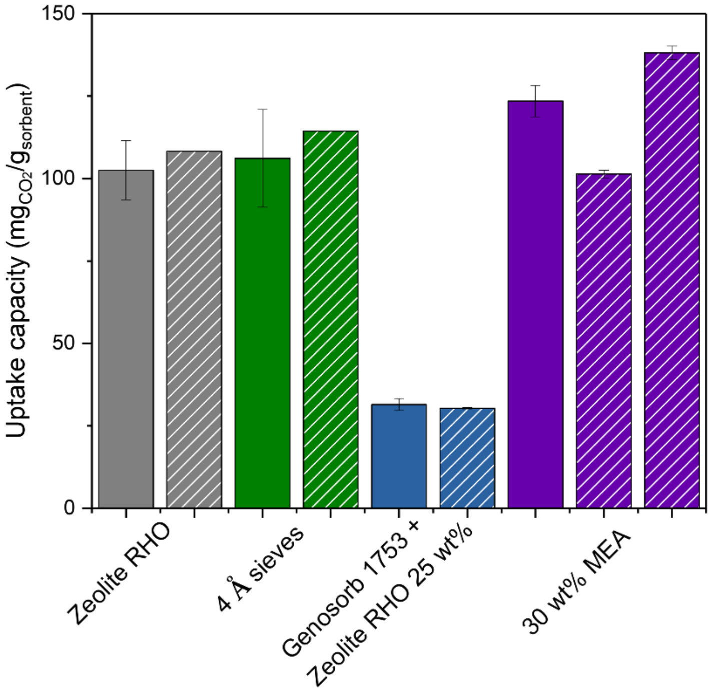


Figure 4 -Experimental uptake data of mole fraction of CO_2 obtained at 1 bar in this work (Solid colour) when compared with uptake data from literature sources (white stripes) showing good agreement with literature data[7–10]

Measurements like these have been carried out with CO_2, CH_4, C_2H_4 and C_2H_6 so far with both solid and liquid systems. These have also been found to yield results which compare well to that of literature. The error, accuracy and deviations from the literature data for these measurements is also being estimated.

Future work

A paper is currently being written about these and other results relating to this GC method for measuring the gas uptake of materials. We hope ton submit to ACS analytical chemistry in the near future.

References

1. F. M. Baena-Moreno, M. Rodríguez-Galán, F. Vega, L. F. Vilches and B. Navarrete, *Int J Green Energy*, 2019, **16**, 401–412.
2. M. R. Rodero, R. Ángeles, D. Marín, I. Díaz, A. Colzi, E. Posadas, R. Lebrero and R. Muñoz, in *Biogas*, Springer, 2018, pp. 239–276.
3. P. G. T. Fogg, *Carbon Dioxide in non-aqueous solvents at pressures less than 200 kPa*, Elsevier, 2017, vol. 50.
4. A. C. Galvão and A. Z. Francesconi, *J Chem Thermodyn*, 2010, **42**, 684–688.
5. A. Kordikowski, A. P. Schenk, R. M. Van Nielen and C. J. Peters, *J Supercrit Fluids*, 1995, **8**, 205–216.

6. A. H. Jalili, M. Shokouhi, F. Samani and M. Hosseini-Jenab, *J Chem Thermodyn*, 2015, **85**, 13–25.
7. J. Cahir, M. Y. Tsang, B. Lai, D. Hughes, M. A. Alam, J. Jacquemin, D. Rooney and S. L. James, *Chem Sci*, 2020, **11**, 2077–2084.
8. Y. E. Kim, J. A. Lim, S. K. Jeong, Y. Il Yoon, S. T. Bae and S. C. Nam, *Bull Korean Chem Soc*, 2013, **34**, 783–787.
9. D. Tong, J. P. M. Trusler, G. C. Maitland, J. Gibbins and P. S. Fennell, *International Journal of Greenhouse Gas Control*, 2012, **6**, 37–47.
10. R. V Siriwardane, M.-S. Shen, E. P. Fisher and J. A. Poston, *Energy & Fuels*, 2001, **15**, 279–284.