QUILL

Quarterly Reports

May - July 2020

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QUILL Quarterly Report

May 2020 – July 2020

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

Valorisation of Products from Waste Plastic Pyrolysis

During this period, I have been working on the preparation of new work packages for an EPSRC proposal. A part from the main goal of the project, which is the oligomerization of α-olefins towards the preparation of lubricating base oils, I have focused on other alternative synthetic routes for the preparation of high-added value products from the same feedstock. The main focus of the WP was on the conversion of α-olefins to cyclic and/or polycarbonates using one-pot synthetic methodology known as “oxidative carboxylation” (Figure 1(a)), and/or cycloaddition of CO_2 with the corresponding epoxides, which can be obtained from α-olefins present in our feedstock (Figure 1(b)). I have prepared a short literature review about the main catalytic systems that can promote this transformation efficiently, while reading patents and journal articles to understand the state of knowledge on this field.

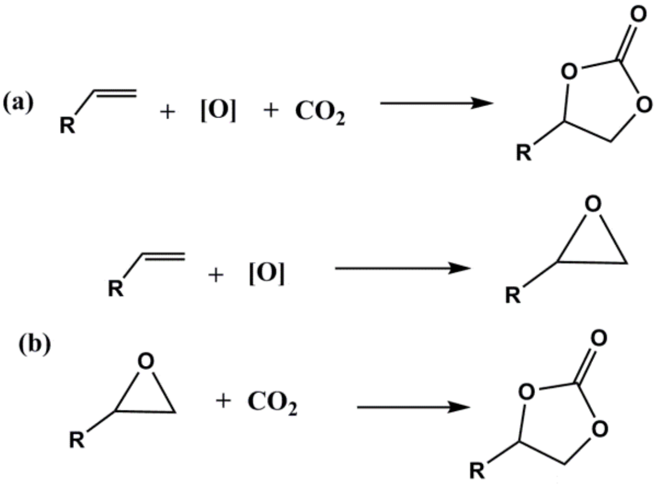

Figure 1 - The direct one-pot route for the preparation of cyclic carbonates from olefins

For what concern the other work packages, I focused with my co-workers on finding other α-olefins valorisation routes, such as the preparation of diols, alkylbenzyl sulfonates, dialkyl carbonates and boric acid esters, while looking in literature for their potential applications in the manufacturing of valuable products, especially lubricating base oils. The progress of the proposal work was followed by the supervisor throughout a virtual group meeting each week.

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Name:	**Marian Borucki**		
Supervisor(s):	Prof Peter Nockemann, Dr Stephen Glover and Dr Małgorzata Swadźba-Kwaśny		
Position:	PhD Student		
Start date:	01.2018	Anticipated end date:	07.2021
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, 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 different cell chemistries will be investigated.

Working from home summary

During the period of the lockdown the previously assembled lithium ion battery samples have been aged and monitored throughout the period using battery analyser remotely. Unfortunately, due to the laboratory work limitation continuous characterisation of samples have not been available as a potentiostat is needed to be used for that purpose. Although the ageing data gathered in pre-lockdown period has been analysed by applying the incremental capacity analysis (ICA). The ICA for one of the samples is to be observed in the figure below. Analysis of the samples provides insight on capacity – voltage dependence, thus it serves as a tool to observe the changes that do occur in sample behaviour of charging and discharging as the sample is aged. In **Figure** we notice an overall decrease in dQ/dV ratio with further cycling which occurs due to increase in discharged capacity observable during the first discharges for lithium samples. Further on with a subsequent cycle the peak does shift to lower voltage region as more lithium ions are incorporated to the cathode structure. Focusing on ICA a further data analysis is developed in order to quantify the energy stored for each process distinguished.

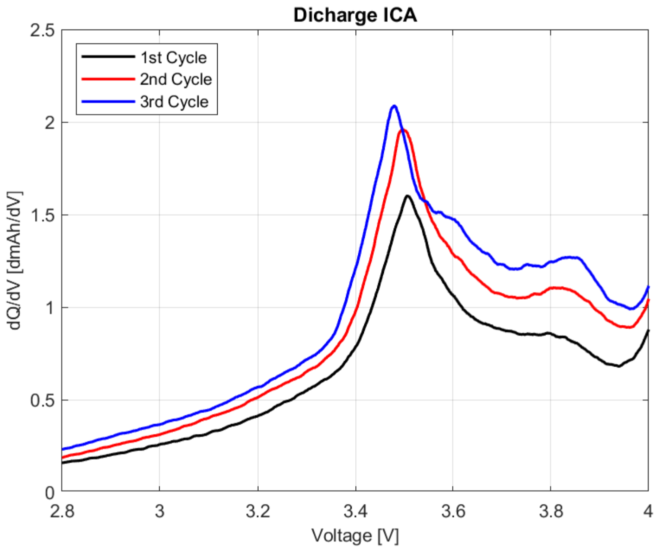

Figure 1 - Incremental capacity analysis of three initial discharges for lithium ion CR2032 coin cell sample assembled from graphite anode, lithium nickel manganese cobalt cathode (NMC 811) of nickel to manganese to cobalt ratio of 8:1:1, with 1M $LiPF_6$ dissolved in ethylene carbonate : ethyl methyl carbonate (1:1 molar ratio) with the addition of 2% of vinylene carbonate as electrolyte, using ceramic coated polypropylene as separator. The discharge cycles have been performed using C/10 current ratio on a battery analyser.

Back to laboratory work tasks

Post-mortem studies – The *post-mortem* case has been designed, 3D printed and tested for laser beam permittivity using Witech alpha 300R microscope with a control sample as for leakage proving to be sealed. The aged samples are planned to be dismantled in a glovebox. The electrodes are to be sliced in half using a ceramic knife into two parts. Four samples, two for cathode and two for anode, are expected to be obtained per sample. The as prepared post-mortem samples are to be used for spectroscopy data collection as well as for structural microscopy studies and crystallographic studies. The obtained data from *post-mortem* studies would provide insights to the specific degradation processes occurring inside the cell as the cell is aged and could be further compared to electrochemical data obtain during sample ageing.

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

Carbon-based anodes spectroscopic ageing comparison – Three carbon-based materials are studied as an anode for the lithium ion cells. A similarity in their ageing mechanism is expected to be investigated. A broad spectroscopy study being carried out to provide insights if the ageing of different carbonaceous materials is able to be observed by obtaining their spectra in the same conditions.

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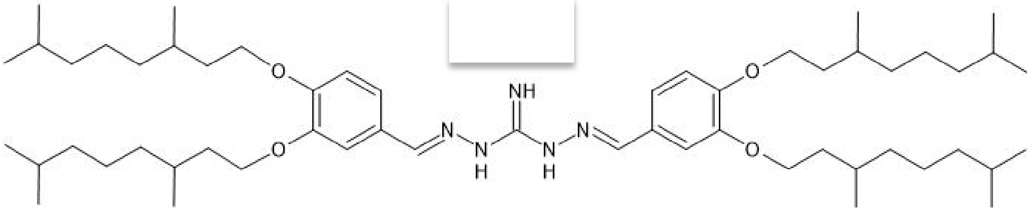
Name:	**Dominic Burns**		
Supervisor(s):	Prof John Holbrey and Dr Gosia Swadzba-Kwasny		
Position:	PhD Student		
Start date:	1st October 2019	Anticipated end date:	31st May 2023
Funding body:	EPSRC		

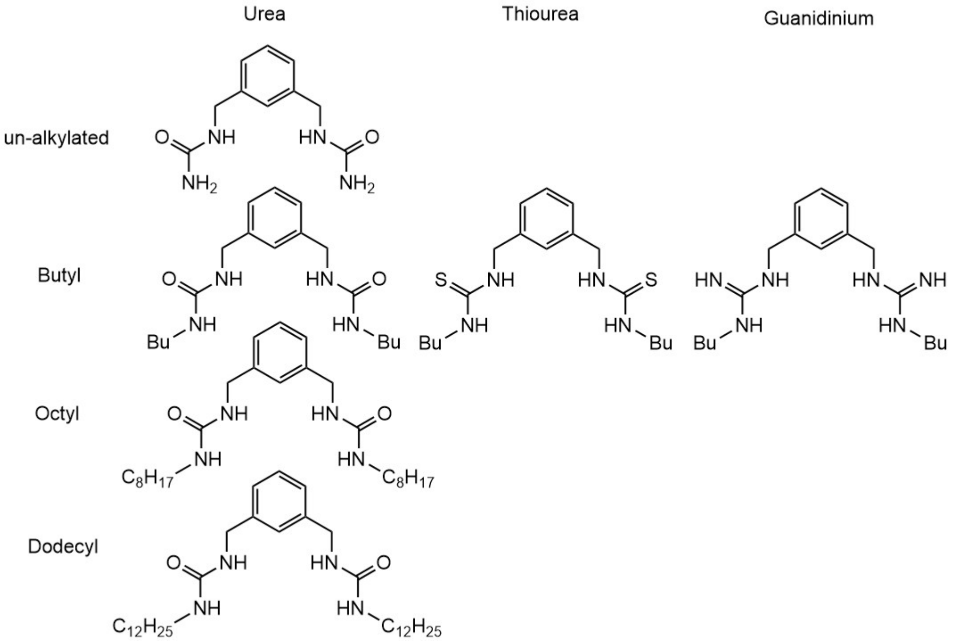
Recycle and Reuse of Process Water Through Sulfate Removal: Developing an Ionic Liquid Technology for Selective Anion Recognition and Extraction

Following studies on using $[P_{66614}]Cl$ as a liquid ion exchanger, I am currently designing and carrying out studies on possible additive extractant molecules that will enhance the selectivity of the extracting phase for sulfate.

Strategy 1 involves the use of a reverse micelle forming extractant reported by Williams *et al* that can extract sulfate into a branch paraffin solvent extracting phase and has a separation factor of 4,300 for sulfate over chloride. (DOI: 10.1039/c8cc05115a)



Strategy 2 is a more traditional approach where a series of bisurea molecules will be assessed by NMR binding studies and small-scale extractions. These anion ligands can coordinate to the sulfate and hopefully pull it into the extracting phase as $[SO_4 L_x]^{2-}$.



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

Designing Functional Liquids

Since the last QUILL report, I have been working from home on the following tasks:

1. A major contribution of this time has been dedicated to writing my thesis and compiling results into graphical form using Origin software.
2. I have finalised amendments and corrections following acceptance of a paper submitted to PCCP on my physio-chemical work on TOPO:carboxylic acid eutectics. I have also spent time writing introduction and experimental sections for a paper based on sulfuric acid:pyridine Brønsted acidic protic ionic liquids for which the results from ISIS neutron scattering data will be included. All these tasks involved reviewing literature in addition to the time spent writing.
3. Finally, as I attended a Chartered Management Institute course on Strategic project management and leadership at the QUB Graduate School, I completed a report on strategic project management which contributed to passing the course and have also attended many webinars on topics such as proposal writing, introduction to patents and thermal analysis for example.

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

Battery Thermal Management and Algorithmic 3D Temperature Prediction

Work being carried out from home

Due to the COVID-19 pandemic, all work on this project is currently being completed from home. As the experimental side of the project involves placing thermal sensors inside a commercial Li-ion cell, a process involving a robotic arm is being developed to ensure safe and accurate placement. Computer vision is currently being explored to add further accuracy to the process as a feedback for the sensor placement. This may be in the form of error correcting or go/no go checks. A mock battery has been 3D printed in order to develop and test the process outside of the lab in a safe manner.

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Name:	**Oisin Hamill**		
Supervisor(s):	Dr Nancy Artioli and Dr Alex Goguet (2)		
Position:	PhD Student		
Start date:	01/10/2019	Anticipated end date:	30/09/2022
Funding body:	EPSRC		

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

Work plan during the university closure and COVID-19 lockdown period beginning from the last week on March 2020 – July 2020:

I compiled a literature review in preparation for my differentiation interview. This review consisted of a background on emission sources; current emission legislations, tests and detection systems; a background on LNT catalysts focusing on ceria; a review of dopants; the effect dopants have on ceria in particular; and a summary of laboratory work completed to date. It finished with a short background to all the techniques used during catalyst characterisation and includes the results acquired from initial tests carried out in the first 6 months of my project. I explained why these techniques were important to understand my catalyst material and how they were performed. I have been reading relevant literature in my field of study and compiling a list of papers I plan to use in future papers as well as interesting experiments and points of interest. I have set out a return to work plan and began preparations in the lab to return to work in August 2020.

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

A Catalytic Gas-to-Liquid Process for CO Valorisation

Background

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

Objective of this work

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

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

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

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

Progress to date

During this period, a Lean Launch Programme (LLP) was attended in order to aid in the commercial aspects of the work, mainly focusing on the market discovery, market testing, and customer analysis. During this period, it had been found that our initial desired market was unlikely to be effective. Initially the desire was converting digestate waste from anaerobic digestion (AD) plants into fuels. Through market testing during the LLP course, it was found that there would be very little market interest for this as it is more profitable for AD plants to dry the digestate waste and directly sell them as fertilizer. Our goal would have necessitated further digestate waste processing to syngas, which is both energy intensive and expensive. It was found however that there is a substantial interest in CO_2 capture and storage, or CO_2 mitigation. During the course of the LLP, it was found that breweries would have a large interest in cleaning their CO_2 output and reuse. This is a viable market, using carbon capture technology. However, as this deviates from our technology quite substantially, this potential customer base will have to be set aside for a separate project.

CO_2 treatment however remains a viable market as there are industries seeking to resolve this. Contact was made with Aggregate Industries/Lafarge Cement, as they are an industry that produces large quantity of CO_2 emissions. At present, they have expressed some interest, and are interested in converting to natural gas and LPG grade fuels. Further discussions will be had, with regards to technical details and what they aim

As detailed in the previous Quarterly report, due to the Covid-19 lockdown, experimental work that was planned has been postponed until further notice. Thus the techno-economic analysis which was originally planned for a later date, has been pushed forward and may be adapted to become the large bulk of the overall work. Towards this, Aspen Plus has been installed allowing for this to take place remotely. Official Aspen Tech courses were booked and completed.

In other general tasks, with the laboratory opening back up, a previously broken GC system has been repaired. Servicing of an FTIR instrument was also conducted. The system is operational, but as there are missing components that were taken from a research group that worked in the lab previously, new items and equipment are to be purchased.

Conclusions and future work

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

The laboratory has opened back up, so experimental work can begin again. As mentioned above, FTIR accessories and items are to be purchased in order to fully operate the FTIR instrument.

With Covid-19 cutting into the experimental work, the original plans for catalyst optimization may be pushed back in favour of designing a catalytic reactor that we can cater to the customer needs, and also allow us to apply a patent with the goal towards licensing. This reactor design will be a bench-scale, but is designed to simulate a larger scale process. Success with this reactor design mean we are closer to customer specifications for larger scale applications.

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

Chemisorbent Materials for Olefin and Paraffin Separation

Objective of this work

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

Progress to date

Since the last quarterly report, my initial version of my literature review has been completed, and I have moved on to focus more in-depth on synthesis and properties of ionic liquids. This has involved gathering basic properties of the ionic liquids under the experimental conditions (such as temperature of adsorption, and viscosity of the ionic liquids) and impurities in the ionic liquids (*e.g.* water content and halogen salt content). In terms of the solubility of the olefins and paraffins in the ionic liquids, the Henry's Law constant was determined, and how this solubility was measured. This information is collected in a database which initially has focused on experiments consisting solely with pure ionic liquids. This will expand to include mixture of ionic liquids, metal ion containing ionic liquids and other non-ionic liquid material. Also, this will be used to determine functionality groups which promote the solubility of the olefin and paraffin in the ionic liquids.

In terms of the return of the labs, planning has been put in place for the upgrade of the gas rig to the specification to carry out experiments in our facility. The initial steps will to be to benchmark the equipment using carbon dioxide as the gas, and polyethylene glycol 200 (PEG200) as the absorbent. The second phase of the benchmarking will involve using 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (also known as [Bmim][NTf_2]) in the presence of carbon dioxide, and in the presence of ethylene and ethane.

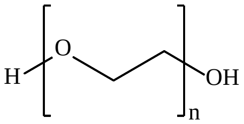

Figure 1 - Chemical structure of PEG200

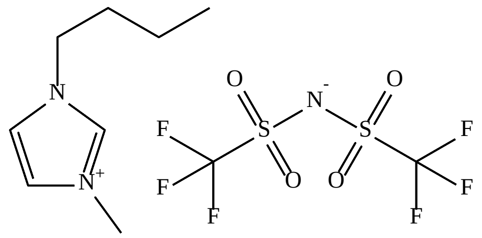

Figure 2 - Chemical structure of [Bmim][NTf$_2$]

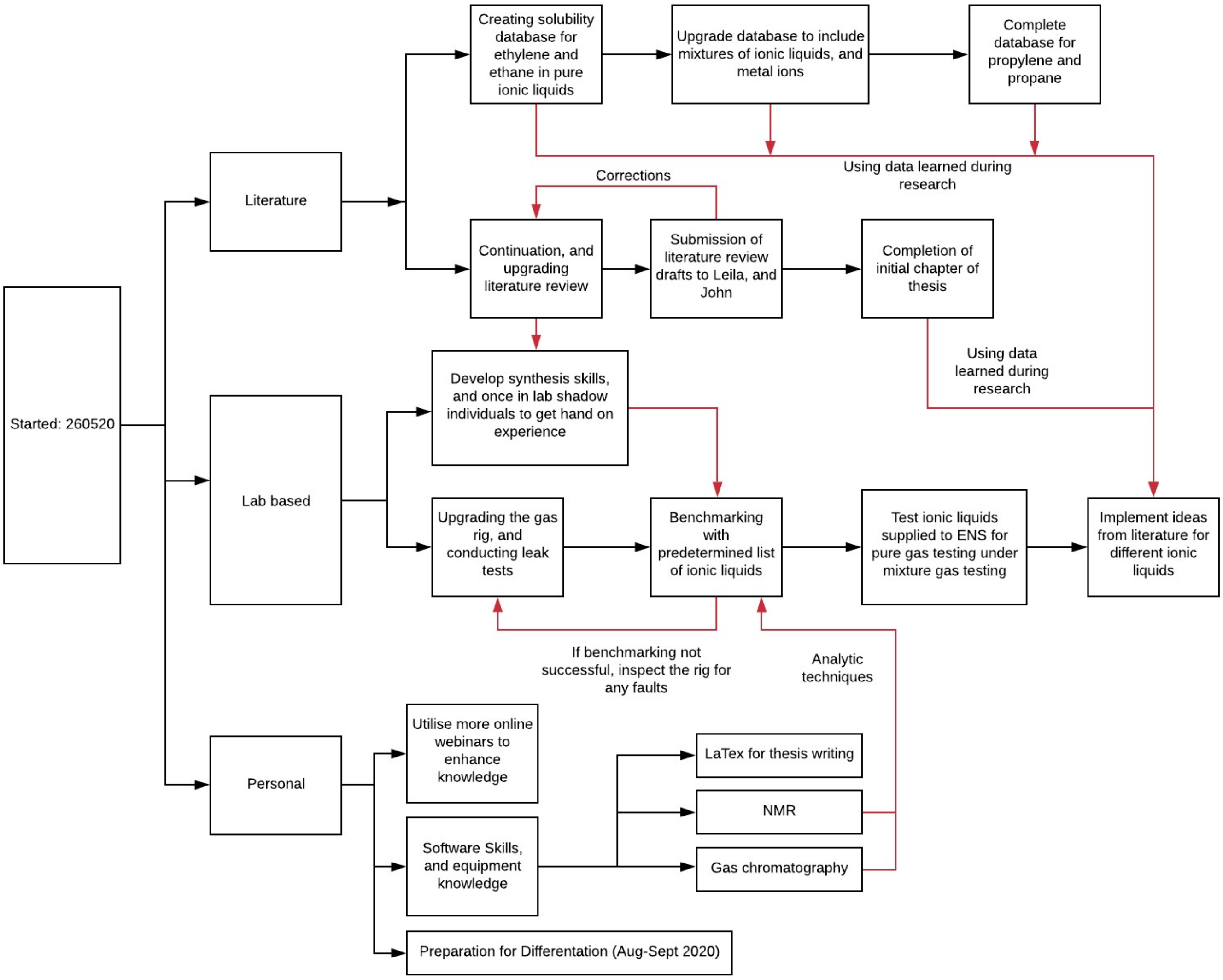

Figure 3 - My development plan since the end of May 2020

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

Selective Reduction of Carboxylic Acids to Alcohols for Use in APIs

Objective of this work

Methods to reduce fatty acids/carboxylic acids such as octanoic acid to produce alcohols which can be used for API in pharmaceuticals.

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 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.

This method is now also being applied to other acids such as benzoic acid for its reduction to benzyl alcohol.

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

Main Group Catalysis in Ionic Liquids

I have been learning how to use EPSR and Dissolve modelling programmes to analyse neutron scattering data. I have been analysing data from recent beamtime and comparing the liquid structure of: (a) neat sulfuric acid, (b) an ionic liquid made of two moles of sulfuric acid and one mole of pyridine, and (c) a mixture of one mole of sulfuric acid, one mole of pyridine and two moles of water. This work will give an important insight into the liquid structure, explaining some of their unique properties and hopefully enabling further optimisation. Analysis of the results so far, show that this model has responded to the experimental data input by generating an un-ionised, molecular representation of sulfuric acid. Furthermore, the results show that pyridine is protonated. Further analysis into the liquid structure and hydrogen bonded network will be undertaken.

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May 2020 – July 2020

Name:	**Hugh O'Connor**		
Supervisor(s):	Prof Peter Nockemann		
Position:	PhD Student		
Start date:	October 2019	Anticipated end date:	March 2023
Funding body:	EPSRC		

Redox Flow Battery Materials for Energy Storage

With the COVID-19 shutdown continuing into May and June, the design and manufacture of 3D-printed Redox Flow Battery test cells was delayed. In the interim, development of a Multiphysics continued. This model couples Computational Fluid Dynamics (CFD) and Electrochemistry to predict the performance of various cell geometries and electrolytes. Results from this model show good correlation with those from literature and will hopefully be validated with experimental data obtained using 3D-printed cells in the battery lab at QUILL. In tandem with the development of this Multiphysics Model, I've finished the "Literature Review" section of my thesis and completed my Differentiation via Microsoft teams, which was interesting!

Towards the end of July, preparation began to make the Labs COVID safe, and in recent weeks, socially distant lab work has resumed. I have spent most of this time improving the design of 3D-printed lab scale test cells, focusing on ease of use and sealing, with some promising results.

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May 2020 – July 2020

Name:	**Scott Place**		
Supervisor(s):	Dr Paul Kavanagh (Primary) and Dr Mark Muldoon (Secondary)		
Position:	PhD Student		
Start date:	October 2019	Anticipated end date:	July 2022
Funding body:	Department for the Economy (DfE)		

Copper-Based Electrocatalysis for Energy Applications and Sensing

The following was achieved in the past quarter:

- Preparation and presentation of my Differentiation report, detailing my research work from September 2019 to April 2020, to CCE academic panel. The panel agreed that the report was well-written and presented, notwithstanding some concerns, which were useful pointers for areas of improvement and are being addressed for later reports. It was agreed that a substantial body of results has been generated over the course of the first year and that I was to progress on to the next year.
- A significant amount of time was spent during lab lockdown improving my theoretical understanding of fundamental and advanced electrochemical topics that underpin my project. I have spent a substantial amount of time studying texts on Electrochemical Fundamentals by Bard and Faulkner, Inorganic Electrochemistry by Zanello and various educational articles on electrochemical kinetics and experimental methods. I have also been working through a series of Electroanalytical Chemistry lectures by David Wipf.
- Drafting of publication entitled "Electrocatalytic oxidation of alcohols using PIPO redox polymer" (working title) for submission to *Chemical Communications* or journal of similar impact. I am currently in the process of conducting several key experiments which will enhance the paper.
- Planning of experiments for studies following the above publication. I will be working on a number of experiments studying the effect of electrode surfaces and solvent-electrolyte system on TEMPO (and TEMPO-Derivative) mediated alcohol oxidations. These studies will be underway immediately after finishing the final experiments for the PIPO study.

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

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

At the end of May the annual progress review was carried out for the second year of my PhD. Most of May was spent preparing the report, presentation and revising for the interview. I passed my APR with a few comments from the reviewers, which have been discussed with my supervisors and a plan put in place to address these. Since then I have continued to review recent relevant literature as well as attending webinars and courses relevant to my research. I recently completed a 5 day course with the RSC and JMP on Design of Experiments and received a certificate as proof of my attendance. Since the end of July it has been possible, with certain restrictions, to work in labs again and so I have been restarting the experimental part of my project and getting the gas rig ready to test samples.

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May 2020 – July 2020

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

Thermochemical Conversion of Biomass Lignin into Mesoporous Carbon Materials

Background

Lignocellulosic biomass feedstock is an indispensable energy resource to achieve net-zero carbon emission globally. As a main component, lignin from biomass holds huge potential for producing nanostructured carbon materials[1,2,3], which represents upper-class valuable products amongst all lignin-based applications.[4] Especially mesoporous carbons (MCs) have gained ubiquitous applications in energy storage, catalysis and separation due to superb physicochemical properties. However, most preparation methods for MCs are empirical, leading to unpredictable topologic and structural properties thus likely unfavourable for aimed downstream applications. Soft-template route was reported successful to prepare highly ordered MCs from lignin but novel promising templates are still in need of development.

Considering that ionic liquids (ILs) are increasingly seen in the dissolution and depolymerisation of lignin and certain ILs with long alkyl chain on the cations exhibit excellent amphiphilic properties, theoretically we could employ ILs as potential structure-directing agents. So this programme aims to investigate the possibility to convert lignin into MCs in the presence of ILs as solvents and templates simultaneously. The effective implementation involves both experimental work and computational investigation via molecular dynamics (MD) simulations.

In my previous report, I have already described the study on micelle evolution process for systems without carbon precursor and cross-linker, which is the key for the proposed preparation method in this programme and determines the resultant meso-structures of carbon materials. Spherical, hexagonal cylindrical and lamellar bilayer structures were observed with the increase in ILs/water ratio and the influence of temperature on morphology evolution was also studied. This report briefly describes the assembly process of system with ILs, water and phenol as a vague model of lignin to study the feasibility of employing amphiphilic ILs as template.

Methodology

Considering that IL model used in my previous work is non-transferable and incompatible with other models (carbon precursor models to be exact), which limits the simulation focusing on systems containing IL and water only. Introducing new components into the system including carbon precursor and cross-linkers (if necessary), requires the employment of transferable and compatible models. Herein, all models used in this report are based on Martini 2 models[5]. 1-decyl-3-

methylimidazolium acetate was selected as template compared with IL used in my previous work where bromide was replaced by acetate as anion to avoid the introduction of toxic halogen, making the preparation technology greener. Specifically, IL cation and anion were chosen from the work by Crespo et al.[6] and Huet et al.[7], respectively. Phenol model was proposed with a SP1 bead and two SC5 beads as shown in Figure 1. Bead distances were constrained by 0.30 and 0.27 nm, respectively. Non-bonded interaction was described by a shifted Lennard-Jones 12-6 and Coulomb potentials with a cutoff of 11 Å and long-range Coulombic interaction by particle-particle particle-mesh (pppm) method with a tolerance of 10^{-5}. Coarse-grained MD simulations were performed using software LAMMPS[8] for different ILs% content and trajectory files from simulation were visualised by VMD. Timestep for simulation is 10 fs. Initial configurations of simulations were built randomly by using PACKMOL[9] to ensure all the simulations start from heterogeneous state.

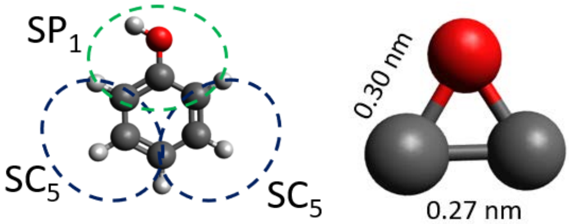

Figure 1 – Proposed phenol model

Results

Figure 2 shows the hexagonal cylindrical morphology of system at room temperature, where the ratio of ILs : phenol : water ranges from 1:1:12 to 1:1:8. Similar with previous modelling, the alkyl chain of imidazolium cation were aggregated into cluster forming the hydrophobic phase and slowly reorganised into hexagonal structure and the head groups were exposed to aqueous phase. For the fabrication of mesoporous carbons, it is critical to study the distribution of carbon precursor, i.e. phenol in this case. From Fig 2c, it can be clearly observed that the phenol was distributed between the imidazolium rings and the alkyl chains, forming hexagonal cylindrical structure as well.

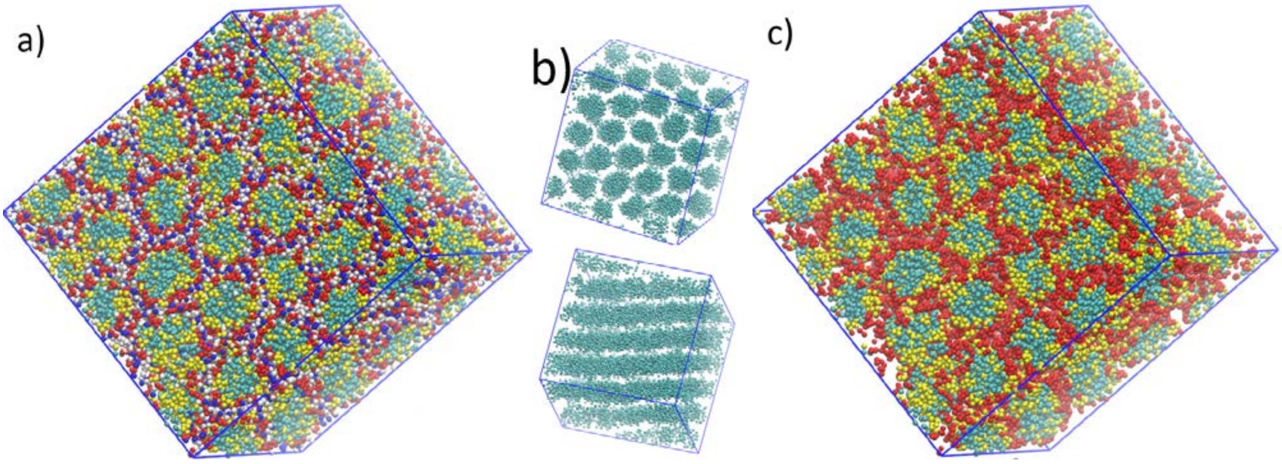

Figure 2 - Snapshots of morphology at 298.15K with components: a) all, b) alkyl chain only with its orthogonal perspective and c) ILs and phenol. Imidazolium rings, hydrophobic alky chains, anion, phenol and water are shown in colour red, cyan, blue, yellow and white, respectively.

Conclusions and future work

1. Conclusions:

Computational investigation on system with carbon precursors indicates that carbon precursors also slowly re-organised into hexagonal cylindrical distribution. Amphiphilic ILs showed high potential as soft templates to prepare highly ordered mesoporous carbons even in the presence of carbon precursor phenol. However, to make the hexagonal structure stable, it is necessary to add cross-linking reagents forming thermally stable frameworks so as to alleviate mesopore structure from collapsing after carbonisation.

2. Future work:

1) Add cross-linkers into system. Glyoxal could be potential candidate compared with formaldehyde in term of toxicity. The ratio of glyoxal to phenol is constrained as constant 1 to enable the formation of linear polymer frameworks.
2) DFT calculations will be performed to investigate the major driven forces for this self-assembly.
3) Experimental work including the synthesis of ILs and MCs will be carried out.

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QUILL Quarterly Report

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Modelling the use of Flow Batteries in Transport Applications

Background

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

Objective of this work

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

Progress to date

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

Conclusions and future work

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