QUILL

Quarterly Reports

February - April 2020

Contents

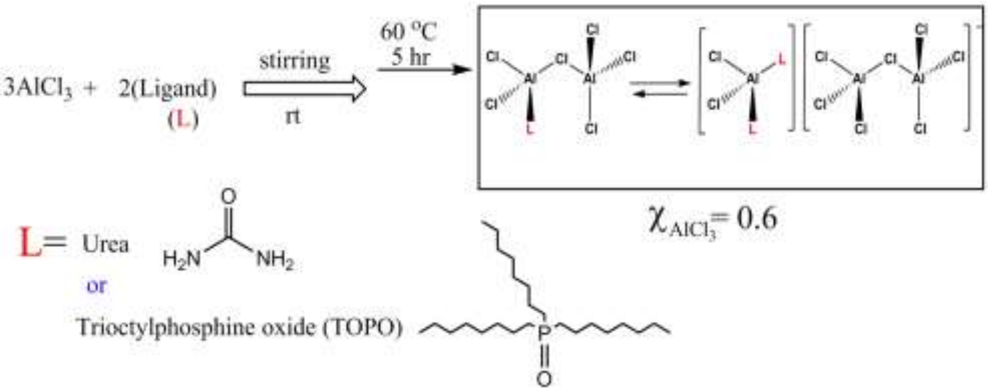
QUILL Quarterly Report

February 2020 – April 2020

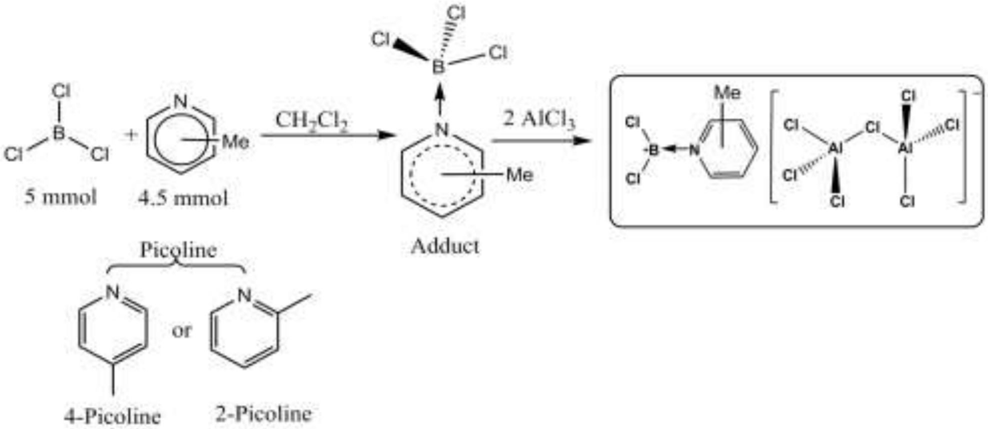
Name:	Dr Issam Abdalghani		
Supervisor(s):	Dr Gosia Swadźba-Kwaśny		
Position:	Post-doctoral Research assistant		
Start date:	10/12/2019	Anticipated end date:	December 2020
Funding body:	Invest Northern Ireland (Proof of Concept Funding Scheme)		

Chemical Conversion of Waste Plastic to Lubricating Base Oils using Lewis Acidic Ionic Liquids

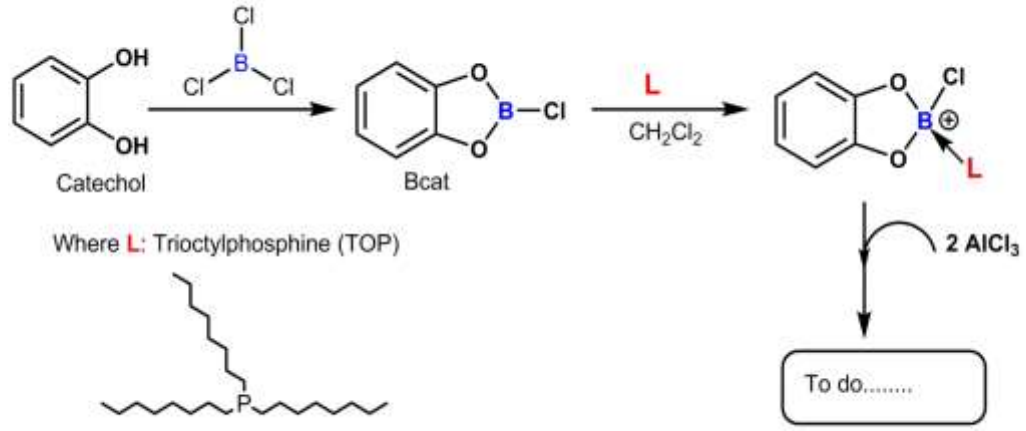
Before the lockdown and the closure of the university, I was working on the synthesis of some Lewis acidic ionic liquids such as: liquid coordination complexes (**Scheme 1**) and borenium ionic liquids (**Scheme 2**). I have been working also on the synthesis of new boron based-ionic liquids using b-chlorocatechol (BcatCl) as shown in **Scheme 3.**



Scheme 1 - Synthesis of liquid coordination complexes (LCCs) using O-donor ligands.



Scheme 2 - Synthesis of borenium ionic liquids.



Scheme 3 - Synthesis of b-chlorocatechol (BcatCl), and boron complexes using trioctylphosphine as ligand.

During the last weeks, I have been working on writing a literature review about the main catalytic systems used in the oligomerization of α-olefins for the preparation of polyalphaolefins (PAOs). I have read many patents and journal articles in order to familiarise myself with the current state of knowledge on this topic, while trying to develop my theoretical framework, as well as, to provide a general overview of the key findings on the main homogeneous catalysts used for the oligomerization of olefins.

Briefly, I have focused my reading on the Lewis acid catalysts system such as aluminium chloride ($AlCl_3$) and boron trifluoride (BF_3), metallocene catalysts, chromium and titanium based-catalysts, and ionic liquids and the progress of this work was discussed with supervisor and co-workers throughout a weekly virtual group meeting every Monday. I have also followed the online main-group chemistry seminars every week as it is a very interesting field of research, while learning new key findings from international experienced scientists.

QUILL Quarterly Report

February 2020 – April 2020

Name:	**Marian Borucki**		
Supervisor(s):	Prof Peter Nockemann, Dr Stephen Glover and Dr Małgorzata Swadźba-Kwaśny		
Position:	PhD Student		
Start date:	01.2018	Anticipated end date:	04.2021
Funding body:	Bryden Centre, Horiba Mira		

Lithium ion batteries degradation study using spectroscopy techniques

Background

Lithium ion batteries (LIB) are secondary (rechargeable) batteries 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 dependent on the environment, which results in discontinuous energy supply. In order to store excess energy that has been generated during times where lower amounts of energy are consumed within a day, energy storage stations based on LIB are used. The other, yet not less important application for LIBs is replacing the fossil fuel by storing the energy in the 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 towards expanding the market of HEV, EV and FCEV, thus the supply for lithium ion batteries will grow. The Automotive Council UK has in their roadmap reports on lithium ion batteries that have gathered up the issues that need to be addressed if the automotive of EV, HEV and FCEV is to grow. Such issues are based on the need for improving the safety of battery usage, lowering the costs of the batteries, researching 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, minimisation of the losses related to cell joining, their thermal management, increasing the lifespan of the batteries as well as increasing their recyclability, therefore, require further research towards the next generation of batteries.

In order to meet all the requirements a thorough study of the current battery technology as well as the development of a new chemistries is needed. Lifespan and the safety of the battery is of very high importance when it comes to the battery application in the transportation market. Battery life is limited by the degradation mechanism that occur inside the cell. Currently there is a known number of such mechanisms occurring, even though the proper investigating techniques allowing *in operando* study have not been developed yet. Moreover, the degradation is very much 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, which are non-toxic, environmentally friendly, non-flammable as well as of high performance should be developed. By developing the new electrolytes, often the development of the electrodes is also needed since the electrolyte stability as well as the energy density of the battery depends highly 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 its operation. In order to achieve the goal a development of an experimental method based on the spectroscopic analytical 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.

Aims for working from home period

Due to the university lockdown we are required to work from home and lab work has been suspended. The main objective of the working from home period is to review the scientific literature in the field. Additional activities include performing data analysis and training in different software; MatLab, Origin etc. Attendance at webinars will be undertaken if in area of interest (e.g. chemical analysis of Li-ion batteries by Raman spectroscopy and beyond on Monday 11th of May by Horiba US).

QUILL Quarterly Report

February 2020 – April 2020

Name:	**Dominic Burns**		
Supervisor(s):	Prof John Holbrey and Dr Gosia Swadzba-Kwasny		
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

Background

Water purification is essential to the modern world but in order to be most efficient with our resources we must use the correct purification method depending on the level of purity required. For example, if we were to distil all of the worlds drinking water that would be a waste of energy when an acceptable level of purity can be achieved by reverse osmosis.

ILs have been well studied on their ability to extract metal ions from aqueous environments but to date no work has been published on their ability to remove anions. Incorporating coordinating motifs in the IL phase may increase the sulfate removal similar to extractants in metallurgy.

Objective of this work

To design and synthesise a hydrophobic IL that can selectively extract sulfate from an aqueous phase in the presence of competing anions during bi-phasic extraction.

Work before Lockdown

In the month and a half before lockdown:

- Mutual solubilities of water and $[P_{66614}]Cl$ were determined.
- Sulfate extractions with ion exchange resins were performed as a comparison.
- Synthesis of a sulfate ligand, 1,1'-(1,3-phenylenebis(methylene))bis(3-butylthiourea).
- This ligand was dissolved in $[P_{66614}]Cl$ to try and increase its sulfate extractant ability but results were inconclusive.

Current work in lockdown

This has been a good opportunity to take a step back and review the work done to date and the current literature of the surrounding research topic. Since lockdown has started I have been working on a literature review of the current ways in which sulfate is removed, the fundamentals of anion coordination and how to specifically target sulfate as a ligand target.

I have also been working on my PhD progression by preparing for my differentiation on the 20th of May which involves compiling my literature review with all the work I have done to date followed by a plan for future research.

QUILL Quarterly Report

February 2020 – April 2020

Name:	**Emily Byrne**		
Supervisor(s):	Dr Małgorzata Swadźba-Kwaśny and Prof John Holbrey		
Position:	PhD Student		
Start date:	October 2017	Anticipated end date:	October 2020
Funding body:	DfE (Department for the Economy)		

Protic ionic liquids based on sulfuric acid

Background

Protic ionic liquids are prepared using the general formula below *via* hydrogen transfer (Eq. 1), whereby incorrect assumptions about complete ionicity are made where weaker acids and/or bases are used.[1–5]

$$HA + B \rightarrow [BH]^{+} + [A]^{-} \qquad \text{(Eq. 1)}$$

Instead hydrogen transfer is said to be dependant on the difference in pk_a between the acid and base,[6] the ratio of acid:base used[7] and the ability of the base to hydrogen bond.[8] Protic ionic liquids have been considered a cost-effective one-step acid-base hydrogen transfer synthesis alternative to expensive ionic liquids (*e.g.* $[N_{1222}][HSO_4]$ cost evaluation = US\$1.24 kg^{-1}).[9] They have been used in industrial applications including conversion of methanol to dimethylether (DME) for fuels[10] or in plasticiser synthesis[11] for example.

The sulfuric acid based subset of Brønsted acidic protic ionic liquids are particularly interesting due to their low price (sulfuric acid is a cheap commodity chemical)[9] and in some cases equivalent or improved performance when compared to their benchmark.[9,11] Industrial catalytic applications of these sulfuric acid based Brønsted acidic protic ionic liquids include ε-caprolactam[12] and plasticiser[11] synthesis and in biomass pre-treatment.[9,13,14] Pre-treatment of biomass studies also report that addition of 10-40% water is added to the protic ionic liquid used to promote fractionation.[13–15]

Brønsted acidic protic ionic liquids use excess acid component instead of 1:1 stoichiometry resulting in the presence of undissociated acid in the mixture whether strong acids/bases are used or not. When based on sulfuric acid, this undissociated acid usually tends to associate with $[HSO_4]^{-}$ ions as anionic clusters of $[(HSO_4)(H_2SO_4)_n]^{-}$ (Eq. 2).[11,12]

$$nH_2SO_4 + B \rightarrow [HB]^{+} + [(HSO_4)(H_2SO_4)_{n-1}]^{-} \qquad \text{(Eq. 2)}$$

However, although these species are known to exist in Earth's upper atmosphere,[16–19] this speciation was not confirmed in sulfuric acid based ionic liquids by the group until 2014.[11] Nevertheless, structural studies on cluster formation in ionic liquids,[20–25] anionic clusters in acidic ratios of acid-base reactions based on carboxylic acids[1,26] and hydrogen bonded systems based on carboxylates have been well established.[8,27–29] Previous studies by the group have considered the relationship between these anionic clusters and the physiochemical properties (*e.g.* density, viscosity, conductivity, acidity) using aliphatic, aromatic and alicyclic amines as cationic component and structure confirmed using spectroscopic techniques (*e.g.* ^{1}H NMR, IR).[11,12]

In addition to these spectroscopic structural studies on Brønsted acidic protic ionic liquids based on sulfuric acid, the group has also conducted research into structural studies of pyridine-acetic acid mixtures using neutron scattering to elucidate liquid structure.[7] The results from this indicate that proton transfer does not occur as outlined (Eq.1), but instead the time averaged bulk structure indicates that pyridine inclusions are present amongst hydrogen bonded acetic acid chains; highlighting the importance of real system structural studies using techniques such as neutron scattering.

Other work surrounding mixed anionic clusters based on $[(HSO_4)(H_2SO_4)_n(H_2O)_m]^-$ have been described as species existing in the stratosphere.[19] These species are stable, however, clusters become unstable when $n > 1$.[19] Here, infra-red spectroscopy band changes involving the S=O bond change upon hydration (*i.e.* hydrogen bond network appears disrupted), whereas when $n < 1$ this does not happen.[19] In addition, H_2SO_4 has greater affinity towards existing in a cluster with $[(HSO_4)(H_2SO_4)_n]^-$ than H_2O (ΔG = -59 and -26 kJ mol^{-1} respectively)[30] as a result of H_2SO_4's greater ability to hydrogen bond to an anionic core than H_2O.[19,31]

Motivation for this work

There are two strands of research to which liquid structural studies would be of benefit. The first is in protic ionic liquids based on $[HB][HSO_4]$ used in the pre-treatment of biomass where water has an advantageous effect on the fractionation of products such as lignin.[9,13–15] The second is in Brønsted acidic protic ionic liquids based on $[HB][(HSO_4)(H_2SO_4)_{n-1}]$ used in the synthesis of ε-caprolactam[12] and plasticisers[11] where n = 2 or 3.

Therefore, firstly, structural studies using both spectroscopic and neutron scattering techniques highlighting the effect of water on $[HB][HSO_4]$ systems is interesting to determine its role effective biomass pre-treatment. Secondly, structural studies using spectroscopic and neutron scattering techniques to elucidate structure of $[HB][(HSO_4)(H_2SO_4)_{n-1}]$ systems where n = 2 and 3 is interesting to better tailor industrially relevant catalytic systems to achieve increased performance.

Progress to date

Four sample sets were prepared for neutron scattering experiments (Table 1). Samples were based on pure sulfuric acid (1:0:0), sulfuric acid:pyridine:water (1:1:2) and sulfuric acid:pyridine (2:1 and 3:1) were prepared and their corresponding isotopic substitution[32] - protiation (H), deuteration (D) or 50:50 protiation:deuteration (H/D) used.

Table 1 - Sample compositions used for neutron scattering experiments as ISIS including ratios of acid:pyridine:water and their levels of protiation and/or deuteration.

Sample number	χ_{H2SO4}	Acid:Pyridine:Water	Sulfuric acid	Pyridine	Water
1	1.00	1:0:0	H		
2	1.00	1:0:0	H/D		
3	1.00	1:0:0	D		
4	0.25	1:1:2	H	D	H
5	0.25	1:1:2	H/D	D	H/D
6	0.25	1:1:2	D	D	D
7	0.25	1:1:2	D	H	D
8	0.25	1:1:2	D	H/D	D
9	0.25	1:1:2	H	H	H
10	0.25	1:1:2	H	H/D	H
11	0.67	2:1:0	H	D	
12	0.67	2:1:0	H/D	D	
13	0.67	2:1:0	D	D	
14	0.67	2:1:0	D	H	
15	0.67	2:1:0	D	H/D	
16	0.67	2:1:0	H	H	
17	0.67	2:1:0	H	H/D	
18	0.75	3:1:0	H	D	
19	0.75	3:1:0	H/D	D	
20	0.75	3:1:0	D	D	
21	0.75	3:1:0	D	H	
22	0.75	3:1:0	D	H/D	
23	0.75	3:1:0	H	H	
24	0.75	3:1:0	H	H/D	

In the case of sulfuric acid:pyridine:water (1:1:2) samples, deuteration level of water was chosen based on the sulfuric acid deuteration level as hydrogen/deuterium exchange would only occur between labile hydrogen/deuterium species.

Corrosion tests on TiZr sample cans with our least and most corrosive samples showed that sample acidity did corrode TiZr cans (Figure 1).

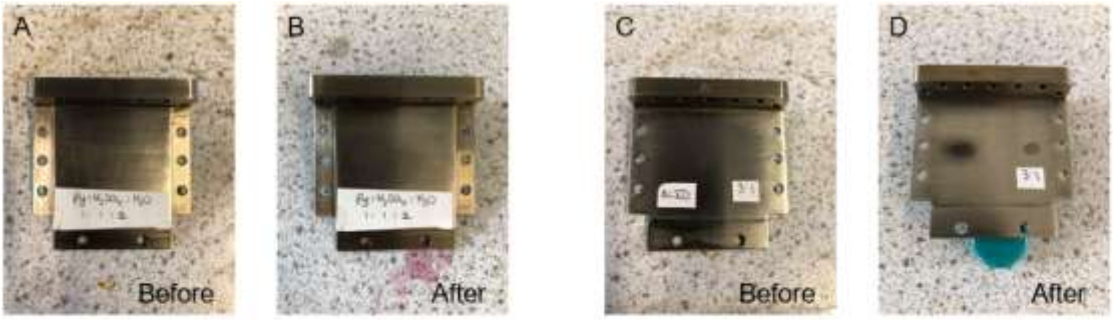


Figure 1 - TiZr sample can corrosion tests. Photos (A,C) show TiZr can before sample added. Photos (B,D) show corrosion of TiZr cans after the least corrosive sample 1:1:2 H_2SO_4:py:H_2O (B) and the most corrosive samples H_2SO_4 (left) and 3:1 H_2SO_4:py (right) (D).

Sample 1:1:2 H_2SO_4:py:H_2O shows very mild corrosion to the TiZr sample can (B), however, the most acidic sample H_2SO_4 shows considerable corrosion and 3:1 H_2SO_4:py also shows visible corrosion to the TiZr sample can (D). As a result, quartz cells were used as sample holders instead as they are better resistant to acidic corrosion.

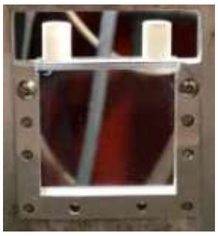


Figure 1 - Quartz cell sample holder with 2 mm internal cavity, filled with sample 6 (χ_{H2SO4} = 0.67) in place on the beam line autosampler and held in place with brackets. These quartz sample holders are more resistant to acidic samples than the archetypal $Ti_{0.68}Zr0._{32}$ alloy cans typically used.

Neutron scattering data was gathered from seventeen samples (1-17, Table 1) as a result of beamtime cut short due to COVID-19, however, we successfully collected scattering data on three complete datasets (*i.e.* χ_{H2SO4} = 1.00, 0.67 and 0.25 – pure sulfuric acid, sulfuric acid:pyridine mixtures and sulfuric acid:pyridine:water mixtures respectively). Each quartz cell had an internal cavity thickness of 1 or 2 mm. 2 mm cells were used for samples with high deuteration levels (*i.e*. sample numbers 2, 3, 5-8, 12, 13, 15 - **Error! Reference source not found.**), 1 mm cells for samples with lower deuteration (*i.e.* sample numbers 1, 4, 9-11, 14, 16, 17 – **Error! Reference source not found.**) and up to 1000 μA of data collected on each.

Physical characterisation (*e.g*. NMR spectroscopy, density, viscosity, infra-red spectroscopy and thermogravimetric analysis) have been studied. However, for the purpose of length, only density will be discussed.

Density of samples 1-24 (Table 1) were studied as a function of temperature between 20-50 °C. The density of all samples decreased with increasing temperature as expected. However, in contrast to previous studies considering the density of Brønsted acidic protic ionic liquids based on sulfuric acid,[12] there was minimal change to the linear trendline gradient with increasing χ_{H2SO4} from 0.67 to 0.75 (~8×10^{-4} g cm^{-3} K^{-1}); suggesting that the hydrogen bonding network in the samples is less easily disrupted with temperature or a greater prevalence of columbic interactions prevail. Sample density as a function of χ_{H2SO4} is outlined and discussed below (Figure 3).

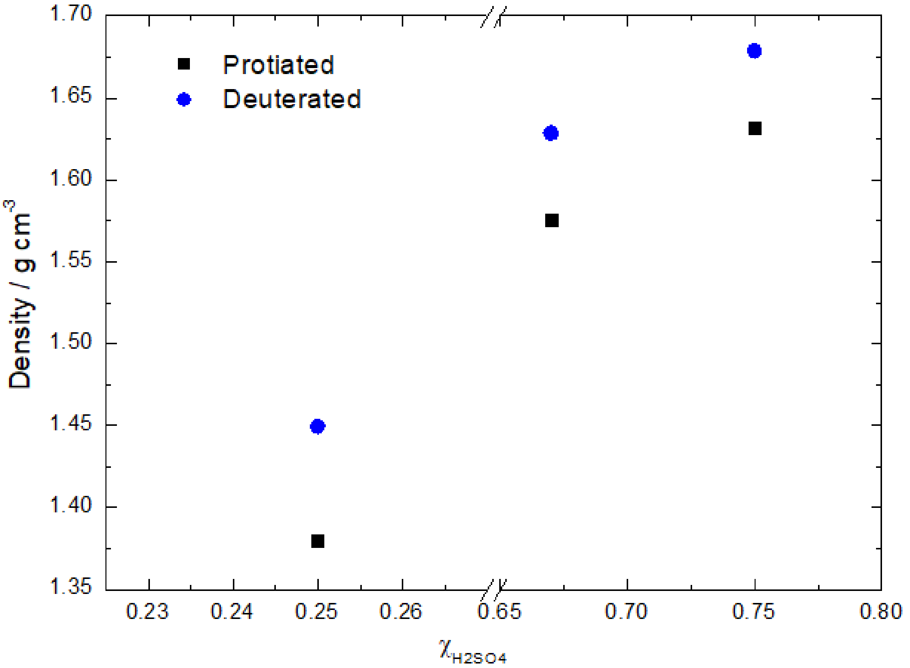


Figure 3 - Density of 1:1:2 H_2SO_4:py:H_2O ($\chi_{H2SO4} = 0.25$), 2:1 H_2SO_4:py ($\chi_{H2SO4} = 0.67$) and 3:1 H_2SO_4:py ($\chi_{H2SO4} = 0.75$) at 20 °C. Black squares represent fully protiated samples (samples 9, 16, 23). Blue circles represent fully deuterated samples (samples 6, 13, 20).

Samples are, as expected, less dense than pure protiated and deuterated sulfuric acid (1.8365 and 1.87235 g cm^{-3}) respectively and more dense than pure protiated and deuterated pyridine (0.9833 and 1.04815 g cm^{-3}) respectively at 20 °C. They show a trend of increasing density with increasing χ_{H2SO4} from $\chi_{H2SO4} = 0.25$-0.75. However, the trend between $\chi_{H2SO4} = 0.25$ and $\chi_{H2SO4} = 0.67$-0.75 is not linear as $\chi_{H2SO4} = 0.25$ also has two moles of water present which is not present in samples $\chi_{H2SO4} = 0.67$-0.75 and appears to lower its density quite significantly. In addition, isotopic substitution of pyridine, sulfuric acid and water substituents from protiated to deuterated increases the density of the samples. These experimental results for H_2SO_4:py:H_2O and H_2SO_4:py show an increase in density with 'heavier' components in a similar manner to experimental results[33] and computational calculations[34] using the path integrated Monte Carlo method for isotopically substituted water (*i.e.* $\rho_{water} = {}^1H < {}^2D < {}^3T$). This is likely due to the atomistic density for these H_2SO_4:py:H_2O and H_2SO_4:py samples remaining the same, however, with an added neutron from ^1H to ^2D, the mass of each atom increases, increasing their mass per volume (g cm^{-3}).

In addition to this, I have been writing a paper based on these results in preparation for submission to RSC PCCP.

Conclusions and future work

Finally, twenty four samples were prepared with varying levels of protiation/deuteration and structural studies using neutron scattering were undertaken on samples 1-17 at the Rutherford Appleton Lab's ISIS pulsed neutron and muon source in Oxfordshire. Corrosion tests revealed that regular TiZr sample holder cans were not appropriate for sample analysis, therefore, quartz cells were used as sample holders. Physical characterisation (*e.g.* NMR spectroscopy, density, viscosity, infra-red spectroscopy and thermogravimetric analysis) have been carried out on each of these twenty four samples. Analysis of density results reveal that in contrast to previous studies concerning Brønsted acidic protic ionic liquids based on sulfuric acid,[12] there was minimal change to the linear trendline gradient across the temperature range 20-50 °C with increasing χ_{H2SO4} from

0.67 to 0.75. This suggests either that there is a greater prevalence of columbic interactions in these systems or that the hydrogen bonding network present is less easily disrupted with increasing temperature. In addition, H_2SO_4:py:H_2O and H_2SO_4:py samples show an increase in density with 'heavier' components (*i.e.* higher levels of deuteration). This is unsurprising given that with constant atomistic density, an additional neutron to each hydrogen species will increase the mass per unit volume (*i.e.* density).

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QUILL Quarterly Report

February 2020 – April 2020

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

Work being carried out from home

Due to the COVID-19 pandemic, all work on this project is currently being completed from home. Therefore, all planned experimental work has been postponed and focus has been shifted to computer-based work. Currently this includes investigating the application of time-series forecasting deep learning networks in conjunction with a 3D thermal model for prediction of internal battery temperature using external thermal measurements. If successful, this would allow for computationally efficient thermal predictions by a vehicle battery management system.

QUILL Quarterly Report

February 2020 – April 2020

Name:	**Oisin Hamill**		
Supervisor(s):	Dr Nancy Artioli and Dr Alex Goguet		
Position:	PhD Student		
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

Work plan during the university closure and COVID-19 lockdown.

I am currently compiling a literature review in preparation for my differentiation interview later this month. This review consists of a background on emission sources; current emission legislations, tests and detection systems; a background on LNT catalysts focusing on ceria; a review of dopants; the effect dopants have on ceria in particular; and a summary of laboratory work completed to date. It finishes with a short background to all the techniques used during catalyst characterisation and includes the results acquired from initial tests carried out in the first 6 months of my project. I also will explain why these techniques were important to understand my catalyst material and how they were performed.

QUILL Quarterly Report

February 2020 – April 2020

Name:	**Jerry Pui Ho Li**		
Supervisor(s):	Dr Nancy Artioli and Prof Peter Nockemann		
Position:	Research Fellow		
Start date:	9/12/2019	Anticipated end date:	8/12/2020
Funding body:	Invest Northern Ireland (INI)		

A Catalytic Gas-to-Liquid Process for CO Valorisation

Background
The project being contracted for is titled: A Catalytic Gas-to-Liquid Process for CO Valorisation. This is largely work with more emphasis towards commercialisation and business, with some towards academic goals (when possible).

Objective of this work
This is work based around the commercialisation of a catalytic process, requiring first to identify the market area and reaction. This is followed by a work plan (WP) broken down into several stages:

1. Identifying the type of catalyst required followed by optimising the catalyst.
2. Designing a lab scale multi-channel reactor using the optimised catalyst in WP1.
3. Perform a techno-economic analysis of a scaled-up process, using the work from WP1 and 2 as the core basis.

The project also requires more business-oriented tasks, making industrial contacts, partners, and mentors through and outside of tradeshows and conferences.

Other work beyond the project itself involve the technical support for the research group itself, whether it be laboratory maintenance or to provide aid to the students.

Progress to date
With the system in operation as stated in the previous quarterly report, continued guidance was provided to 2 groups of Masters students working on their final year project which requires the use of the reaction setup, making sure all the results make sense within the confines of the work. Due to the Covid-19 lockdown, the experimental work was cut short and as a result the students could only use the results that they had on hand. During March, the organisation of their results and presentation work was conducted remotely as WFH orders were in place.

In work more directly related to the project, some benchmark catalyst samples have been synthesized and awaiting characterisation. In the meantime, chemical materials have been ordered in order to fully begin WP1 work.

The 2nd quarter report for the INI funding was written and submitted. Due to the Covid-19 lockdown, experimental work that was planned has been postponed until further notice. Thus the techno-economic analysis which was originally planned for a later date, has been pushed forward and may be adapted to become the large bulk of the overall work. Towards this, Aspen Plus has been installed allowing for this to take place remotely. However, as little experience has been held for this software, official Aspen Tech courses have been booked to learn how to use the software. The first course (Introduction to Aspen Plus) has been completed during 20-22 April. The other courses have been booked for May and June.

In addition to the techno-economic analysis and the courses, a course on starting and running small businesses was attended on 30th April, which details how to design a business canvas, how to approach the design, and how to pitch an idea. During the course, some contacts were made in order to see if help can be conducted for market research and partnership. A follow up course which details the grants, is slated for 7th May. Additional online courses have also been recommended by the university and INI which should also bolster increase the knowledge for the commercial and business side of the project. A Lean-Launch program has been registered for, which will also be prudent for the market research component of the PoC work.

In further unrelated work, 3 papers were submitted for publication prior to QUB starting period was accepted. As of the time of this report, 2 have been accepted and published, while 1 is under review.

Conclusions and future work

At the time of this report, there are no results beyond the successful synthesis of the catalyst benchmarks and some of the data obtained by the Masters students which can be used towards the techno-economic analysis.

Having taken the Aspen Tech training course (Introduction to Aspen Plus), work is in progress towards practicing how to use the Aspen Plus software by replicating case studies, which by design also has similar setup to how we aim to approach our process design. However, more courses will happen during May, which will allow for further optimisation of the processes.

Some business courses have also been attended, and at least 2 contacts have been made in order to see if help can be conducted for market research and partnership. This will be an ongoing process as being in touch with new business partners is somewhat more difficult. Thus the sooner the techno-economic analysis yields results, the better the position we are for going ahead and pitching to companies and partners.

QUILL Quarterly Report

February 2020 – April 2020

Name:	**Sam McCalmont**		
Supervisor(s):	Dr Leila Moura and Prof John Holbrey		
Position:	PhD Student		
Start date:	Jan 2020	Anticipated end date:	2023
Funding body:	Royal Academy of Engineering and EPSRC DTP		

Chemisorbent material 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 material benchmarked for testing under industrial conditions.

Progress to date:
With the current status of being house bound with COVID-19 I am focusing most of my attention upon my literature review. The current status of which is the key headings and information has been included, however, areas of which are of interest to me (such as ionic liquids) I want to expand into a more detailed collection of data for experiments going forward, rather than simply a broad range of data for my literature review. I plan for my literature review to be completed by the end of May 2020.

My initial review is planned to be completed virtually by the end of May 2020. Within my initial review I will be focusing on my literature review, and my research plan for the return to the lab once the current restrictions due to COVID-19 has eased. Within my research plan is the upgrading of the rig that has been erected currently and development of personal skills on nuclear magnetic resonance (NMR), and headspace gas chromatography (HSGC). In turns of experimental work, I plan on completing pure (single), olefin and paraffin experiments (pure binary), and experiments introducing contaminates to mimic true gas streams after steam cracker. These experiments used to determine the material capacity, and the selectivity of the olefin to the paraffin. Furthermore, these experiments will be completed on the gas rig as shown in Figure 1.

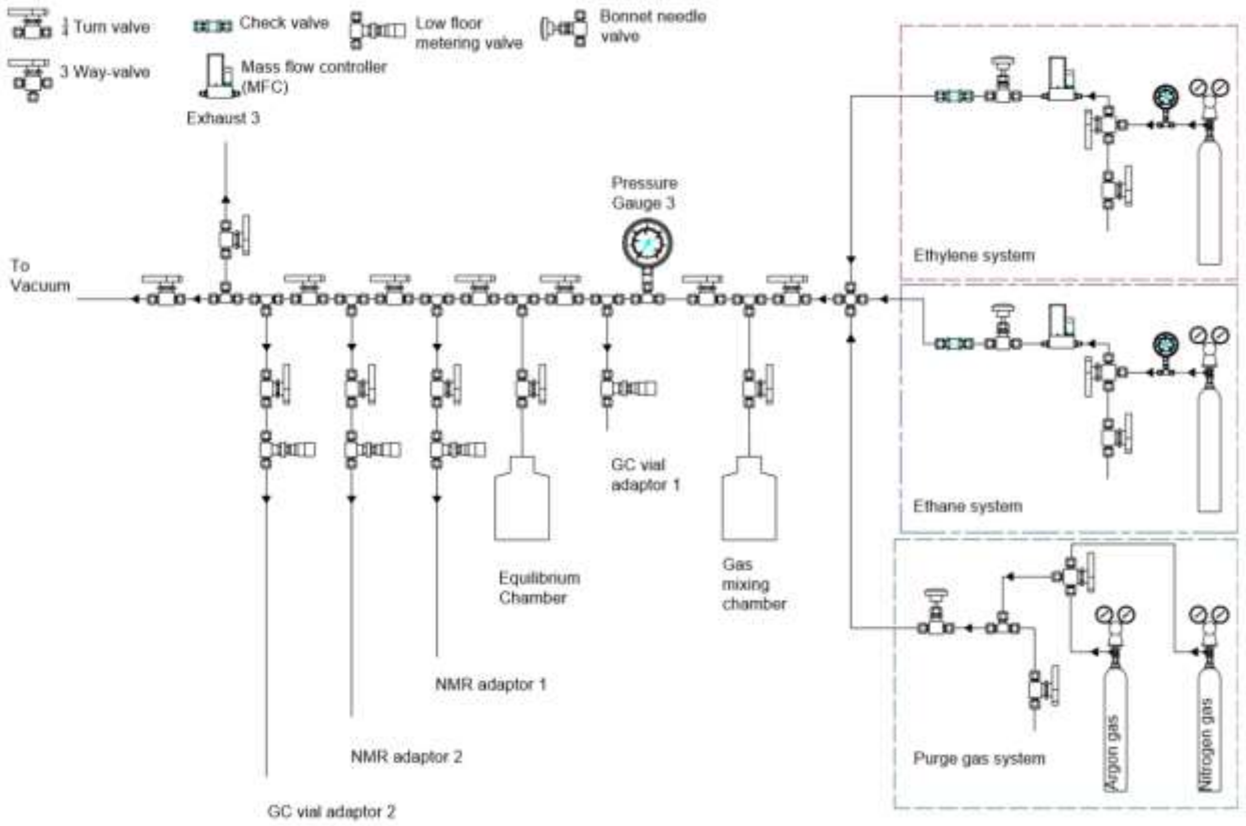

Figure 2 - The desired design of rig. ¼ turn valve being binary on/off. 3-way valve allowing a two directional flow option. Check valve prevents back flow occurring. Low floor metering valve, and bonnet needle valve both are used to control the flow of gas.

QUILL Quarterly Report

February 2020 - May 2020

Name:	**Stephen McDermott**		
Supervisor(s):	Dr Haresh Manyar and Prof Peter Nockemann		
Position:	PhD Student		
Start date:	1st October 2019	Anticipated end date:	1st March 2023
Funding body:	EPRSC		

Catalytic Production of biomass-derived liquid transportation fuel additives

Objective of this work

Methods to reduce fatty acids/carboxylic acids such as octanoic acid to produce liquid transportation fuel additives using ionic liquids and sodium borohydride.

Progress to date

We have achieved a conversion of octanoic acid using sodium borohydride and ionic liquid $[P_{6,6,6,14}]$ $[N(CN)_2]$ using THF as a solvent. I am in the process of writing a review article on the various hydrogenation methods of carboxylic acids. I am also preparing for differentiation. Due to the pandemic, there is no access to the lab and therefore lab research is suspended. On return to the lab, I will further analyse the products using GC-MS to identify unknown peaks.

Next stage is to perform the reaction at different conditions to determine the selectivity of the reaction to the products (Alkane or Alcohol) and the conversion of the acid into the products. The conditions of the reactions to be varied are temperature of reaction mixture, stirring speed, amount of ionic liquid, amount of sodium borohydride, amount of acid, amount of solvent and solvent used.

I obtained conversions to alcohols, aldehydes and alkanes at room temperature using ionic liquids. I am now trying to improve the selectivity of the reaction towards one of the products of the reaction.

Conclusion

I am looking to optimise the reaction and try to scale up the reaction for larger batch reaction.

QUILL Quarterly Report

February 2020 – April 2020

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

Main Group Catalysis in Ionic Liquids

I am currently working on writing my report for my differentiation and preparing for my presentation. This has involved reading up to date literature, reading around my subject and writing up results and discussion and experimental sections. I am also learning how to use the EPSR and Dissolve modelling programmes, used to analyse neutron scattering data. I attended the disordered materials user group meeting and EPSR and Dissolve data analysis workshop in January. This involved the opportunity to learn about new features available in the data analysis programme EPSR26, as well as its new graphical user interface. Furthermore, I was able to learn and try the new analysis package, Dissolve. This training is incredibly beneficial to analyse results from neutron scattering experiments carried out at the ISIS neutron and muon source at the Rutherford Appleton Laboratory, UK. Neutron scattering is a very powerful technique and one that I will use throughout my PhD. I will continue to build on what I learned at the 2-day data analysis workshop. I will analyse data from beamtime looking at the FLP, $P(^tBu)_3$ and BCF, in the ionic liquid $[C_2mim][NTf_2]$. I will also analyse data from recent beamtime looking at the liquid structure of sulfuric acid and derived protic ionic liquids.

QUILL Quarterly Report

February 2020 – April 2020

Name:	**Hugh O’Connor**		
Supervisor(s):	Prof Peter Nockemann and Dr Stephen Glover		
Position:	PhD Student		
Start date:	01 October 2019	Anticipated end date:	23 March 2023
Funding body:	EPSRC		

Redox Flow Battery Materials for Energy Storage

Before the COVID-19 work was ongoing on the design and manufacture of a fully 3D-printed redox flow battery test cell. Sealing tests were successful and initial charge/discharge cycling tests were being carried out. Vanadium electrolyte similar to that used in industry was synthesised and various 3D-printable polymers were being tested for chemical compatibility. Since Lab work has been suspended, development of a Multiphysics Model has continued. This model will be used to evaluate the performance of different flow cell topologies and has shown good correlation with models found in Literature. I have also been writing the “Literature Review” section of my thesis and preparing for my differentiation.

QUILL Quarterly Report

February 2020 – April 2020

Name:	**Scott Place**		
Supervisor(s):	Dr Paul Kavanagh		
Position:	PhD Student		
Start date:	October 2019	Anticipated end date:	2022/23
Funding body:	Department for the Economy (DfE)		

Copper-Based Electrocatalysis for Energy Applications and Sensing

Background
This is a PhD research project focusing on electrochemical alcohol oxidation reactions using organic nitroxyl redox mediators and abundant, relatively low-cost earth metals. Modern methods for the oxidation of alcohols to aldehydes and ketones produce stoichiometric quantities of waste and require reagents and conditions which are often hazardous. Electrochemical methods have the potential to eliminate the need for chemical terminal oxidants and significantly reduce waste in synthesis, improving this highly valuable reaction's environmental impact whilst also leading to safer conditions.

Alcohol oxidations also have the potential to be used as a competent energy source in fuel cells, with mediators opening up the possibility of more challenging fuels, such as bio-sources, for use in these cells by alleviating a number of engineering problems with current direct-oxidation fuel cells relating to reaction surface area and activation energy, among others. With the use of surfactants, it may be possible to achieve an all-aqueous, bio-mimetic alcohol oxidation fuel cell using a copper-TEMPO catalysis system. (TEMPO being a common and highly effective nitroxyl redox mediator, as well as a competent aerobic oxidation catalyst).

This project also serves as an opportunity to benchmark a number of nitroxyl mediators under controlled conditions, with the aim of understanding how structure relates to specific performance for different reactions; i.e. electronically-activated alcohols vs. otherwise, or primary vs. secondary, etc. With this guide, it would be possible to exploit the tuneable nature of organic nitroxyl mediators for optimisation purposes.

Finally, mediators can be used as tuneable organic charge-storage molecules. Certain derivatives of TEMPO, such as the polymer variant, PIPO, may be useful as charge storage molecules in redox-flow cells, whilst reducing overall cell cost by relaxing the constraints on ion-exchange membranes, which often account for a significant portion of cell cost. This specific application has potential to make use of ionic liquids as a solvent/electrolyte for this TEMPO derivative.

Objective of this work
From my own perspective, this project serves as an educational experience with the end goal of earning a PhD qualification. From an academic perspective, the aim is to produce useful results that will be beneficial for the field, whilst exploring and developing green energy systems.

Progress to date

A good amount of time was spent on reproducing high-impact results in the field of mediated electrocatalytic alcohol oxidations as both a training exercise and as a test of reproducibility and competence before building further on these results. Happily, results were replicated well, demonstrating competence with the techniques used.

Studies so far have focused mostly on the use of polyamine immobilised piperidinyl oxyl, PIPO, a commercially available polymer-derivative of TEMPO. We have shown for the first time that PIPO is an effective electrocatalyst and have explored its potential as a catalyst to be immobilised onto an active support, for improved recyclability, activity and versatility. With the latter, we have encountered challenges, but have learned a lot about how this type of system could work. We have also shown that PIPO is electroactive, still transferring electrons with the electrode rapidly, in the ionic liquid, $P_{66614}NTf_2$, which is a promising preliminary result for PIPO's potential as a charge storage molecule in this sort of system. We have begun to work with the Nockemann group on developing this flow cell on a proof-of-concept scale.

Throughout the PIPO study, we have also observed some connections between solvent and reaction mechanism, with results suggesting that the rate determining step of the oxidation mechanism is, in part, dependent on solvent. This has served as kindling for a new idea: a study on solvents and electrolytes and their effect on reaction mechanism and rate in the context of this oxidation.

Current work in lockdown

Given the situation of the COVID-19 global pandemic, lab work has temporarily ceased. In the time out from the lab, time has been spent writing up the differentiation report for this project and a presentation is currently being prepared for the interview. Though this report has taken up the vast majority of the time at home so far, background reading is underway on advances in aqueous alcohol oxidations using surfactants and copper-TEMPO to pick up a running start on the biomimetic fuel study upon returning to the lab.

Conclusions and future work

The PIPO study has made up the bulk of the work so far, in which this commercially available polymer has been demonstrated to be electroactive under a number of conditions with potential for a range of applications, and the vast majority of data is compiled for preparation of a publication in the coming months. The next step in the project will be work on the aqueous, biomimetic fuel cell, as this appears to be an area of excitement in the field and is a good opportunity to produce a high-quality, high-impact paper. Additionally, we hope to develop further the redox flow cell using PIPO in ionic liquids with the Nockemann group.

QUILL Quarterly Report

February 2020 – April 2020

Name:	Zara Shiels		
Supervisor(s):	Dr Artioli, Prof Nockemann and Dr Harrison		
Position:	PhD Student		
Start date:	Feburary 2019	Anticipated end date:	2022
Funding body:	Interreg (Renewable Engine Project)		

Developing New Nanocatalysts for the Direct Conversion of Biogenic Carbon Dioxide (CO2) to Sustainable Fuels

Since having to suspend all experimental work due to Covid-19, I have been working on an updated literature review. I have circulated the first draft of the first chapter of my thesis to my supervisors for corrections and hope to have this completed by the end of lockdown. I have also been working on a report for my annual progress review (APR). I circulated a first draft to my supervisors and have received some corrections which I have worked on and submitted a new draft of the abstract, introduction and aims for their review. Next, I plan to work on the experimental, results and discussion sections of the APR report and submit this also for review. Finally, if time permits, I also wish to start writing up the first experimental chapter of the thesis, since all the results and data have not yet been collected it will be a framework that can be filled in at a later date.

QUILL Quarterly Report

February 2020 – April 2020

Name:	**Yaoguang Song**		
Supervisor(s):	Prof Peter Nockemann & David Rooney, Dr Xiaolei Zhang (Strathclyde) and Dr Szabolcs Pap (UHI)		
Position:	PhD 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

Since last quarter, I kept running simulations to predict the micelle morphologies at ILs in aqueous solution with Coarse-grained models. More concentrations were studied. The influence of temperature on micelle morphology transition was investigated at 343.15 K compared with 298.15 K. Surface tensions and self-diffusion coefficients for different mixing systems were calculated at 298.15 K from simulation, expecting to serve as criteria to indicate the morphology transformation. Experimental measurements were carried out to get surface tension value, so that we could compare results from simulations and experiments to verify the prediction of simulations. Besides, owing to COVID-19 pandemic, experimental work has been significantly delayed. In addition to running simulations, I started to write manuscript for publication and prepare the coming APR.

QUILL Quarterly Report

February 2020 – April 2020

Name:	**Jiajun Sun**		
Supervisor(s):	Prof John Holbrey		
Position:	MPhil Student		
Start date:	01/10/2019	Anticipated end date:	30/9/2020
Funding body:	Self-funded		

Gelled Polyaromatic-Functionalised Ionic Liquids as Electrolytes

Background

The ionic liquids are widely studied in the applications of catalysis, solvents and electrolytes. The ionic liquids are called as 'designer solvent'.

Although the properties of the ionic liquids could be designed through adding the functional groups, there are still some controversial properties which are hard to be achieved through the synthesis of specific ionic liquids. Therefore, the ionic liquids mixtures could achieve these potential properties. And there might be some molecular interactions between these ionic liquids like charge-transfer structure or π-π interaction. These interactions may change the viscosity, density and conductivity of the mixtures.

Normally, the binary ionic liquid mixtures are quite ideal mixing. The physical properties of the ionic liquid mixtures are corresponding to the anticipation. There is a little deviation from the anticipating line.

The self-assemble effect is a kind of π-π interaction which is existed in the aromatic ionic liquids with the electron-rich structure like naphthalene rings. It is used in the synthesis of the zeolites[1]. The formation of the larger holes of the zeolite could use this effect.

The charge-transfer complexes are consisted of the electron-withdrawing structures like pyridinium, and imidazolium cation and electron-rich structure like naphthalene. This complex could be different from the ingredients like the UV-Vis absorption[2].

Objective of this work

Synthesize the imidazolium ionic liquids with naphthalene rings. Mix the pyridinium ionic liquids with these imidazolium ionic liquids. According to the self-assemble effect, the complex like charge-transfer complex might be formed. The solid-state of mixtures could be used as the electrolytes or some other applications.

Progress to date

In February, the 1-butyl-3-(2-naphthalenylmethyl) imidazolium bistriflimde was synthesised and characterise the ionic liquid through the NMR. The pure ionic liquid has been made. Otherwise, the 1-methyl-4-cyanopyridnium bistriflimde is also made and the purity of sample is also detected through the NMR. The mixtures of imidazolium ionic liquids and pyridinium ionic liquid. The mole fractions are from 10% to 90%. The DSC and TGA are detected and recorded.

In March, the 1-(2-naphthalenylmethyl)-4-cyanopyridinium bistriflimide and 1-(2-naphthalenylmethyl)-3-cyanopyridinium bistriflimide are made and characterised through the NMR. The mixtures of these two pyridinium ionic liquids and three imidazolium ionic liquids are also formed from 25% to 75%. The UV-Vis absorption of the ionic liquids is detected through the equipment. All ionic liquids are solved in the ethyl acetate. And the self-isolation began because of the COVOID-19.

In April, the academic writing for the thesis and APR have begun with the COVOID-19.

Conclusion

The π-π interactions are existed in 1-(2-naphthalenylmethyl)-4-cyanopyridinium bistriflimide and 1-(2-naphthalenylmethyl)-3-cyanopyridinium bistriflimide through UV-Vis absorption. There is a peak only existing in high concentrations.

The melting points of mixtures can't show any obvious conclusions because there is no trend with the mole fractions change.

Future work

The conductivities of the single ionic liquids and ionic liquids mixtures will be measured through equipment. And make sure whether the linear relationships are existing in the mixtures. And the other physical properties like viscosity and glass transition temperatures will also be detected.

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QUILL Quarterly Report

February 2020 – April 2020

Name:	**Richard Woodfield**		
Supervisor(s):	Dr Stephen Glover, Prof Peter Nockemann and Dr Robert Watson		
Position:	PhD Student		
Start date:	06/2019	Anticipated end date:	12/22
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

A literature review has been performed, and initial flow-battery models have been developed. Flow-battery testing was due to start, though it has been impacted by the current epidemic. This has caused a shift in my work towards more detailed modelling systems, as well as hybrid energy storage system modelling. Once testing is able to resume, the models can be validated and populated with data.

Conclusions and future work

The initial battery/energy storage models will be further developed and validated, then integrated into vehicle models.