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(up to December 2023)

QUILL

Quarterly Reports

August - October 2020

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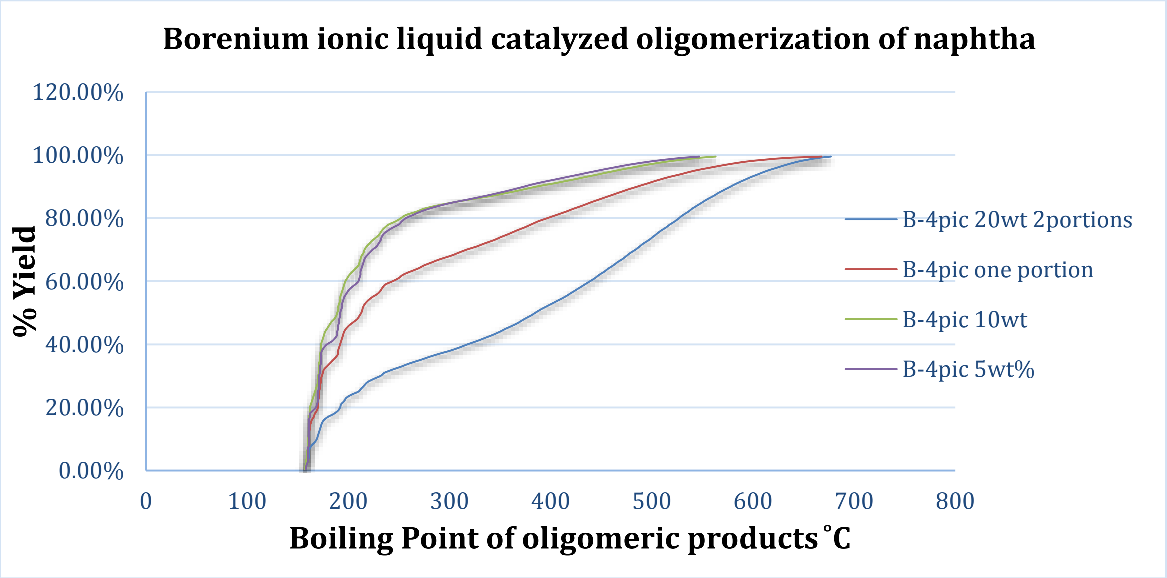
QUILL Quarterly Report

August 2020 – October 2020

Name:	**Issam Abdalghani**		
Supervisor(s):	Dr Gosia Swadźba-Kwaśny		
Position:	Research Fellow		
Start date:	10/12/2019	Anticipated end date:	31/03/2021
Funding body:	Invest Northern Ireland (Proof of Concept Funding Scheme)		

Valorisation of Products from Waste Plastic Pyrolysis

During my previous research work period, I resumed practical experiments after the opening of lab (Post-lockdown) and worked on the existing project. The focus of the work was on the screening of the catalytic activity of a series of Lewis acidic ionic liquids for the oligomerization of the olefinic mixture present in the real feedstock (naphtha) towards the preparation of base oil. Lewis acidic ionic liquids such as, liquid coordination complexes LCC, chloroaluminate ionic liquids and borenium ionic liquids were prepared, characterized and tested in the oligomerization of real feedstock under different conditions. The oligomerization was also investigated on other Lewis acidic catalysts such as, $AlCl_3$ and/or $AlCl_3/TiCl_4$. All reactions were performed using a battery of 8 HEL reactors in parallel, and the products (oligomers) were separated, purified and analysed by Simulated -Distillation GC. As main results, most of catalysts showed activity in the oligomerization of the feedstock, which partially reacted to afford oligomers. However, borenium ionic liquids showed better reactivity and selectivity. The focus of the next experiments will be using this catalyst, under different conditions (e.g., temperatures, catalyst loading and method of adding catalyst).



QUILL Quarterly Report

August 2020 – October 2020

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

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

The overarching objective of this project is to design, synthesis and investigate the chemistry of new main-group anionic coordination complexes that may be suitable candidates to produce the next generation of hydrophobic ionic liquids that incorporate non-coordinating anions.

The initial strategy within this research plan is to investigate modifications to current boron-based anions, within the context of ionic liquids, building on the existing work with tetrafluoroborate ($[BF_4]^-$), tetracyanoborate ($[B(CN)_4]^-$), tetraalkylborate ($[BR_4]^-$), and *bis*(oxalatoborate ($[BOB]^-$). A detailed literature review is underway, exploring how known boron-based anions are used to prepare ionic liquids, and more broadly the development of main-group borate anions. This will be used as a guide or 'stepping stone' to develop and test new experiments that could lead to the development of new anions for functional ionic liquids.

This will be achieved through synthesis, characterisation and testing of the anion's functionality. Within this strategy, the first stages are to replicate literature data to test the accuracy and reliability of the results, followed by modifications of synthetic pathways to the anion. The modifications will be used to develop versatile and flexible methods for preparation of families of functionalised borate anions.

The two functional targets identified for the first studies are (i) aryltrifluoroborates (Figure 1) and (ii) new borate ester anions (Figure 2). The general routes to obtain these two sets of anions are shown below.

<u>Aryltrifluoroborates</u>:
Aryltrifluoroborates with *ortho-* and *para-* chloro substituted groups have been previously prepared.[1] The general reaction scheme is shown in Figure 1. This work will be replicated, with the melting point and viscosities of the generated tetraalkylammonium salts determined and compared with the literature as benchmarks.

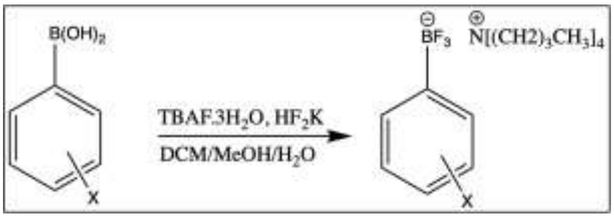


Figure 1 - General reaction scheme for synthesis of tetraalkylammonium aryltrifluoroborate salts.[1]

The effect of functional groups and substitution positions (especially with electron withdrawing groups) in the aryl substituent on the physical characteristics of aryltrifluoroborate salts will be investigated. EWGs including nitrile, sulfonyl and nitro groups are of interest, as are the effects of *meta*-substitution compared to *ortho*-substitution.

Borate Ester Anions:

A number of borate ester anions have been previously studied as ionic liquid forming systems, including bis(oxalate)borates ($[BOB]^-$) and esters formed with diols. In this study, non-halogenated borate esters will be prepared and investigated. Chiappe *et al.* have described the formation of glycerol-borate ester anions through reaction with boric acid.[2] The reaction scheme is shown in Figure 2. Relative stability and formation of cyclic five- and six-membered chelates were discussed.

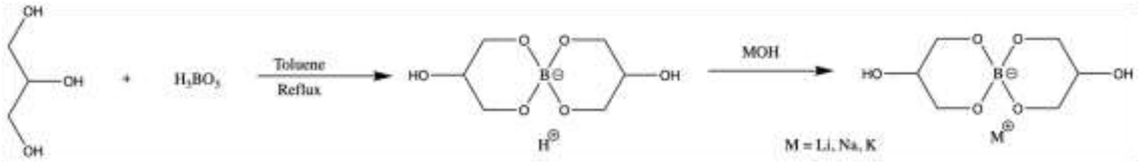


Figure 2 - Reaction scheme to form glycerol borate ester salts.[2]

Since this borate is known to dissociate in water, which is not ideal as shown by the project title, the development of hydrophobic anions, modified diols (1,3 and 1,4) will be investigated containing more hydrophobic peripheral functions. An example is through the reaction of glycerol/glycidol with fatty acids to obtain hydrophobic monolipid chelating agents. Alternatively, the -OH group can be replaced with different functional groups. Furthermore, instead of using glycerol it would be interesting to see how the physical/chemical properties would change if diols of varying carbon length were used instead.

References:

1. S. Brown, C. Drummond, J. Marchand, S. Marcuccio, K. Stockton and T. Greaves, *Phys. Chem. Chem. Phys.*, 2020, **22**, 23374-23384.
2. C. Chiappe, F. Signori, G. Valentini, L. Marchetti, C. Pomelli and F. Bellina, *J. Phys. Chem. B*, 2010, **114**, 5082-5088.

QUILL Quarterly Report

August 2020 – October 2020

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

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

Objective of this work

The aim of the PhD programme is focused on investigating the lithium ion battery (LIB) degradation processes occurring inside the cell during its operation. In order to achieve the goal a development of an experimental method based on the spectroscopy analysis techniques will be needed. A proper method would allow to observe and measure the changes that occur *in operando* inside the lithium ion battery. During the PhD programme the 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 characterization of samples have not been available as a potentiostat is needed to be employed for that purpose. Although the ageing data gathered in pre-lockdown period has been analysed by applying the distribution of a relaxation times (DRT) analysis. Firstly, due to the fact that DRT is able to estimate only resistive and capacitive-resistive behaviour of studied system a pre-processing of impedance data needs to be undertaken. The pre-processing has been investigated and performed as it could be observed in Figure 1. The first step is based on obtaining the impedance spectra, a raw data set by sample Electrochemical impedance spectroscopy (EIS) measurement. A validation by Kramers-Kroing test is further preformed. If the $\|Z - Z_{kk}\|$ residuals are found to be of relatively low a data set is treated as valid. However, if the residuals are observed to be occur throughout the entire measured spectrum or are considerably high an EIS measurement should be repeated until acceptable level of Z' and Z'' residuals are met. After the raw data validation an equivalent circuit is modelled and fit to the data. Here a knowledge of the studied system is of great importance as model is assumed *a prori*, thus grey box modelling in undertaken. Nonetheless there are a number of equivalent circuit models established for lithium ion batteries of various chemistries in the literature, thus could serve as a framework for the ECM development for studied system. Finally, the convergence of the established model is studied and if achieved a model is presumed to be valid. Then a removal of any diffusive and inductive elements should be subtracted from the ECM, so the DRT requirements are met. Eventually a new set of data is simulated based on a modified model.

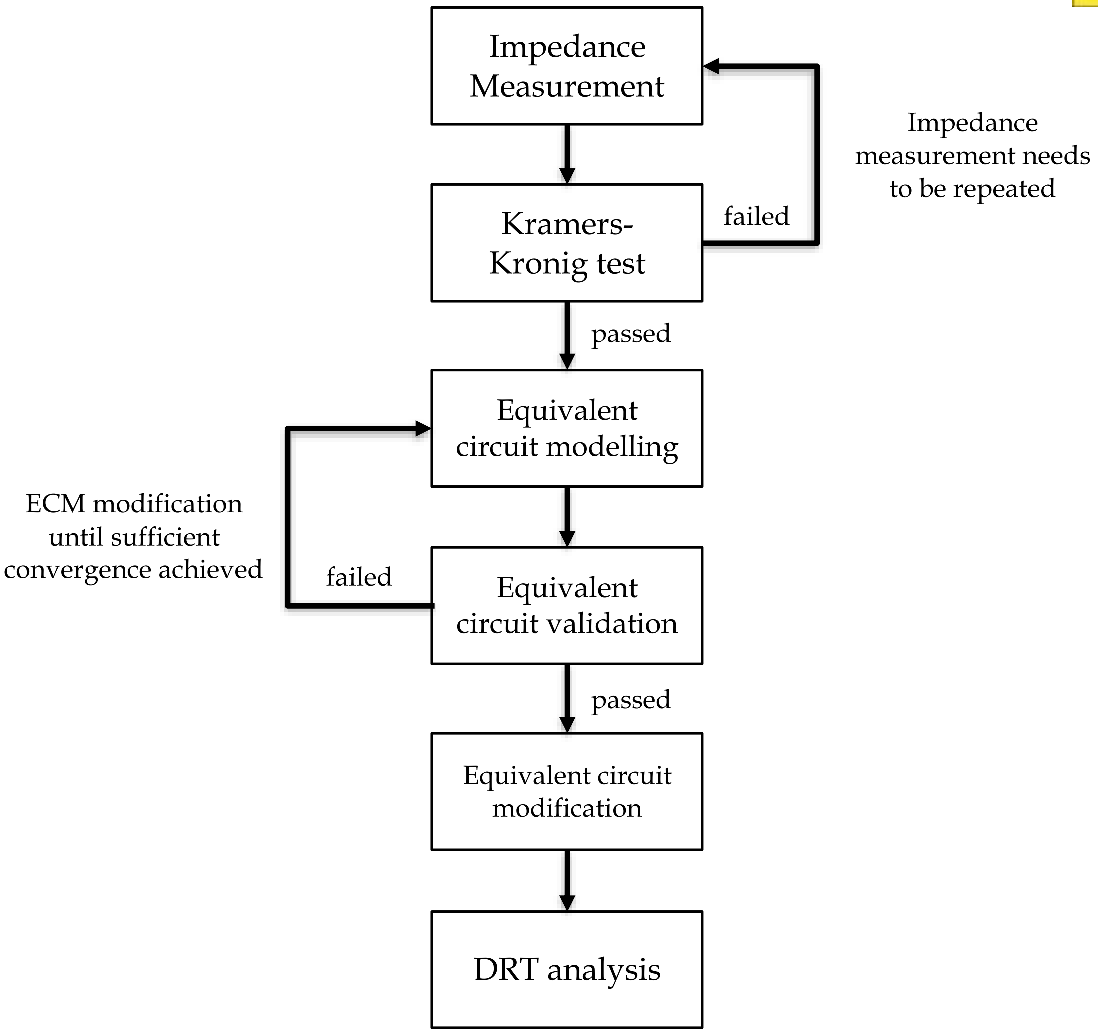


Figure 1 - Pre-processing of an impedance measurement for the distribution of relaxation times analysis

Additionally, an investigation of DRT analysis itself has been performed. The DRT analysis could be performed either using the piecewise linear approach or by the use of radial basis function (RBF) for discretization of an EIS data, thus both approached has been tested. Therefore, a set of radial basis function that has been included in DRTtools MatLab® toolbox as well as piecewise linear based analysis has been performed using MatLab® software. The RBF discretization methods that has been studied are shown in Table 1.

Table 1 - Radial Basis Functions included within DRTtools toolbox

Discretization method	$\phi_\mu(x)$
Gaussian	$\exp(-(\mu x)^2)$
C^2 Matérn	$\exp(-\lvert\mu x\rvert)(1+\lvert\mu x\rvert)$
C^4 Matérn	$\exp(-\lvert\mu x\rvert)(1+\lvert\mu x\rvert+\frac{1}{3}\lvert\mu x\rvert^2)$
C^6 Matérn	$\exp(-\lvert\mu x\rvert)(1+\lvert\mu x\rvert+\frac{2}{5}\lvert\mu x\rvert^2+\frac{1}{15}\lvert\mu x\rvert^3)$
Inverse Quadratic	$1/(1+(\mu x)^2)$
Inverse Quadric	$1/\sqrt{1+(\mu x)^2}$
Cauchy	$1/(1+\lvert\mu x\rvert)$

However, The DRT analysis is heavily dependent on the parameters used that are not commonly discussed, especially for specific electrochemical systems. Firstly, the optimal regularization λ and RBF shape factor μ parameters as well as the regularization derivative has been investigated. DRT has been investigated using a set of various regularization parameter. The investigation should thus result in obtaining the most optimal set of regularization parameters. The DRT has been performed on a LIB CR2032 coin cell sample of NMC811 cathode and graphite anode at the 10-cycle point of life. The regularization parameter value investigation could be seen in Figure 2.

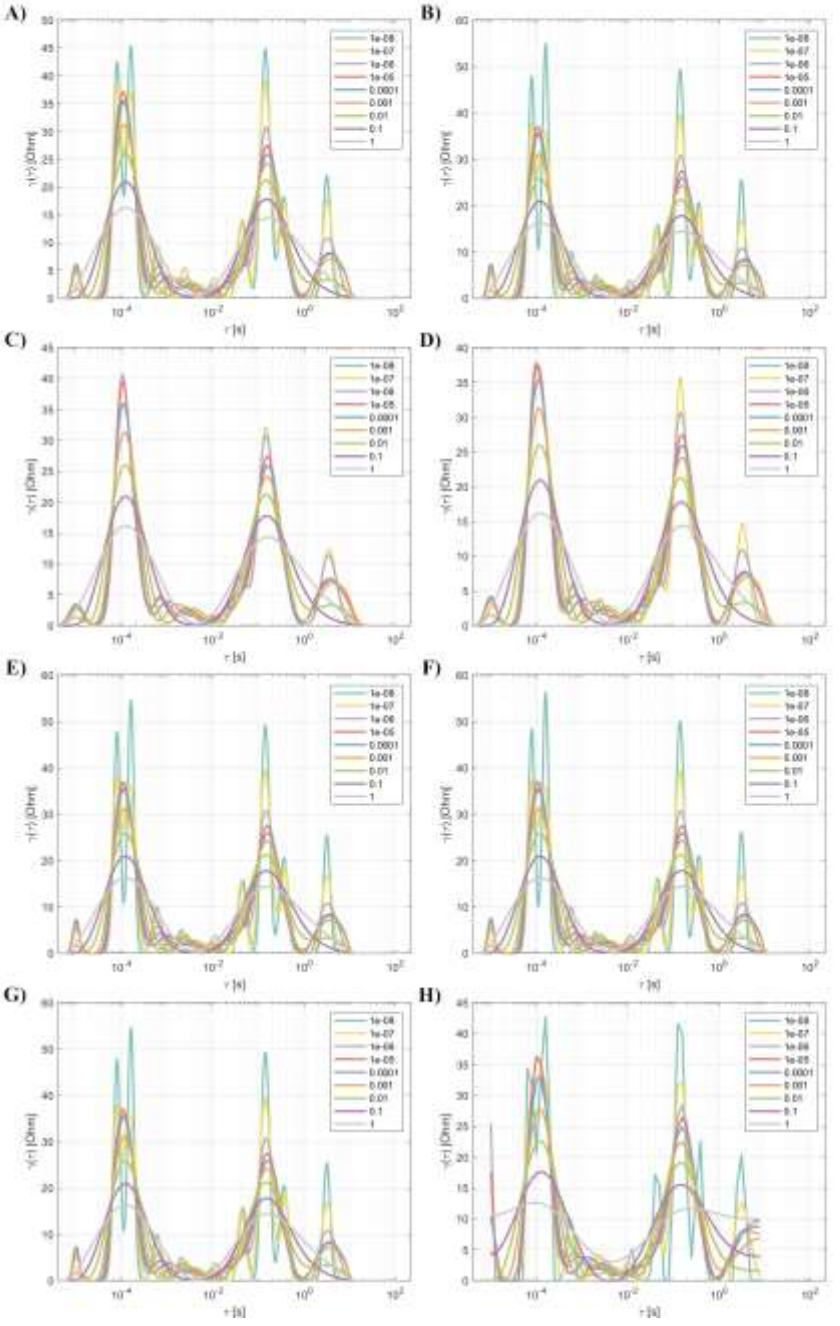


Figure 2 - Regularization parameter investigation of DRT analysis performed on LIB CR2032 coin cell NMC811 vs Graphite pre-processed EIS data at 10 cycle of life. DRT with candidate values of regularization parameter has been used with discretization methods of A) Gaussian, B) C^2 Matérn, C) C^4 Matérn, D) C^6 Matérn, E) Inverse Quadratic, F) Inverse Quadric, G) Cauchy, H) Piecewise Linear

The value of the regularization parameter is of important measure as the shape of calculated DRT data depend on it significantly. It has been shown that the value if to low would result in oscillation, yet if to large an over smoothing of data would occur. An optimal value of the regularization parameter will be chosen by optical examination of the DRT curves, making explicit attention to occurring oscillations and smoothing of data. In order to achieve the optimal value a set of candidate values has been proposed starting from unit decreasing up to 10^{-8} by steps equal to an order of magnitude. The range has been chosen as the regularization parameters in literature has vary from 10^{-2} up to 10^{-5}, thus the aim was to cover the regularization parameters that has been used by other research groups, yet also to explore the DRT behaviour pass the proposed in literature values. After analysing each DRT an approximate optimal value for each discretization method has been found to be between 10^{-5} and 10^{-4} for Gaussian, 10^{-6} and 10^{-5} for C^2 Matérn, 10^{-5} and 10^{-4} for C^4 Matérn and C^6 Matérn, approximately 10^{-4} for Inverse Quadratic and Inverse Quadric, 10^{-5} for Cauchy and 10^{-4} for Piecewise Linear. In order to estimate a more precise value for the regularization parameter a new set of predefined candidate values has been created for each discretization method basing on the approximate value observed when previous range of candidate parameters has been employed. Therefore, the DRT has been calculated using the new sets of values. Eventually, the optimal parameter values and derivative order has been found for each of the discretization method that could be employed with DRTtools Matlab® toolbox. The found values could be found on Table . It could be seen that the value of regularization parameter varies from 10^{-5} up to 10^{-4} for all the discretization methods. The RBF shape parameter highest used value of a unit is employed with Gaussian discretization while the lowest of 0.1 with C^4 Matérn and C^6 Matérn. The derivative of first order has been found to be suitable for most of the discretization method except for the C^2 Matérn where a second order of derivative was found to produce data with more uniform peak shape.

Table 2 - The regularization, RBF shape parameter estimated values and derivative order for DRT analysis performed on LIB CR2032 coin cell NMC811 vs Graphite EIS data at 10 cycle of life sample with discretization methods included in DRTtools Matlab® Toolbox

Discretisation method	λ_{reg}	μ	Derivative order
Gaussian	10^{-4}	0.5	1^{st}
C^2 Matérn	2×10^{-5}	0.3	2^{nd}
C^4 Matérn	5×10^{-5}	0.1	1^{st}
C^6 Matérn	5×10^{-5}	0.1	1^{st}
Inverse Quadratic	10^{-4}	0.5	1^{st}
Inverse Quadric	2×10^{-4}	0.3	1^{st}
Cauchy	5×10^{-5}	0.5	1^{st}
Piecewise Linear	10^{-4}	-	-

Back to laboratory work tasks

Disclaimer: Due to lack of chemicals and equipment back to lab work it is impossible. Some orders dated February have not been delivered till this day.

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 ceramic knife into two parts. A 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 is needed 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 studies is in order to provide insights if the ageing of different carbonaceous materials is able to be observed by obtaining their spectra in the same conditions.

In operando studies – The methodology for cutting electrodes to shape has been investigated resulting in foil metal cutters to provide with the finest cuts suitable for electrode reshaping. The *in operando* casing has been developed using AutoCAD® software and its to be printed on Ultimaker® 3D printer. Assessing the needed components for the Raman microscope is undertaken. The studies are planned for February.

QUILL Quarterly Report

August – October 2020

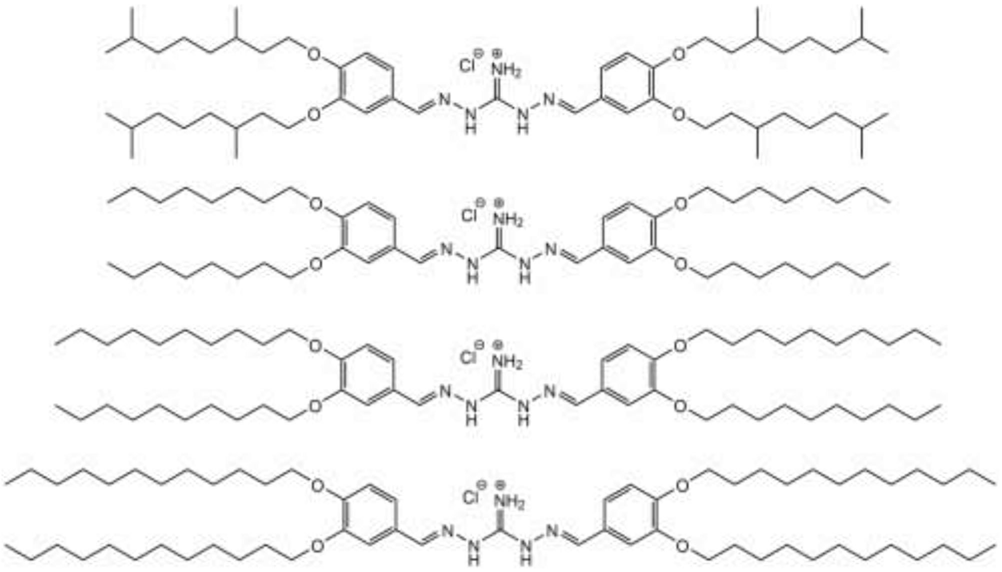
Name:	**Dominic Burns**		
Supervisor(s):	Prof John Holbrey & Dr Gosia Swadzba-Kwasny		
Position:	PhD Student		
Start date:	01/10/2019	Anticipated end date:	31/05/2023
Funding body:	EPSRC		

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

Following studies testing the ability to use [P_{66614}]Cl as a hydrophobic liquid anion exchanger materials to remove sulfate from aqueous streams previously reported, I am currently designing and carrying out investigations on extractant molecules that will enhance the selectivity of the extracting phase for sulfate through selective complexation and discrimination.

The main body of my work in the last quarter is based on a reverse micelle forming extractant reported by Moyer and co-workers that can extract sulfate into a branch paraffin solvent extracting phase with a separation factor of 4,300 for sulfate over chloride (DOI: 10.1039/c8cc05115a).

I am currently synthesising this extractant (show as top, below) as well as a series of homologues with a range of alkyl chain substituents to test how the structure can alter the self-assembly of these molecules and how that can then change its ability to extract sulfate from aqueous solutions.



Some time was also spend synthesising and testing bisurea/thiourea anion receptors as possible sulfate extractants but this work was set aside due their limited solubility in common laboratory solvents as well as [P_{66614}]Cl.

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August 2020 – October 2020

Name:	**Andrew Forde**		
Supervisor(s):	Dr Stephen Glover, Dr Rob Watson & Prof Peter Nockemann		
Position:	PhD Student		
Start date:	03/06/2019	Anticipated end date:	03/12/2022
Funding body:	Horiba-MIRA & EPSRC		

Battery Thermal Management and Algorithmic 3D Temperature Prediction

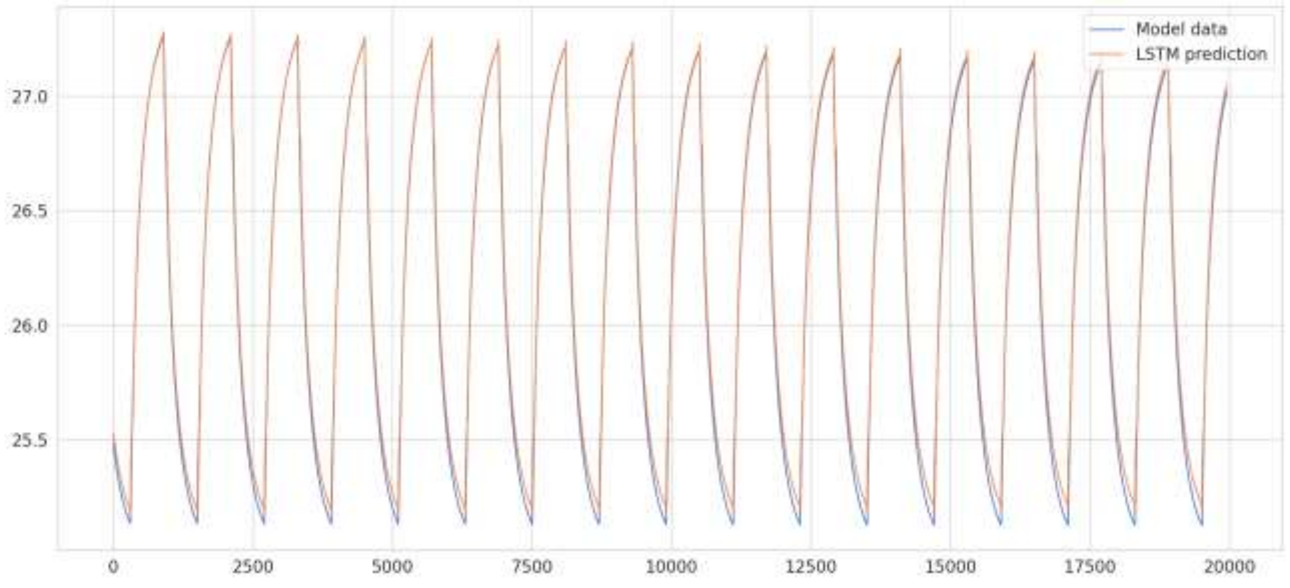
Experimental work being carried out from home

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.

A computer vision system has been developed to allow to robotic arm to accurately locate the sensors and battery relative to itself. This was necessary as the homing mechanism usually carried out by the arm is not possible when confined within a glovebox. A custom end effector is now being designed to allow for maximum accuracy when lifting and placing thermal sensors. This will ensure that risk of damaging the battery during instrumentation is minimised.

Machine Learning

A bidirectional LSTM network has been developed using the Keras machine learning library. Initial training using results from the battery numerical model show high accuracy for prediction of a point temperature measurement at the centre of the battery. Prediction of response to a 0.5C pulse discharge cycle is shown below



QUILL Quarterly Report

August 2020 – October 2020

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

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

Background

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

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

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

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

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

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

Objective of this work

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

Progress to date

- Addition of water CEM to rig in order to create a more consistent and stable water flow rate in feed lines.
- Addition of Krypton gas line to rig to act as a standard which will show the differentiation between lean and rich compositions.
- Addition of Helium gas line to rig for calibration purposes.
- Mass spectrometer calibration experiments. Gases cycled on and off at a set concentration in order to determine the ion current that corresponds to the fed concentration of gas.
- Calibration of all feed and product gases was performed in order to accurately map experiments. Mass spectrometers must be calibrated after every period of 6 months or in the event of an unplanned shut down or electrical fault.
- Replacement of 2 gas regulators for micromeritics chemisorption machine.
- Defined TPR method for catalyst samples and analysis of TCD vs Temp graph to ensure results are as expected.
- Shipment of mass spectrometer to England to fix vacuum pump fault.
- SEM/EDX training for sample characterisation.

Conclusions and future work

- No experimental results obtained, during this period, to draw conclusions from.
- Next steps involve completing TPR characterisations and SEM/EDX characterisations as well as performing LEAN/RICH cycling experiments.
- Analysis of experiments will be discussed once results from these types, mentioned above, have been obtained.

QUILL Quarterly Report

August 2020 – October 2020

Name:	**Jerry Pui Ho Li**		
Supervisor(s):	Dr Nancy Artioli & Prof Peter Nockemann		
Position:	Research Fellow		
Start date:	9/12/2020	Anticipated end date:	8/02/2021
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, more focus has been placed on the experimental work of the proof of concept (POC) project. At present we are able to satisfy the goals of CO_2 conversion, upwards of 25%. The product distribution produced requires further optimisation however.

On the commercial end of the work, engagement has been made with Aggregate (also known as LaFarge) concrete manufacturing. They are keen on any carbon conversions technology as one of the bigger CO_2 emitters globally, and have shown interest in discussions. This had resulting in an introductory meeting with representatives of Aggregate, with all those involved in the POC in attendance. It would appear that there has been interest, with parties on both sides drawing up NDA agreements before further discussion. Within the meeting, an introduction to our proposed technology was made, showing conversion of CO_2 to hydrocarbons. Preliminary results were presented, introducing the type of catalyst to be used, and some reaction data. Aggregate meanwhile, have highlighted their need for carbon emission control but also highlighted the purity of their flue gas. It would appear that in addition to the conversion, the flue gas requires some cleaning and purification.

For technical work, synthesis and testing of a few batches of the nanodispersed catalyst. As the laboratories have only just recently opened up. At the time of this report, 3 types of catalysts were prepared, with one being tested. It should be noted that although ionic liquids have been cited to be reusable, it would appear that due to the high temperatures required of the synthesis methods, they cannot be used more than 2 cycles, with the 1st cycle producing the most yield, 2nd cycle with less, and the 3rd producing undesired products.

In the initial test batch, results showed ~25% conversion of CO_2 to C_1-C_4 hydrocarbons, but low amounts of higher chain hydrocarbons. The other catalysts produced relatively similar conversions, but product distribution remains in the C_1-C_4 range, thus further optimisation is required.

Technoeconomic assessment of a larger scale process is ongoing. At present preliminary figures can be produced but still requires several components to complete this: real process data from Aggregate (i.e. annual emissions output and its composition), usable experimental data, and optimisation to allow for error-free simulations. As it stands it can be used as the initial sales pitch but ultimately needs to be complete in the end.

In other general tasks, 3 virtual conferences were attended: ICEC2020, UKCSCST2020, and the QUILL meeting, where oral presentations were given in each, and a prize being awarded during the QUILL meeting.

Conclusions and future work

At the time of this report, Aggregate have shown interest in collaboration with NDA's being drawn from both them and the university, thus showing a market interest for the technology and satisfying a portion of the POC goals. For technical work, catalyst optimisation will be ongoing, first by attempting to replicate results from literature (to be used as a benchmark), followed by iterating on the benchmark.

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.

QUILL Quarterly Report

August 2020 – October 2020

Name:	**Sam McCalmont**		
Supervisor(s):	Dr Leila Moura & 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, I have returned to the laboratory and have been able to put what theory I learnt and prepared for during the lockdown period into practice. On top of this I have completed my first QUILL biyearly meeting and the differentiation of my PhD.

The main objective over the 3 months has been to move forward with the commissioning of the gas system. The main step to begin with is the installation of the gas system. This has included the thought process behind the placement of the individual components to enable the system to be used for multiple purposes at the same time. On top of this for the pressure-volume-temperature (pVT calculations), the assembly and wiring of the pressure transmitters was completed. Volume determination of the chambers containing the gas has also been completed. The gas system is currently being leak tested before the validation of the system can be begin.

The second objective upon return was to synthesise my first ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Bmim][NTf_2]) *via* [Bmim]Br. [Bmim][NTf_2] will be utilised for the validation of the gas system, alongside polyethylene glycol 200 (PEG200). This synthesis has proven to be more of a challenge than initially thought. However, the synthesis has proven to be a positive learning curve towards my work, improving my knowledge and skills in synthesis. These skills include the usage of the correct solvent for the synthesis and purification of the ionic liquid and a better understanding of the reaction mechanism.

QUILL Quarterly Report

August 2020 – October 2020

Name:	**Stephen McDermott**		
Supervisor(s):	Dr Haresh Manyar		
Position:	PhD Student		
Start date:	October 2019	Anticipated end date:	October 2023
Funding body:	EPRSC		

Selective reduction of carboxylic acids under ambient conditions

Investigating the role of ionic liquids in the reduction of carboxylic acids to alcohols for their use in API's in the pharmaceutical industry. The use of Bronsted acidic ionic liquids such as $[P_{6,6,6,14}][(H_2SO_4)(H_2SO_4)_x$ alongside sodium borohydride as a route for the reduction of carboxylic acids. In the past few months, we have tried various cations such as ET_3NH^+ and $Hmim^+$ without achieving the required conversion of benzoic acid and selectivity towards the alcohol. The phosphonium based ionic liquid $[P_{6,6,6,14}][(H_2SO_4)(H_2SO_4)_x$ has achieved 85% conversion with 98% selectivity towards the alcohol.

I have been characterising the ionic liquids by ^1H NMR, TGA, DSC, CHNS Analysis and FTIR. The characteristics match those in literature confirming the structure and process of production.

QUILL Quarterly Report

August 2020 – October 2020

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

Boron Lewis acids: structure and applications

Background

Transition metals are widely recognised for their ability to function as good catalysts, but they have major drawbacks such as low abundance, high cost and toxicity. Boron is a main group, non-metallic, earth-abundant element with the potential to replace transition metals.[1] Many boron-based species show very strong Lewis acidity (*i.e.* excellent electron-pair acceptors).[2] However, understanding, quantifying and predicting Lewis acidity is very challenging, which limits the development of boron-based catalysts. Usually, measurement of Lewis acidity is probe-dependent, therefore order of strength on Lewis acidity scale may vary, depending on the probe used and the methodology adopted. In addition, there are limited experimental measurements of electronic structure of boron compounds. A major challenge for obtaining experimental electronic structure data is the presence of the boron centre. The boron 1s core orbital has an energy of ~200 eV, meaning that vacuum conditions are required for any electronic structure measurements. I am currently working on a study which will utilise liquid-microjet x-ray spectroscopy using the soft x-ray synchrotron BESSY II, Berlin, to determine the valence electronic structure of boron-containing samples. This research will be done in collaboration with Dr Kevin Lovelock from the University of Reading, who will be analysing the results. The aim is to use this data to better quantify, understand and predict the Lewis acidity of boron-based species. By understanding how the electronic structure relates to chemical reactivity, it will help aid the design of new boron based catalytic systems. To achieve this goal a combination of liquid-jet sample delivery with x-ray photoelectron spectroscopy (XPS), resonant XPS (RXPS) and x-ray absorption spectroscopy (XAS) will be used to study a range of boron-containing samples. These include reference samples and a selection of 3 and 4 coordinate boron-based species with formal charges -1, 0, +1. Suggested samples are shown in Table 1.

Boron 1s XPS, along with calculations, will be used to probe the atomic charge of the boron centres; this is important for understanding and predicting reactivity. The atomic charge for ligands bonded to boron will also be probed (O 1s, Cl 2p, P 2p).

RXPS is a site-specific technique involving resonant core level excitation followed by de-excitation through Auger electron emission. The boron-based molecular orbitals (MO) for all compounds are expected to be at a similar binding energy to solvent MOs. Using standard XPS, identification of boron-based solute MOs would be very difficult due to how they are swamped by signal from solvent MOs. RXPS of B 1s will allow identification of these boron-based MOs. Furthermore, RXPS will allow identification of MOs from ligands bonded to boron (O 1s, Cl 2p, P 2p).

B 1s XAS will be recorded using partial Auger yield detection (as part of the RXPS measurements). XAS, along with time-dependent DFT calculations, will be used to identify the boron-based unoccupied MOs. In addition, unoccupied MOs for ligands bonded to boron will be identified (O 1s, Cl 2p, P 2p).

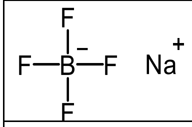
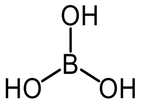
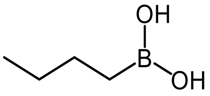
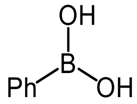
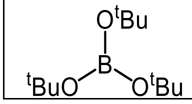
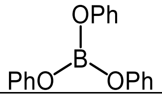
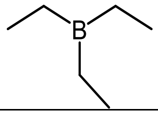
Objective of this work

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.

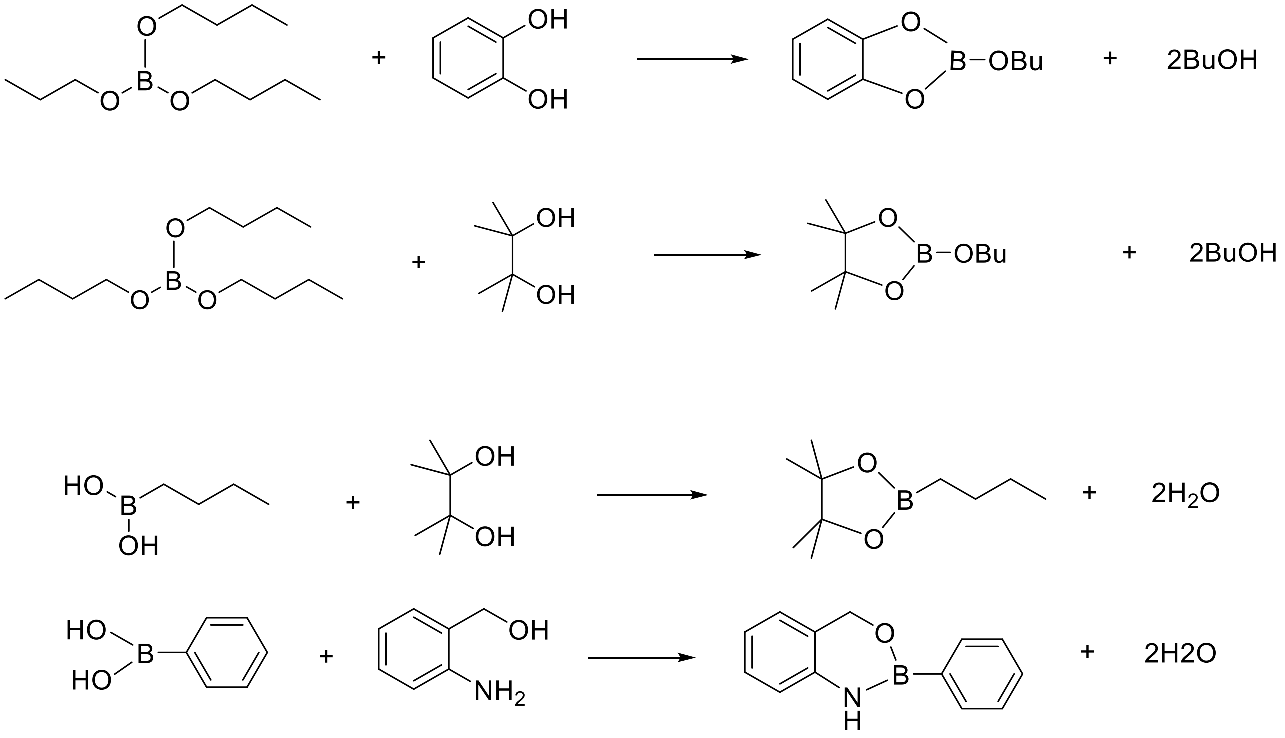
Progress to date

I have been designing the sample set of boron compounds to be tested at BESSY II in January. Table 1 shows some of the compounds that will be tested and Scheme 1 shows the synthesis that I am currently working on, that are able to be made on a large scale (30 – 40 g) which is required for the experiments.

Table 1 - Structures of the samples along with the coordination number and formal charge

Molecule/ion	**Coordination number**	**Formal charge**
	4	-1
     	3	0

Scheme 1 - Synthesis of boron containing compounds



These compounds will be made by adding 1 equivalent of the starting materials and heating to reflux in toluene, followed by distillation of butanol or collection of water in dean-stark apparatus. The compounds will be fully characterised using NMR, mass spec, DSC and TGA. The sample set has been designed to enable comparisons to be made between boron compounds of different coordination numbers and different charges. Other ligands such as trioctylphosphine oxide can be added to these three coordinate compounds in Scheme 1 to investigate four coordinate boron compounds.

Conclusions and future work

Preparations are in progress to run experiments at BESSY II in January. The sample set is evolving to contain more boron compounds and to ensure that useful comparisons can be made. This work will give an important insight into the electronic structure of these compounds which will help to better quantify their Lewis acidity and to aid the design of new catalytic systems.

I have also 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.

References

1. M. A. Legare, C. Pranckevicius and H. Braunschweig, *Chem. Rev.*, 2019, **119**, 8231-8261

2. S. Coffie, J. M. Hogg, L. Cailler, A. Ferrer-Ugalde, R. W. Murphy, J. D. Holbrey, F. Coleman and M. Swadźba-Kwaśny, *Angew. Chem.-Int. Edit.*, 2015, **54**, 14970-14973.

QUILL Quarterly Report

August 2020 – October 2020

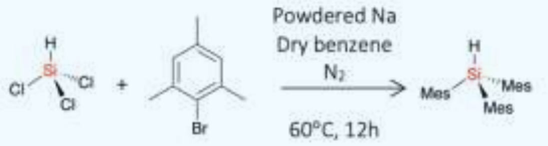
Name:	**Shannon McLaughlin**		
Supervisor(s):	Dr Gosia Swadźba-Kwaśny		
Position:	PhD Student (1st year)		
Start date:	October 2020	Anticipated end date:	July 2024
Funding body:	Department for the Economy		

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

The main aim of this project is to further research Lewis acidic main group cations such as tin, aluminium, gallium, indium and silicon. There is a particular interest into cationic silicon compounds in this project and the first goal is to synthesise the 'free' trimesitylsilylium cation first isolated by Lambert *et al.*[1] The synthesis of trimesitylsilane, chlorotrimesitylsilane, and allyltrimesitylsilane will follow methods described by Lappert *et al.*,[2] Zigler *et al.*[3] and Lambert *et al.*[4] respectively. The allyltrimesitylsilane will be used to synthesise the 'free' trimesitylsilylium cation following the method described by Lambert *et al.*[1] Silylium ions are usually quite a reactive species but the bulky mesityl groups in compound **1** help to shield the silicon centre from attack by large nucleophiles. These steric interactions also prevent the silylium ion reacting with the solvent and the product alkene making it much more stable.

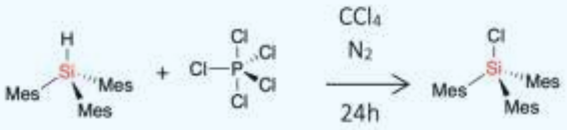
Synthesis of Allyltrimesitylsilane:

1. Synthesis of Trimesitylsilane



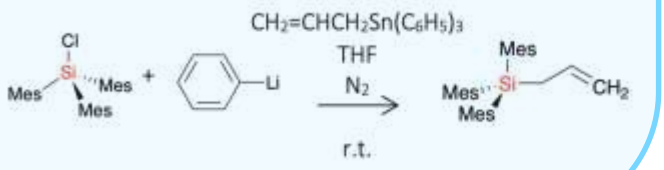
Lappert *et al.*[2]

2. Synthesis of Chlorotrimesitylsilane



Zigler *et al.*[3]

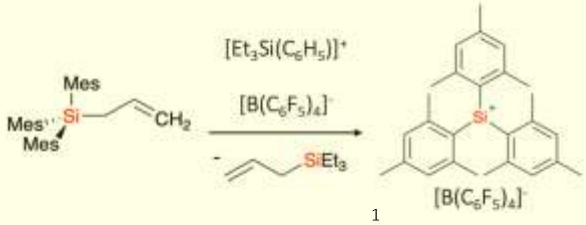
3. Synthesis of Allyltrimesitylsilane



Lambert *et al.*[4]

Synthesis of a 'Free' Trimesitylsilylium Cation:

allyl leaving group method



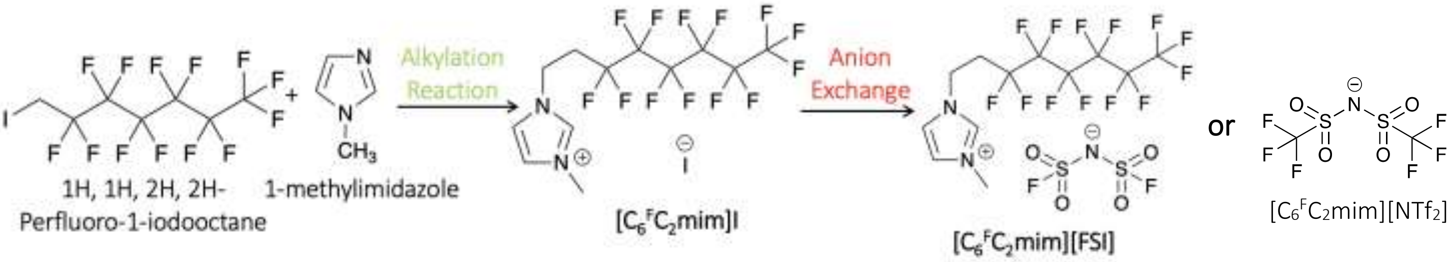
Lambert *et al.*[1]

1

An allyl leaving group method is used to generate the free silicon cation and the corresponding alkene. The driving force for this reaction is provided by the relief of steric strain around the original tetracoordinate silicon centre.

These salts are difficult to crystallise properly and instead they tend to form oils or liquid clathrates. Therefore, there is a potential to use these materials for unique applications such as ionic liquids. They will also be employed as a potential catalyst for both racemic and enantioselective Diels-Alder reactions, activation of strong carbon-fluorine bonds and the Friedel-Crafts silyation of heteroaromatic compounds.

Synthesis of Perfluorinated Ionic Liquids
(Continuation of Master's Project Work)



The synthesis of two perfluorinated ionic liquids will be continued from Master's project work.

1-methylimidazole and 1H, 1H, 2H, 2H-perfluoro-1-iodooctane will be refluxed together at 80°C to produce $[C_6^FC_2mim]I$. Reaction will be monitored using ^1H, ^{13}C and ^{19}F NMR spectroscopy. Once the alkylation reaction is complete and no more 1-methylimidazolium is remaining the $[C_6^FC_2mim]I$ will be converted to the corresponding $[C_6^FC_2mim][NTf_2]$ and $[C_6^FC_2mim][FSI]$ salts *via* anion exchange.

Approximately 5 ml of 1-methyl-3-(1H, 1H, 2H, 2H-perfluorooctyl) imidazolium bis(fluoromethylsulfonyl)-imide/bis(trifluoromethylsulfonyl)imide will be synthesised.

QUILL Quarterly Report

August 2020 – October 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

Following the COVID-19 shutdown, lab work on developing 3D-printed redox flow battery cells has resumed. An experimental setup has been assembled and Vanadium electrolyte from literature has been mixed. Various 3D-printed polymers have been evaluated for compatibility with this electrolyte with two suitable polymers identified – PP and ABS. A 3D-printed cell has been successfully printed, assembled and cycled with charge/ discharge experiments being carried out. A CNC machine has also been set up to manufacture custom current collectors and bipolar plates in QUILL. Work is ongoing to characterise these 3D-printed cells and to compare their performance to existing devices outlined in literature.

QUILL Quarterly Report

August 2020 – October 2020

Name:	**Scott Place**		
Supervisor(s):	Dr Paul Kavanagh (Principal) & Dr Mark Muldoon (Secondary)		
Position:	PhD Student (2nd Year)		
Start date:	01/10/2019	Anticipated end date:	31/07/2022
Funding body:	Department for the Economy (DfE)		

Electrocatalysis for Energy Applications and Sensing

From the month of August, I have been able to spend more time working in the lab collecting data for publications. In this time, I:

- Worked with Dr Kavanagh to compile and present data for our study on PIPO (polymer-immobilised TEMPO) in a publication draft. Throughout this process, we identified areas of weakness in the publication drafts and I went back to the lab to collect data required to fill the gaps and strengthen the work. Dr Kavanagh and I also met with Dr Mark Muldoon to discuss the paper, where he offered a number of helpful comments from a non-electrochemical perspective. Over the next two weeks, we will be implementing his feedback into the publication.
- Attended my first QUILL meeting in September (virtual), where I presented my work on PIPO and answered questions from a number of industrial partners.
- Contacted and met with Dr Peter Klusener (Shell) to begin an Industrial Mentor partnership. In this meeting, I again presented my work in PIPO in the context of energy storage and flow cells.
- Began work on the next major study in my PhD: investigation into the effect of electrode surface material on TEMPO-mediated alcohol oxidation kinetics.
- Attended a number of virtual seminars hosted by the School of Chemistry and Chemical Engineering including those by Peter Crowley (Macrocycle-mediated Protein Frameworks) and Thomas Wirth (Electrification of Synthesis and Flow Chemistry).
- Attended the Royal Society of Chemistry Webinar on Science and Stormont, with a focus on climate science and sustainability in public policy.
- Began working with the School of Chemistry and Chemical Engineering on marking and providing feedback for undergraduate work in Physical Chemistry.

QUILL Quarterly Report

August 2020 – October 2020

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

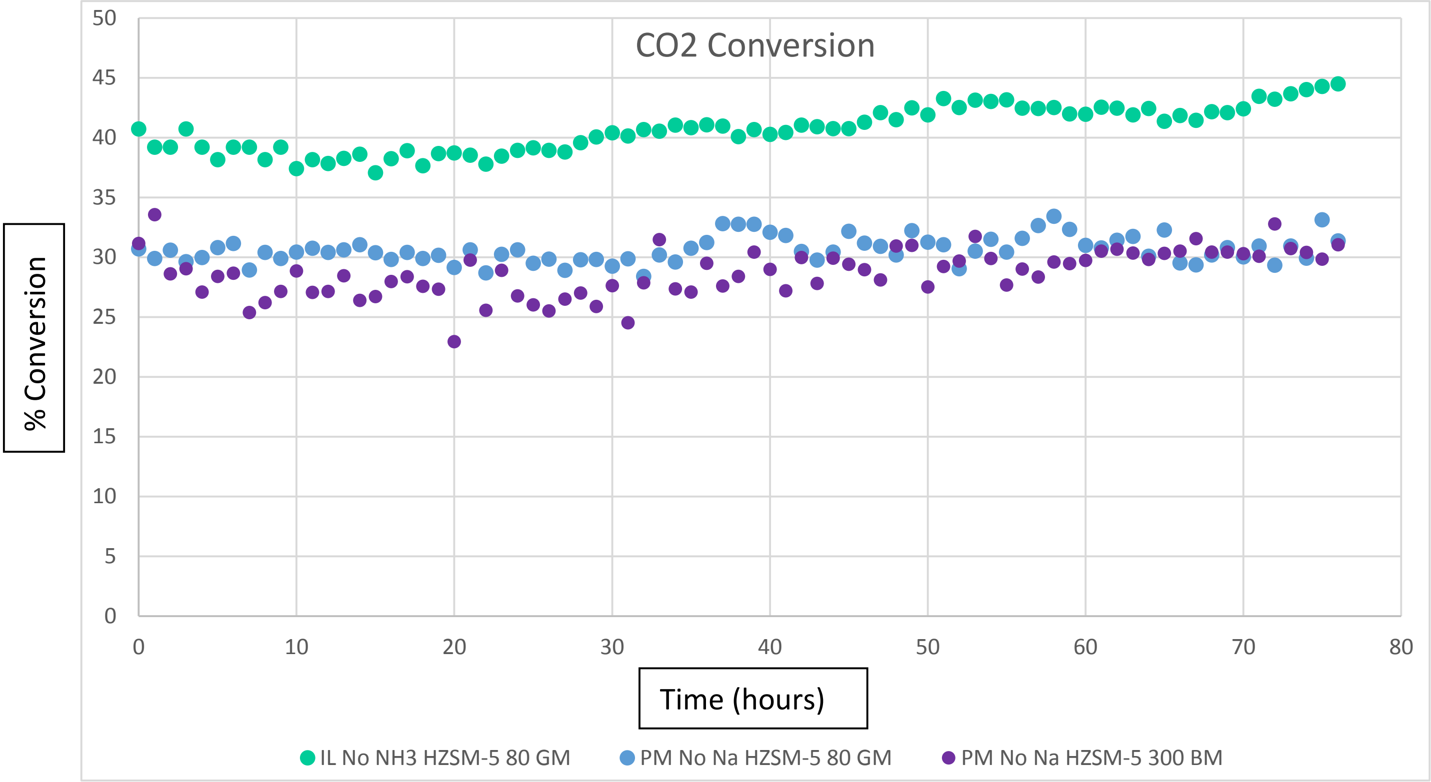
Developing New Nanocatalysts for the Direct Conversion of Biogenic Carbon Dioxide (CO_2) to Sustainable Fuels

Since returning to the lab in July, time has been spent getting the gas rig ready to restart testing of catalyst under reaction conditions. This involved ensuring no leaks, correct gas flows, mass flow controllers all working correctly. There was also some time spent re-evaluating the method for the GC. Initial testing of four different catalysts has been carried out and analysed, with a further three tested recently with the results not having been analysed sufficiently they will be included in the next report.

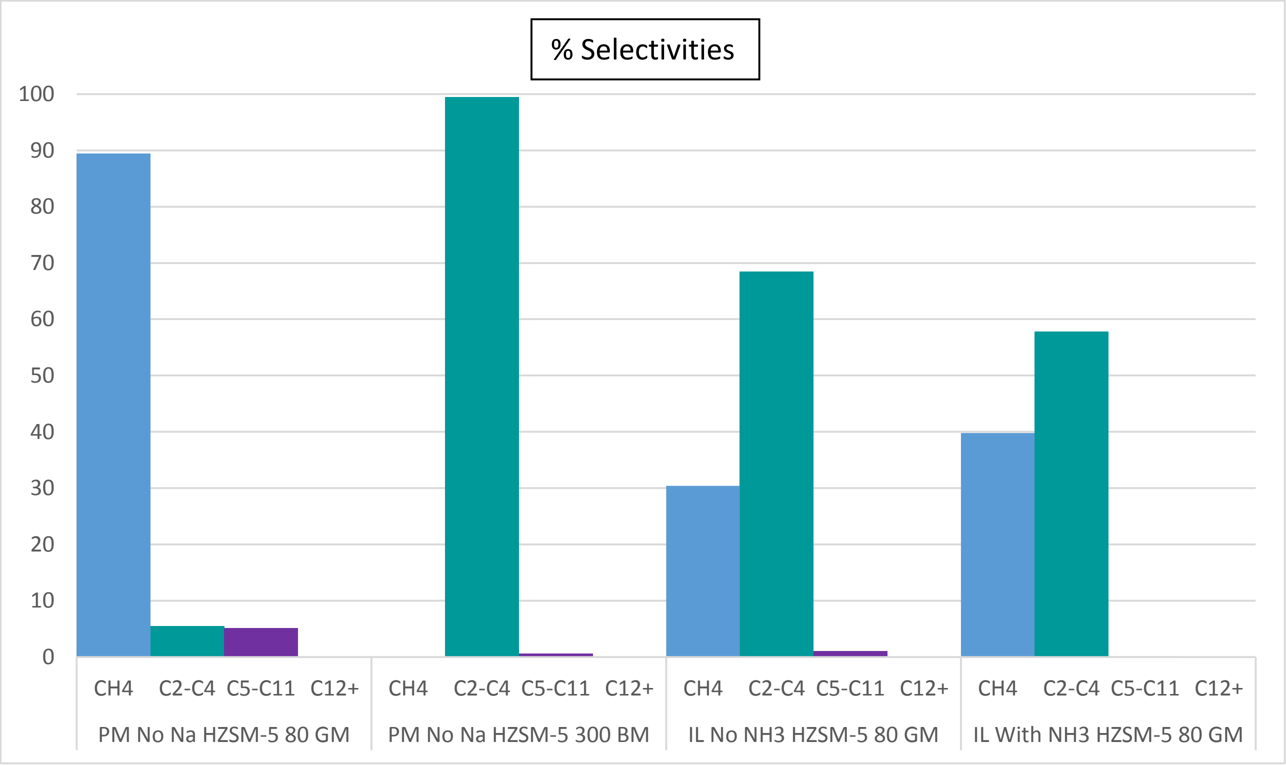
The table below shows the samples which have been tested and will be reported here.

Synthesis Method	**Conditions**	**Support Used**	**Method of Combination**	**Sample Name**
Precipitation	No Na	HZSM-5 (80)	Granular mixing	PM-NoNa-HZSM-5(80)-GM
Precipitation	No Na	HZSM-5 (300)	Ball Milling	PM-NoNa-HZSM-5(300)-BM
Ionic Liquid	No NH_3	HZSM-5 (80)	Granular mixing	IL-NoNH_3-HZSM-5(80)-GM
Ionic Liquid	With NH_3	HZSM-5 (80)	Granular mixing	IL-NH_3-HZSM-5(80)-GM

The samples were tested in a fixed bed stainless steel reactor under the following conditions: 3:1 gaseous mixture of H_2 and CO_2, GHSV = 4000 $mLh^{-1}g_{cat}^{-1}$, temperature: 320 ^{o}C, pressure: 25 bar.



The precipitation method CO_2 conversion is in line with what was reported in literature. The above graph shows that a higher CO_2 conversion is achieved with the sample prepared using ionic liquid. It also shows that there is little to no difference in CO_2 conversion when using different acidities of support or in how they are combined with the iron oxide. This is evidenced by the fact that the CO_2 conversion of the precipitation method samples are very similar.



The above graph shows the differences in selectivities towards different chain length hydrocarbons achieved by the different sample preparation methods. When comparing the precipitation method samples, it is clear there is a difference caused by the acidity of the support and the combination method. The next samples tested under reaction conditions compare the effect of these two conditions in order to gain further understanding of their effects.

QUILL Quarterly Report

Aug 2020 – Oct 2020

Name:	**Yaoguang Song**		
Supervisor(s):	Prof Peter Nockemann & Prof 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.

My last quarterly report introduced the computational study, coarse-grained MD simulations to be exact, on 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. The molar ration of ILs/phenol was constrained as 1/1. Spherical, hexagonal cylindrical and lamellar bilayer structures were observed with the decreasing water content in the three component systems. In this report, we will discuss the influence of hydrogen bonds on the self-assembly as well as the distribution of phenolic compounds.

Methodology

Benzene, phenol, resorcinol, phloroglucinol were employed as vague lignin models due to their increasing number in hydroxyl groups linked to the aromatic ring. Consequently, above mentioned four compounds could form 0, 1, 2, and 3 hydrogen bonds as H donor with ILs or water, respectively. Similar to my previous report, 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. Phenolic compounds model was proposed based on benzene model 3 SC5 beads, while hydroxyl groups were coarse-grained with SP1 bead to introduce polarity. 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.

Results

Figure 1 shows the morphology of system at 358 K. Alkyl chain of imidazolium cation were aggregated into cluster forming the hydrophobic phase and slowly reorganised into columnar hexagonal or smectic lamellar bilayer phase and the head groups were exposed to aqueous phase. Based on simulations, at same molar ratio and temperature, the introduce of increased hydroxyl group influenced the morphology.

For the fabrication of mesoporous polymers or mesoporous carbons, it is critical to study the distribution of carbon precursor as well. From Figure 1, it can be clearly observed that the carbon resource transferred from alkyl chain phase to aqueous phase with increased hydroxyl groups.

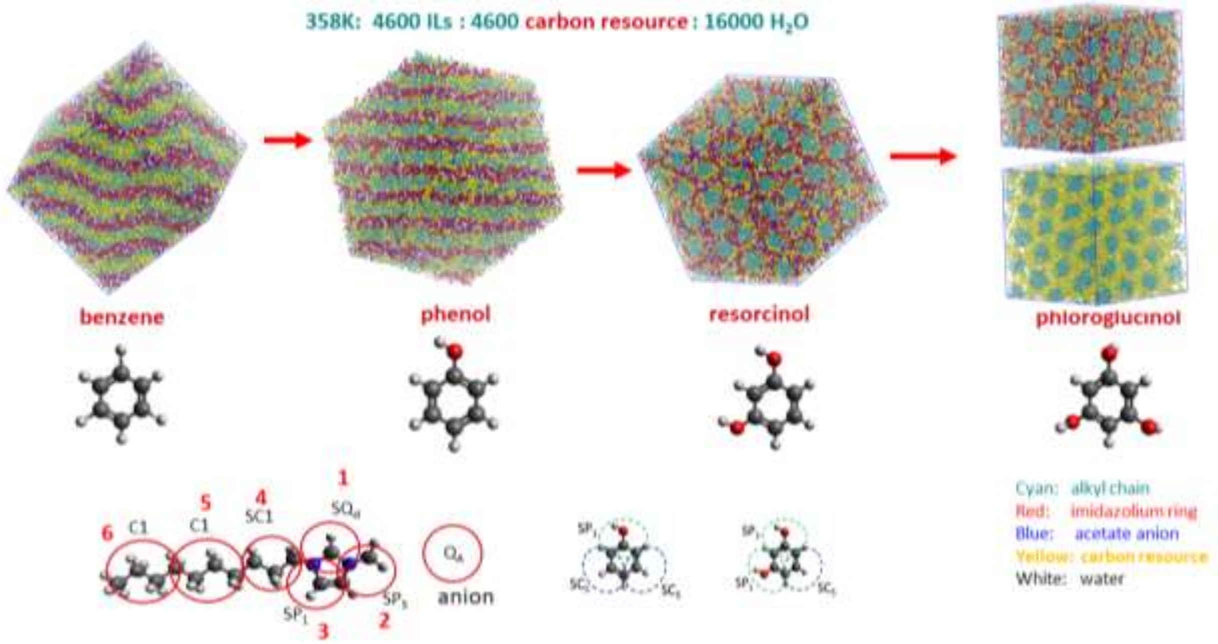


Figure 1 - Snapshots of morphology at 358.15K with components. Imidazolium rings, hydrophobic alky chains, anion, phenol and water are shown in colour red, cyan, blue, yellow and white, respectively

Figure 2 shows the bead-bead radial distribution function (RDF), which indicates the correlation preference between two beads. With the increasing hydroxyl group, the correlation between carbon resource and ILs cation tail become weaker, while the correlation with water become stronger. This results coincide well with the distribution preference of carbon resource in Figure 1.

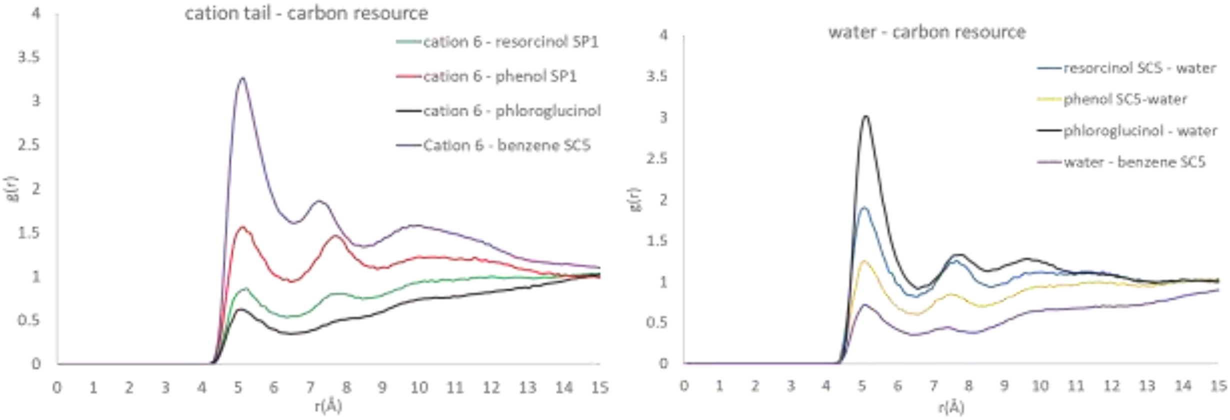


Figure 2 - Bead-bead RDF between carbon resource and ILs (left), and water (right)

Conclusions and future work

1. Conclusions:
Computational investigation on system with carbon precursors indicates that carbon precursors also slowly re-organised into columnar hexagonal or smectic lamellar bilayer structures. With increased hydroxyl groups, the morphology of three-component system evolved from lamellar bilayer to columnar hexagonal phase. Besides, the distribution of carbon resource also transferred from hydrophobic phase to aqueous phase.

2. Future work:
1) DFT calculations will be performed to investigate the major driven forces for this self-assembly, especially how hydrogen bonds influence the morphology evolutions.
2) Prepare ILs to make three component systems to verify the simulation results by performing SAXS or solid-state NMR.

References

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QUILL Quarterly Report

Aug 2020 – Oct 2020

Name:	**Richard Woodfield**		
Supervisor(s):	Dr Stephen Glover, Dr Robert Watson & Prof Peter Nockemann		
Position:	PhD Student		
Start date:	06/2019	Anticipated end date:	12/2022
Funding body:	EPSRC		

Modelling the Use of Flow Batteries in Transport Applications

Background

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

Objective of this work

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

Progress to date

Battery testing was due to start before the pandemic, and the focus has shifted towards the modelling side of the project for the time being. Flow-battery models have been developed, including an electrical and thermal model of a vanadium redox flow-battery coastal ferry, which shows promise.

Conclusions and future work

Battery testing will commence soon, allowing some initial models to be further validated. Hybrid vehicle models will be developed further too.

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Name:	**Mark (John) Young**		
Supervisor(s):	Dr Leila Moura and Prof John Holbrey		
Position:	PhD student		
Start date:	1/10/2020	Anticipated end date:	1/4/2024
Funding body:	EPSRC		

Gas separation technologies

Biomethane is obtained through the upgrading of biogas produced from anaerobic digestors. It consists of mainly methane and carbon dioxide with many trace compounds including hydrogen sulfide, ammonia, silioxanes, terpenes and water vapour. Biomethane must be of a purity equal to or better than that of natural gas if it to be utilised for grid injection therefore a methane purity of above 96% must be achievable from any prospective technology. Carbon dioxide should make up 2.5-4% of the remaining volume with contaminants such as sulfer and siloxanes being limited to 10 mg/m^3 and 0.1 mg/m^3 respectively. Due to the major biogas components being carbon dioxide and methane it is this separation we will focus on in this project.

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

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

Before any experiments can be carried out with new potential sorbents we must first create a methodology for fast screening of samples. We plan to utilise headspace GC where we add various compositions and pressures of carbon dioxide and methane to multiple GC vials and allow for equilibration to occur. Headspace GC will then be used on the samples and concentrations of headspace gas calculated. Using this information, the known concentration of gas pre-equilibration will be compared to that of post-equilibration to give an approximate uptake and selectivity of the sample. This methodology should allow for many samples to be screen simultaneously. Any “hits” can then be fully tested using the full gas rig to accurately determine gas uptakes at various temperatures and pressures of up to 5 bar.

Before the end of the year the goal is to complete the GC methodology having constructed accurate calibration curves for application to our samples in order to be able to calculate uptakes. I also will synthesise and test various new sorbents for their gas uptakes via headspace GC.