CONFIDENTIAL
(up to August 2024)

QUILL

Quarterly Reports

May - July 2021

Contents

QUILL Quarterly Report

May 2021 – July 2021

Name:	Haris Amir		
Supervisor(s):	Prof John Holbrey		
Position:	Postgraduate (PhD)		
Start date:	01/10/2020	Anticipated end date:	30/09/2023
Funding body:	ESPRC/UKRI		

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

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, separations and extraction of metals and waste. In this work, the design and investigation of functional borate anions for ionic liquid applications, synthesis and investigation of borate anion complexes with O/N-chelators.

The ionic liquid tetrabutylphosphonium $[P_{4444}]^+$ of different borate anions incorporating O- and N/O-donor ligands is described to carry out single crystal XRD studies. The thermal stability and decomposition of these ionic liquids (ILs) is also reported.

Thermogravimetric Analysis (TGA)

Dynamic thermogravimetric analysis (TGA) was used to study the thermal stability and decomposition pathways of the ionic liquids synthesised. The percentage of the mass loss upon gradual heating (1˚C/min) of the samples was used as a method of describing the thermal stability of these products. Initially all the samples were prepared by using a standard aluminium pan, as a result the samples could only be heated to 600˚C.

Figure 1 shows the TGA curve of $[P_{4444}][B(gly)_2]$, it shows that it was quite stable up to 250˚C as there was weight loss of less than 7%. As the temperature ramped up to 323˚C there was a weight loss of more than 50%, there was then gradual weight loss between 323 and 500˚C. As it shows in figure 1 there is still 15.32% of weight left over, implying that the sample has not fully decomposed at the parameters chosen to run.

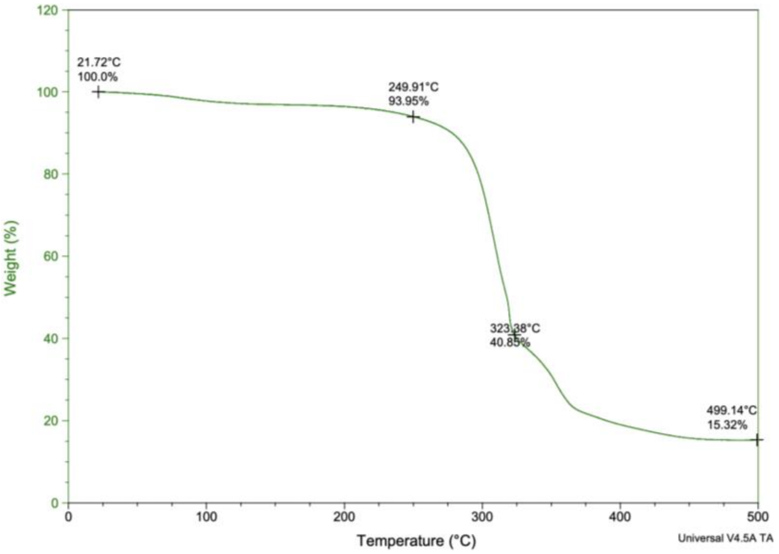

Figure 1 - TGA curve of $[P_{4444}][B(gly)_2]$

$[P_{4444}][B(C_4H_8O)_2]$ (figure 2) shows a gradual decrease, losing about 70% weight at 207˚C, this was then followed by a slow decrease as the temperature ramped to 308˚C only 4% loss in weight. At 370˚C it is noted that there is about 9% weight of the sample left, what is interesting and yet not fully understood is as the temperature increases to 500˚C the % weight increases to 10.95%. $[P_{4444}][B(C_2H_4O)_2]$ showed similar gradual weight loss as the temperature increased, there was no increase in % weight as shown for $[P_{4444}][B(C_4H_8O)_2]$. What was noticeable was the fact as temperature reached 500˚C there was still 31.77% weight, this suggests that the $[B(C_2H_4O)_2]$ anion has a strong coordination to the boron centre making it more thermally stable when compared to the $[B(C_4H_8O)_2]$ anion.

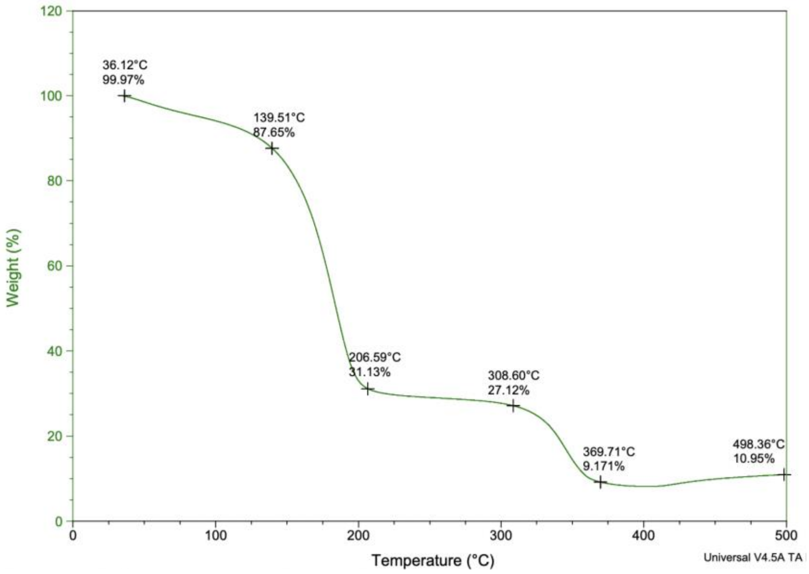

Figure 2 - TGA curve of $[P_{4444}][B(C_4H_8O)_2]$

The boron anions containing N/O- donor ligands all showed greater thermal stability than compared to the boron anions with O- donor ligands. The TGA curves show that after 150˚C $[P_{4444}][B(C_2H_5NO)_2]$, $[P_{4444}][B(C_3H_7NO)_2]$ and $[P_{4444}][B(C_3H_7NO)_2]$ only lost between 4-12% weight. All three showed very similar slopes of weight loss as the temperature gradually increased. All three also showed that after 500˚C there was still more than 35% weight left over, an example is shown

in figure 3 where there is still more than 50% weight of the sample. Indicating when replacing one O- with an N- greatly increases the thermal stability of
these boron anions.

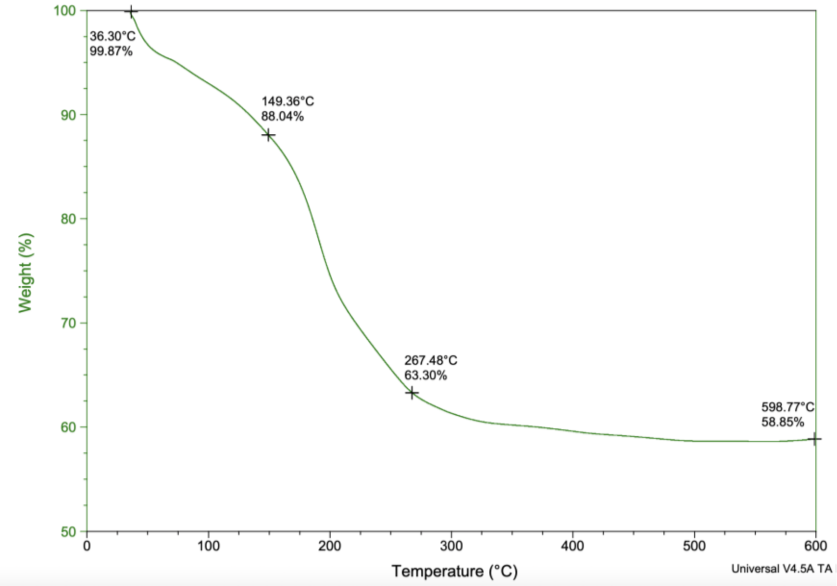

Figure 3 - TGA curve of $[P_{4444}][B(C_3H_7NO)_2]$

Crystal Data

Crystal studies of these anions are still on going, currently the anion $[B(C_2H_4O)_2]$ has been analysed and given the crystal structure as expected. The crystal structure of this anion is shown below. Future work will include the ongoing effort of obtaining presentable crystal structure of these boron anions. Along with continuing to run TGA at higher temperature to achieve full decomposition, this will then be followed by differential scanning calorimetry (DSC).

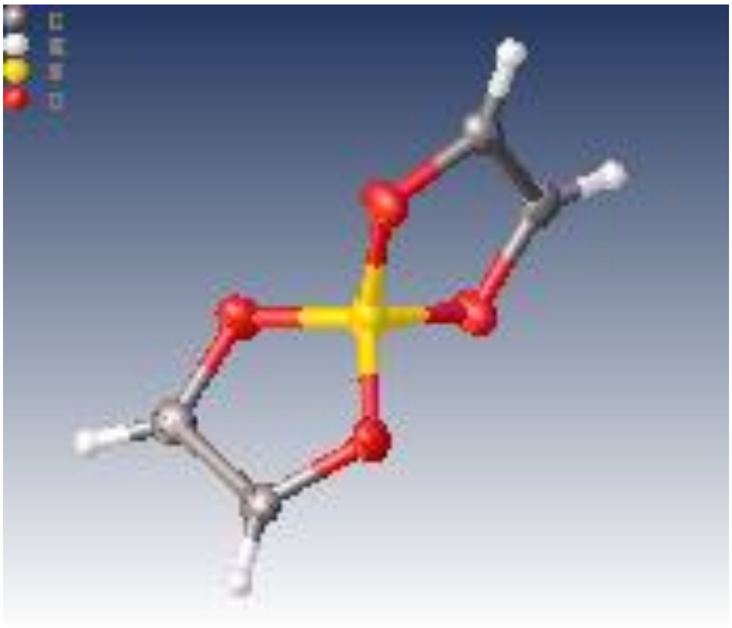

Figure 4 - Crystal structure of $[B(C_2H_4O)_2]$, yellow = boron, red = oxygen, grey = carbon and white = hydrogen

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Name:	Marian Borucki		
Supervisor(s):	Prof Peter Nockemann, Dr Stephen Glover & Prof Gosia Swadźba-Kwaśny		
Position:	PGR Student		
Start date:	01.2018	Anticipated end date:	09.2021
Funding body:	Bryden Centre, Horiba Mira		

Lithium-ion batteries degradation study using spectroscopy techniques

Background

Lithium-ion batteries (LIB) are a secondary (rechargeable) battery that are currently the main energy storage device. LIBs are applied in various applications as in portable devices, grid energy storage, grid current regulation as well as in hybrid- and electric vehicles. Energy harvested by the renewable energies is often environmental dependent, what results in discontinuous energy supply. In order to store energy that have been over generated during less energy consuming times of a day, energy storage stations based on LIB are used. The other, yet not less important, application is one where LIBs are replacing the fossil fuel by storing the energy for transport sector, namely in hybrid (HEV) and electric vehicles (EV). The trend of replacing the fossil fuels both in energy sector by supplementing them with renewable energy power plants as well as by supporting the market of HEV, EV and fuel-cell vehicles (FCEV) is growing. New policies of EV30@30 and New Policy Scenario are the programmes that are aimed in expanding the market of HEV, EV and FCEV, thus the supply for lithium-ion batteries will grow. Yet, for the market to growth the research, ones that solve current issues, are needed. Automotive council UK in their roadmap report for the lithium-ion batteries have gathered up the issues that are needed to be addressed if the automotive of EV, HEV and FCEV is to grow. Such an issues are based on the need of improving the safety of battery usage, lowering the costs of the batteries, researching a new materials for the batteries that will allow to store more energy and provide more power, thus be fast chargeable, issues concerning the battery pack and modules combination, one that will allow to minimalize the losses related to cell joining, as well as their thermal management, increasing the lifespan of the batteries as well as increase their recyclability, eventually the research on the next gen batteries is needed.

In order to meet all the requirements a thrill study of the current batteries as well as the development of a new chemistries is needed. Lifespan as well as the safety of the battery is nowadays ones of the most important factor when it comes to the battery application in the transportation market. Battery life is limited by the degradation mechanism, ones that occur inside the cell. Currently there are known number of such mechanism occurring, even though the proper investigating technique allowing *in operando* study have not been developed yet. Moreover, the degradation is highly chemistry dependent so whenever the new chemistry is tested for the battery the new degradation mechanism could occur. On the other hand, the safety of the battery is limited by the usage of the organic based electrolyte, which is highly flammable and might lead to battery explosion. Proper electrolyte, non-toxic, environmentally friendly, non-flammable as well as of high performance should be developed. With developing the new electrolyte, often the development of the electrodes is needed as the electrolyte stability as well as the energy density of the battery highly depends on them.

Objective of this work
The aim of the PhD programme is focused on investigating the lithium-ion battery (LIB) degradation processes occurring inside the cell during it operation. In order to achieve the goal a development of an experimental method basing on the spectroscopy analysis techniques will be needed. A proper method would allow to observe and measure the changes that occur *in operando* inside the lithium-ion battery. During the PhD programme an analytical data of LIB degradation will be acquired, using various analytical techniques including electrode surface examination, electrolyte composition. Acquired spectroscopy data will be linked with the rest of the data gathered in order to develop the sensing method. Eventually, batteries of a different cell chemistries will be investigated.

Laboratory work
Electrochemical studies – The distribution of relaxation times (DRT) curves have been obtained for studied half and full cell lithium-ion battery samples. The impedance spectra for DRT analysis have been obtained at varying temperature range, 25℃ - 55℃ with 10℃ step and at varying SoC levels on one full battery discharge from 100% to 0% of SoC with 10% steps. The cathode half-cells have displayed limited impedance dependence on the temperature, whereas the dependence of anode half cell was significant. The full cell sample also did exhibit a temperature dependence however to a smaller extent than anode half cells. The obtained spectra for all the samples at altered SoC levels did show battery impedance dependency. Performing the DRT analysis on the obtained impedance spectra did allow to observe the polarization processes separately as 5 peaks have been observed for cathode half cells, 6 for anode half cells and 7 for full cells providing the most complex DRT curve. However, by observing the specific peak temperature and SoC dependency characteristics a tool for peak interpretation for full cell DRT has been obtained. The temperature study did allow to obtain the activation energy for all the peaks investigated as Arrhenius behaviour for processes has been observed. The SoC dependency studies reveal which of the observed peaks and to what extend were SoC dependent by monitoring shifts in their position, changes in their height and polarization process resistance obtained by differentiation of area under the specific peak. Finally, an interpretation of acquired full cell responses enhanced by the half-cell study is undergoing.

***Post-mortem* studies** – The *post-mortem* case has been designed, 3D printed and tested for laser beam permittivity using Witech alpha 300R microscope with a control sample as for leakage proving to be sealed. The aged LIB samples are being disassembled in a glovebox. Prior to disassembly procedure cells are discharged to 0% SoC, thus 2.7 V. Both electrodes and separator are extracted from the dismantled cells. The electrodes are further dried to remove the electrolyte residues using vacuum mode in Schlenk line for overnight drying. Then electrodes are cut using ceramic scissors into four parts if the shape of electrode does allow for the operation.

The obtained electrodes and separators from aged lithium-ion batteries, further referred as post-mortem samples are to be used for spectroscopy data collection as well as for structural microscopy studies and crystallographic studies. The obtained data from *post-mortem* studies would provide insights to the specific degradation processes occurring inside the cell as the cell is aged and could be further compared to electrochemical data obtain during sample ageing. Due to high sensitivity of XPS study, which is aimed to investigate the top layer (10nm) of electrodes providing insights into interfacial film properties the XPS investigation will be carried out first.

Semi-solid electrolyte 'Ionogel' studies – Mechanical properties investigation in cooperation with school of aerospace and mechanical engineering in planning as interschool laboratory access is limited. Synthesis optimization – establishing the substrates molar ratio which result in product of highest ionic conductivity as well as the most optimal mechanical characteristics. Lithium transference number for electrolytes of each substrate ratio is needed to be studied.

Carbon-based anodes electrochemical investigation – Post Graduate Taught student project based on coating GNP/IL mixtures on top of Graphite electrodes and use of IL as an electrolyte. Due to IL high viscosities low specific capacities were obtained. Therefore, an organic electrolyte – IL mix has been proposed for electrolyte to be studied. The coating of GNP/IL mixture has been found to be hard to optimize as cracks in coated electrodes has been observed even when most optimal binder ratio, sonification time and drying temperatures has been found. Therefore, electrodes as a mix of Graphite and GNP/IL have been proposed for study.

***In operando* studies** – The cells for in operando spectroscopic studies has been assembled and formation cycles and well as quality control and further cycling has been undertaken using the battery tester introduced into the glovebox. The batteries displayed specific capacities about 70% lower of theoretical specific capacity, however the capacity was stable upon cycling.

The cells have been placed inside the airtight vials which were placed in airtight container for sample transport to the Horiba UK where spectroscopic studies were to be undertaken. The samples have been transported by plane as their low capacitive specification did allow for this form of transport. At Horiba UK the samples have been studied by Raman Spectroscopy with cycling procedure implemented simultaneously. However, after a day of testing a shortcut of all battery samples has been found. The sample behaviour was connected to the fact that the study was not carried in inert atmosphere, like preliminary studies, yet in air. However, the samples stored inside the airtight container has also displayed the shortcut. It was possible that the pressure change did influence the sample properties to the extent that samples were shortcut. Therefore, a newly assembled samples this time were placed on ship cargo for transportation. The new samples have displayed higher stability as their worktime was about 20h until deviations from standard charge-discharge characteristics occur. Finally concluding that the sample design needs to be updated for airtightness itself.

The update of design is based on three ideas: 1) increasing and evenly distributing the mechanical stress across battery by the use of 3 mm thick stainless steel external casing, 2) Sealing the optical window area by the use of separator from the inside of battery and by the use of fast curing silicon sealing from the outside, 3) Use of the potting compound for the current collector outputs. The design for external stainless steel casing part has been updated and could be seen on **Figure 1**. The job for stainless steel machining has been submitted and a new lithium-ion cell will be assembled as son as external casing is ready. However due to limited possibilities of using the Horiba UK equipment a Witec Raman microscope at Queens will be used for in operando study.

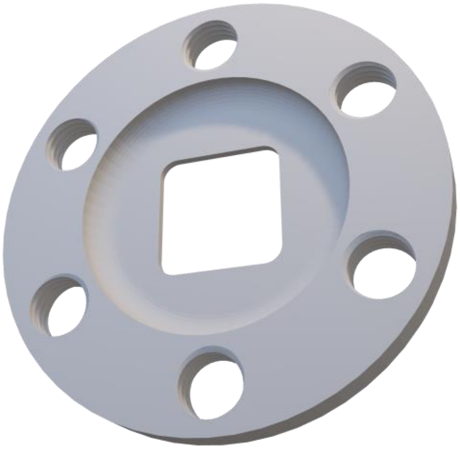

Figure 1 - Updated external case design for in operando lithium-ion cells. Material: Stainless steel. Thickness 3 mm. Threaded M5 holes distributed with 60° angle.

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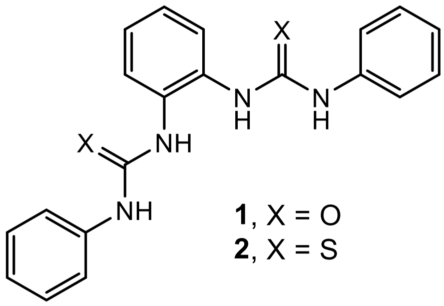
Name:	Dominic Burns		
Supervisor(s):	Prof John Holbrey, Prof Gosia Swadzba-Kwasny and Dr Hye-Kyung Timken		
Position:	PhD Student		
Start date:	1st October 2019	Anticipated end date:	31st May 2023
Funding body:	EPSRC		

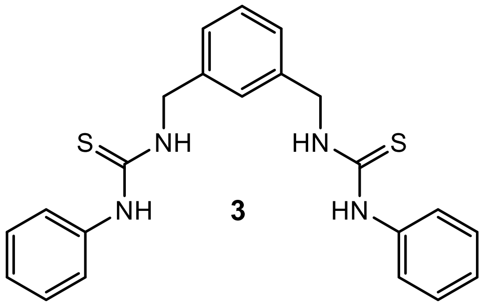
Recycle and Reuse of Process Water Through Sulfate Removal: Developing an Ionic Liquid Technology for Selective Anion Recognition and Extraction

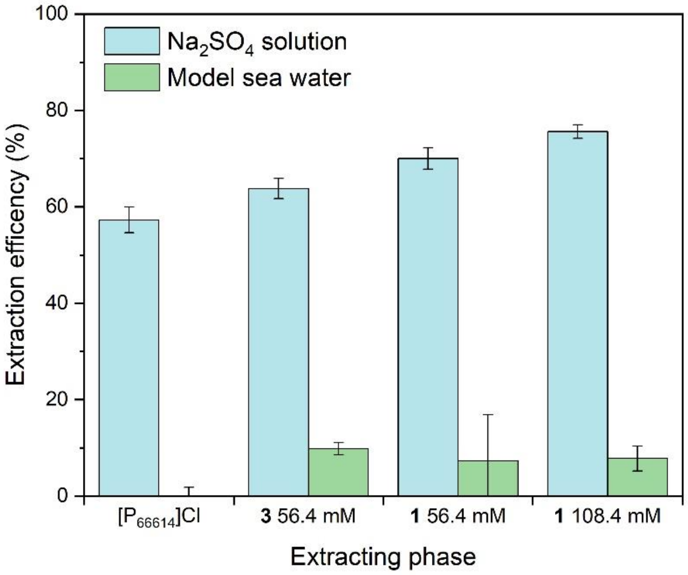
This is an ESPRC industrial CASE project in collaboration with Chevron EL, to explore liquid technologies to treat saline process water with the initial objective of selective sulfate removal from highly competitive aqueous streams. Initial work began by characterising $[P_{66614}]Cl$ as a liquid anion exchanger. This work showed that sulfate can be extracted by $[P_{66614}]Cl$ from `ideal' sodium sulfate solutions via anion exchange as shown in the graph below. However, when chloride is already present in the aqueous phase this blocks the exchange process reducing the extraction to almost zero. The current main approach is a liquid-liquid extraction where sulfate specific receptors are dissolved into the IL phase which can then bind to the sulfate. Other approaches currently on pause include micelle forming receptors that have previously been reported on and thiouronium ILs that are known to be good moieties for anion complexion.

Receptors **1**, **2** and **3** have been selected as they are relatively simple to synthesis with affordable starting materials and have either been previously reported to bind and poorly extract sulfate in the case of **3**[1] or in the case of **2** and **3** are simpler structures of successful sulfate receptors[2]. The use of very strongly binding receptors has been purposefully avoided as to make the IL re-useable the receptors will need to release the bound sulfate, the exact K_a values are hard to estimate but are around 15,000 in DMSO and in the order **3** < **1** < **2.** UV binding studies are planned for future work to accurately determine each binding constant.

These receptors are mostly insoluble in common organic solvents however, they are remarkably soluble in $[P_{66614}]Cl$. This is thought to be from the receptors binding to the chloride anion although further investigation is required to verify this.


1, X = O
2, X = S


3



The graph above shows how the extraction efficiency of sulfate from water increases upon the addition of the receptors into the IL phase. $[P_{66614}]$Cl will extract 57.3% of sulfate from an `ideal' sodium sulfate solution (sulfate = 2600 ppm) via an ion-exchange mechanism. However, in a model sea water solution (sulfate = 2600 ppm, chloride = 19000 ppm) the high concentration of chloride already in the aqueous phase strongly inhibits this process.

The addition of **3** to the IL at 56.4 mM increases the ideal extraction efficiency to 63.8% by binding to the sulfate and pulling it into the extracting phase while also removing 9.8% of sulfate from the model sea water solution. Addition of **1**, again at 56.4 mM performs even better as expected from its higher binding constant, increasing the extraction to 70.0%. Further addition of **3** up to 108.2 mM again increased the ideal extraction to 75.6% although no clear increase was observed from the model sea water, still at 7.8% sulfate removal.

This approach shows good promise for the removal of sulfate from saline streams although much more work is needed to fully understand the mechanism, selectivity of the receptors for sulfate over chloride, re-useability and if receptor **2** will perform better than **1** or **3** due to its larger predicted binding constant.

References

1. T. Shioya, S. Nishizawa and N. Teramae, Anion recognition at the liquid-liquid interface. Sulfate transfer across the 1,2-dichloroethane-water interface facilitated by hydrogen-bonding ionophores [13], *J. Am. Chem. Soc.*, 1998, **120**, 11534–11535.
2. R. Li, Y. Zhao, S. Li, P. Yang, X. Huang, X. J. Yang and B. Wu, Tris chelating phosphate complexes of bis(thio)urea ligands, *Inorg. Chem.*, 2013, **52**, 5851–5860.

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May 2021 – July 2021

Name:	Andrew Forde		
Supervisor(s):	Dr Stephen Glover, Dr Rob Watson and Prof Peter Nockemann		
Position:	PhD Student		
Start date:	03/06/2019	Anticipated end date:	03/12/22
Funding body:	Horiba-MIRA & EPSRC		

Battery Thermal Management and Algorithmic 3D Temperature Prediction

Experimental

One aim of this project is to place thermal sensors close to the active materials in a prismatic cell for model validation purposes. In order to carry this out, an instrumentation process has been designed and tested on a 3D printed model of the cell.

The chosen cell for this instrumentation work has changed, therefore the new cell was modelled for 3D printing. This was initially modelled around information from the manufacturer. Scans have now been taken to allow for a new model to be created which is more representative of the cell.

As this process relies heavily on the accuracy of sensor placement, accuracy tests have been designed for the equipment being used. This should ensure that minimal contact is made with the active material when placing a sensor inside the cell. One key accuracy metric is the placement error in the horizontal plane which has previously been shown to be sufficient. However, as a new cell design has been chosen for this work, this test is to be redesigned and repeated to align with the new process.

Numerical Model

The numerical model was run over various drive cycles in order to test and collect data for validation purposes. This data can be compared to experimental results before and after instrumentation in order to validate the model and observe any performance differences after instrumentation.

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Name:	Oisin Hamill		
Supervisor(s):	Dr Nancy Artioli and Dr Alex Goguet		
Position:	PhD		
Start date:	01/10/2019	Anticipated end date:	30/09/2022
Funding body:	EPSRC		

Mechanism Understanding of NOx storage, release and reduction on Pt/doped ceria catalysts

Background

Due to strengthening emission legislations in Europe, North America and the rest of the world, there is a need for further optimisation of existing emission after-treatment catalytic converters for automotive applications. New legislations focus primarily of NO_X abatement and consequently the exhaust emissions of lean-burn gasoline and diesel vehicles. After treatments systems must utilise new technologies to reduce this that offer low temperature activation and high stability.

High surface area ceria is successfully employed as an excellent support of metals (Pd, Rh, Pt, etc.) in commercial catalytic systems for the oxidations of carbon monoxide and propane and automotive emission control. Ceria is a unique material with a rich and complex chemistry. It possesses high oxygen storage capacity (OSC), a unique redox property by the cycle of Ce^{4+}/Ce^{3+} redox pairs and it can be further enhanced through using dopants. Platinum supported on ceria can show enhanced NO_X storage at low temperature, as reported in the literature, together with an improved carbon monoxide/hydrocarbon light off.

Ceria supported catalysts, in general, do not operate efficiently at low temperatures and therefore must be modified in order to overcome this problem. For this reason, addition of enhancing materials is currently being considered in detail. This addition of a material that increases the performance of an already functional catalyst is called doping. The main function of this dopant is to allow the catalyst to function outside of the normal working temperature range and operating conditions to increase catalyst efficiency.

It has been proposed that the dopants, such as rare-earth and transition metal oxides, increase the concentration of surface vacancies which affect the ionic conductivity, oxygen mobility and oxygen storage capacity of the ceria. It can be speculated that all these properties are responsible for the enhanced oxidation activity by promoting oxygen diffusion and formation of more "reactive oxygen" species. Furthermore, the oxygen species play a role in the mechanism of the reaction, favouring the NO_X storage.

Additionally, presence of dopants can reportedly modify the platinum reducibility and platinum-ceria interaction, allowing more readily activation during rich purge.
This project aims to better understand the NO_X storage mechanism on the doped materials and give new insights into the activation/lean deactivation mechanisms in the presence of different dopants.

Objective of this work

The main objective considered in this project is to improve the understanding of the NO_X storage mechanism, together with the mechanism of rich purge on ceria supported platinum. We aim to gain a deeper knowledge of the rich activation and lean deactivation mechanisms as well as determine the structure of the active sites under reaction conditions. We look to develop a method to differentiate between active species and spectator species through transient methods. We will also strive to develop a global kinetic model for the reaction and all involved species. This will enable the determination of the relative importance of different reactions within the catalyst bed as well as a measurement of the exact gas compositional conditions present during the reactions. With this approach in depth information relevant to mechanistic understanding and reaction engineering application will be obtained.

Progress to date

- BET characterisation completed for Pr and Sm doped ceria based catalysts.
- XPS analysis on 0.25Pt loading, doped and undoped Nd/Ce completed.
- TEM analysis on 0.25Pt loading, doped and undoped Nd/Ce completed.
- EXAFS BAG call proposal submitted and accepted for August 2021.
- TPR completed for Sm doped catalysts.
- XRD characterisation performed on all new dopants.
- ICP characterisation performed on all new dopants.

Conclusions and future work

- NSC tests for all doped and undoped catalysts including new dopants.
- Lean/Rich cyclic experiments for new dopants to compare to Nd effect.
- Complete TPR characterisation on new dopants.
- TPR calibration experiments to do on Cu_2O to calibrate TCD graphs.
- Submit new dopants for XPS & TEM.
- Begin in-situ TEM experiments.
- Analyse EXAFS results when experiments have been completed.

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May 2021 – July 2021

Name:	Sanskrita Madhukailya		
Supervisor(s):	Prof John Holbrey and Dr Leila Moura		
Position:	PhD Student (first year)		
Start date:	19th April 2021	Anticipated end date:	20th April 2024
Funding body:	Tezpur University/QUB joint PhD scholarship		

Design of supported ionic liquid catalysts for the synthesis of 5-substituted tetrazoles to be used as draw fluids for forward osmosis in water desalination

We know that from space our planet looks more water than earth. But despite the water covering 71% of the planet's surface, more than half the world's population endures water scarcity for at least one month a year. Population growth, industrialization, environmental deterioration, and economic evolution have resulted in great demand for freshwater, and the current estimates predict that by 2040, up to 20 more countries would be experiencing water shortages.[1] Separation membrane technologies are considered the most promising methods for water treatment and recovery. To date, pressure-driven membrane processes (reverse osmosis) are widely deployed, however, these processes consume a high amount of energy and can result in membrane fouling. On the other hand, osmotically driven membrane (forward osmosis) offers the potential for efficient renewable desalination systems with significantly reduced energy demands.[2]

Forward osmosis (FO) takes the advantage of osmotic pressure gradient to draw water across a semi-permeable membrane from a feed solution at a lower osmotic pressure to a draw solution at a higher osmotic pressure. Due to lower hydraulic pressure requirements, FO involves less energy input and high-water recovery over other pressure-driven membrane processes.

In my research, ionic liquids showing lower critical solubility temperature (LCST) phase behaviour based on functionalised 5-phenyl-tetrazolate anions[3] will be developed and investigated as thermally responsive draw solutes in the forward osmosis process, to compare with isosteric phenyl-sulfonate and phenyl-carboxylate analogues.

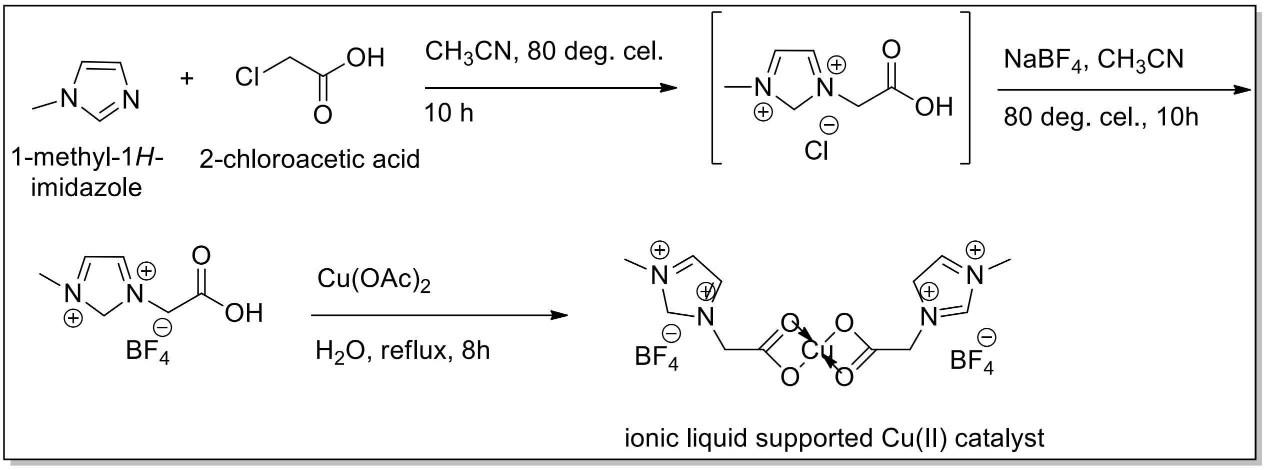
The objective of this work

The primary objective of my work is to investigate and develop, new improved approaches to synthesize functionalised 5-phenyltetrazoles using robust, green methods with easily available catalysts. The tetrazoles will then be used as the anionic component of ionic liquids with potential LCST phase behaviour, extending the work with the ionic liquid, $[P_{4444}]$[Ph-Tet] previously studied by Moura *et.al.* Synthesising various substituted phenyl tetrazoles, examining the effects of modification and functional group substitution at the phenyl-ring and determining the cloud-point and LCST properties of the ionic liquids will be a part of my work. Finally, the best ionic liquid systems will be used as draw fluids to demonstrate a forward osmosis process to treat wastewater.

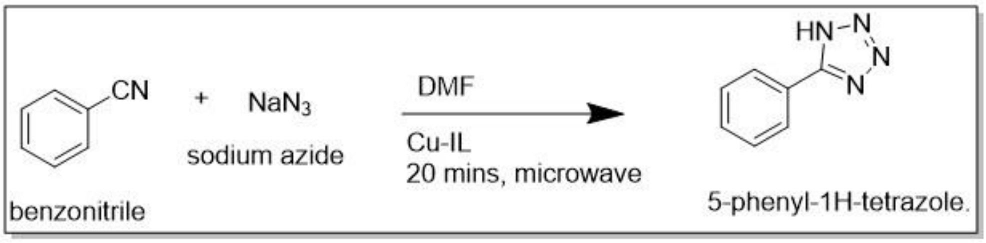
Progress to date

Initially, methods to prepare the core 5-phenyl-1*H*-tetrazole have been examined using a series of catalysts selected from a screen of the literature: Catalysts have been synthesized and the cyclisation of benzonitrile with sodium azide and with 1-butyl-3-methylimidazolium azide under conventional and microwave heating conditions is underway.

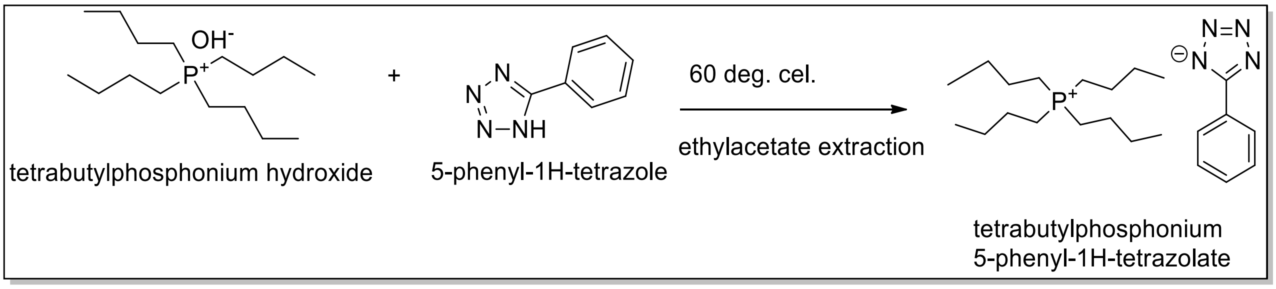
Synthesis of ionic liquid supported Cu-catalyst:



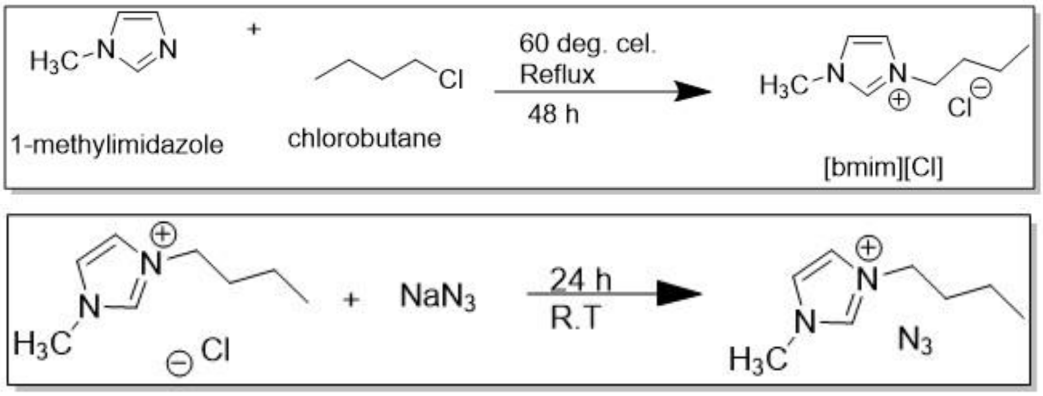
Synthesis of 5-phenyltetrazole by cyclization of benzonitrile and azide (both in microwave & conventional heating):



Synthesis of $[P_{4444}]$[Ph-Tet] from tetrabutylphosphonium hydroxide and 5-phenyl-1H-tetrazole:



Synthesis of [bmim][N_3] used as azide source to prepare 5-phenyl-1H-tetrazole:



Conclusion and future work

1. The formation of the ionic liquid supported Cu-catalyst was confirmed by ^{1}H-NMR. Cyclisation of benzonitrile with sodium azide using this catalyst, resulted in formation of 5-phenyltetrazole (detected by TLC and ^{1}H-NMR). However, preparation of this catalyst was time-consuming and so less efficient in terms of reaction throughput. Microwave heating allowed the reaction to be conducted at higher temperatures than conventional heating (sealed reactor under pressure) allowing more rapid production of 5-phenyltetrazole.

2. The ionic liquid [P_{4444}][Ph-Tet] was prepared from 5-phenyltetrazole synthesised by metathesis/neutralisation with tetrabutylphosphonium hydroxide solution. Characterised by ^{1}H-NMR.

3. Synthesis of the azide source [bmim][N_3] is under progress, as an organic azide source for preparation of the tetrazole.

4. A series of (literature) catalysts for tetrazole synthesis from azides/nitriles will be screened using the standardised conventional and microwave reaction conditions investigated with the copper-catalyst above, to identify the *best* catalyst systems to take forward.

5. After catalyst selection, substituted 5-phenyltetrazoles will be prepared, starting with 2-hydroxy-5-phenyltetrazole which is the isostere of salicylic acid. The phase behaviour of the [P_{4444}][2-HO-Ph-Tet] ionic liquid with water, specifically potential formation of LCST system will be studied and compared with that from the phenyltetrazolate anion (and the relative differences between the behaviours of the comparative benzoate and salicylate systems) to understand the influence of the 2-hydroxy function on performance.

References

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2. J. Wang, X. Liu, *Journal of Cleaner Production*, **2021**, 280, 124354; W. Wu, Y. Shi, G. Liu, X. Fan, Y. Yu, *Desalination*, **2020**, 491, 114452.
3. L. Moura, L. C. Brown, M. Blesic and J. D. Holbrey, *ChemPhysChem.*, **2017**, 18, 3384-3389.

QUILL Quarterly Report

May 2021 – July 2021

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:	2023
Funding body:	EPSRC Doctoral Training Partnership		

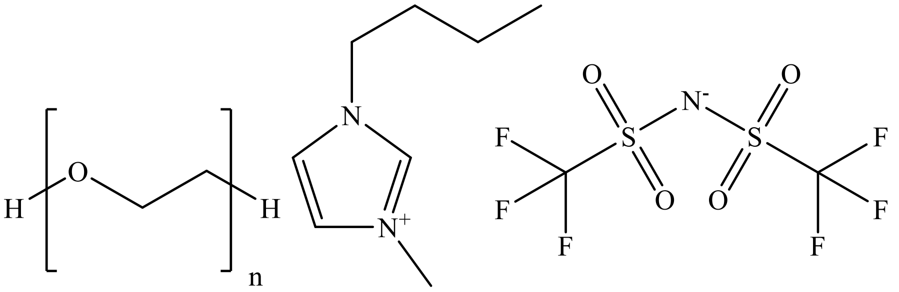
Chemisorbent materials for olefin and paraffin separation

Objective of this work:

Develop and test new chemisorbent materials for the separation of light olefins and paraffins. In this, achieving high capacity and selectivity for the selected materials. To test this, equipment will be installed, commissioned, and benchmarked for testing under approximate industrial gas stream compositions.

Progress to date:

The gas solubility system (GSS) as of the last quarterly report has been fully calibrated and benchmarked with PEG200 and [Bmim][NTf2] (both shown in figure 1) as the test material and carbon dioxide as the gas. The GSS is now being prepared to test new materials with the solubility of ethylene and ethane. These materials include cyanopyridinium based ionic liquids and ammonium based ionic liquids (figure 2).[1] This has involved the synthesis of ethylammonium nitrate and the current ongoing characterisation of the ionic liquid. The cyanopyridinium based ionic liquids was suggested by Nimal Gunaratne, as the cyanopyridinium have been shown to form charge-transfer complexes with electron-rich aromatics via π-cation interactions.[1]



PEG200 [Bmim][NTf_2]

Figure 1 - Polyethylene glycol 200 (PEG200) and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Bmim][NTf_2]).

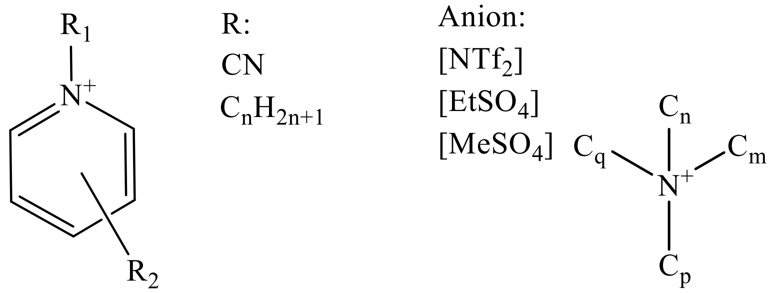


Figure 2 - Cyanopyridinium cations and corresponding anions (left) and ammonium-based cation (right)

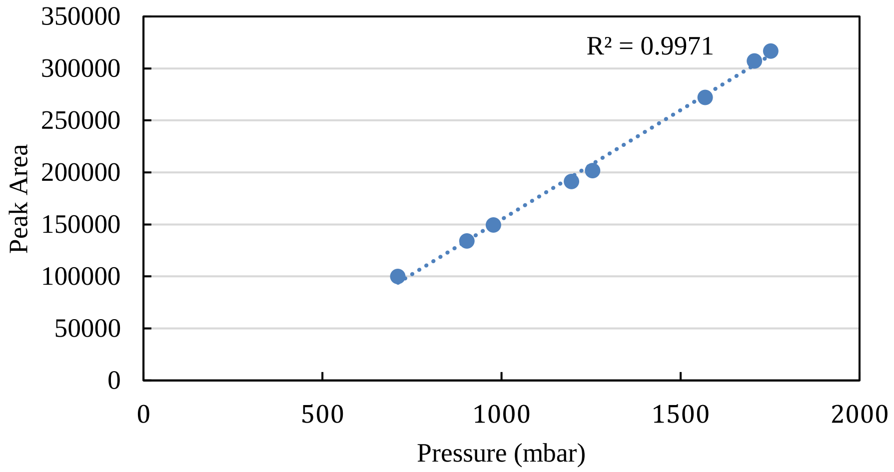


Figure 3 - Calibration curve of pressure within the glass vials against the peak area produced from the HSGC

The work completed by Mark Young on using headspace gas chromatography (HSGC) as a means of screening the solubility of carbon dioxide in different test materials has now also been applied to ethylene. The initial calibration curve has shown direct correlation can be made between the peak area of the HSGC and the corresponding pressure in the vial, achieving an R^2 value of 0.9971 (figure 3). This calibration is currently being reproduced, and the cyanopyridinium ionic liquids are now being screened using this method.

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QUILL Quarterly Report

May 2021 – July 2021

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

Main group catalysis in ionic liquids

Structural study of frustrated Lewis pairs (FLPs) by neutron scattering

In June, neutron scattering data were recorded at the Small Angle Neutron Diffractometer for Amorphous and Liquid Samples (SANDALS) beamline at ISIS, which is designed for the study of liquid samples. Data was recorded for samples of P^tBu_3 and BCF at a concentration of 160 mmol in protiated (H), deuterated (D) and in a 1:1 H/D mixture of the ionic liquid $[C_2mim][NTf]_2$. Previous work by the group has demonstrated the potential of neutron scattering as a viable technique for observing the formation and concentration of transient encounter complexes.[1] The result corroborate well with previously reported DFT model and are in agreement with 2D NMR spectroscopy. A “solvent separated” association between BCF/P^tBu_3 in benzene was demonstrated, through the detection of modelled interatomic distance between boron and phosphorus around 8 Å. The low concentration of encounter complexes which has been experimentally observed was suggested to be *ca.* 5% of FLP molecules. The group then revealed how the population of encounter complexes of FLP can be enhanced using ionic liquids. The selected ionic liquid was 1-decyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, $[C_{10}mim][NTf_2]$ (Figure 1). These results indicated an increase in both concentration and stability of the encounter complex to >20%. As a continuation of this study, the FLP $P(^tBu)_3$/BCF in the ionic liquid $[C_2mim][NTf_2]$ (Figure 2) was studied by the same method of neutron scattering. $[C_2mim][NTf_2]$ was selected as $[C_{10}mim][NTf_2]$ (previously used) was impossible to model due to its long alkyl chain length.

The neutron scattering data will be processed using the Gudrun software[2,3] and modelled using empirical potential structure refinement (EPSR). EPSR uses a Monte Carlo simulation approach coupled with Lennard-Jones potential approximation.[2,3] These programmes will provide information on the separation distance between boron and phosphorous, enabling verification of the encounter complex. The data for the FLP in $[C_{10}mim][NTf_2]$ will also be analysed using Dissolve. Dissolve is a new code for the simulation of total scattering data and implements methodology similar to EPSR code but is built to process complex and larger systems. The main difference in the code is that Dissolve employs a standard force field to better describe molecules.

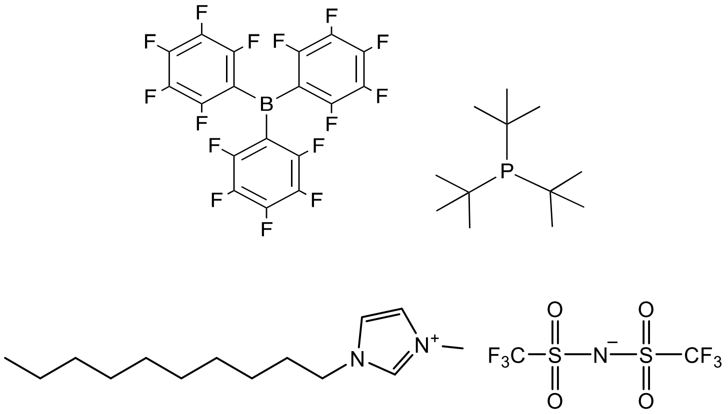


Figure 1: Structure of the FLP $P(^{t}Bu)_3$/BCF and the ionic liquid $[C_{10}mim][NTf_2]$

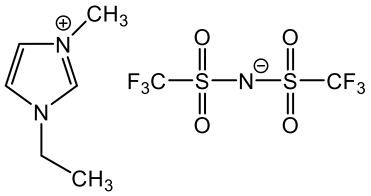


Figure 2: Structure of $[C_2mim][NTf_2]$

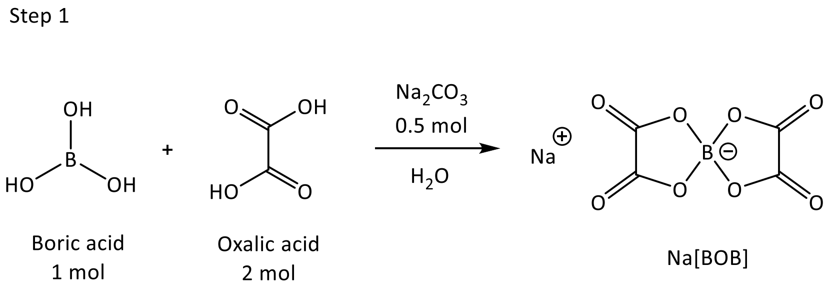
Structural study of H_2SO_4 by neutron scattering

Neutron scattering data was collected using the instrument SANDALS at ISIS and analysed using EPSR[2,3] software. The time-averaged liquid structures of pure sulfuric acid ($X_{H2SO4} = 1.00$) sulfuric acid:pyridine mixtures ($X_{H2SO4} = 0.67$) and sulfuric acid:pyridine:water mixtures ($X_{H2SO4} = 0.25$) were visually made clear by producing three dimensional models of component arrangement based on their spatial density function. Several different approaches of modelling the data were undertaken. Initial approaches ensured that minimal structural assumptions were inputted into the model. Detailed analysis of the results was carried out including examining the network of hydrogen bonding and the influence of water on the systems. PCCP publication of the results is in preparation.

The results are also currently being analysed by Dissolve software as a comparative study between EPSR and Dissolve. I have built the model for analysing sulfuric acid and pyridine mixtures. This involved working with Tristan Youngs (the developer of Dissolve) to incorporate an appropriate force field into the code. I also worked with Tristan as a tester of the software and reported back on bugs, possible improvements, and consistencies between EPSR and Dissolve data. There are still improvements to be made with the code and it is currently in the beta testing phase.

Synthesis of sodium bis(oxalato)borate, Na[BOB]

I have also successfully prepared sodium bis(oxalato)borate, Na[BOB] (Scheme 1). The next step is to add $P_{66614}Cl$ to form trihexyl(tetradecyl)phosphonium bis(oxalato)borate, $[P_{6,6,6,14}][BOB]$.



Scheme 1: Synthesis of sodium bis(oxalato)borate, Na[BOB]

Experimental

Oxalic acid (1.8 g, 20 mmol) and boric acid (0.618 g, 10 mmol) were separately dissolved in water and then mixed together under constant stirring. Na_2CO_3 (0.53 g, 5 mmol) was slowly added to the mixture with vigorous stirring. The turbid solution was heated in an oil bath at 120 °C until a dry white powder was obtained. The crude product was dispersed in hot acetonitrile at 60 °C and stirred for one more hour. Then a white powder was isolated using vacuum filtration. The product was further washed with cold ethanol and the powder was dried in an oven at 60 °C for 12 hours.

References

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2. A. K. Soper, *Chem. Phys.*, 1996, **202**, 295–306.
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QUILL Quarterly Report

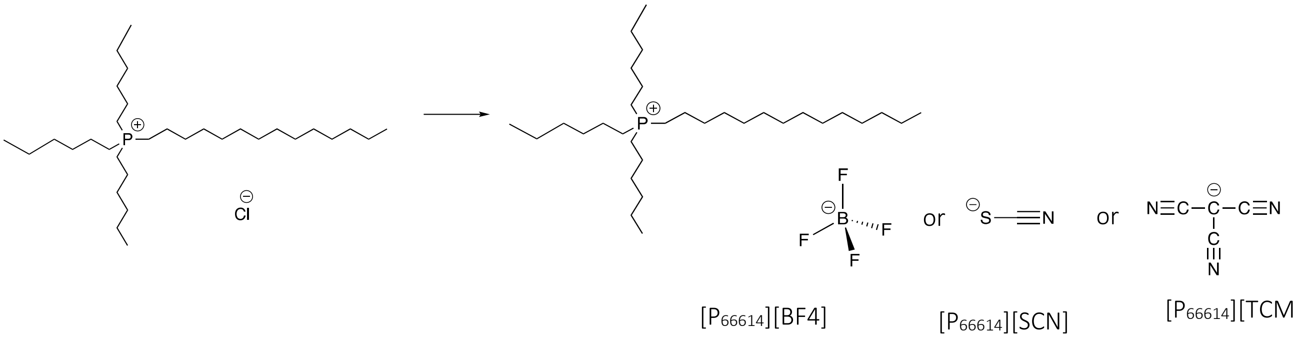
May 2021 – July 2021

Name:	Shannon McLaughlin		
Supervisor(s):	Prof Gosia Swadźba-Kwaśny		
Position:	PhD Student (1st year)		
Start date:	October 2020	Anticipated end date:	July 2024
Funding body:	Department for the Economy		

Thinking inside the (glove)box: Lewis Superacidic Ionic Liquids Based on Main Group Cations

Synthesis of Ionic Liquids:

Scheme 1 - Synthesis of $[P_{66614}][BF_4]$, $[P_{66614}][SCN]$ and $[P_{66614}][TCM]$.



Trihexyl(tetradecyl)phosphonium chloride $[P_{66614}]Cl$ was converted to either trihexyltetradecyl-phosphonium tetrafluoroborate ($[P_{66614}][BF4]$), trihexyltetradecyl-phosphonium thiocyanate ($[P_{66614}][SCN]$) or trihexyl(tetradecyl)phosphonium tricyanomethane ($[P_{66614}][TCM]$) *via* an anion exchange reaction (Scheme 1). Synthesis was conducted on a 50 g scale for each ionic liquid. Both ionic liquids were washed initially with a deionised water salt solution and DCM. 10 -15 subsequent washes were performed with the corresponding deionised water and salt solution. Solutions were tested with silver nitrate solution and XRFs were taken until the chloride content was below 100 ppm. $[P_{66614}][BF_4]$, $[P_{66614}][SCN]$ and $[P_{66614}][TCM]$ will be utilised in a collaborative study with the Wojnarowska group.[1] This group classifies ionic liquids under extreme pressure and studies phase transfer as a function of pressure instead of temperature.

$[P_{66614}][BF_4]$:

Chloride content = 69.0 ppm (LLD = 2.35)

^1H NMR (600 MHz, d_6 -DMSO) δ: 0.37-0.52 (m, 12H), 0.62-0.85 (m, 18H), 0.86-0.95 (m, 14H), 0.96-1.05 (m, 8H), 1.06-1.23 (m, 8H), 1.56-2.03 (m, 8H).
^{13}C NMR (600 MHz, d_6 -DMSO) δ: 12.92, 12.98, 16.98, 17.29, 20.26, 21,41, 21.74, 27.94, 28.47, 28.53, 28.77, 28.85, 29.31, 29.41, 29.68, 29.78, 30.00, 30.16, 31.02.

^{11}B NMR (600 MHz, d$_6$ -DMSO) δ: -1.55
^{19}F NMR (600 MHz, d$_6$ -DMSO) δ: -149.35
^{31}P NMR (600 MHz, d$_6$ -DMSO) δ: 32.53

[P$_{66614}$][TCM]:

Chloride content = 89.3 ppm (LLD = 2.80)

^{1}H NMR (600 MHz, d$_6$ -DMSO) δ: 0.47-0.65 (m, 12H), 0.80-0.98 (m, 18H), 0.98-1.07 (m, 14H), 1.08-1.17 (m, 8H), 1.17-1.32 (m, 8H), 1.69-2.00 (m, 8H).
^{13}C NMR (600 MHz, d$_6$ -DMSO) δ: 4.87, 13.54, 13.68, 18.12, 18.43, 20.92, 20.95, 21,96, 22.34, 28.33, 28.92, 29.02, 29.21, 29.33, 29.36, 29.38, 29.87, 29.97, 30.20. 30.29, 30.49, 31.06, 31.59, 120.83.
^{31}P NMR (600 MHz, d$_6$ -DMSO) δ: 33.96

[P$_{66614}$][SCN]:

Chloride content = Non – detectable (LLD = 15.5)

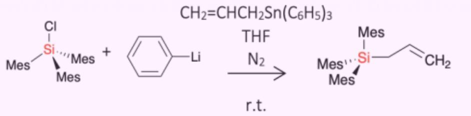
^{1}H NMR (600 MHz, d$_6$ -DMSO) δ: 0.36-0.57 (m, 12H), 0.67-0.90 (m, 18H), 0.91-1.04(m, 14H), 1.05-1.19 (m, 8H), 1.20-1.44 (m, 8H), 1.88-2.34 (m, 8H).
^{13}C NMR (600 MHz, d$_6$ -DMSO) δ: 13.56, 18.46, 18.78, 21.35, 22.01, 22.14, 22.27, 27.64, 28.07, 28.59, 28.97, 29.07, 29.28, 29.36, 30.03, 30.13, 30.38, 30.48, 30.70, 31.09, 31.54, 130.67.
^{31}P NMR (600 MHz, d$_6$ -DMSO) δ: 32.58

Future Work

Synthesis of trimesitylsilane:
Future work will involve completing the final two steps of the proposed synthesis of the 'free' trimesitylsilylium cation.

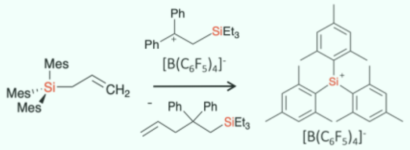
Allyltrimesitylsilane and trimesitylsilylium tetrakis(pentafluorophenyl)borate (compound 1) will be synthesised following methods described by Lambert *et al*.[2] and Lambert and Zhao[3] respectively (Scheme 2 and Scheme 3). After compound 1 has been successfully synthesised, it will be combined with commonly used anions such as [NTf$_2$]$^-$ and [FSI]$^-$ to conduct characteristic studies of the cation.

Scheme 2: Synthesis of allyltrimesitylsilane.



Lambert *et al.*

Scheme 3: Synthesis of a 'free' trimesitylsilylium cation.



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Lambert and Zhao.

The next aim would be to combine the trimesitylsilylium cation with borate anions or cyanoborate anions (Figure 1) in hope of generating new Lewis superacidic ionic liquids. Applications of these newly developed ionic liquids will then be investigated for potential use as solvents and catalysts.

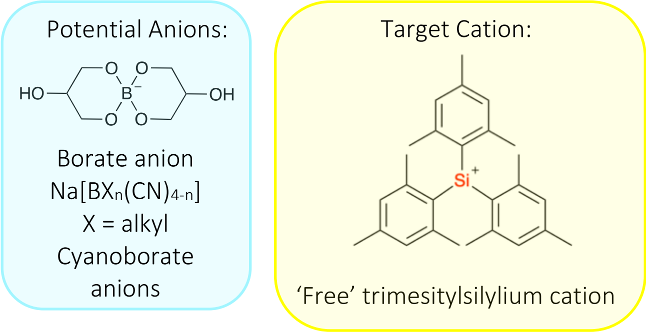


Figure 1 - Structure of the target trimesitylsilylium cation and potential borate anions or cyanoborate anions

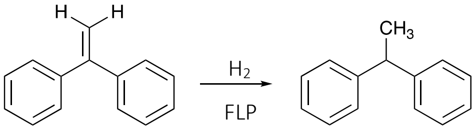
Hydrogenation Splitting using Frustrated Lewis Pairs

The FLP/IL mixtures mentioned in the previous quarterly report will be used in two areas of research.

Hydrogenation of Organic Substrates

The first area of research involves an ongoing study into frustrated Lewis pair (FLP) catalysis in ionic liquids. The FLP systems that successfully split hydrogen will be used to hydrogenate organic substrates. 1,1-diphenylethylene was chosen as the first substrate to be investigated as it has been previously observed to be effectively reduced by FLP systems[6,7] (Scheme 4). 0.1 ml of 1,1-diphenylethylene will be added to each FLP system and pure hydrogen will be bubbled through the FLP solutions at a rate of 2 ml/min for 12 hours. The progress of hydrogenation will be monitored using ^{1}H, ^{13}C, ^{19}F, ^{31}P and ^{11}B NMR spectroscopy.

Scheme 4 - Reduction of 1,1-diphenylethylene to 1,1-diphenylethane.



Collaborative Studies

The second area of research utilises the FLP/IL systems as potential electrolyte media for hydrogen detection. Previous studies into room temperature ionic liquids (RTILs) have shown promise as potential air stable and non-volatile electrolytes for amperometric gas sensors (Figure 2).[4-6] 0.5ml samples of $[C_2mim][NTf_2]$, $P(^tBu)_3/B(C_6F_5)_3$ in $[C_2mim][NTf_2]$ before hydrogenation and $P(^tBu)_3/B(C_6F_5)_3$ in $[C_2mim][NTf_2]$ after hydrogenation will be sent to the Silvester[5] research group for further investigation.

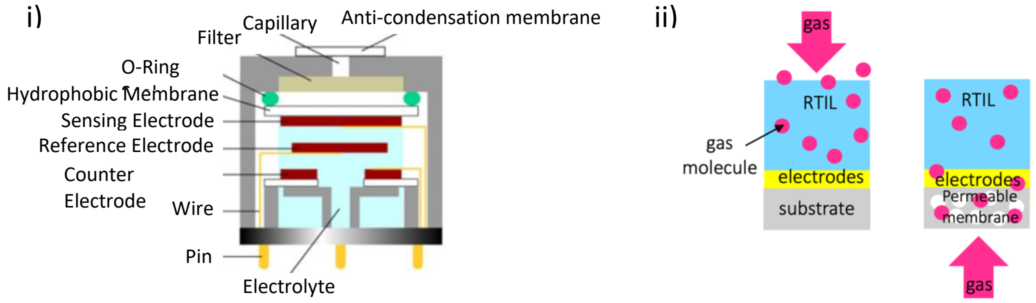


Figure 2 - Schematic diagrams of i) the structure of an amperometric gas sensor ii) diffusion of gas molecules from gas phase through IL to the electrode

References:

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3. K. C. Kim, C. A. Reed, D. W. Elliott, L. J. Mueller, F. Tham, L. Lin and J. B. Lambert, *Science.*, 2002, **297**, 825–827.
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5. D. S. Silvester, *Curr. Opin. Electrochem.*, 2019, **15**, 7–17.
7. I. Cretescu, D. Lutic and L. R. Manea, in *Electrochemical Sensors Technology*, InTech, 2017.

QUILL Quarterly Report

May 2021 – July 2021

Name:	Hugh O'Connor		
Supervisor(s):	Prof Peter Nockemann and Dr Stephen Glover		
Position:	PhD Student		
Start date:	October 2019	Anticipated end date:	June 2023
Funding body:	EPSRC		

Redox Flow Battery Materials for Energy Storage

Testing of 3D-printed redox flow battery cells has continued, with the cells being used to investigate the performance of vanadium and iron electrolytes. Graphene/ ionic liquid nanocomposites of both polypropylene and TPU have been successfully 3D-printed, and work is underway on increasing the amount of graphene present in the materials to increase electrical conductivity. 3D-printed electrodes with a high surface area have also been investigated, with early results showing promise. Larger size, industrial scale stacks have also been test printed for feasibility, along with a stackable design.

QUILL Quarterly Report

May 2021 – July 2021

Name:	Scott Place		
Supervisor(s):	Dr Paul Kavanagh (Principal), Dr Mark Muldoon (Secondary)		
Position:	PhD Student (2nd Year)		
Start date:	Oct 2019	Anticipated end date:	Jul 2022
Funding body:	Department for the Economy (DfE)		

Electrocatalysis for Energy Applications and Sensing

Following my leave of absence due to COVID-19, I returned to the lab at the beginning of June. Since then, I:

- Published work with Dr Paul Kavanagh on the electroactivity of a commercially available nitroxide radical polymer (PIPO) in *Electrochimica Acta* (https://doi.org/10.1016/j.electacta.2021.139044), to which I contributed in investigation, methodology, formal analysis, and visualisation. Work is now underway on the next publication on the electrocatalytic performance of PIPO, which should be submitted in the coming months. The data has been collected and the report is being drafted, with expected publication in *Chemical Communications* or another journal of similar impact. More data may be required, subject to reviewers' comments.
- Presented the above work at the International Society of Electrochemistry (ISE) annual conference, which was my first presentation on a completed study.
- A significant amount of time was spent writing the report and presentation for my annual progress review (APR) with Profs. John Holbrey and AP de Silva. The report detailed the work I have completed since April of 2020. The panel agreed that the report was well-written and presented, notwithstanding some concerns, and concluded that I am able to discuss my work effectively. It was agreed that I was to progress on to the next year of my studies.
- Recent time in the lab has been spent working on data collection for our TEMPO-derivative benchmarking study for electro-organic synthesis. We aim to apply the Saveant framework for benchmarking electrocatalysts using cyclic voltammetry in combination with longer-term electrolysis reactions, in which we will oxidise substrates with a variety of catalysts and determine their conversion percentages and selectivity using GC. We aim to determine a framework in which one could use fast physical chemistry methods to screen catalysts for organic reactions, without needing to do full syntheses to determine their activity. This work is in early stages and will require a significant amount of data. As it progresses, I will be responsible for drafting the paper for publication in full.

QUILL Quarterly Report

May 2021 –July 2021

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

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 programme, 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:

Preparation of appropriate model ionic liquids

Characterisation of aqueous/ionic liquid phase behaviour as a function of aqueous component salinity, pH, temperature and to draw strucutre-performance relationships with the ionic liquid cation/anion components.

Develop and validate an automated screening approach to determination of liquid/liquid critical phase behaviour through cloud-point determination

Optimize ionic liquid to use as draw fluid, developing a proof-of-concept ionic liquid-based RO desalination demonstrator for benchmarking

Measure the energy consumption and compare with typical method of water treatment

Progress to date

Experimental: The target ionic liquid tetrabutylphosphonium 5-phenyltetrazolate ([P_{4444}][Ph-tet]) has been synthesised and fully characterised by NMR spectroscopy and comparison with the literature data previously reported from QUILL.

Training: Handling materials under inert (dry) conditions using a Schlenk vacuum/inert gas manifold. Operation of the Crystal16 system.

Liquid/liquid phase determination: Validation of a new application of an Avantium Technologies (currently Technobis) Crystal16 crystallisation screening system to determine liquid-liquid critical behaviour in model LCST and UCST (upper critical solubility temperature) mixtures is under development. Critical variable under investigation including sample volume (between 0.5-2.0 mL), stirring rate, heating and cooling profiles, and system reproducibility with liquids of different viscosity. Data on model LCST/UCST mixtures: phenol/water and triethylamine/water, and validation of the ionic liquid [P$_{4444}$][Ph-tet]/water system have been completed, comparing the results to literature.

Conclusions and future work

The Crystal16 system is very convenient and efficient for measuring cloud points. In the studies to date the ability to use the system, originally designed for screening thermal crystallisation profiles, to identify liquid/liquid cloud points has been demonstrated and the method and operational parameters validated.

The next steps are to use this rapid screening methodology, where up to 16 samples can be studied in parallel, to examine the LCST response of [P$_{4444}$][Ph-tet] in aqueous mixtures as a function of added electrolyte strength mimicking inorganic salt concentrations and compositions between pure and sea water, and as a function of aqueous pH.

QUILL Quarterly Report

May 2021 – July 2021

Name:	Yaoguang Song		
Supervisor(s):	Prof. Peter Nockemann & David Rooney (QUB), Dr Xiaolei Zhang (Strathclyde), Prof. Stuart Gibb & Dr Szabolcs Pap (UHI)		
Position:	PGR Student		
Start date:	3rd Dec 2018	Anticipated end date:	31 Dec 2021
Funding body:	EU INTERREG VA Programme, managed by SEUPB		

Thermochemical Conversion of Biomass Lignin into Mesoporous Carbon Materials

Background

As a main component, lignin from biomass holds huge potential for producing mesoporous carbons (MCs)[1,2,3], which represents upper-class valuable products amongst all lignin-based applications.[4] However, most preparation methods for MCs are empirical, leading to unpredictable topologic and structural properties thus likely unfavourable for aimed downstream applications. Soft-templating synthesis was reported successful to tune nanostructures effectively, but novel promising templates are still in need of development.

A good option is long-chain ionic liquids (ILs) comprised of solely ions, as they can form lyotropic liquid crystals (LLCs), micelles, and (micro) emulsions that have been used for templating synthesis as well. Besides, ILs are also increasingly seen in the dissolution and depolymerisation of lignin. Therefore, this programme aims to investigate the possibility to convert lignin into MCs by employing ILs as both structure-directing agent and solvent. The effective implementation involves both multiscale modelling for computational design of preparation method and tangible experimental validation.

In my last quarterly report, we studied the self-assembly of ternary mixtures containing IL template, phenolic compounds as precursor, and water as solvent by employing both experiments and multiscale modelling including coarse-grained (CG) molecular dynamics (MD) simulations and density functional theory (DFT) calculations. The influence of materials precursor on the self-assembly of IL template was emphasised. Results indicate that the precursor influences not only the morphologies of IL template but the distribution of phenolic compounds themselves. Based on these studies, we could select appropriate precursor and control the mixing ratio to fabricate porous polymer and carbon materials (Figure). Therefore, this report briefly introduces our explorations.

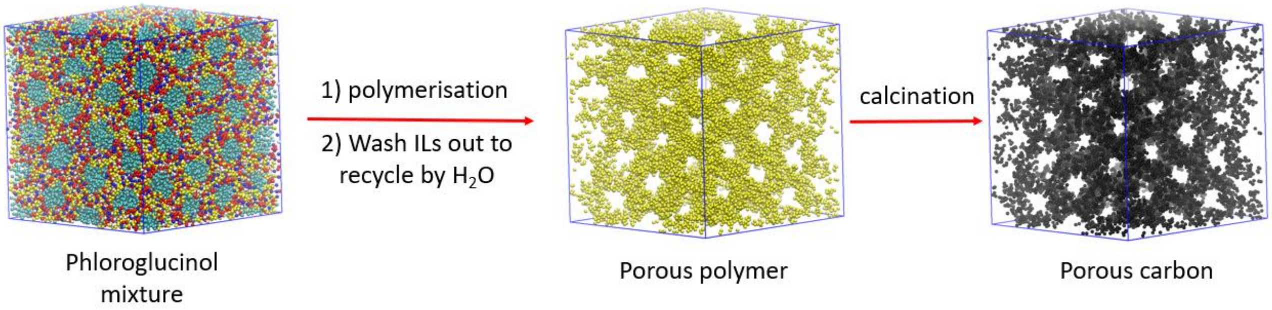

Figure 1 - Scheme for the fabrication of porous polymer and carbon materials using IL templates

Methodology

i. Preparation of porous polymer and porous carbons

For a typical run, 2.52 g of phloroglucinol and 5.65 g of [C_{10}MIM][OAc] synthesised in lab were mixed together in a vial equipped with a stir bar. The vial was tightly sealed with a screw cap and placed at 85 °C using an oil bath until phloroglucinol was fully dissolved when mixture appeared orange colour. The mixture was cooled down to room temperature. 2.90 g of glyoxal solution (40 wt%) was added dropwise then the mixture kept stirring vigorously at room temperature for another 20 min. Additional water was added to adjust the ratio between ILs and water. The boiling tube was heated up to 85 °C for polycondensation until homogeneous orange resin formed. The polymer was ground into powder and washed with deionised water. ILs were recycled after removing the water in filtrate by rotavapor. The polymer powder was dried at 85 °C overnight, labelled C10-P1.

The calcination took place under N_2 with a flow rate of 100 mL/min. The resin was heated from 20 °C to 800 °C at a rate of 1 °C/min and maintained at 800 °C for 1 h, followed by cooling down naturally. The resultant carbon material was labelled as C10-C1. For comparison, we also selected another mixing ratio where the relative IL content was 50% with spherical structures. Products were labelled as C10-P2 and C10-C2, respectively.

Evaporation induced self-assembly (EISA) technique was also employed for comparison. Ethanol was chosen as co-solvent to dissolve all starting materials. The liquid mixture was poured into a petri dish for solvent evaporation for 2 d at fume hood, then cured at 85 °C. All other experimental conditions kept unchanged. The new samples are labelled as C10-E-P1 and C10-E-C1, respectively.
Tentative investigation on tuning pore structures was alsoo performed by employing [C_{18}MIM][OAc] as template. Resultant polymer material was labelled as C18-E-P1.

ii. Characterisation

Surface area and porosity analysis: BET surface area and pore volume for samples were analysed by N2 adsorption-desorption at 77 K under a TriStar II 3020 analyser.

Scanning electron microscopy (SEM): Morphologies of resultant polymers and carbons were characterised on JEOL JAM-6500F field emission scanning electron microscope.

Results

IL as potential template showed a hexagonal array in ternary mixture containing phloroglucinol when the relative IL content reached 82%. The distribution of phloroglucinol also favours the preparation of highly ordered mesoporous polymer/carbons, so tentative explorations were carried out to make these materials, namely C10-R1 and C10-C1.
Table 1 shows the BET surface area and pore volume of carbon materials. Both carbon samples possess dominating micropores with average pore size around 16 Å. Measurements of polymers are in progress. Based on the difference of textural property in polymer and carbon material, it is possible to know the influence of the calcination on pore structures.

Table 1 - Textural properties of resultant samples

Sample	BET surface area (m^2/g)	Micropore area (m^2/g)	Total pore volume (cm^3/g)	Micropore volume (cm^3/g)	Average pore size (Å)
C10-C1	275.6	250.8	0.112	0.098	16.3

C10-C2	224.8	193.3	0.094	0.076	16.7

Figure 2 shows the representative morphology of samples before and after calcination. Unfortunately, no highly ordered pore structures were observed though there are uniform pores on the surface of polymer material. Several possible reasons are: 1) the mixtures did not reach equilibrium before polymerisation due to the high viscosity of IL; 2) The addition reaction of glyoxal with phloroglucinol and sequential polymerisation took place almost in the same time and progressed so rapidly that the morphology of IL templates were destroyed; and 3) polymers kept crosslinking and pore collapsed after the removal of the template. In combination with the small pore volume, most of the BET surface areas possibly came from those tiny particles produced during milling.

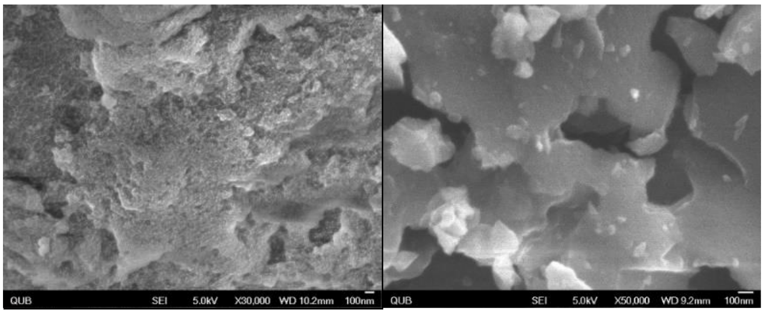

Figure 2 - Representative SEM images of sample C10-P2 (left) and C10-C2 (right)

To investigate the first assumption, EISA technique was employed and equilibrated for 1d. The morphologies of new samples (C10-E-P1 and C10-E-C1) were shown in Figure **3**. Though there are no highly ordered hexagonal pores, the distribution of pores on the surface seemed more uniform for polymer sample. This indicates that EISA technique may be effective to optimise the preparation. For the second assumption, a sol-gel process was employed, where the addition reaction of phloroglucinol with glyoxal took place first, followed by solvent evaporation and cross-linking reaction at 85 ˚C. The characterisation of pore structures is on-going. Considering that milling could destroy the nanostructures and increase “pseudo” surface area, the polymers were chopped into chunks instead of milling. However, this brings difficulty in the removal of ILs that are usually washed out by water. Therefore, we are currently investigating the use of Soxhlet extractor to extract ILs out of polymers without milling.

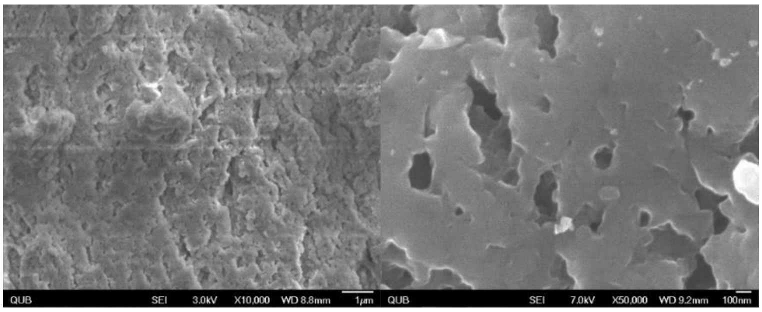

Figure 3 - Representative SEM images of sample C10-E-P1 (left) and C10-E-C1 (right)

Tentative investigation was carried out by employing longer-chain ILs in the meanwhile aiming for tuning nanostructures. Phase behaviour for ternary mixtures containing [C_{18}MIM][OAc] is being studied by CGMD simulations to find out the mixing ratio at which hexagonal structures form. The morphology of [C_{18}MIM][OAc] showed spherical when the relative contents of [C_{18}MIM][OAc] by weight were below 51%. IL contents between 62% and 71% saw the coexistence of spherical and cylindrical clusters. Simulations for higher contents is under running. As shown in Figure **4**, polymer C18-E-P1 showed much uniform lamellar structures alongside random pores. The relative IL content in this mixture was around 50%, where spherical structures were predicted. There are two possibilities in the discrepancy: 1) CGMD results went wrong; and 2) such lamellar structures were caused by the uniform shear force during milling. To exclude the second possibility, polymer material was prepared in the same condition without milling. The morphology of this material will be characterised.

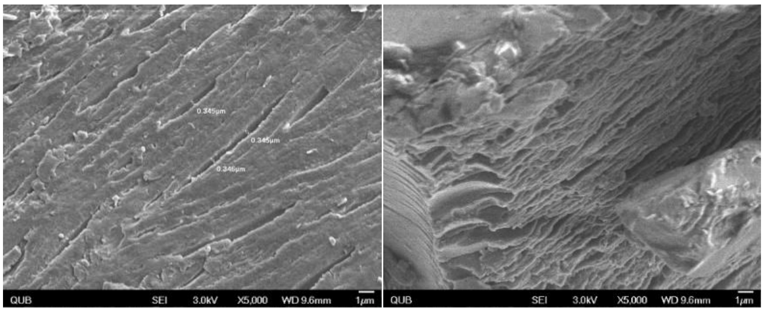

Figure 4 - Representative SEM images of sample C18-E-P1

Conclusions and future work

With the guidance of the study on self-assembly of ILs for templating synthesis, tentative explorations were carried out though failed to produce highly ordered hexagonal mesopores. These explorations, on the other hand, provided valuable feedback on how to optimise the preparation method: 1) ensure that mixtures containing templates and starting materials reach equilibrium; 2) prevent violent reactions from destroying the self-assembled structures of templates; and 3) avoid milling the products that would create surface area factitiously. In the future, more explorations will be performed to obtain highly ordered mesopores.

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QUILL Quarterly Report

May 2021 – July 2021

Name:	Richard Woodfield		
Supervisor(s):	Stephen Glover, Robert Watson, Peter Nockermann		
Position:	PhD Candidate		
Start date:	06/2019	Anticipated end date:	12/2022
Funding body:	EPSRC		

Modelling the use of Flow Batteries in Transport Applications

Background

Flow batteries have received significant attention in the past years for use in grid storage applications. The decoupling of the relationship between power and energy density offers a very unique way to store energy to suit the user's particular needs. The extremely long cycle life of a flow-battery is another attractive asset, as the electrodes do not undergo cyclic stressing in the same way Li-ion and other chemistries do. Flow-batteries have received very limited attention regarding their use in transport applications. There is untapped potential in the fact that the discharged electrolyte of a flow-battery could be rapidly swapped at a traditional gas-station, where the infrastructure is already half in-place with storage tanks under the stations. With the electrolyte being entirely re-usable, the station would use an on-site flow-battery to recharge their reservoir and provide passing vehicles with opportunity to swap their electrolyte with readily charged fluid.

Objective of this work

The overall goal of the project is to identify viable electric or hybrid modes of transport that would benefit from the use of a flow-battery, given the refillable nature of the flow-battery electrolyte reservoirs. Even the applications rendered not viable will have outcomes, as the amount by which the energy density of the electrolyte would need to improve by is also providing electrolyte chemists with targets to aim for. The investigations will be carried out using software to model battery and vehicle behaviour, primarily Simulink.

Progress to date

Modelling work has shown that coastal ferries are a very good candidate for RFB technology, and a paper has been submitted in this area.

Conclusions and future work

Modelling work is now shifting towards bus applications, exploring a range of system architectures and control strategies.

QUILL Quarterly Report

February 2021 – April 2021

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 digestors. 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 form any prospective technology. Carbon dioxide should make up 2.5-4% of the remaining volume with contaminants such as sulfer and siloxanes being limited to 10 mg/m^3 and 0.1 mg/m^3 respectively. Due to the major biogas components being carbon dioxide and methane it is this separation we will focus on in this project.[1]

Currently biogas upgrading is multistep and scrubbing is mainly used for carbon dioxide and methane separation. This involves the use of liquid amines where the carbon dioxide uptake occurs through a chemisorption process. This requires high energy for amine regeneration 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 vast 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 liquify leaving a pure methane stream. However the energy cost associated with this method is massive which makes it less sustainable and exceedingly costly.[2]

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

Work to date

The HS-GC screening methodology has been my major focus since the last report and has improved considerably. Calibration curves for both CO_2 an CH_4 have been completed giving R^2 values > 0.995 which shows direct correlation between GC peak area and initial pressure as can be seen in figure 1. This was achieved through the use of correct vial components so as to full reseal the vial after puncture with a 23 gauge needle. Much testing and methodology development was carried out in order to achieve these results including the testing of many vial components and HS-GC method alterations.

Figure 1 also shows equilibrated samples with [Bmim][NTf_2] which from literature we know should have a high CO_2 capacity[3] and low CH_4 capacity.[4] These samples were plotted using initial pressure injected into the vial where variation in the peak area is attributed to the sample. The Peak area of what we expect from the calibration curves of CO_2 is substantially higher than what we see with equilibrated samples. This indicated that differences are attributed to gas uptake by the ionic liquid when we consider control vials remain on the calibration curves after being allowed to equilibrate for the same amount of time. This rules out leaks as a possible source of peak area decrease. As expected the equilibrated sample with CH_4 shows almost no change when compared with the calibration curve.

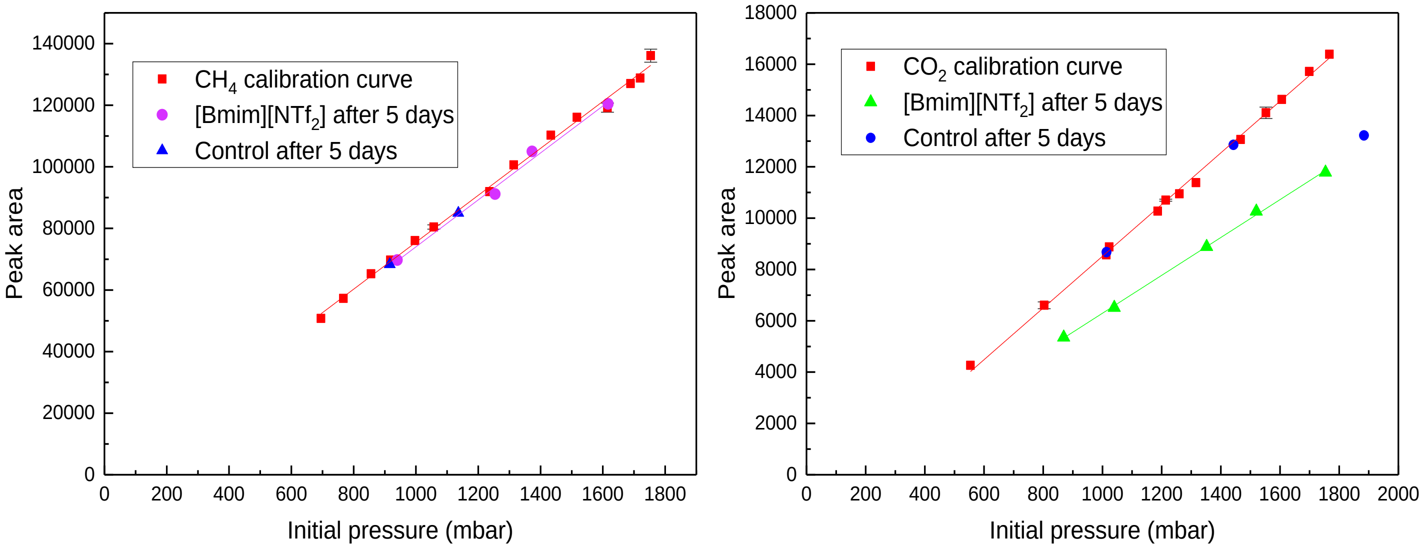

Figure 1 - Calibration curves with both CO_2 (left) and CH_4 (right) along with first material testing of [Bmim][NTf_2] with both gasses

It was also found that the maximum pressure that this testing can be carried out at is around 1800 mbar (figure 2). This was initially though to be due to septa leaks but more recently it has been found that different septa are following the exact same trend. These septa can be viably seen holding pressure up to 3 bar with no leaks. This indicated that the GC is limiting maximum pressure. We hope to in future carry out experiments with our own HS-GC to alleviate this issue.

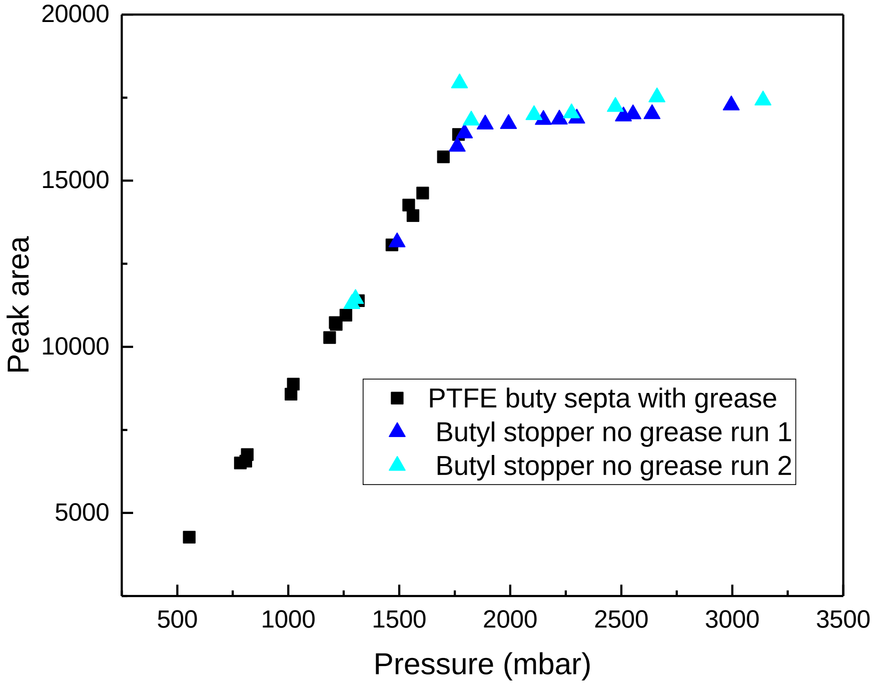

Figure 2 - Calibration curves with CO_2 using two different kinds of septa showing the same trends.

Initial material testing has begun with novel liquid sorbents. Initial experiments have involved making low melting mixtures (LMMs) from adding 10 wt% β-CD to a [Ch]Cl:U 1:2. These were prepared through simple mixing of the components at 30°C. 2.8 mL of this new sample was then added to vials and vials pressurised with CO_2. These were allowed to equilibrate for one week and the results can be seen below in figure 3. This data shows an increased capacity over that of pure [Ch]Cl:U 2:1 with the addition of 10 wt% of β-CD. This is likely brought about through host guest interactions between the β-CD and the CO_2, this is as of yet unconfirmed. It must be noted that is data form a single experiment and replicants are yet to be generated but are underway. It is however promising for future work due to the number of data points.

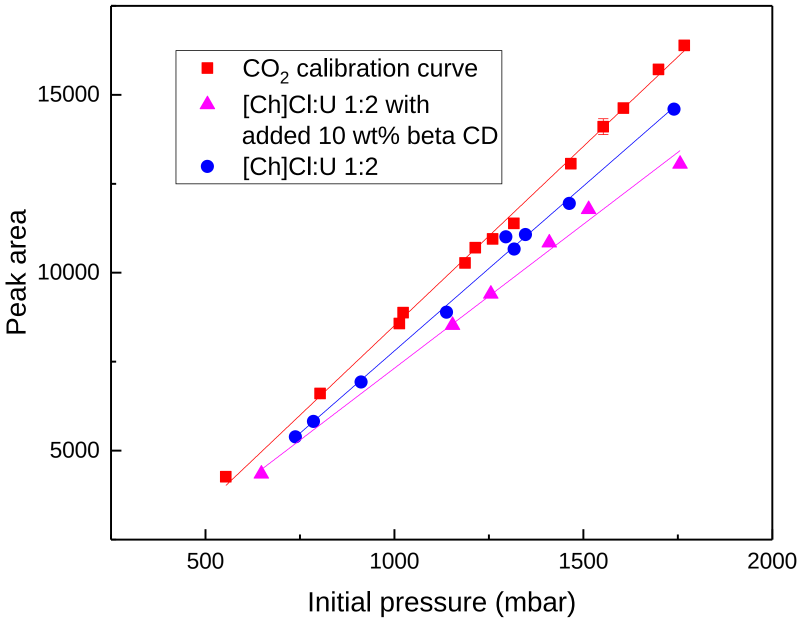

Figure 3 - Results of equilibrated samples of [Ch]Cl:U 1:2 as synthesised (blue) and with an added 10 wt% of β-CD (pink) all compared to a CO_2 calibration curve (red).

Testing of solid β-CD did not show any substantial decrease in peak area with CO_2 as can be seen from figure 4. This experiment was carried out with only 0.1g of β-CD so more may need to be added it is however interesting witness this change in behaviour when the β-CD is in the solid and liquid phase. Testing was also carried out with other solids we plan to test such as α and γ CD in conjunction with LMMs. Testing has also been carried out on cucurbiturils in the solid phase these as expected showed some capacity for CO_2. It remains to be seen if we can use these in conjunction with LMMs to increase their capacity.

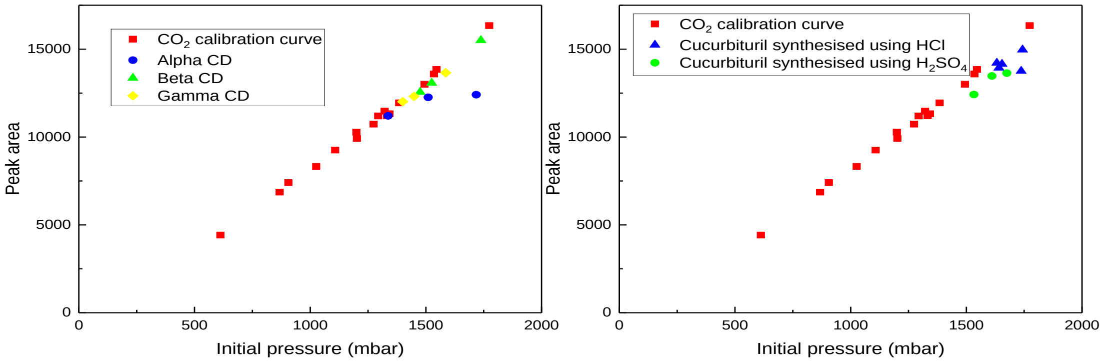

Figure 4 - Comparison of equilibrated solid macrocycle samples to CO_2 calibration curves testing their gas uptake properties in the solid state

Future work

Synthesis of new materials such as macrocycles and novel LMMs will take continue. These will subsequently be fully characterised via NMR, TGA, DSC and Karl Fisher. After characterisation these materials with then be tested using the described screening method for CO_2 and CH_4 capacity along with CO_2/CH_4 selectivity using mixed gasses. Work will also be continued with [Ch]Cl:U 1:2 in conjunction with CD this will include replication of results, use of different gasses, variation of CD type and amount of CD added.

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