QUILL

Quarterly Reports

November 2019 – January 2020

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QUILL Quarterly Report

November 2019 – January 2020

Name:	**Issam Abdalghani**		
Supervisor(s):	Dr Gosia Swadźba-Kwaśny		
Position:	Research Fellow		
Start date:	10 December 2019	Anticipated end date:	9 December 2020
Funding body:	Invest Northern Ireland (Proof of Concept Funding Scheme)		

Chemical Valorisation of the Products of Waste Plastic Pyrolysis to Lubricant Base Oils Using Lewis Acidic Ionic Liquids

Background

Plastic is the largest growing waste stream and is considered as a major issue due to the rise of global production of plastic. While this material is quite resistant to degradation which makes it persist in our environment for a prolonged time. The conversion of waste plastic to high value added products and energy has been investigated and is considered as a promising strategy to be employed for more efficient waste management method. The use of pyrolysis technology, which is a thermal decomposition process of long-chain hydrocarbon molecules (polymer) into smaller units under high temperature conditions (450-800^{0}C) and in the absence of oxygen. Pyrolysis of polyolefin plastics (polyethylene - PE, polypropylene - PP) generates a series of products from solid carbon (char), to volatile hydrocarbons which can condensate as naphtha, fuel and wax, and non-condensable as gaseous fuel.[1-3] Once the plastic is converted to naphtha, then the feedstock can be used for the production of wide range of chemicals. One example of a product that can be generated from this feedstock is the synthetic polyalphaolefins (PAOs), and other, lower grade base oils for automotive lubricants.[4]

Prior work carried out in QUILL, on the synthesis of Lewis acidic catalysts for the synthesis of PAOs from 1-decenem inspired the idea of testing them for mixed olefin feedstock from plastics pyrolysis. The most promising feedstock is the naphta fraction, that has about 50% of 1-olefins, including 13% of 1-decene (Figure 1).

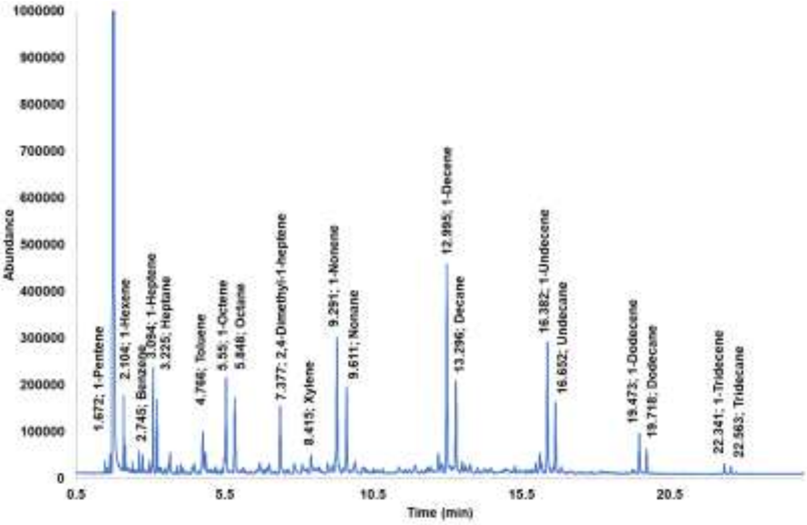

Figure 1 - Gas Chromatography-Mass Spectrometry(GC-MS) of naphtha.

Objective of this work

The investigation of the catalytic activity of a series of Lewis acidic ionic liquids in the oligomerisation of a mixture of olefins present in naphtha as feedstock under optimal reaction conditions. Then based on the results of the reactions, we will develop new catalysts, new ligands and new reaction conditions towards the preparation of the desired PAOs.

Progress to date

During the first two months, I have prepared and characterised several types of Lewis acidic ionic liquids IL such as: chloroaluminate ILs, liquid coordination complexes (LLCs) and borenium ionic liquids as well as being trained on the use of Simulated Distillation Gas Chromatography (SimDist GC) for the characterisation of the products of the oligomerisation reactions(PAOs). In addition, I have tested the catalytic activity of chloroaluminate ionic liquid [C4mim][Al_2Cl_7] for the oligomerisation of 1-decene using schlenck techniques in order to familiarize myself with the oligomerisation reaction and the workup of the crude mixture which was analyzed by SimDist GC.

Conclusions and future work

At the time of writing this report, the battery of reactors that will be used for a complete study of the catalytic activity is undergoing commissioning. I am focusing on the design of new borenium ionic liquids to further progress the development of very active and inexpensive Lewis acidic catalysts. Once reactors are commissioned, I would like to optimise the reaction conditions towards the preparation of the high quality lubricant base oils.

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QUILL Quarterly Report

November 2019 – January 2020

Name:	**Marian Borucki**		
Supervisor(s):	Prof Peter Nockemann, Dr Stephen Glover and Dr Małgorzata Swadźba-Kwaśny		
Position:	PhD Student		
Start date:	January 2018	Anticipated end date:	April 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.

Progress to date

The studied lithium-ion electrochemical cells are a CR2032 coin (button) cell type. The chemistry of a cell is based on graphite anode and $LiNi_{8/10}Mn_{1/10}Co_{1/10}O_2$ (NMC811) as a cathode material, which are coated on the thin foil (~0.01 mm) of copper and alumina current collators, respectively. In the 'commercial' cell setup a supporting electrolyte of 1 M $LiPF_6$ is dissolved in ethylene carbonate (EC) : ethylene methylene carbonate (EMC) as 1:1 molar ratio solution with 2% vol. vinylene carbonate (VC) which is used as film-forming agent. Since the electrolyte is liquid, a polyolefin separator of good ionic conductivity characteristics is needed in order to prevent the short-circuit in event of physical contact of electrodes. The assembly of Li-ion cells are undertaken in glovebox, with inert atmosphere (Ar based) and low concentration of water and oxygen (< 0.1 ppm) due to the use of an organic electrolyte. The 'commercial' lithium-ion cell scheme both as a technical inscription and graphitic representation can be observed in Figure 1.

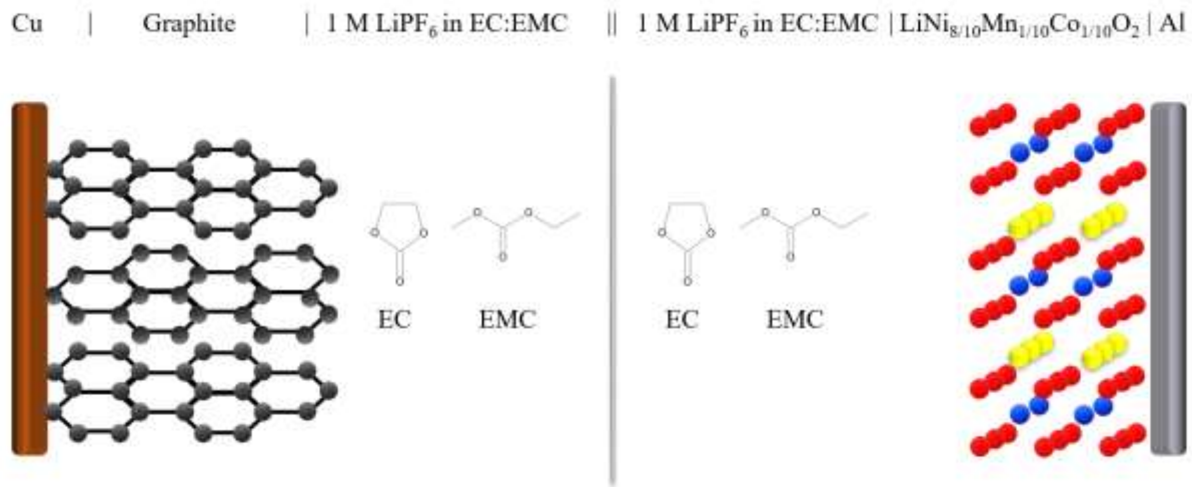


Figure 1 - Lithium-ion cell inscription and scheme.

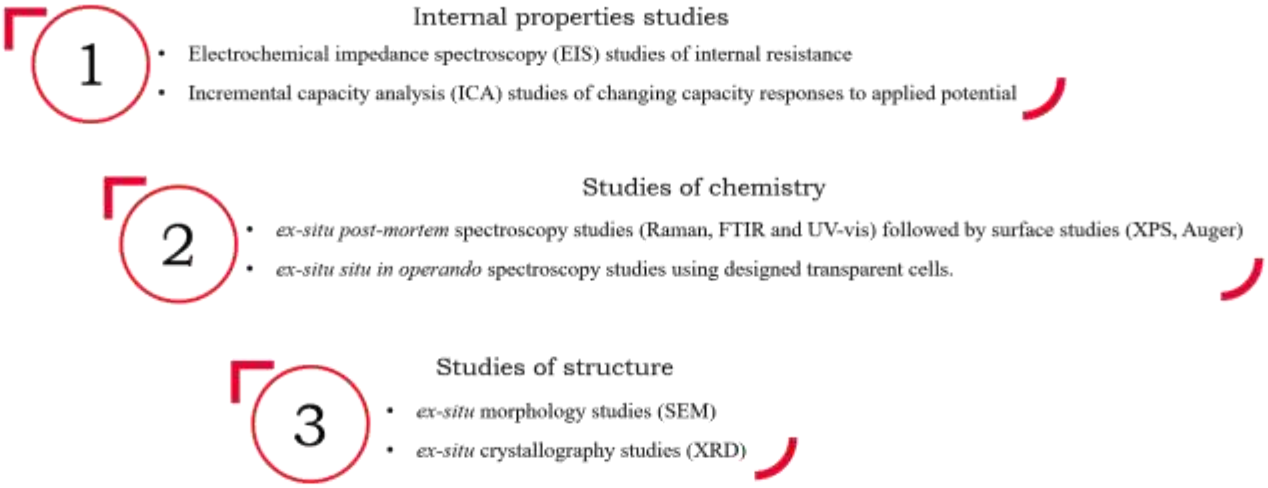
In the above figure, individual parts of the studied cell can be distinguished, from the left to the right: a copper current collector, graphite anode, electrolyte separated by the polyolefin film, NMC811 as cathode material and alumina current collector. All these cell components are arranged in the same pattern inside the studied samples.

Further to the assembly process of lithium-ion batteries, their quality control and testing procedures are implemented. Four procedures can be distinguished, each with different purpose. These procedures are:

a) Three charge-discharge cycles at theoretical 0.1 C current rate – establishing the properties of the cell.
b) Four series of three cycles with varying current rates – studying the cell stability in various current rates.
c) Single discharge with varying current – performing control of the power characteristics of the cell.
d) Dynamic stress testing (DST) cycles – performing the charge/discharge cycles with changing power outputs.

The a), b) and c) procedures are implemented for the purpose of quality control, the samples that do not meet the requirements can be identified and rejected. Due to such approach only the samples that are considered to be stable are further studied according to DST procedure.

As it can be seen on the degradation studies scheme (Figure 2), three types of studies need to be undertaken in order to fully characterise the cell from a chemistry, electrical and material point of view. Firstly, a range of studies that allow to monitor and investigate the change in the electrical properties of the lithium ion cell such as its voltage response to current, power outputs, capacity etc. need to be conducted. Such studies include charge-discharge testing with discharge reference cycles (DRC), electrochemical impedance spectroscopy (EIS), incremental capacity analysis (ICA) and distribution of relaxation times analysis (DRT). A huge advantage of these studies is the fact that they are non-destructive methods. The ICA, EIS and DRT examination of a cell is performed together with dynamic stress testing (DST) procedure at set stages of cell life. The internal properties studied are followed by both studies of chemistry and structure, yet in opposition to electrochemical examination these studies are not only invasive but also are needed to be performed post-mortem, so a disassembly of a lithium-ion cell is needed. The disassembly of a lithium-ion cell is performed at various stages of battery life which corresponds to stages of life when the electrochemical examination taken place. Simultaneously to standard sample ageing a transparent coin cell design of a sample is undertaken in order to perform spectroscopic studies *ex situ, in operando*. Data gathered from the transparent cell spectroscopy studies is due to be collected, analysed and compared to one acquired from standard CR2032 samples.


1

Internal properties studies

- Electrochemical impedance spectroscopy (EIS) studies of internal resistance
- Incremental capacity analysis (ICA) studies of changing capacity responses to applied potential

2

Studies of chemistry

- *ex-situ post-mortem* spectroscopy studies (Raman, FTIR and UV-vis) followed by surface studies (XPS, Auger)
- *ex-situ situ in operando* spectroscopy studies using designed transparent cells.

3

Studies of structure

- *ex-situ* morphology studies (SEM)
- *ex-situ* crystallography studies (XRD)

Figure 2 - Degradation studies scheme.

In a previous report a number of EIS data was described, one that have been collected at different stages of battery life from its initial charging and quality control up to 100 cycles of dynamic stress testing (DRT). Since then a new data points at 250 and 500 DST cycles has been analysed for studied samples. The Nyquist plots taken in different stages of life of a representative sample are shown in Figure 3 A. From the obtained spectra it can be seen that the second semicircle of the sample at initial state was significantly larger than one obtained after 10 cycles of DST performed on the studies sample. However, with further cycling the second semicircle is observed to be growing, which implicate growing value of cell resistance with further cycling. The first semicircle seems to follow the trend of continuous growth as the cell is aged. From the Equivalent circuit model seen at Figure 3 B the obtained semicircles by EIS study can be connected to their respective phases present in the cell. The first semicircle is observed due to the SEI layer formation on the anode surface within the cell whereas the second semicircle could be connected to the charge transfer processes occurring at the electrode surface.

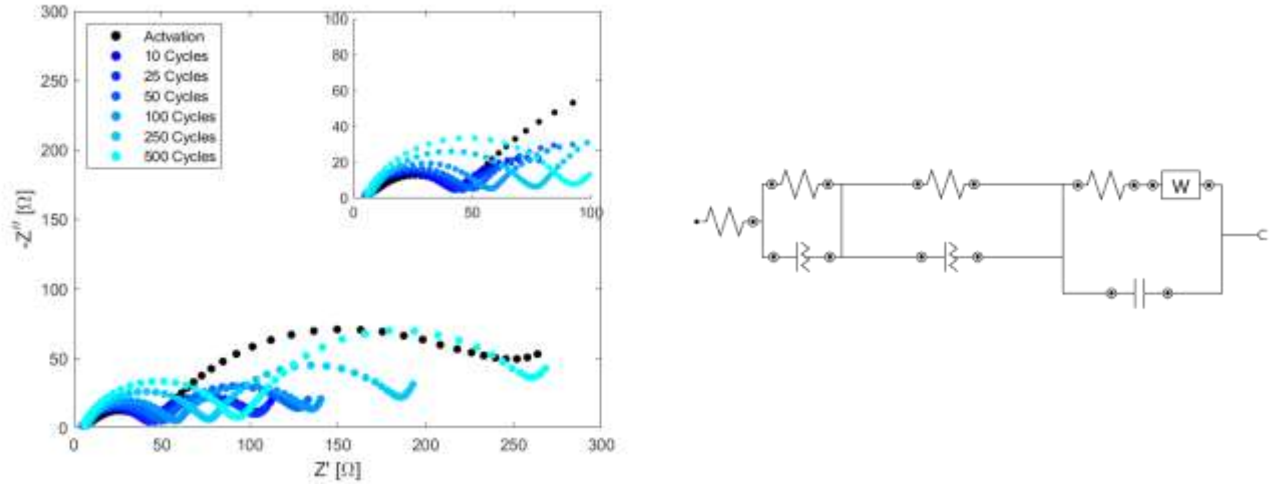


Figure 3 - A) Nyquist plots of the lithium ion cell examined at the begining of life (activation) as well as atfter 10, 25, 50 , 100 , 250 and 500 cycles of life, B) The equivalent circuit of a tested cell obtained from data fitting simullation.

Based on the DRC an ICA has been performed as well as DRT of the obtained EID spectra, yet in order to understand the obtained data fully a further study of half-cells as well symmetrical cells is needed.

A transparent cell has been developed in order to study the changes in cell chemistry by the usage of spectroscopic techniques in order to obtain the *in operando, ex situ* data. In order to create such a cell, a shape for the electrodes has been designed, one that will allow the spectroscopic study of both of them at the same time. The electrode, casing and whole cell design was developed using AutoCad software. What was important in the design process was that the proportions in electrode and electrolyte materials should be kept the same both in the transparent coin cell and standard CR2032 so the data obtained from transparent cell would be comparable to the *post-mortem* analysis. A proper machining method for obtaining such a special electrode shape was investigated and decided to be the laser cutting. In order to properly laser cut the electrodes, the electrode material has been sandwiched between two sheets of 2 mm aluminium with countersunk bolts in it in order to ensure the integrity during the cutting process. Additionally, both electrodes as well as quartz glass have been studied using WiTec Raman confocal microscope. The transparency of the quartz glass of 0.15 mm has been established to be sufficient as no peaks from the quartz glass has been observed on the Raman spectra of electrodes. The conclusion has originated from the fact that the peaks of quartz glass seen at ~900 and ~500 cm^{-1} are not present in the spectra of the electrodes that are covered with the quartz glass material. The obtained Raman spectra are shown at Figure 4. The peaks for graphite electrode are clearly visible at ~1300, ~1600 and ~2700 cm^{-1} corresponding to D, G and 2D bands observe for graphite materials. The peak for the NMC 811 is observed slightly around the value of 500 cm^{-1} of Raman shift. The magnitude of the peak is related to the type of study, as the acquisition times were set to low values (2s whereas one used in literature are set around 3 min) due to the nature of the studies being preliminary.

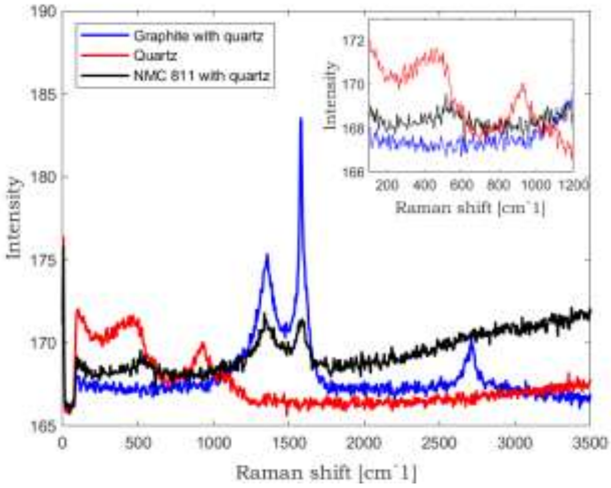


Figure 4 - Raman spectra of quartz glass alone as well as both electrodes covered by the quartz glass.

Conclusions and future work

Conclusions:

- Based on the EIS study and literature review an equivalent circuit model of studied cell has been simulated and fitted to obtained data.
- EIS of the studied cell sample shows continuous steady increase of first semicircle related to SEI growth during cycling of the cell.
- The second semicircle related to charge-transfer processes has been identified to be highly resistive during the battery rating and quality control as the huge impedance drop has been observed after first cycles of battery ageing.
- The individual elements of transparent cell have been designed.
- The quartz glass of thickens of 0.15 mm has been identified to not be interfering with the obtained electrode materials Raman spectrum.

Future work:

- Design and manufacture a swagelok like cell that would allow for symmetric and half cell study.
- Half-cell and symmetric cell studies are needed to be performed in order to fully understand the Ica and DRT analysis of the samples.
- Ageing the lithium ion cells and study their performance by DRC, EIS, Ica and DRT.
- Assembling the transparent coin cell as designed, and further performing *ex situ, in operando* study of lithium ion cell.
- Further studies of new lithium-ion battery electrolytes, focusing on the optimisation of the synthesis.
- Performing studies of promising anode materials.
- Verifying the equivalent circuit model of lithium ion cells by DRT data using the analysis of half- and symmetric cells.

QUILL Quarterly Report

November 2019 – January 2020

Name:	**Dominic Burns**		
Supervisor(s):	Prof John Holbrey and Dr Gosia Swadźba-Kwaśny		
Position:	PhD Student		
Start date:	1 October 2019	Anticipated end date:	31 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 world's drinking water that would be a waste of energy when an acceptable level of purity can be achieved by reverse osmosis.

High sulfate and calcium levels is an issue in many industries, some of which include metallurgy, nuclear waste and mining. Calcium and sulfate cause permanent hardness in water and so can precipitate in pipes causing scaling. Many of these industries must comply with regulated discharge limits on the total dissolved solids or specific limits for sulfate and/or calcium.

Many different approaches to sulfate removal have been developed over the past few decades to address the issues face by industry, these can be divided into three main categories; chemical, physical and biological extraction. As well as advances in these processes, much research has also been done in synthesising molecular chemical receptors for anion recognition and removal.
Many of the methods used to remove sulfate (eg. SAVMIN^{TM} process and ultrafiltration to name a few) are also effective methods to remove calcium ions. Selective extraction of calcium can be difficult because of its similar properties to other metals and so, most of the existing literature describes general metal extraction, which is already a large area for ionic liquid (IL) research.

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. Aisling McGuigan and Dr Syed Nasir Shah had previously worked on removing sulfate using a trihexyltetradecyl-phosphonium chloride IL for QUILL but their results were inconclusive as barium precipitation followed by gravimetric analysis is not a reliable way to quantify the extraction efficiency.

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. Then to design another IL to do the same with calcium cations.

Progress to date

To date, $[P_{66614}]Cl$ has been characterised on its ability to extract sulfate by anion exchange from aqueous solutions in terms of the:

- Initial sulfate concentration
- Phase volume ratio
- Mixing time
- Extraction from model seawater
- Effect of pre-washing the $[P_{66614}]Cl$

Thermodynamic sulfate extractions using ion exchange resins have also been conducted as a comparison and the mutual solubilities of water and $[P_{66614}]Cl$ have been studied.

Conclusions and future work

From the work to date it has been shown that $[P_{66614}]Cl$ can extract up to 81% of sulphate from a 0.025 M solution when stock $[P_{66614}]Cl$ is used in a 2 : 1, water : IL phase weight ratio in one hour. Using water saturated IL, sea water levels of chloride or lower phase volume ratios all reduce the extraction efficiency and it is suspected that acid in the supplied IL is assisting in the extraction.

The problem is that the sulfate has a very large hydration enthalpy of -1080 kJ mol^{-1} compared to chloride at -340 kJ mol^{-1}. Therefore in a 2 : 1 ion exchange, there is a 400 kJ mol^{-1} deficit as sulfate is going into an essentially hydrocarbon environment.

To overcome this, urea based neutral molecular sulfate ligands are going to be synthesised and dissolved in the IL phase to bind to the hydrophilic sulfate via hydrogen bonding in much the same way that ligands are used to assist in the extraction of metals.

QUILL Quarterly Report

November 2019 – March 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)		

Physical Characterisation of Functional Liquids

Background

It is proposed that deep eutectic solvents 'DES' are a chemical component mixture composed of hydrogen bond donors and acceptors which have intermolecular interactions that result in a freezing point which is lower than that of the isolated individual components of the system with no interactions between each other.[1] They are asymmetric species which, due to their orbitals' inability to overlap well and thus, pack into a regular lattice arrangement, have low lattice energy and so do not require a large amount of energy in order to exist as a liquid and as a result tend to have low melting points.

The most common and well renowned DES are those prepared with the combination of organic salts such as choline chloride, which act as a hydrogen bond acceptor and carboxylic acids or alcohols with a hydrogen bond donating role.[2–5] However, these solvents are generally miscible with water and so their application is quite limited. Therefore, work was undertaken by van Osch *et al.* which led to the publication of the first hydrophobic deep eutectic solvent using a carboxylic acid hydrogen bond donor and a long chain quaternary ammonium salt in 2015.[6] In addition to this, DES have since been formed using alcohols and fatty acid hydrogen bond donors in combination with organic salts to form deep eutectic solvents which can be used for extraction of metals[7] and natural products[8,9]. In addition to this, in an attempt to reduce the viscosity associated with these charged DES species, Ribeiro *et al.* developed DES systems using D-menthol and carboxylic acid hydrogen bond donors where the individual components used are non-ionic species.[10] More recently, DES made with the combination of trioctylphosphine oxide (TOPO) and phenol have been published and its use as a uranyl extractant shown.[11]

TOPO has a number of uses such as capping agents[12–16] in nanoparticle synthesis, metals[17,18], organic acids[19–22] and phenolics[23–26] extraction and so a number of DES will be prepared using a range of hydrogen bond donors most suited to the potential application.

Objective of this work

In this work, a route to synthesising sodium silicate without the need for caustic conditions used in industry was proposed using glass cullet from used glass. By providing a mildly basic medium in the form of a χ_{TOPO} = 0.50 TOPO:phenol DES and a cheap source of sodium (i.e. sodium salicylate), the aim was to provide a novel route to synthesise sodium silicate; a widely used industrial feedstock in applications such as production of cement.[27]

Progress to date

A range of preliminary experiments were conducted using different DES components, reaction time and temperature of reaction as illustrated in Table 1 below.

Table 1 - Glass cullet / sodium salicylate experiment variables

	DES used	
	χ_{TOPO} = 0.50 TOPO:phenol	χ_{TOPO} = 0.50 TOPO:salicylic acid
Temperature / °C	50	50
	80	
	100	
Time / h	24	24
	96	

In the interest of length, the results discussed will focus on a χ_{TOPO} = 0.50 TOPO:phenol DES with varying reaction time. Glass cullet, excess sodium salicylate and χ_{TOPO} = 0.50 TOPO:phenol were added together in a sealed pressure tube, stirred at 500 rpm and heated to 100 °C for either 24 or 96 hours. The resulting solid was separated from the liquid eutectic phase via centrifugation, washed with absolute ethanol and placed in an oven at 80 °C overnight to remove residual ethanol. Solid phases were analysed using XRD and XRF while liquid phases were analysed with NMR and XRF.

Initially, samples were heated at 100 °C for 24 hours, the XRD and XRF results of the solid phase analysis are shown in Figure 5 and Table 2 respectively below.

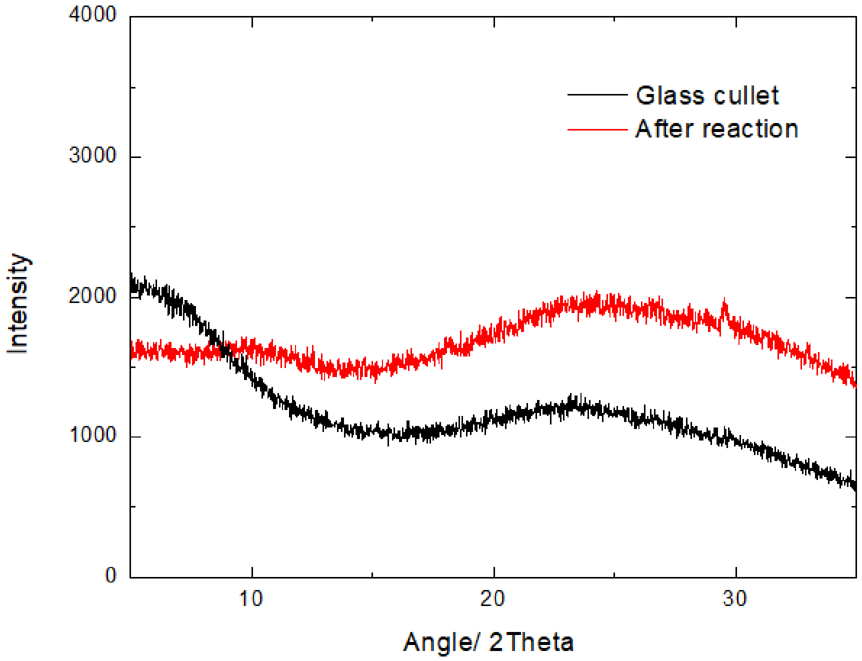


Figure 5 - XRD of glass cullet and the ethanol washed solid present after reaction. Reaction conditions: sealed pressure tube, 100 °C, 24 h, 500 rpm

Results from XRD analysis indicate the presence of a broad peak centred around 2θ = 25 ° and is indicative of an amorphous material. This is also shown in the XRD of glass cullet which suggests that the solid present after reaction is unreacted glass cullet. In addition to this, XRF analysis shows that the Si:Na ratio in glass cullet is ~2.6. This ratio is approximately constant after reaction at ~2.4 and therefore indicates that no reaction has taken place and that the isolated solid is unreacted glass cullet.

Table 2 - Composition of glass cullet before and solid isolated after reaction. Reaction conditions: sealed pressure tube, 100 C, 24 h, 500 rpm

	Mass %	
Element	Before	After
Si	33	21
O	45	65
Na	13	9

There is a larger mass % of O present in the sample after reaction, however, it is thought that this is due to unevaporated ethanol used to wash the solid still present.

Analysis of the liquid phase was done using NMR and XRF and the results are shown in Figure 6 below.

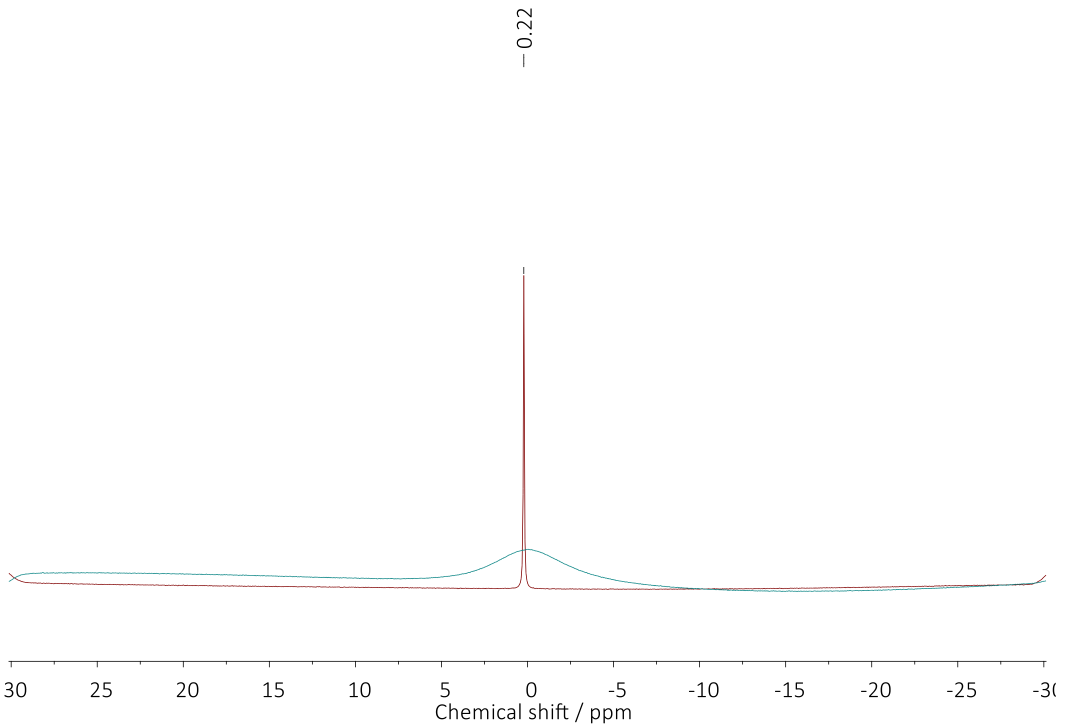


Figure 6 - Blue line: ^{23}Na NMR of χ_{TOPO} = 0.50 TOPO:phenol liquid phase after reaction. Red line: 0.1 M NaCl in D_2O standard. Reaction conditions: sealed pressure tube, 100 C, 24 h, 500 rpm.

NMR spectroscopy showed the presence of a small hump in the ^{23}Na spectrum, however, this was not a sharp peak characteristic of ^{23}Na. XRF analysis of the liquid phase also showed a presence of 7% phosphorus, but 0% sodium present. Therefore, it is not thought that sodium dissolved into the eutectic in this case.

As a result, the time for reaction was increased from 24 h to 96 h and ethanol used to wash the isolated solid phase was dried using 3 Å molecular sieves activated in a furnace. Analysis of the solid phase is shown in Figure 3 below.

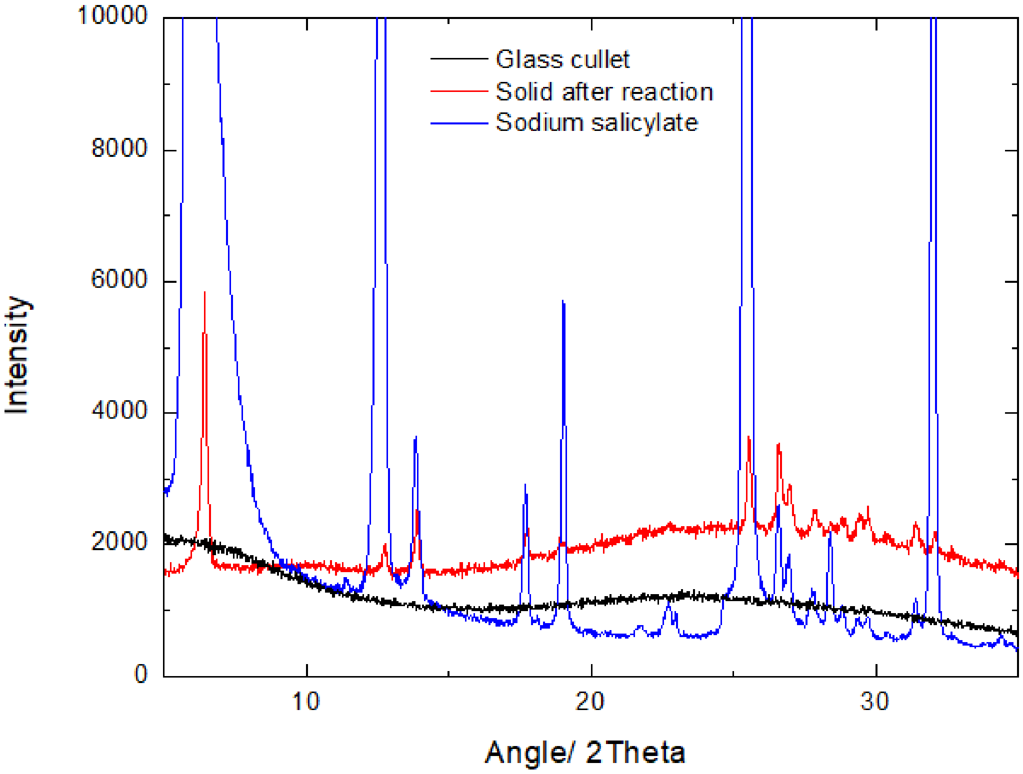


Figure 7 - XRD of glass cullet (black line), sodium salicylate (blue line) and the ethanol washed solid (red line) present after reaction. Reaction conditions: sealed pressure tube, 100 °C, 96 h, 500 rpm

Similar to results shown in Figure 5, there is a broad peak indicative of amorphous materials present centred around 2θ = 25 ° as shown by glass cullet (black line). There are however, the presence of small peaks across the 2θ range shown. As shown by the XRD of sodium salicylate (blue line), these peaks correspond to sodium salicylate present in the sample which have not been washed away by ethanol and are not indicative of sodium metasilicate crystals as hoped. In addition to this, XRF analysis shown in Table 3 indicates that the Si:Na ratio in glass cullet is ~2.6. This ratio is approximately constant after reaction at ~2.0 and does not correspond to Na_2SiO_3, therefore indicating that no reaction has taken place and that the isolated solid is unreacted glass cullet.

Table 3 - Composition of glass cullet before and solid isolated after reaction. Reaction conditions: sealed pressure tube, 100 C, 96 h, 500 rpm

	Mass %	
Element	Before	After
Si	33	27
O	45	52
Na	13	13

Again, the larger mass % of O present in the sample after reaction is thought to be due to unevaporated ethanol used to wash the solid still present.

Analysis of the liquid phase was done using NMR and XRF and the results are shown in Figure 8 below.

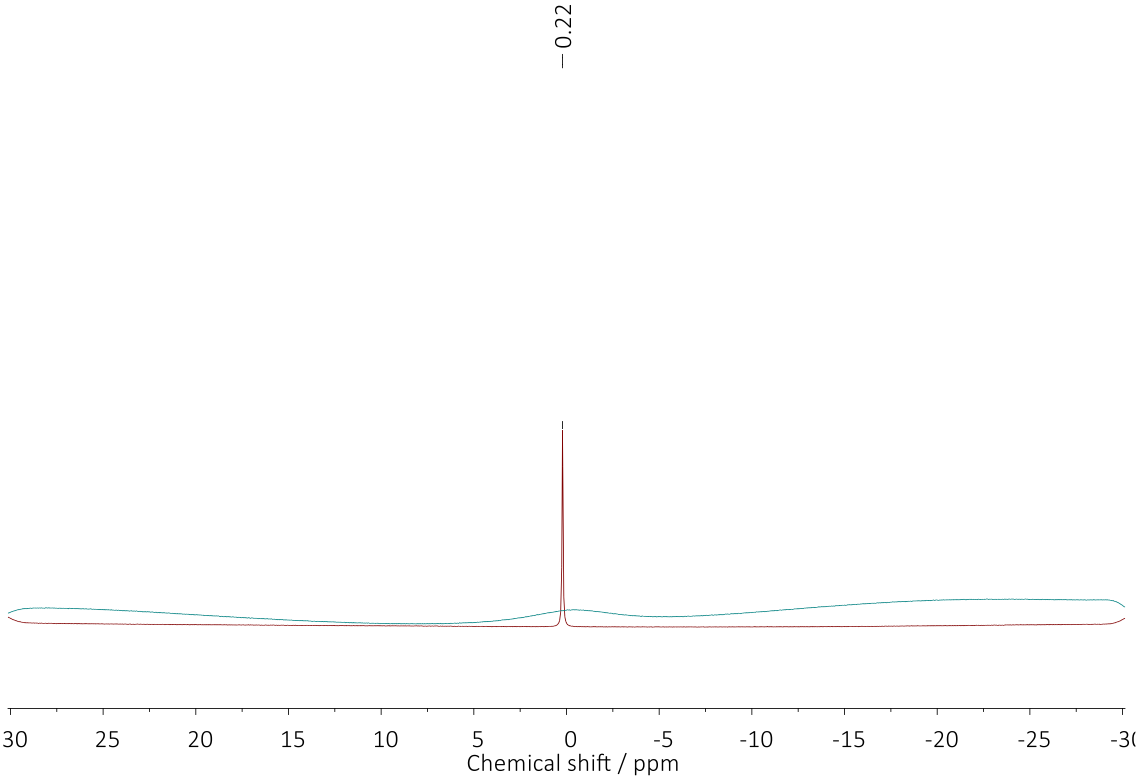


Figure 8 - Blue line: ^{23}Na NMR of χ_{TOPO} = 0.50 TOPO:phenol liquid phase after reaction. Red line: 0.1 M NaCl in D_2O standard. Reaction conditions: sealed pressure tube, 100 C, 96 h, 500 rpm.

NMR analysis did not indicate the presence of sodium in the liquid phase. In addition, XRF analysis of liquid phase showed 7% phosphorus, but 0% sodium present therefore showing that no sodium had been dissolved into the χ_{TOPO} = 0.50 TOPO:phenol liquid phase and that the reaction has been unsuccessful.

Conclusions and future work

To conclude, analysis of the solid phase isolated after reaction by XRD analysis indicated the presence of an amorphous material in both 24 and 96 h reaction times; attributed to unreacted glass cullet. XRF also highlighted that the Si:Na ratio in solids measured before (*i.e.* ~2.6) and after reaction (*i.e.* ~2.4 and ~2.0) were approximately equal and therefore did not indicate the presence of Na_2SiO_3 by a reduction in the Si:Na ratio (*i.e.* 0.5).

Analysis of the liquid phase isolated after reaction by NMR did not indicate any sharp peaks indicative of ^{23}Na NMR spectroscopy, despite a small hump present in the NMR spectrum after the 24 h reaction. In addition to this, XRF analysis indicated that there was no sodium present in the eutectic phase after reaction highlighting that no sodium from sodium salicylate has dissolved in the eutectic liquid phase. Although sodium does not have a strong x-ray absorbance using XRF analysis, the presence of an excess of sodium salicylate compared to glass cullet in the reaction mixture, it is thought that had sodium been dissolved; it would be detected to some extent.

Future work will include taking a different approach to research conducted in this area as reactions to produce sodium silicate have been unsuccessful.

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QUILL Quarterly Report

November 2019 – January 2020

Name:	**Andrew Forde**		
Supervisor(s):	Dr Stephen Glover, Dr Rob Watson and Prof Peter Nockemann		
Position:	PhD Student		
Start date:	3 June 2019	Anticipated end date:	3 December 2022
Funding body:	Horiba-MIRA & EPSRC		

Battery Thermal Management and Algorithmic 3D Temperature Prediction

Background

As governments across the world attempt to address the issues posed by climate change, electrification of vehicles has been identified as a key area of focus. This has led to new legislation with the aim of accelerating development and public uptake of electric vehicles (EVs). It is commonly observed that the main barriers to public uptake are performance and price of EVs, both of which are extremely dependent on the battery of the vehicle, which makes up over half of the total vehicle cost [1]. Development of battery technology is therefore vitally important in producing EVs which can compete with current internal combustion engine vehicles.

The performance, safety, and lifespan of batteries is highly dependent on battery temperature. Temperature management is therefore critical if optimised performance and safety of lithium-ion batteries is desired. Batteries are currently monitored using external thermocouple sensors which take measurements at either a cell or pack level, with many EVs containing only three or four thermocouples for thermal management of hundreds of cells. This method is not indicative of the temperature of active materials in the cell as thermal gradients within the jelly roll can arise due to internal heating, battery cooling/heating systems, and thermal inertia. A temperature difference of 4.7 °C has been observed for small pouch cells using no active cooling [2], which leads to a difference in battery reaction kinetics, k, of 37.8% according to Arrhenius law [3]. This temperature difference also becomes significant when considering the narrow optimal temperature range for lithium-ion batteries. Thermal gradients may be greater when using more complex cooling methods, such as phase change material, which can incite a difference of $T > 14$ °C ($k = 152.4\%$) [4]. Effective battery thermal management will therefore play a large role in enabling new battery technologies, such as self-heating batteries and extreme fast charging [5], to become viable.

In order to reliably monitor a cell, the accurate temperature of the active materials should be known. Therefore, accurate estimation of internal temperature is essential for an optimised battery. Existing methods often involve optical sensors which, while providing precise measurements, require specialist equipment to operate and are restrictive in their suitable areas of placement [6][7][8]. These methods require heavy modification of the cell casing, which would not be desired in commercial application. Structural modifications are also often required, such as the addition of extra separator layers during cell manufacture, therefore performance may deviate from the standard cell design.

Little work has been carried out on instrumentation of prismatic type cells, with most work of this type being focussed on cylindrical and pouch cells. Therefore, current work on thermal management of prismatic cells focuses on bulk thermal properties or the use of thermal imaging of the cell surface, both of which assume that the cell exhibits some degree of homogeneous behaviour across its volume. As homogeneous thermal behaviour across electrodes reduces with larger format cells, this assumption is becoming less valid with the increase in capacity of prismatic EV cells [9].

A method for predicting internal temperatures within a prismatic lithium-ion cell is therefore required for development of future battery technology. By increasing the understanding of temperature distribution within the cell, performance can be further optimised while ensuring the cells are kept within a safe temperature range.

Objective of this work

The aim of this research is to produce an algorithm for 3D temperature prediction in a lithium-ion cell which can be integrated with a Horiba-MIRA battery management system for automotive application. This aims to provide a more effective technique for battery management, improving both performance and lifetime of EV batteries.

Progress to date

To date, an initial literature review has been completed, investigating the state-of-the-art in topics relevant to this project.

CT scan data of prismatic cells has been converted to 3D models, allowing for a better understanding of battery internal structures. This has also allowed for development of a simplified 3D model to be used for testing of battery instrumentation equipment. Using an accurate model of the chosen battery allows for accuracy and repeatability testing of equipment in real-life scenarios, giving an accurate indication as to the suitability of the equipment.

Two preliminary models have been developed. First, an equivalent-circuit model (ECM) was developed as this is a standard efficient model commonly used in both academia and industry. A preliminary numerical model was then developed using the Fortran 90 language. This is a coupled electrical-thermal model which observes the battery thermal reaction to an applied current cycle. The ECM treats the cell as a lumped system, giving a 1-D output. Whereas the numerical model uses the finite difference method to investigate heat diffusion throughout the volume of the cell, treating the jelly roll as a stack of planar layers of the active materials. Results of the numerical model are shown in Figure 1 for a constant discharge of 0.5C with no active cooling. This model can then be used to simulate a battery response and the ECM model can be run using the same inputs to compare accuracy and efficiency between modelling methods.

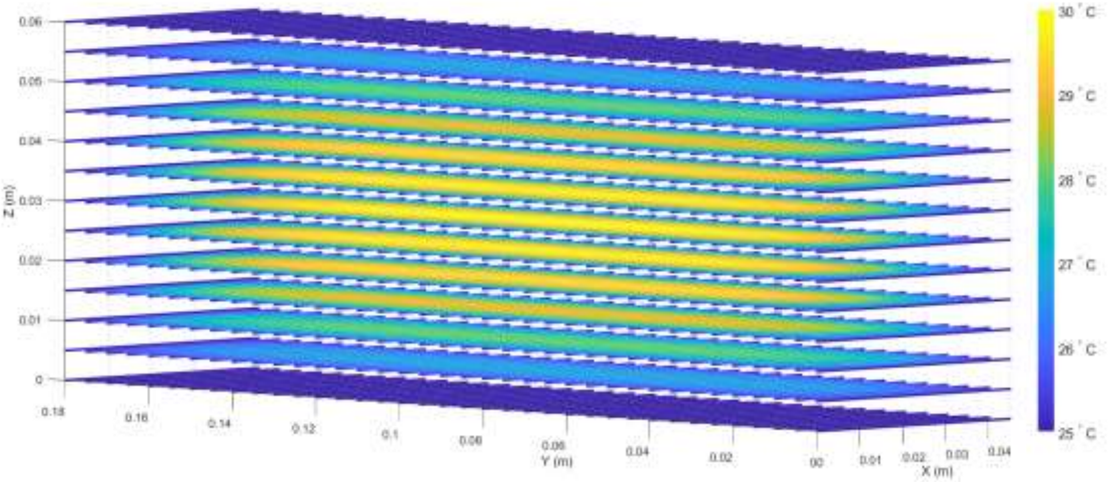

Figure 1 - Results of numerical model (0.5C discharge for 30 minutes)

Development of a process for battery cell instrumentation has been planned. Equipment for this process has been identified and procured. This equipment is currently being tested using a 3D printed model of the chosen prismatic cell. This will provide an indication of the suitability of the equipment for this process. The process will include using a CNC machine to drill holes in pre-defined locations, after which, a robotic arm will be used to place thermocouples in the folds of the jelly rolls. This will allow for accurate temperature measurement of the active materials within the cell and how they relate to the external temperature measurements taken by battery management systems. This will be carried out in an inert environment using a glovebox as shown in Figure 2.

Figure 2 - Diagram of equipment arrangement

Conclusions and future work

Two preliminary models have been developed. Instrumentation of a prismatic battery cell has been planned and equipment has been secured. When instrumentation has been successfully carried out this will serve as a method for tuning and validation of the models.

Future development of the numerical model involves investigating novel methods for modelling prismatic cells. This includes investigating how the folds of the jelly roll are to be modelled, as these are commonly ignored in literature. Another future development is the inclusion of machine learning to create an efficient and accurate model which can incorporate battery ageing effects.

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QUILL Quarterly Report

November 2019 – January 2020

Name:	**Oisin Hamill**		
Supervisor(s):	Dr Nancy Artioli and Prof Alex Goguet		
Position:	PhD Student		
Start date:	1 October 2019	Anticipated end date:	30 September 2022
Funding body:	EPSRC		

Mechanism Understanding of NOx Storage, Release and Reduction on Pt/Doped Ceria Catalysts

Background

Due to the strengthening emission legislation both in Europe and North America, there is a need for further optimisation of existing emission after-treatment catalytic converters for automotive applications. 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 which shows marked structure sensitive properties that can be assessed through shape-controlled synthesis. It possesses high oxygen storage capacity (OSC), a unique redox property by the cycle of Ce4+/Ce3+ redox pairs and it can be further enhanced through using dopants. Platinum supported on doped ceria can show enhanced NOx storage at low temperature, as reported in the literature, together with an improved carbon monoxide/hydrocarbon light off. [1] It is not clear whether this is due to the presence of a higher number of active sites (dopants create a more favourable environment for NOx storage), same number of sites but intrinsically more active, or enhanced NO oxidation activity (rate determining step).

It has been proposed that the dopants 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 NOx storage.
Studies also suggest that the purge efficiency of doped systems can be lower compared to the un-doped catalyst. [2] This may be related to the different surface intermediate species observed during preliminary NOx storage and IR experiments. However, it is unknown how this relates to the presence of dopants (modification of the rate of redox reaction, different electronic environment which allows stronger NOx adsorption).

Additionally, presence of dopants can reportedly modify the platinum reducibility and platinum-ceria interaction, allowing more readily activation during rich purge. [3]

This project aims to better understand the NOx storage mechanism on the doped materials and give new insights into the activation/lean deactivation mechanisms in the presence of different dopants.

This will involve different techniques to characterise the catalyst (in-situ TEM, EXAFS, IR) and study its reactivity. Reactivity studies will involve using transient and space-resolved techniques.

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Objective of this work

- Improve the understanding of NOx storage mechanism together with the mechanism of rich purge on ceria supported Pt.
- Gain more knowledge of the rich activation/lean deactivation mechanisms.
- Determine the structure of the active sites under reaction conditions and differentiate between active species and spectators by transient methods.
- Development of a global kinetic model.

Progress to date

Some initial characterisations completed.
Characterisations completed include: XRD, XRF, SEM, ICP, BET
Characterisations in progress include: TPR
Gas cylinders attached to inlet lines and safety & handling course completed.
Automated switching valve which is used to switch and control lean and rich condition switching times is now built and fully operational.
Testing rig built and now functional and fit for purpose.
Initial lean/rich cyclic testing began (no meaningful results yet).

Conclusions and future work

Catalysts partly characterised and testing equipment now fully ready for use.

Future work to include:
Completion of TPR characterisations on all catalysts.
Completion of Lean/Rich cyclic testing on all catalysts.
Attend Johnson Matthey Academic Conference (JMAC) – March/April 2020 and present poster.

QUILL Quarterly Report

November 2019 – January 2020

Name:	**Jerry Pui Ho Li**		
Supervisor(s):	Dr Nancy Artioli and Prof Peter Nockemann		
Position:	Research Fellow		
Start date:	9 December 2019	Anticipated end date:	8 December 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 in to 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

The majority of the time upon contract start, involved repair and maintenance work of a key reaction setup. The setup has been restored and upgraded, and is now in operation. With the system in operation, guidance is 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 resu

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.

As the 1st quarter report for the INI funding is due, a commercialisation roadmap and business canvas was drawn up, along with making arrangements for the tradeshows and conferences to be attended in the near future.

In further unrelated work, a publication submitted prior to QUB starting period was accepted. As of the time of this report, a DOI has not been assigned. In addition, various training courses have been undertaken (Safety, solvent waste disposal, compressed gases, liquid nitrogen, and in addition all compulsory online courses QUB staff is required to take).

Conclusions and future work

At the time of this report, there are no results beyond the successful synthesis of the catalyst benchmarks. The repaired and upgraded reactor system is currently in operation.

Plans have been made to build a completely separate instrument setup that is dedicated solely to the current project at hand. Thus far space has been assigned but no further update. A specialist is on-call to setup the apparatus whenever the space is ready.

As soon as the chemicals arrive, WP1 can fully begin. There are also plans to optimise the process, involving a design of a home-made electromagnet. The synthesis methodology for the catalyst samples are straight-forward, but there is sample loss in the separation process. However, it is noted that the sample is also magnetic. A design and build of a benchtop electromagnet will allow for ease of product separation.

There is also an abstract submission deadline for a conference in September. Thus, there is an aim towards obtaining some preliminary results of which to build an abstract around.

QUILL Quarterly Report

November 2019 – January 2020

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

Chemisorbent Material for Olefin and Paraffin Separation

Background

Propylene plays a vital part in day to day life, a major portion going towards polypropylene (67%).[1] Polypropylene is for plastic parts (toys to automobile products), reusable products (Containers), technology (loudspeakers), and laboratory equipment. Other uses for propylene include:

- Propenoic acid (5%) which is used for acrylic polymers, present in cosmetic material.
- Propenonitrile (6%) is used for fabrics and carpets.
- Cumene (4%) used to make phenol and acetone.
- Epoxypropane (7%) used for the manufacture of polyurethanes.
- Butanol (3%) used as a solvent for surface coatings.

Ethylene also plays a key role, a major portion of produced ethylene going towards polyethylene (60%).[2] Polyethylene can be used for food packaging, waste bins, transportation pipes (*e.g.* for carrying liquid), and fuel tanks. Other uses include:

- Polyvinyl chloride (PVC) (11%) is used for pipes, and electric cables. Also, many buildings use PVC including the guttering system.
- Polyphenylethane (5%), better known as polystyrene, is used for food packaging, domestic appliances, consumer electronics, and construction.
- Ethylene Oxide (16%) is used to produce ethane-1,2-diol (used for de-icing aircraft prior to take off), and healthcare sterilant.

These gases are mainly sourced from crude oil, and natural gas, thermally cracked down into lighter olefins. This thermal process produces hydrocarbon mixtures that require separation and purification before further application.

To date the current industrial method for separating olefin and paraffin mixtures is cryogenic distillation.[5] This separation process is currently one of the most energy intensive processes but it is necessary due to the similar chemical properties of olefins and paraffins (similar boiling point). As of 1991, the total estimated energy required for cryogenic distillation was 10^{15} BTU (British thermal units), 9 times more than the total energy requirements for the UK population in 1991. Thus, with an ever-growing goal of greener technology while sustaining our demand for propylene and ethylene there is a desire to reduce this energy consumption. The motive behind my work shall be converting from an energy dominant separation to a mass dominant separation.

Previous studies have included:

- Metal-organic-frameworks (MOFs) can exhibit distinctly high adsorption capacity, and preferential binding affinity for ethylene over ethane.[9] However, using MOFs in harsher conditions do produce challenges including thermal, and mechanical stabilities.[11]
- Membranes have also been discussed as a potential use.[12] Membranes do have low operating costs, but also have low permeabilities, and selectivities.
- The addition of transition metals such as copper and silver have shown the ability to complex with the olefin (the pi-bond in olefin allowing the bond to form whereas paraffin doesn't contain the pi-bond).[10]
- Ionic liquids are also a key interest, and will be the initial focus of my work, for olefin and paraffin separation. Generally ionic liquids have been noted to have negligible vapour pressure, and high thermal stability.[8] Ionic liquids can be further enhanced and are relatively easy to functionalise to increase chemisorbent ability.

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

- Initial review, and literature review preparation fully underway.
- Construction of the equipment already arrived.

Conclusions and future work

The current outcome is gaining knowledge on the field and proposing ideas forward. Further work on the literature review to be completed, and further experimental preparation.

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QUILL Quarterly Report

August 2019 – October 2019

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

Ionic liquids such as [$P_{6,6,6,14}$] [$N(CN)_2$] and [$P_{6,6,6,14}$] [NTF_2] have been produced using literature and characterised using NMR ^{1}H, TGA and DSC. They were found to be produced correctly. Calibration curves using GC-FID with internal standard have been produced to analyse the reaction at different time intervals. The calibration curves which have been produced were octanoic acid, octan-1-ol, n-octane and octanal.

The first reaction will involve [$P_{6,6,6,14}$] [$N(CN)_2$], sodium borohydride solution and octanoic acid. The reaction was left to stir in glass reactor at 25 Deg C for 2 Hours. After this time, the mixture products are extracted using dibutyl ether and analysed using GC-FID.

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. Investigate the cascade reaction by taking the aldehyde and alcohol and subject them to the hydrogenation in the same way.

QUILL Quarterly Report

November 2019 – January 2020

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

Main Group Catalysis in Ionic Liquids

Background

The first strongly Lewis acidic borenium ionic liquids of the general formula $[BCl_2L][M_2Cl_7]$ (Figure 1, left),[1] were reported by the Swadźba-Kwaśny group in 2015. These were shown to be very powerful Lewis acidic catalysts;[2,3] however, their applications are hindered by several factors. The high chloride content resulted in issues with corrosion. Furthermore, in combination with the chlorometallate anion these ILs can have multiple Lewis acidic sites, which limits control over reactivity and becomes a challenge in designing specific catalytic applications.

The second generation of borenium ionic liquids was subsequently developed to address these issues. These systems maintain strong Lewis acidity, while being chloride-free and featuring one, well-defined Lewis acidic centre, located in the cation. This was achieved by introducing a catechol ligand to the boron centre to form adducts of the general formula [B(Catechol)LCl] (Figure 1, middle), which could then be converted to ionic liquids with bistriflimide anion (Figure 1 right).

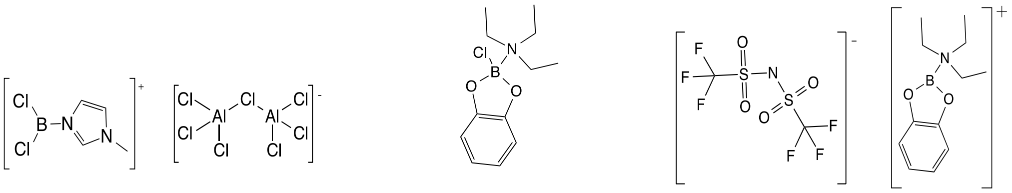


Figure 1 - (left) 1st generation borenium ILs, (centre) boron complex precursor, (right) 2nd generation borenium ILs.

Applications of these new ionic liquids were inspired by the flourishing field of frustrated Lewis pairs (FLPs), which enable metal-free activation of small molecules, in particular metal-free hydrogen splitting.[4] When borenium ionic liquids were combined with equimolar quantities of the sterically-hindered phosphine, such as P^tBu_3, coordinationally saturated boronium ionic liquid were generated, such as $[B(cat)(P_{888})(P^tBu_3)][NTf_2]$ (Figure 2). Owing to the very weak bond between boron and phosphorus in P^tBu_3, such ionic liquids were capable of acting as a latent FLP and activating hydrogen (Figure 2). This is the first frustrated Lewis pair ionic liquid (FLP-IL) reported.

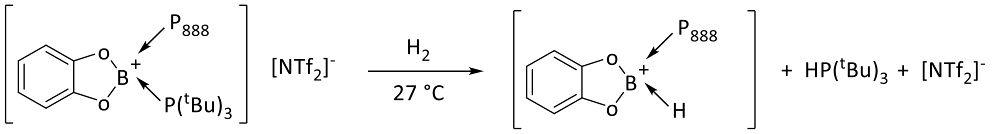
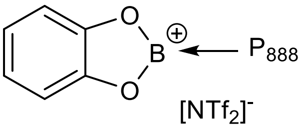


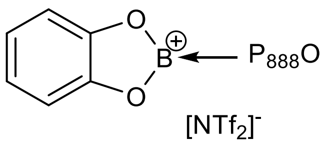
Figure 2 - Hydrogen activation using the boronium ionic liquid, $[B(cat)(P_{888})(P^tBu_3)][NTf_2]$.

Objective of this work
To identify new cations that can be used in FLP chemistry and test their catalytic activity. In order to test their catalytic activity, the goal is to design a set up capable of bubbling gas through ionic liquids, with the results analysed by NMR spectroscopy.

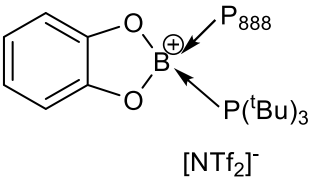
Progress to date
Synthesis and characterisation of four ionic liquids – Bcat$[P_{888}][NTf_2]$, Bcat$[P_{888}O][NTf_2]$, Bcat$[P_{888}][NTf_2]$ with 1 eq. of $P(^tBu)_3$ and Bcat$[P_{888}O][NTf_2]$ with 1 eq. of $P(^tBu)_3$. These ionic liquids were characterised by NMR, TGA and DSC.



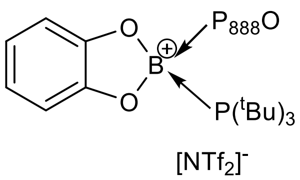
Bcat$[P_{888}][NTf_2]$



Bcat$[P_{888}O][NTf_2]$



Bcat$[P_{888}][NTf_2]$ with 1 eq. of $P(^tBu)_3$



Bcat$[P_{888}O][NTf_2]$ with 1 eq. of $P(^tBu)_3$

I attended the disordered materials user group meeting and data analysis workshop where I got the opportunity to learn about new features available in EPSR26, as well as its new graphical user interface. I also tried out their new analysis package dissolve. This training will aid me in analysing my neutron scattering results from June 2019, as well as previous data reported by the group and data analysis for future experiments.

I have also been researching new cations that can be used in FLP chemistry. Furthermore, I am designing a new set up which can be used to test the catalytic activity of these FLP ionic liquids. The plan is to bubble gas directly through the ionic liquid and monitor the reaction by NMR spectroscopy. Both hydrogenation and dehydrogenation will be performed to see whether the H_2 can be removed from the system under vacuum with or without heating to establish the reversibility of this reaction. If the H_2 is removable that would suggest the potential for their use as a catalyst to reduction reactions. Furthermore, the activation of other small molecules will be investigated.

Conclusions and future work
Future work involves analysing neutron scattering data from experiments performed at ISIS in June. Also, to continue to investigate new cations that can be used in FLP chemistry. The goal is to finalise the design and start to build a setup which enables bubbling of gas into ionic liquids and then test their catalytic activity. An upcoming exciting project involves investigating the electronic structure of boron-based compounds in solution measured by liquid jet photoelectron spectroscopy. These experiments will be performed using the soft x-ray synchrotron in Berlin,

known as Bessy II, in April. The aim is to gain a better understanding of how the electronic structure of boron-based species relate to chemical reactivity which will help aid the design of new boron based catalytic systems. In February I will visit the site to learn more about the technique, the requirements and preparation of the samples.

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1 S. Coffie, J. M. Hogg, L. Cailler, A. Ferrer-Ugalde, R. W. Murphy, J. D. Holbrey, F. Coleman and M. Swadźba-Kwašny, *Angew. Chemie - Int. Ed.*, 2015, **54**, 14970–14973.

2 K. Matuszek, S. Coffie, A. Chrobok and M. Swadźba-Kwaśny, *Catal. Sci. Technol.*, 2017, **7**, 1045–1049.

3 J. M. Hogg, A. Ferrer-Ugalde, F. Coleman and M. Swadźba-Kwaśny, *ACS Sustain. Chem. Eng.*, 2019, **7**, 15044–15052.

4 D. W. Stephan and G. Erker, *Angew. Chemie - Int. Ed.*, 2010, **49**, 46–76.

5 L. C. Brown, A. McGrogan, R. O’Donnell, N. Artioli, J. D. Holbrey and M. Swadźba-Kwaśny, in preparation.

QUILL Quarterly Report

November 2019 – January 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

Background

As fossil fuel supplies dwindle and the climate change problem escalates, the need to harness renewable energy resources increases. However, these energy sources are intermittent and unpredictable, making them difficult to be used in a safe and stable power grid. For this reason, it is important that new energy storage technologies are developed which can shift energy from off-peak demand times to peak demand times. One of the most promising emerging technologies is the Redox Flow battery.

In Redox Flow Batteries, Redox couples are dissolved in electrolyte solutions and stored in separate reservoir tanks. During charge and discharge these electrolytes are pumped from reservoir tanks into half cells where they react in an electrode, either consuming or generating electrons.

This working principle gives rise to a number of key advantages over other conventional battery technologies. In Flow Batteries, power and energy is decoupled; power is controlled by the stack effectiveness whilst energy is stored in the electrolyte reservoir tanks. This makes RFBs highly customisable, allowing them to be tailored to meet the demands of various power grids. They also have a long working life; with the electrolytes stored in separate tanks, the electrodes don't undergo complex redox reactions and experience less structural changes and strain than those found in conventional batteries. One drawback of Redox Flow Batteries however is their low energy density when compared to other energy storage technologies.

Improving the energy density, energy storage efficiency and sustainability could make Redox Flow Batteries an even more promising candidate for large scale energy storage applications. This could also potentially provide a solution in reducing inevitable costs that will occur when implementing a new energy storage technology.

One method of improving the energy density of Redox Flow Batteries is designing better performing flow fields, manifolds and cell topologies resulting in a better performing cell stack.

Objective of this work

This project is focused on the investigation into increased performance and efficiency of redox flow batteries by improving their energy density. This will be achieved by investigating new novel flow field/ manifold designs and various cell topologies. CFD (Computational Fluid Dynamics) and Multiphysics modelling will be used to drive cell design and 3d printing will be used to rapid prototype flow cells to test at QUILL.

Progress to date

A thorough literature review has been carried out with a particular focus on work detailing the development and evaluation of high-performance cell designs. Furthermore, as I come from a Mechanical Engineering background and the field of Redox Flow Batteries falls at a crossroads between Chemistry and Chemical, Mechanical and Electrical Engineering, substantial time has been spent developing my understanding of these other disciplines and how they relate to Redox Flow Battery Technology. A number of promising avenues for future research have been identified such as the development of Flow Cells with novel manifold and flow field topologies and development of 3d printing technologies.

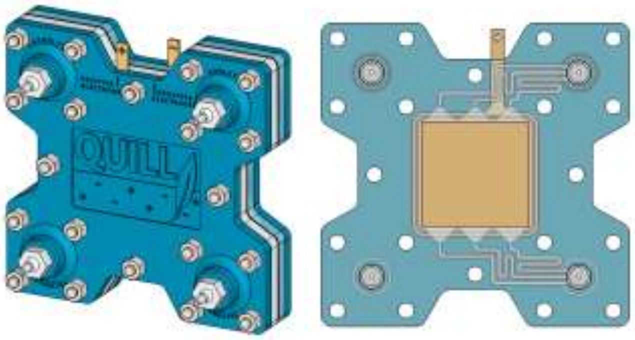


Figure 1 - 3d Printable Lab Scale Test Cell

Our own 3d printer has been procured and is operational in the Battery Lab in QUILL. Extensive work has been carried out utilising FDM (Fused Deposition Modelling) 3d printing to develop a fully 3d printed lab scale flow battery test cell. Optimal print settings for flow cell production and most suitable materials for electrolyte compatibility have been identified and tested thoroughly to ensure adequate sealing of the battery to prevent electrolyte leakage. Different novel cell designs have been drawn up, some of which have been manufactured and evaluated in the Battery Lab in QUILL. Novel designs such as an “all in one” and “stackable” lab scale flow cell and low material costs show great promise in providing researchers with a more accessible and affordable lab scale test cell with a design that is easier to use than existing test cells.

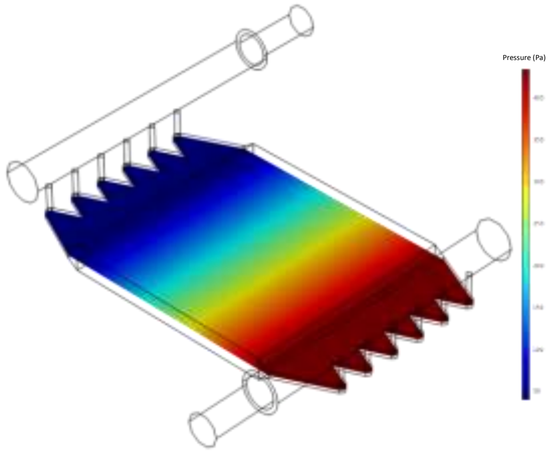


Figure 2 - CFD showing pressure distribution in Half Cell

In tandem with the ongoing cell production a Multiphysics model coupling CFD (computational fluid dynamics) and an Electrochemical Model is being developed with the end goal of evaluating and optimising the performance of new flow cell designs. The model is being validated from existing models in literature and will be compared to test results obtained in the Battery Lab in the near future. The results from these simulations should also help develop a better understanding of the key performance influencers involved in flow cell design. This model is also being developed in collaboration with the School of Mechanical and Aerospace Engineering to ensure high quality CFD results to accurately predict flow cell performance.

Conclusions and future work

In conclusion, Redox Flow Batteries with novel flow field and stack topologies appear to have great promise in developing Flow Cells with higher energy densities and the development of a workflow incorporating Multiphysics modelling in tandem with 3d printing presents an effective pathway to exploring this. I am also in the early stages of writing a paper detailing the “Design and Manufacture of a Low-cost Laboratory Scale Redox Flow Battery test cell to facilitate researchers investigating new Electrolyte technologies.”

Scale up of the manufacturing and Multiphysics modelling being developed towards kW/ industrial scale Redox Flow Battery stacks is also planned and will be conducted over the coming months.

QUILL Quarterly Report

November 2019 – January 2020

Name:	**Scott Place**		
Supervisor(s):	Dr Paul Kavanagh		
Position:	PhD Student		
Start date:	01 October 2019	Anticipated end date:	2022/23
Funding body:	Department for the Economy (DfE)		

Copper-Based Electrocatalysis for Energy Applications and Sensing

Background

The conversion of alcohols to aldehydes and ketones is very valuable in synthesis for pharmacy and other industries. Often these reactions are performed with stoichiometric quantities of, often toxic, oxidant for the regeneration of the catalysts. We are investigating the use of electrochemical techniques for the regeneration of TEMPO and TEMPO-derivative systems, eliminating the need for chemical oxidants. TEMPO derivatives are organic, stable radicals and can often be very cheap to buy or easy to make. They often function very well as a charge-storage molecule and are excellent electron-transfer mediators. Their ability as a mediator allows electrocatalytic oxidations of specific alcohols, rather than the alcohols oxidising directly at the electrode surface. The pathway by which the alcohol is now oxidised, using TEMPO systems, allows for much lower redox potentials to be used, as it has a lower activation energy. This is attractive since it allows alcohol oxidations to happen more easily for electro-organic synthesis, and it peaks interest for use in fuel cells, as the lower redox potential would result in a higher electrical output of the cell, something we aim to investigate. We will be investigating a variety of these systems and benchmarking them, deriving some rationale for their activity, allowing future work to be done on intentionally tuning them for specific purposes.

Objective of this work

To produce a handful of simple but high-utility publications over the course of the next few years in peer-reviewed journals, in addition to producing enough data and gain the skills needed for a successful PhD thesis.

Progress to date

We are drawing close to writing up our data for the first publication of the project. Substantial work has gone into analysis of PIPO (a TEMPO-based redox polymer) for alcohol oxidation. Solvent studies were undertaken. We have also found that PIPO functions as a competent electrocatalyst in homogeneous solution and when immobilised onto an active support surface, such as a graphite electrode. Kinetic analysis has revealed that PIPO can transfer electrons with ease and shows good overall stability when acting as a homogeneous catalyst over extended periods of time. Currently we are working on improving the stability of the graphite-immobilised PIPO, as immobilising the catalyst is desirable for a number of applications and for improvements in recyclability. It does appear to be possible to achieve a stable immobilised system, but we’re currently troubleshooting for optimum reaction conditions, concentration of crosslinker etc.

In addition to collecting together the data for our publication, I successfully completely my Initial Review and am on track for Differentiation in the coming months. I have also been invited to present verbally and by poster at the upcoming QUILL meeting.

Conclusions and future work

I have demonstrated the potential for PIPO to be used as a redox-mediator in electrocatalytic alcohol oxidations under low-toxicity conditions and have begun development of immobilised versions of the reaction system for more specialised use-cases. I have completed the first stages of my PhD project up to the Initial Review and will soon be working on my Differentiation. Future scientific studies within this project will include: kinetic analysis of several TEMPO derivatives, kinetic analysis of alcohol oxidations on a variety of electrode surfaces, the use of ionic liquids and TEMPO-derivatives in redox-flow cells and the use of TEMPO-derivatives in bio-mimetic fuel cells.

QUILL Quarterly Report

November 2019 – January 2020

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

Using Ionic Liquids as Draw Fluids for Separation and Water Treatment

Background

1. New Ionic liquid materials that exhibit lower critical solubility temperature (LCST) phase behaviour in mixtures with water and with saline solutions have been identified. In mixtures of materials exhibiting LCST behaviour with water, on heating a solution it splits at the LCST into two phases, one that is lean in IL and one that is rich. Such materials have the potential to be used as draw fluids for forward osmosis water desalination using low grade energy to address global challenges to deliver clean water to all the world's populations.

Objective of this work

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. My program includes:

- Preparation of ionic liquids tetrabutylphosphonium salts with phenyltetrazolate (QUB, Moura et al.), benzenesulfonate (Cai *et al.*, Singapore and Urban, USA) and benzenecarboxylate (Ohno, Japan) anions for evaluation and comparison.
- Characterisation of ionic liquid/water and ionic liquid/water/salt cloud points and LCST behaviour.
- Establishing operating conditions for using of ionic liquid draw fluids in forward osmosis.
- Integration of ionic liquids in hydrogel membranes for active transport of water from saline solutions across a thermal gradient.

Progress to date

Experimental

first ionic liquid salts for studies: tetrabutylphosphonium phenyl-tetrazolate ([P_{4444}][Ph-tet]) and tetrabutylphosphonium salicylate (Ando et al., *Chem. Commun.*, 2013, **49**, 10248 have been prepared following the methods described by Moura et al (*ChemPhysChem.*, 2017, **18**, 3384) and characterised.

In the next stage, their LCST behaviour in mixtures with water and with aqueous salt solutions will be characterised using visual cloud point observation and by developing a repeatable and robust procedure to make use of the groups Avantium Crystal16 parallel crystalliser to detect cloud-point behaviour by automated turbidity measurement. This will enable high-throughput derivation of

IL/water/salt LCST phase diagrams and unify different methods of measurement following the disussions by Zhang et al (*Mater. Horiz*. 2017, **4**, 109).

Training
I have received training in use of schools NMR spectrometers and analysis of ^{1}H, ^{13}C, and ^{31}P NMR spectra using Topspin NMR software.

Lecture
School lectures (My future)

Work
My program initial review report has been submitted for assessment. Due to delays on returning from China after new year due to COVID19 travel restrictions, my initial review has not yet taken place.

Conclusions and future work

- Initial progress starting the research program has been made: Two (of the three) initial target phosphonium ionic liquids for screening and comparative evaluation have been prepared and characterised ready for LCST evaluation.
- In the next stage, a methodology for cloud point turbidity measurements using the Avantium Crystal16 parallel crystalliser will be developed, benchmarking against standard phenol/water and against direct observation critical points for the IL/water mixtures.
- IL/water/salt LCST behaviour will be characterised (cloud point turbidity phase diagrams and phase composition using ^{1}H NMR and XRF elemental analysis) as a function of salt electrolyte composition. This will establish the operating conditions for thermally-switchable forward osmosis and the draw fluid efficiency.
- Beam-time was ISIS has been awarded (May 2020) to study the hydration behaviour of phenyltetrazolate anions using neutron scattering.

QUILL Quarterly Report

February 2019 – April 2019

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

Developing New Nanocatalysts for the Direct Conversion of Biogenic Carbon Dioxide (CO_2) to Sustainable Fuels

Background

Rising CO_2 emissions, global warming, ocean acidification and a reliance on a diminishing source of fossil fuels are all factors having a detrimental effect on the environment, making our current way of living unsustainable.[1] In recent years, there has been a large emphasis on research that addresses these issues. Global warming is a serious problem and therefore, many governmental protocols and objectives have been put in place to tackle the issue, for example the Kyoto protocol in 1997, the Paris protocol[2] published in 2015 and the Clean Power Plan (CPP)[3] announced by President Obama in 2015. More recently a proposal has been signed to repeal the CPP in 2017, therefore now, more than ever, there needs to be action.[4] One solution that has been proposed as a means of relinquishing our need for fossil fuels, is to use waste CO_2 from processes (such as anaerobic digestion) and convert this to fuels.

Typically, for gas conversion reactions to occur efficiently, a catalyst is required and in the case of CO_2 conversion to hydrocarbon fuels, iron oxide nanoparticles have exhibited high activities. Furthermore, in a drive to reduce the use of toxic solvents in chemical processes, ionic liquids can be used in the preparation of this catalyst, whilst controlling the size of the nanoparticles without the need for additional capping agents and allows for dispersion which can prevent agglomeration of the particles. Several authors have reported that by employing this synthetic method, a multi-action catalyst was obtained, with three different sites for conversion of CO_2 to hydrocarbons in the C_5-C_{11} range.[5,6,7]

This report proposes two different possible catalyst synthesis routes that utilise these necessary ionic liquids. The first synthesis method involves the thermal decomposition of an iron precursor in a high temperature solution phase reaction. Once the reaction is complete, the produced iron (III) oxide can be separated through decantation and washed with hexane. Once fully separated, the iron (III) oxide will then be embedded within a zeolite structure for pH control and as a solid support for the final catalyst

The second novel method involves use of two iron precursors, already in the desired oxidation states, heated while stirring in the presence of a specifically chosen ionic liquid and requires less energy than previously reported syntheses. Through varying the ionic liquid utilised as the reaction solvent it is hoped we can achieve the capping capabilities of the previous reaction without the need for additional reagents.

Characterisation will be carried out at each stage of the process by a variety of methods: Nuclear Magnetic Resonance (NMR) Spectroscopy, Powder X-Ray Diffraction (PXRD), Temperature Programme Reduction (TPR), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Brunauer-Emmett-Teller (BET) Surface Area analysis and so on.

Objective of this work

The overall aim of this project is to develop a reproducible method of synthesising a nanocatalyst for conversion of CO_2 to sustainable fuels. Synthesis and use of different ionic liquids in the preparation of the Fe_3O_4 catalyst will be carried out, as well as varying the zeolite support used, characterisation and finally high pressure testing under reaction conditions. A control will also be prepared in order to compare the novel catalyst with a conventional method.

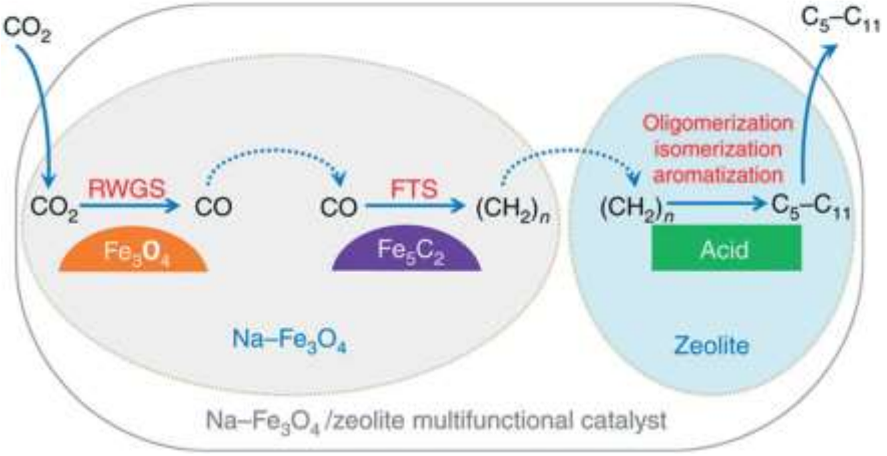


Figure 1 – Depiction of the multifunctional catalyst required for conversion of CO2 to hydrocarbons

Progress to date

Progress to date has involved synthesis and characterisation of different methods of preparing iron oxide nanoparticles. The precipitation method, which is used as a benchmark catalyst, has been synthesised with varying amounts of sodium as a promoter. Three different samples were prepared with either no sodium, low sodium or high sodium. Iron oxide nanoparticles have also been synthesised using two different ionic liquid methods: methods 1 and 2. Method 1 uses iron pentacarbonyl and $[C_4MIM][NTf_2]$ along with additives such as 1,2-hexadecandiol, olelyamine and oleic acid in order to control the particle size and morphology. Method 2 utilises iron(II) chloride and iron (III) chloride with a $[C_4MIM][OAc]$ ionic liquid instead. Method 1 requires a much higher temperature of 280°C compared to method 2 which requires 50°C. However, method 1 produces crystalline material whereas the material produced in method 2 is amorphous and requires further calcination at 420°C under N_2. Samples produced by the different methods have been characterised by PXRD, TPR and TEM, as shown in the graphs, images and tables below.

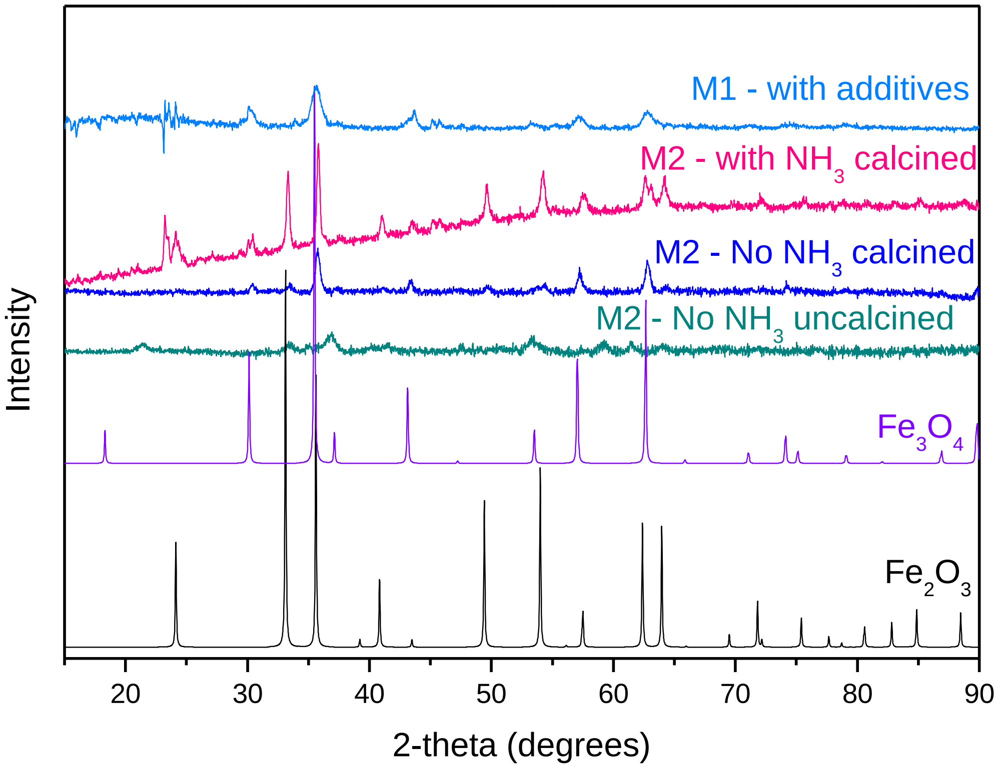


Figure 2 - Graph showing PXRD patterns of Method 1 and Method 2 against simulated Fe_2O_3 and Fe_3O_4

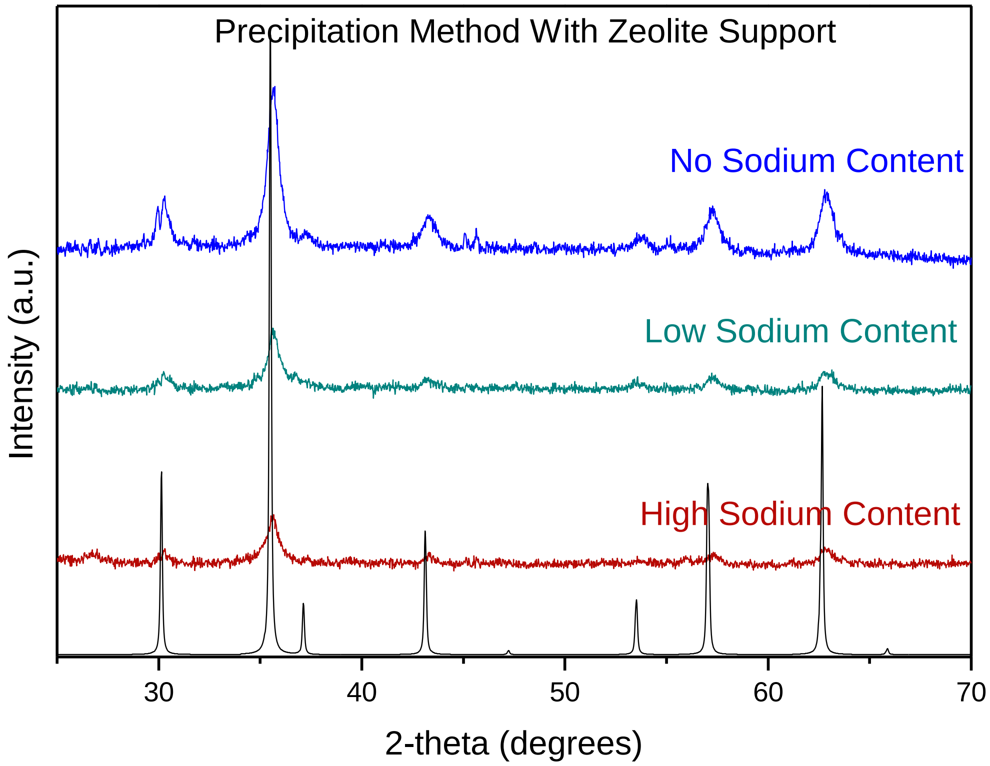
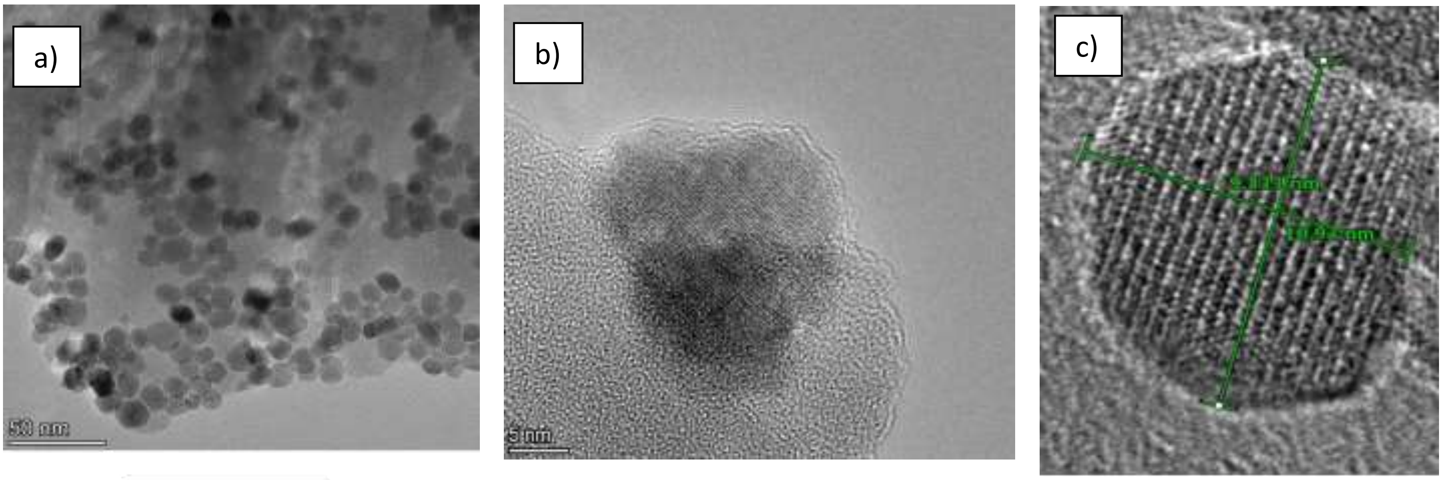


Figure 3 – Graph showing PXRD patterns of precipitation method against simulated Fe_3O_4



245,000 x

390,000 x

630,000 x

Figure 4 - TEM images of a) Method 1 – avg particle size 10-12 nm, b) Method 2 – with NH_3 – avg particle size 20-30 nm, and c) Precipitation method – no sodium – avg particle size – 10-12 nm

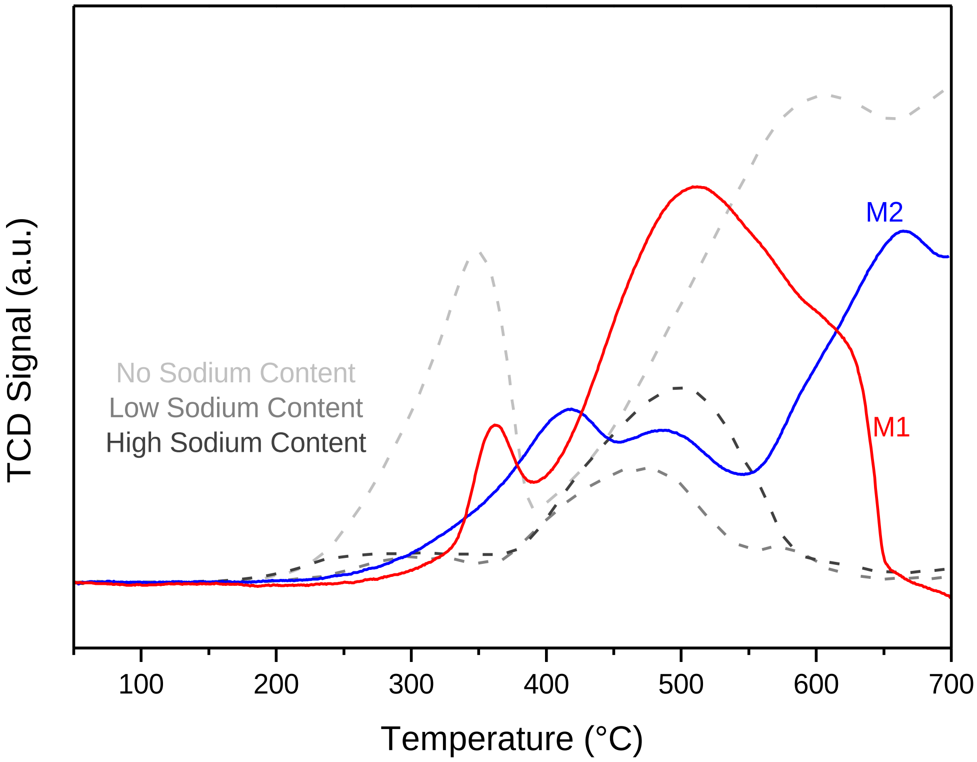


Figure 5 – Temperature Programmed Reduction graphs of precipitation method against method 1 and method 2.

Method	Calcined?	Total Area Under the Curve (mV/min)
1	N	0.74
2 – No NH_3	N	1.23
2 - No NH_3	Y	1.43
2 – With NH_3	N	1.38
2 – With NH_3	Y	**1.501**
PM – No Na	N	0.51
PM – Low Na	N	0.31
PM – High Na	N	0.52

Table 1 – TPR results summary from above graph

Method	Calcined?	Area Under the Curve up to 400°C (mV/min)
1	**N**	**0.08**
2 – No NH_3	**N**	**0.21**
2 - No NH_3	**Y**	**0.15**
2 – With NH_3	**N**	**0.12**
2 – With NH_3	**Y**	**0.14**
PM – No Na	**N**	**0.45**
PM – Low Na	**N**	**0.07**
PM – High Na	**N**	**0.096**

Table 2 – TPR results showing area under the curve up to 400°C (pre-reduction temperature)

Recent work has involved modifying the gas rig used to test the synthesised catalysts and modification of the GC setup as well as the method. Originally the GC consisted of an in series system with an HP-5 column, a Carbon plot, a TCD and an FID. By use of a switching valve it was possible to isolate a column and not allow sample to pass completely through it to the detectors until you wished and switched the valve back again. The HP-5 column was utilised to see shorter chain hydrocarbons and methanol, where we wish to see C5-C11 hydrocarbons being produced by the catalyst. Therefore, we changed this column to a CP-PONA Sil column, which can see longer chain hydrocarbons such as the ones we expect to see. This did not solve our issue and we could not get the GC to work for our reaction, so we required a visit from the Agilent technician, who changed our whole configuration. We are now running an in parallel system where our sample is taken in and split between two different sample loops which then feed into two separate columns fitted to separate detectors. The CP-PONA is connected to the FID, while a new mol-sieve column called a SHIN-Carbon is connected to the TCD. After substantial testing and modifying the system is now setup for running our reaction on and capable of collecting data for a wide range of hydrocarbons should they be produced.

Alongside all the modifications to the GC, there were a range of issues to be fixed with the gas rig itself. During testing it was discovered that the carbon was not balancing. The alumina trap utilised for making sure the CO_2 gas was a pure stream was actually capturing and releasing the CO_2 at random time rather than a steady stream. It was also found that there were a number of leaks. The alumina trap is now by-passed and the leaks have all be found and fixed. The rig is currently in use for testing of the catalyst. This is carried out by using 750mg of catalyst in the fixed bed reactor. The catalyst is then pre-reduced under a flow of H_2 at 400°C for 8 hours. After returning to room temperature the flow is changed to N_2 before increasing the temperature to 320°C (the temperature at which the reaction is carried out). Whilst the temperature is increasing the CO_2 and H_2 mixture is increased to 80% with N_2 at 20%. Once the correct mixture of gases is achieved the pressure is slowing increased over 2hrs to achieve 20bar. The reaction is then run for a 100 hour period in order to assess both the activity and stability of the catalyst.

Conclusions and future work

The samples produced by the different methods were characterised by PXRD, TEM and TPR in order to understand their particle size and morphology and hopefully once we have tested them on the gas rig under reaction conditions this will give an insight into how this affects the catalytic activity. Promisingly the novel method without NH_3 uncalcined has shown high reducibility, second only to the conventional precipitation method sample with no sodium. Once all the samples have been tested under reaction conditions on the gas rig, the activity and selectivity will be assessed and based on this the preparation of the catalyst will be modified. Different ionic liquids may be considered, as well as different iron salts. Another area of interest in the project is changing the zeolite utilised in the catalyst, either to change the acidity of the zeolite or change the zeolite completely to a different zeolite or perhaps a metal organic framework (MOF).

QUILL Quarterly Report

November 2019 – January 2020

Name:	**Yaoguang Song**		
Supervisor(s):	Prof Peter Nockemann, Prof David Rooney, Dr Xiaolei Zhang (Strathclyde) and Dr Szabolcs Pap (UHI)		
Position:	PhD Student		
Start date:	3 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

Lignocellulosic biomass feedstock represents an indispensable neutral even negative carbon emission energy resource, which triggered amounts of research effort on its valorisation into green fuels and sustainable chemicals to alleviate the reliance on petroleum consumption. As a main component of biomass, lignin holds the second most abundant reserve and possesses C element content as high as nearly 60%[1,2], accounting for 30% terrestrial non-inorganic carbon[3], thus endows itself with huge potential for producing carbonaceous materials.

On the other hand, advanced carbon materials represent upper-class products amongst all lignin-based applications in terms of economic worth.[4] Especially mesoporous carbon materials that feature many superb physicochemical properties have gained ubiquitous applications in various scientific/industrial fields, like energy storage, catalysis and adsorption. However, most preparation methods for inorganic materials are somewhat empirical or less oriented, leading to resultant topologic and structural properties high unpredictable and hence unsuitable for aimed downstream applications. An exception was found in self-assembly based soft-template route, which proved itself successful to prepare highly ordered mesoporous carbons from lignin. Nevertheless, reported soft-template route still remains limitations and novel promising preparation methods are still in need of development.

Ionic liquids (ILs) as a novel kind of green solvents are gradually seen in the dissolution and depolymerisation of biomass lignin. Certain ionic liquids with long alkyl chain on the cations exhibit excellent amphiphilic properties and theoretically could act as structure-directing agents. So this programme aims to convert biomass lignin into high value added mesoporous carbons in the presence of ionic liquids as solvents and structure-directing agents simultaneously. The effective implementation involves both experimental work and molecular dynamics simulations since the latter could offer insight into internal mechanism at an atomistic/molecular level.

For the proposed preparation method in this programme, the micelle formation process is the key and the templating micelle structures determine the final meso-structures of carbon materials from lignin. Therefore, the first step is to investigate the spontaneous self-reorganisation process, especially how to control the morphologies of micelle structure so as to tailor the resultant mesostructured of as made carbons. Both coarse-grained molecular dynamics (MD) simulations and experimental techniques will be employed to study this process.

Objective of this work

Our ultimate aim is to convert biomass lignin into mesoporous carbon materials aiming for various applications by employing ionic liquids as solvents and templates simultaneously. However, micellization process is the key in our whole project, my current objective mainly includes controlling the micelle morphologies of ionic liquids in aqueous solutions, where concentration and temperature are two key factors that we focus on.

Progress to date

Micelle formation controlling of ionic liquids in aqueous solution. Amphiphilic ionic liquid $C_{10}MIM^+ Br^-$ was selected. Coarse-grained MD simulations were performed using software LAMMPS[5] for different ILs% content and trajectory files from simulation were visualised by VMD. The coarse-graining way mainly followed “3 heavy atoms into 1 bead” strategy, where ionic liquid $C_{10}MIM^+ Br^-$ is represented by 7 beads[6] and three water molecules are coarse-grained into one single bead[7]. Initial configurations of simulations were built randomly by using PACKMOL[8] to ensure all the simulations start from heterogeneous state.

Table 1 listed all simulated systems and corresponding physical and structural properties, where the pending areas mean that the simulations are still under running.

Table 1 - Computed molar concentration, density and micelle morphologies at different ILs wt%

ILs wt%	Computed molar concentration at 298 K (mol/L)	Computed density at 298 K (g/cm^3)	Micelle morphology	
			298.15 K	343.15 K
1 wt%	-	-	-	-
4 wt%	0.14	1.005	spherical	-
8 wt%	0.26	1.010	spherical	-
30 wt%	1.03	1.043	spherical	-
46 wt%	1.63	1.072	spherical/rod-like	spherical/rod-like
56 wt%	2.02	1.081	rod-like/cylindrical	Hexagonal cylindrical
63 wt%	2.27	1.084	worm-like cylindrical	Hexagonal cylindrical
68 wt%	2.44	1.077	Hexagonal cylindrical	-
72 wt%	2.54	1.082	Hexagonal cylindrical	Transition stage
77 wt%	-	-	Transition stage	-
79 wt%	-	-	Lamellar bilayer	-
81 wt%	-	-	Lamellar bilayer	-
84 wt%	-	-	-	-
89 wt%	-	-	-	-
94 wt%	-	-	-	-

Figure 1 shows three main morphologies of ILs in aqueous solution at room temperature from simulations, where spherical, highly ordered hexagonal cylindrical and lamellar bilayers strutures are observed at different ILs wt%.

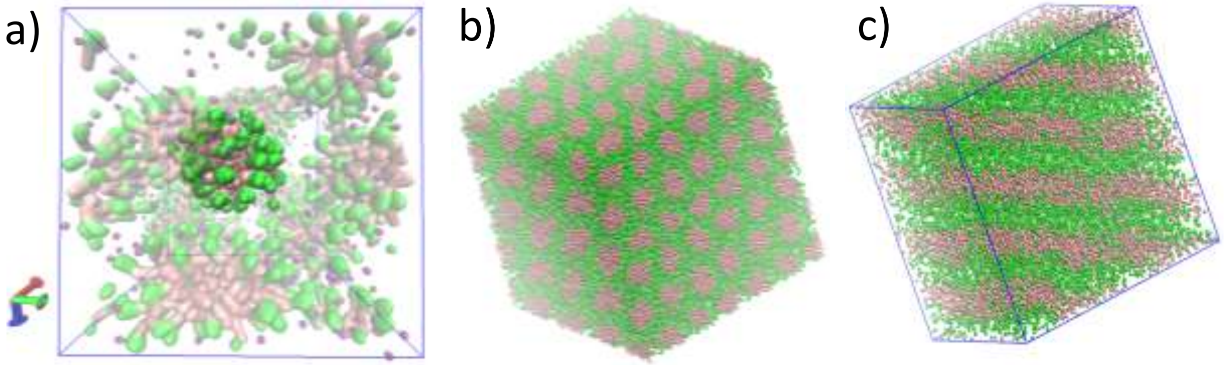


Figure 1 - Snapshots of micelle morphologies at 298.15K: a) spherical at 30 wt%, b) hexagonal cylindrical at 72 wt% and c) lamellar bilayers at 79 wt%. Imidazolium rings and hydrophobic alky chains are shown in green and pink, respectively. For the ease of visualisation, water and anions are not shown.

Conclusions and future work

1. Conclusions:

1) With the increasing in ILs wt%, micelle morphology of ILs in aqueous solution changes from spherical to disordered cylindrical, then to highly ordered hexagonal cylindrical, and even lamellar bilayer structures.

2) When the temperature arises from 298.15K to 343.15K, the turning points of micelle morphologies shift to lower concentrations.

2. Future work:

1) Calculate surface tension of different systems as a criterion with simulation to find out the turning point in morphology.

2) Experimental measurements will be carried out to get density, molecular concentration and surface tension, so that we could compare results from simulations and experiments to verify the prediction of simulations.

3) Study the hydrothermal/ionothermal process by employing CG-MD to predict the structures of micelles.

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QUILL Quarterly Report

November 2019 – January 2020

Name:	**Jiajun Sun**		
Supervisor(s):	Prof John Holbrey		
Position:	MPhil		
Start date:	1 October 2019	Anticipated end date:	30 September 2020
Funding body:	Self-funded		

Polyaromatic-Functionalised Ionic Liquids as Electrolytes

Background

The ionic liquids have been widely studied in many fields such as catalysis, solvents, and electrolytes. The ionic liquids could be designed for many different functions through connecting different functional groups.

Some ionic liquids incorporating cations with aromatic rings that incorporate electron withdrawing groups such as nitrile (-CN) or trifluoromethyl (-CF_3) have been previously shown to form highligh coloured charge trasnfer (CT) complexes in the presence of electron-rich polyaromatic molecules such as naphthalene (Hardacre et al., *Phys. Chem. Chem. Phys.*, 2010, **12**, 1842).

Single crystal analysis has shown that self-assembly of the aromatic cations and electron-rich organic donors leads to co-planar π-π interactions, and these persist in the liquid state. This overlap and aromatic interactions may form electron-tunnels through the liquid mixtures enabling rapid electron transport in addition or conventional ion transport in ionic liquids, i.e. formation of liquid wires.

Objective of this work

The overall objective of this work is to investigate whether electron-conductive ionic liquid composites, particularly room temperature ionic liquid materials, can be formed from mixtures of ionic liquids incorporating electron-deficient (*acceptor*) and electron-rich (*donor*) functional groups. Ionic liquids containing pendent donor polyaromatic groups (benzene, naphthalene, and anthracene) and ionic liquid incorporating aromatic acceptor cations (cyanopyridinium salts) will be prepared and the thermophysical and electrolytic phase behaviour of mixtures investigated.

At the onset of this work it is not known whether mixtures of ionic liquids with e.g. nathphthylimidazolium and cyanopyridinium cations will produce higher-melting CT-complexes stabilised by π-π association, or eutectic forming mixtures with suppressed melting points and this initial characterisation of phase behaviour as a function of the nature of the donor, acceptor, and peripheral substitution patterns will be the major focus of the work.

Progress to date

1. Ionic liquids containing **pendent aromatic groups as electron-rich donors** have been synthesised and characterised.

- 1-methyl-3-(2-naphthalenylmethyl)-imidazolium bistriflimide (mp <313K)

- 1-ethyl-3-(2-naphthalenylmethyl)-imidazolium bistriflimide (rt liquid)

2. Ionic liquids incorporating electron deficient aromatic cores derived from cyanopyridine have been synthesised.

- 1-methyl-4-cyanopyridinium bistriflimide (colourless crystals)

3. Characterisation of ionic liquid mixture phase diagrams has been initiated.

QUILL Quarterly Report

November 2019 – January 2020

Name:	**Richard Woodfield**		
Supervisor(s):	Dr Steve Glover, Dr Rob Watson and Prof Peter Nockemann		
Position:	PhD Student		
Start date:	June 2019	Anticipated end date:	December 2022
Funding body:	EPSRC		

Investigating 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

To date I have spent three months with the sponsor, and six months at Queens. In the past six months I have conducted a literature review and I am now preparing for Differentiation. Initial findings from the literature are already revealing some potential applications such as bus and ferry transport. I am currently preparing test routines and have acquired a lab-scale flow-cell, which will be used to characterise battery models, which will feed into vehicle models.

Conclusions and future work

Some initial findings reveal promise in certain modes of transport, which provide a good starting point for the vehicle models. Before this, battery characterisation tests will be conducted, which will feed into battery models.