

The 7th Australian Symposium on Ionic Liquids

Newcastle, Australia 2016



Welcome!

It is great pleasure to welcome you to the 7th Australian Symposium on Ionic Liquids (ASIL) in Newcastle, Australia, the 2nd largest city in NSW, the 3rd oldest in Australia, and one of the world's 10 best cities.¹

The scientific topics of ASIL7 2016 cover all aspects of ionic liquid research, ranging from breakthroughs in fundamental research to progress in industrial applications. The conference brings together scientific researchers and engineers to exchange ideas, present new findings, and establish new collaborations. The conference is also designed to engage the next generation of researchers, through opportunities for PhD students and early career researchers to get involved in a scientific setting.

The first ASIL meeting was held in Clayton in 2003, a locally run workshop. Subsequent ASIL took place every second year, and attracted much interest from attendees all over the world. ASIL1 – 4 were held in Clayton, Victoria. ASIL5 moved to Clapytron, and ASIL6 was held by UNSW in Coogee in 2014. We don't know where ASIL 8 will be, but it won't be Clapytron.

We would like to thank all participants, committee members and sponsors and student helpers for their joint efforts on making this conference a very successful event.

Once again, welcome to Newcastle. Enjoy the city, its sparking beaches and its prominent architecture.

Rob Atkin, Grant Webber, Alister Page
The Organising Committee

Conference Organisers

Prof. Rob Atkin, Director, Priority Research Centre for Advanced Fluids and Interfaces, University of Newcastle, Australia

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Peter Cooper

Andre Cook

Ryan Stefanovic

Josh Cummings

Dr Trang To

Dr Hua Li

Dr Zhengfei Chen

Conference Program

MONDAY May 23		
	Seaview Room	
	Chair: Rob Atkin	
11:00	Registration Opens	
13:00	Opening Remarks - Rob Atkin	
13:10	O1: Tom Welton	
13:45	O2: Jenny Pringle	
14:20	Welcome from UoN DVC-R Kevin Hall	
14:25	O3: Ed Castner	
15:00	coffee	
	Seaview Room	Harbour Lights Room
	Chair: Castner	Chair: Webber
15:30	O4: Christina Pozo-Gonzalo	O9: Mark Rutland
15:55	O5: Pat Howlett	O10: Hua Li
16:20	O6: Diogo Moulin Cabral	O11: Peter Cooper
16:40	O7: Fengling Zhou	O12: Seiya Watanabe
17:00	O8: Ben McLean	O13: Shuhei Ogawa
17:20	Seaview Room	
	Chair: Welton	
17:25	O14: Blake Simmons	
18:00	Close	

Conference Program

TUESDAY May 24		
	Seaview Room	
	Chair: Padua	
9:00	O15: Claudio Margulis	
9:35	O16: Katya Pas	
10:10	coffee	
	Seaview Room	Harbour Lights Room
	Chair: Margulis	Chair: Espinosa-Marzal
10:40	O17: Barbara Kirchner	O21: Luke O'Dell
11:05	O18: Alister Page	O22: Rebecca Hawker
11:25	O19: Oldamur Holloczki	O23: Sinead Keaveney
11:45	O20: Ryan Stefanovic	O24: Owen Curnow
12:05	Lunch	
	Seaview Room	Harbour Lights Room
	Chair: O'Dell	Chair: Rutland
13:35	O25: Debbie Silvester	O29: Rosa Espinosa-Marzal
14:00	O26: Chuan Zhao	O30: Anthony Somers
14:25	O27: Karin Schaffarczyk McHale	O31: Grant Webber
14:45	O28: Ana Santos	O32: Shouhei Kawada
15:05	coffee	
	Seaview Room	
	Chair: Ueno	
15:35	O33: Jim Wishart	
16:10	O34: Jason Harper	
17:00	Poster Session	
19:00	Close	

Conference Program

WEDNESDAY May 25		
	Seaview Room	
	Chair: Harper	
9:00	O35: Agilio Padua	
9:35	O36: Kenji Takahashi	
10:10	coffee	
	Seaview Room	Harbour Lights Room
	Chair: Aldous	Chair: Simmons
10:40	O37: Bill Price	O41: Kalpit Shah
11:05	O38: Tamar Greaves	O42: Nolene Byrne
11:30	O39: Hiroshi Abe	O43: Trang To
11:50	O40: Majid Asnavandi	O44: Haihui Joy Jiang
12:10	Lunch	
	Seaview Room	Harbour Lights Room
	Chair: Wishart	Chair: Byrne
13:40	O45: Kazuhide Ueno	O49: Leigh Aldous
14:05	O46: Daniel Eyckens	O50: Qi Han
14:25	O47: Jeffrey Black	O51: Will Hart
14:45	O48: Luke Henderson	O52: Aaron Elbourne
15:05	coffee	
	Seaview Room	
	Chair: McFarlane	
15:35	O53: Chris Hardacre	
16:10	O54: Jim Davis	
16:45	Free time	
19:00	Conference Dinner	

Conference Program

THURSDAY May 26		
	Seaview Room	
	Chair: Hardacre	
9:00	O55: Masa Watanabe	
9:35	Seaview Room	Harbour Lights Room
	Chair: Hardacre	Chair: O'Dell
9:40	O56: Zhengfei Chen	O59: Mega Kar
10:05	O57: Saffron Bryant	O60: Masahiro Yoshizawa-Fujita
10:25	O58: Samila McDonald	O61: Sowmiya Theivaprakasam
10:45	Coffee	
	Seaview Room	
	Chair: Davis	
11:15	O62: Doug McFarlane	
11:50	Closing remarks - Rob Atkin	
11:55	Close	

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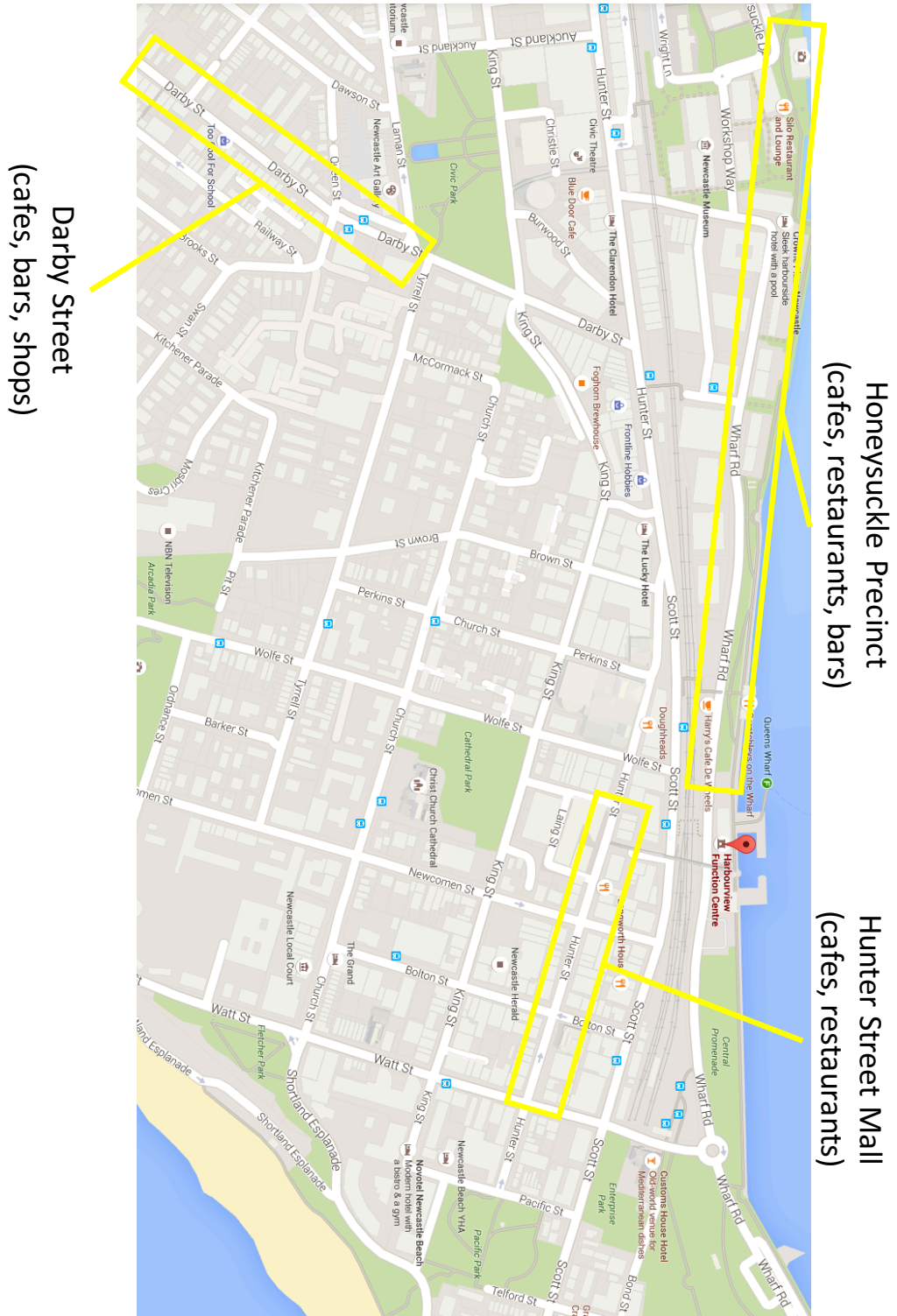


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Conference Location



Ion Diffusion in Ionic Liquids: Single Molecule Fluorescence Spectroscopy

Joshua B. Edel, Aleksander Ivanov, Alastair J. S. McIntosh, Tom Welton*

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An ionic liquid is an ionic substance in which its constituent ions are in motion. Consequently, it is not possible to understand the nature of an ionic liquid without understanding how its constituent ions move. However, gaining a thorough understanding the nature of ion motion in ionic liquids remains a fundamental challenge.

Single molecule fluorescence (SMF) confocal spectroscopy offers a powerful, but as yet largely underutilized tool to measure the diffusion of probe ions in an ionic liquid under a variety of conditions.

To enable SMF measurements, it was necessary to develop the synthesis of ionic liquids with very low background fluorescence. The SMF derived diffusivity of the cationic probe Rhodamine 123 in dilute (ca. 100 pM) solutions in [C₄C₁im][NTf₂] solutions was compared to diffusivity of the ionic liquid cations derived from Pulse Gradient Stimulated Echo NMR measurements. The SMF derived diffusivity of the cationic probe Rhodamine 123 was measured under various applied potentials and throughout the system's relaxation back to its unperturbed state. This relaxation was found to be markedly slower than in salt solutions in molecular solvents.

Ionic liquid-based redox electrolytes for thermal energy harvesting

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Thermoelectrochemical cells are increasingly promising devices for harvesting waste heat, offering an alternative to the traditional semiconductor-based thermoelectrics. This technology offers the promise of continuous and cheap operation at moderate temperatures, particularly <200 °C, e.g. using waste heat from power plants or geothermal sources, with low maintenance and no carbon emissions. Thermoelectrochemical cells utilise two electrodes, held at different temperatures, separated by an electrolyte containing a redox couple (Figure 1). The temperature dependence of the electrochemical redox potential results in a potential difference across the device. The magnitude of this temperature dependence is given by the Seebeck coefficient, S_e .

Until recently, research into thermoelectrochemical cells had primarily focused on aqueous media, predominantly with the ferri/ferrocyanide redox couple.¹ However, the good thermal and electrochemical stability, non-volatility and non-flammability of many ionic liquids makes them promising alternative electrolytes for these devices. Potential advantages include increased thermoelectrochemical device efficiencies, longer lifetimes and the ability to utilise waste heat sources in the 100 – 200 °C temperature range.

The highest power outputs to-date for thermoelectrochemical cells using ionic liquid electrolytes have been achieved through use of a high entropy change $\text{Co}^{(\text{II/III})}$ redox couple.^{2,3} Here we discuss our research into the influence of different ionic liquids on the temperature-dependant thermodynamics of the redox couple, reflected in S_e , and how use of a mixture of ionic liquid and molecular solvent can yield significant improvements in thermoelectrochemical cell power output.

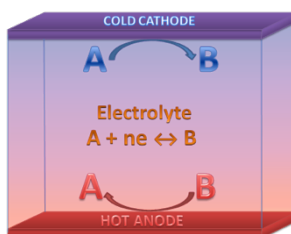


Figure 1. Illustrative example of thermoelectrochemical cell operation.

References

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- [3] M. A. Lazar, D. Al-Masri, D. R. MacFarlane, J. M. Pringle *Phys. Chem. Chem. Phys.*, 2016, 18, 1404-1410.

Ionic Liquids: Mixtures, Structures, Interfaces and Reactivity

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Ionic liquids (ILs) research in our group combines several approaches for studying the bulk structure and transport for interesting ILs and for mixtures of ILs with neutral solvents, including both polar (water) and non-polar (hexane). While the bulk structure of the ILs seems to be minimally perturbed on addition of neutral co-solvents, the measured diffusivities of the neutral species are an order of magnitude larger than hydrodynamic predictions. We normally obtain quantitative agreement between liquid structure factors measured using X-ray scattering and those calculated from molecular dynamics (MD) simulations, which enables detailed deconstruction of the local structure into polar/nonpolar, ionic, and sub-ionic partitions that reveal unique spatial distributions. An example of such polar-nonpolar partitioning is shown in the figure below for the MD simulation box at left, and the polar-nonpolar partitioning of the structure factor at right. I will present results from three classes of ILs: cyano-anions (such as selenocyanate through tetracyanoborate), a comparison between straight- vs. branched- alkyl-substituents on both pyrrolidinium vs. imidazolium cations with NTf₂ anions, and several series of silicon-substituted IL cations.

Other projects in our group continue to explore rates and mechanisms for bimolecular photo-induced charge separation using ILs both as solvents and as reactants. Mechanistic studies also include intramolecular charge separation in covalently linked donor-bridge-acceptor probe molecules in IL solutions. A newer research area for our group has been to prepare ultrathin films of ILs grown on Cu(100) and Au(111) using physical vapor deposition. Film thicknesses range from sub-monolayer to multiple monolayers. Analysis of these results shows stronger cationic interactions and reduced surface diffusivity for copper relative to gold surfaces.

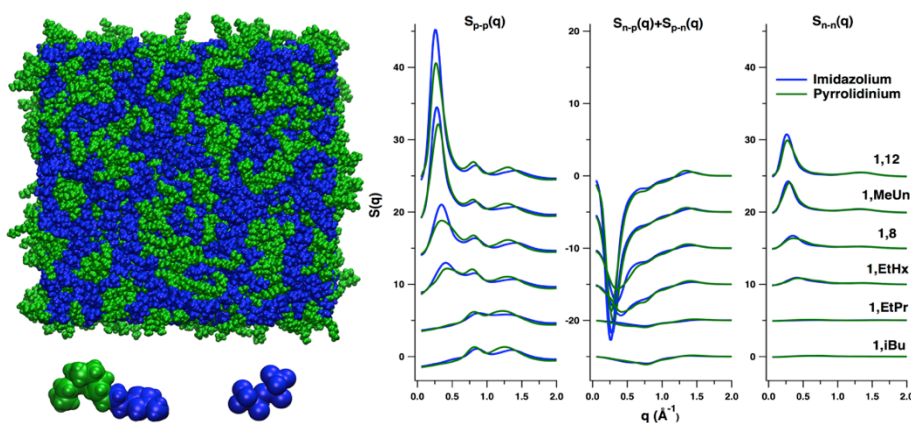


Figure 1. (left) MD box for 1-dodecyl-3-methylimidazolium NTf₂ for 1,000 ion pairs. (right) Polar-polar, polar-nonpolar and nonpolar-nonpolar partitioning of the structure factor for this IL.

Reduction of oxygen in a trialkoxy ammonium-based ionic liquid and the role of water

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The oxygen reduction reaction in a novel trialkoxy ammonium-based ionic liquid, N-ethyl-2-(2-methoxyethoxy)-N,N-bis(2-(2-methoxyethoxy)ethyl)ethan-1-aminium bis(trifluoromethylsulfonyl)imide, [N₂(20201)(20201)(20201)] [NTf₂] has been studied on glassy carbon and gold electrodes, showing faster electrokinetics on glass carbon because of weaker adsorption of the IL. This has been demonstrated by theoretical calculations and electrochemical studies. In the neat IL, the oxygen is reduced to superoxide (O₂^{•-}) through a one electron process; however, better performance is attained in the presence of water (42 mol%), in terms of current density, and onset potential of the reduction process via a reversible 2-electron process. Furthermore, a remarkable increase in cyclic coulombic efficiency is observed for the wet IL (66 % in comparison with the neat IL (24 %), showing the practicality of a reversible O₂/H₂O₂ system for energy storage.¹

References

1. Pozo-Gonzalo, C.; Kar, M.; Jónsson, E.; Howlett, P. C.; MacFarlane, D. R.; Forsyth, M., Reduction of oxygen in a trialkoxy ammonium-based ionic liquid and the role of water. *Electrochimica Acta* **2016**, *196*, 727-734.

Electrolytes For Lithium And Sodium Metal Devices – Towards High Stability, High Efficiency And High Utilisation Electrochemical Cycling

P. C. Howlett, D.R. MacFarlane, M. Armand and M. Forsyth



The holy grail of energy storage is battery technology based on Lithium or Sodium metal anodes, which offer intrinsic benefits of lightweight and high potential. Both Li and Na provide possibilities for reversible, high energy density devices for use from electric vehicles to grid storage, with Sodium metal also offering the advantage of lower cost and possibly, greater safety. These may include conventional devices where an intercalating cathode is used, or in Li/Na-sulphur or Li/Na-air configurations.

A well-known problem with both metals is the ability to cycle the electrode without creating dendritic morphology and ‘disconnected’ deposits, which can cause poor cycling efficiency, dangerous short circuits and failures in a battery. Polymer electrolytes, and more recently ionic liquid based systems, have shown great promise for stable cycling of Li and Na. This presentation will span the trajectory of polymer, plastic crystal and ionic liquid electrolytes, including novel single ion conducting ionomers and highly concentrated mixed ionic liquid electrolytes. The latter appear to produce a stable interphase layer, that, despite possessing somewhat lower ionic conductivities than the traditional organic solvent electrolytes, allow excellent device performance.

Electrochemistry of tris(2,2'-bipyridine) complexes of cobalt (II), nickel (II) and iron (II) in ionic liquids and aprotic solvents.

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The 2,2'-bipyridine (bpy) ligand is one of the most widely used in coordination chemistry. It was first synthesized at the end of the 19th century, with the iron(II) tris(bpy) being the first complex of this ligand ever observed[1]. Over the years a diversity of metals complexed with bpy have been synthesized and extensively studied, and recently some applications of these complexes have been proposed, e.g. the use of iron (II) and nickel (II) tris(bpy) complexes for non-aqueous electrolytes of batteries[2] and the use of cobalt (II) tris(bpy) for thermo electrochemical cells[3]. Also, currently there is a growing interest in using ionic liquids (ILs) for electrochemical applications, because they usually present some interesting properties, such as low volatility, non-flammability and intrinsic ionic conductivity[4].

The purpose of this work was to study the electrochemistry of the tris(bpy) complexes of cobalt (II)[5], nickel (II) and iron (II) in ILs and organic solvents, thus contributing to the understanding of how these compounds behave in these media. The basic electrochemical properties were investigated, including the redox potentials and the chemical and electrochemical reversibility of the redox reactions, as well as the kinetics of the oxidation reactions. An example of the results is in figure 1, which presents the cyclic voltammograms of 10 mmol.l⁻¹ solution of the three complexes in the IL 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (C₄mpyr NTf₂).

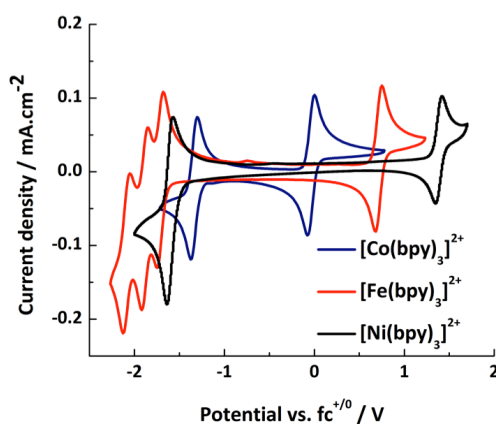


Figure 1. Cyclic voltammograms of tris(bpy) complexes of cobalt (blue), iron (red) and nickel (black), in C₄mpyr NTf₂, on a glassy carbon electrode at 20 mV.s⁻¹.

References

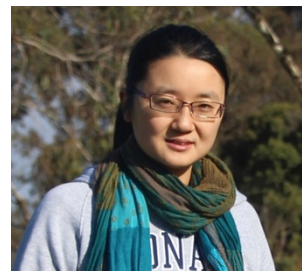
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Enhanced Photo-Electrochemical Water Oxidation on MnO_x in Buffered Organic/Inorganic Electrolytes

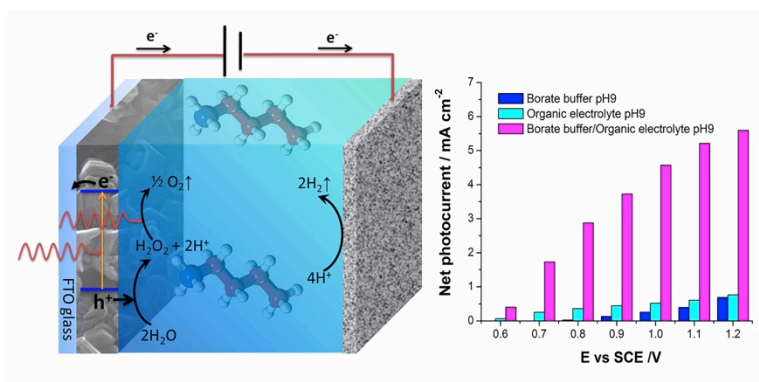
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Manganese oxide (MnO_x) materials have been widely studied as electro-catalysts for the water oxidation reaction. Although the electronic structure of MnO_2 (band gap ~ 2 eV) indicates it could be a promising photo-anode material for solar water splitting, so far only quite small photocurrents have been obtained from manganese oxides. Here, we show that the photo-electrochemical water oxidation performance of MnO_x films can be significantly improved by using buffered aqueous electrolytes containing amine ionic liquids. The buffered conditions to maintain a constant proton activity and the amine salt are both crucial for achieving high photocurrents. Photocurrents as high as 4.5 mA cm^{-2} were obtained at 1.0 V vs SCE ($\eta = 540 \text{ mV}$) in Bi buffered n-butylammonium nitrate (BAN) electrolyte at pH9. The incident photon-to-current efficiency (IPCE) was found to be greater than 3 % at 400 nm and 4% at 370 nm. Both H_2O_2 and O_2 are produced simultaneously in this system, with the potential subsequent decomposition of the H_2O_2 to form oxygen. An acceleration of the decomposition of H_2O_2 under illumination is proposed to explain the photocurrent improvement.



A remarkable improvement in the photo-electrochemical water oxidation on MnO_x has been achieved by employing buffered amine ionic liquid electrolytes.

References

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Nanostructure of Deep Eutectic Solvents at Graphite Electrode Interfaces as a Function of Potential

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Deep Eutectic Solvents (DESSs) are mixtures of salts and hydrogen bond donors that exhibit large freezing point depressions from their precursor materials.¹ The freezing point depression is attributed to a weakening of the lattice energy of the salt due to charge delocalisation as a result of hydrogen bonds forming between the anion and molecular hydrogen bond donor.¹ Atomic force microscopy (AFM), density functional theory (DFT) calculations, and contact angle measurements have investigated the liquid–highly ordered pyrolytic graphite (HOPG) electrode interface for three deep eutectic solvents (DESSs) as a function of applied potential. The DESSs examined are 1:2 molar ratio mixtures of choline chloride and urea (ChCl:urea), choline chloride and ethylene glycol (ChCl:ethylene glycol), and choline chloride and glycerol (ChCl:glycerol). DFT adsorption energy calculations reveal that in all cases the molecular component is excluded from the Stern layer, while chloride and choline enrich this region at positive and negative potentials, respectively. AFM force curves confirm these trends for the Stern layer and show that the near surface layer is predominantly composed of the molecular component. An applied potential increases the extent of near surface ion layering as does the hydrogen bonding capacity of the molecular species. The same trends are seen on a macroscopic level as variation in contact angle with potential is consistent with changes in the Stern layer composition.

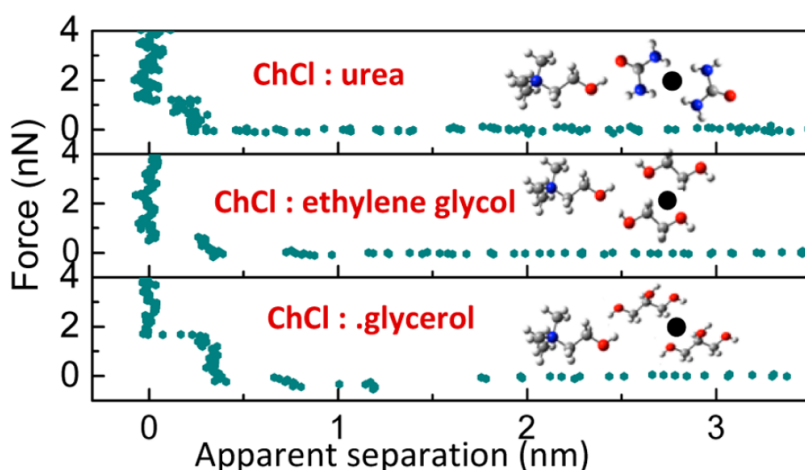


Figure 1. AFM force vs. apparent separation profiles for each choline chloride-based DES.

References

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Ionic liquids at the solid liquid interface –weighing the surface charge and electrorheology

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A method of characterising changes in the surface charge in ionic liquids has been developed using an electrochemical Quartz Crystal Microbalance[1]. The surface charge is effectively weighed by utilising the density differences between the species to explain the change in frequency observed when electrical potentials are applied to a gold surface immersed in IL. The charging process and its relaxation to equilibrium is shown to be diffusion controlled and quantitatively in agreement with NMR diffusion measurements. The capacitance was independently monitored and discharge was also demonstrated to be diffusion limited. The results are discussed in terms of overscreening and crowding by counterions in the light of recent theoretical predictions as to the response of ionic liquid double layers to applied potentials. Equally, the method is appropriate for ionic liquids dissolved in oil. The relaxation behaviour is not as simple as observed for pure ionic liquids, but a measure of the surface charge can be extracted from the exponential decay when the lower conductivity of the oil is accounted for. The adsorbed film at the gold surface consists predominantly of ionic liquid despite low bulk concentrations which is unsurprising given the surfactant-like structures of (some of) the ions. The technique thus allows a quantitative analysis of the changes in surface charge, and has the potential to be able to provide local densities in the surface film.

The QCM in fact is sensitive to both viscosity and density changes in the liquid. It is thus necessary to study whether there are local changes in viscosity – electrorheological effects – in the near vicinity of the surface. A recent paper[2] argues that significant changes in viscosity can be achieved upon applying a potential, so this is a valid concern, as to the quantification of the QCM approach. We demonstrate that artefact is capable of causing significant effects on the measured viscosity, but that when this artefact is accounted for, there is no observable change in the viscosity of the IL measured.

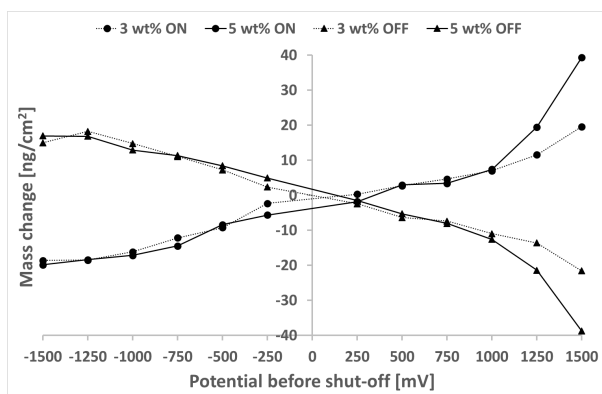


Figure 1. Extracted mass changes are plotted as a function of potential for 3 and 5 wt% [P_{6,6,6,14}][BMB] in oil. Responses both upon application of (circles) and extinguishing the applied potentials (triangles) are shown. The reflection of the data about the abscissa clearly shows that the mass change is reversible.

References

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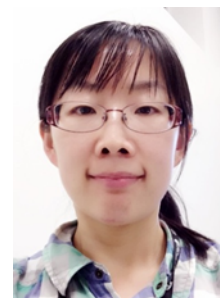
Combined Nano- and Macrotribology Study of Ionic liquids as Lubricant Additives for Titania Surfaces

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Currently one challenge for using titanium and their alloys as moving components in industry is the lack of effective lubricant and lubricant additives. In this work we address this by investigating the nano- and macrotribology of titania surfaces lubricated by one oil miscible IL, P_{6,6,6,14}(ⁱC₈)₂PO₂ and its mixtures with a model base oil, hexadecane.

Both nano- and macrotribological results demonstrate that the integrity and ordering of an IL boundary layer are responsible for the lubrication of the IL and IL-hexadecane mixtures. At both length scales, hexadecane is squeezed out at all contact stresses, leading to direct surface contact, high friction and high wear. For the pure IL and IL-hexadecane mixtures, titania surfaces are well lubricated at low contact stresses, but the friction and wear increase significantly once the contact stress is higher than a critical value. The critical contact stress for IL-hexadecane mixtures increases with IL concentration but always lower than the pure IL. The efficacy of the IL and ZDDP as lubricant additives on titania are investigated under the same macrotribological conditions; the IL shows better lubricity especially at high contact stresses. All these results suggest that IL ions interact more strongly with titania than conventional lubricant oil molecules, therefore, the formed IL boundary layers can protect the titania surface effectively at contact stresses suitable for common applications in industry. The outcomes of this study pave the way for the commercialization of IL lubricants and application of titanium and alloys as moving components in industry.

Tribotronic control of friction using ionic liquids dissolved in base oils

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Ionic liquids (ILs) are promising next generation lubricants. Like high performance lubricants, ILs have low vapour pressure, high thermal stability, and interact strongly with a wide variety of surfaces. These properties make pure ILs effective lubricants at the macro- and nanoscale.^{1, 2} Our group has used nanoscale atomic force microscopy (AFM) and macroscale ball-on-disk experiments to show that lubrication in ILs is determined by the composition of the adsorbed (boundary) layer of IL ions.

A distinguishing feature of IL lubricants from other high performance lubricants is that we can actively control the IL boundary layer by applying an electric potential. The ability to actively control friction *in situ* is called “tribotronics”. Our AFM nanotribology experiments on graphite and gold surfaces showed that we can tribotronically control friction simply by changing the electric potential.^{2, 3} Applying an electric potential to the surface changes the structure and composition of the adsorbed (boundary) layer of IL ions. Applying a positive potential to the surface leads to stronger interactions with the anions, while a negative potential strengthens the attraction of the cations to the surface. Thus by changing the potential in an IL lubricant system we change the boundary layer, which in turn affects lubrication performance of the system.

While the ability to actively control friction via electric potential is exciting, it is limited by the fact that pure ILs are expensive. Our latest work in this area has instead focused on diluting the IL in a base oil.^{4, 5} Our AFM nanotribology experiments have shown that friction forces in IL-oil systems can be controlled by an electric potential in the same way they can be for the pure IL, as shown in Fig. 1, for 5 mol% of the phosphonium phosphinate IL $P_{6,6,6,14}^i(C_8)_2PO_2$. This exciting discovery opens the possibility to actively control friction in oils by adding a small amount of an IL.

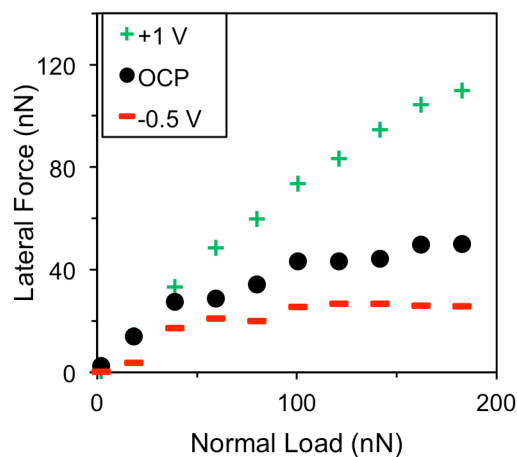


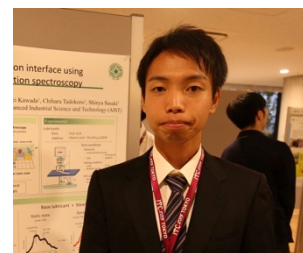
Figure 1. Lateral (friction) force vs. normal load for 5 mol % $P_{6,6,6,14}^i(C_8)_2PO_2$ in hexadecane as a function of electric potential on gold.

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Dynamic observation of ionic liquids at friction interface by Sum-frequency generation spectroscopy

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Ionic liquids are expected as novel lubricants because of their properties such as low volatility, high thermal stability and non-flammability, which make them applicable in extreme condition or maintenance-free desired condition. Properties of ionic liquids can be controlled by changing combination of cation and anion. However, there is no feasible guidepost for development of the ionic liquid for lubricant. For friction reduction, the interfacial structure of molecular adsorbate dominantly affects. In our previous study, we studied the interfacial structure of imidazolium-based ionic liquids on hydrophilic self-assembly monolayer surface by sum-frequency generation (SFG) spectroscopy which can selectively probe the interface and determine the molecular orientation angle.[1] We found the relationship between friction coefficient and orientation angle of imidazolium ring which is associated with the anion size. However, because the interfacial measurement was performed in a static condition, this relationship based on the hypothesis that the interfacial structure of ionic liquids in a static state is same as that in a dynamic state. In this study, we attempt to observe the interfacial structure of ionic liquid at actual friction interface using SFG spectroscopy equipped with prism-on-disk friction tester.

We used a fused quartz hemicylindrical prism and a sapphire disk. To confirm the difference between static and dynamic, static test and disk rotation test were performed. The tests were conducted at a load of 2.5N, and a sliding speed of 10 rpm (2.1 mm/s) for rotation test. 1-buthyl-3-methyl-imidazolium hexafluorophosphate ([BMIM]PF₆) was used as a lubricant. **Figure 1** shows

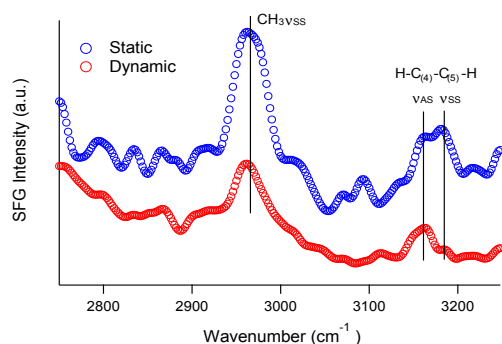


Figure 1. SFG spectra of [BMIM]PF₆ in a static state (blue) and dynamic state (red) with ssp polarization

the SFG spectra of [BMIM]PF₆ in static state and dynamic state with ssp polarization. Peaks at ~2960cm⁻¹, ~3153cm⁻¹ and ~3174cm⁻¹, which were attributed to the vibrational stretching mode of CH₃ symmetric, H-C₍₄₎-C₍₅₎-H asymmetric and symmetric, respectively, were observed in the case of static state. Once disk was rotated, the peak of H-C₍₄₎-C₍₅₎-H symmetric (~3174cm⁻¹) disappeared. This result indicates that the interfacial structure of imidazolium ring was changed by inducing shear force. We will discuss detail of the interfacial structure and its effect on frictional property.

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Control of ionic liquid lubrication by applying electric field

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It is reported that lubrication property of ionic liquids depends on the type of adsorbed ions and their structure on sliding surface. Rob Atkin et al^[1] showed that the applying electric field is effective to control the adsorption state of ionic liquids on the sliding surface. There are, however, few reports about the relationship between the lubrication property and the adsorption state of ionic liquids in macroscale friction phenomena under the electric field.

In this research, we focused on the effect of the electric field on the macroscale lubrication property of ionic liquids in consideration of the adsorption state.

The testing apparatus used in this research is shown in Fig. 1. Ionic liquids used in this research were [BMIM][I], [BMIM][FAP], and [BMIM][PF6], which have the same cation. The detail information of the sliding test specimens are shown in Table 1. The sliding tests were performed at a normal load of 1 N, with a sliding speed of 22 mm/s. The voltage was applied on the ball specimen side, and the disk specimen was connected to the grand. After 10 minutes running-in process without applying voltage, friction measurement was performed for 60 sec at the applying voltage of 2V (or -2V), and for 30 sec under neutral condition.

When the applying voltage was -2V, each friction coefficient showed almost the same value. It is considered that the same cation adsorbed on the ball specimen lead the same frictional behavior. On the other hand, [BMIM][FAP] showed the largest friction coefficient, followed in order by [BMIM][PF6], [BMIM][I] when the applying voltage was 2V. According to the calculation by ChemBio3D, this order is consistent with the order of anion size^[2]. Therefore, the anion size has an important role on the lubrication property of ionic liquids.

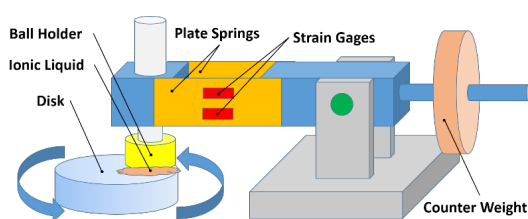


Figure 1. Schematic of testing apparatus

Table 1. Molecular structure of ionic liquid

		Disk	Ball
Size		[mm]	$\phi 24 \times t 7.9$
Substrate material		SUJ2	
DLC	Type of DLC	H-free-DLC	
	Deposition method	Arc Ion Plating(AIP)	
	Film thickness	[μm]	1
	Surface roughness	[μm]	0.01

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Development of Renewable Ionic Liquids for Biomass Pretreatment

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Ionic liquids (ILs), solvents composed entirely of paired ions, have been used in a wide variety of process chemistry and renewable energy applications. Imidazolium-based ILs show remarkable abilities to dissolve biomass, and are thus an ideal media for biomass pretreatment and depolymerization^[1]. Although very efficient, imidazolium cations are currently expensive and therefore their large scale use and industrial deployment, e.g. in biorefineries, is limited^[2]. In an attempt to replace imidazolium-based ILs with ILs derived from renewable sources that retain their efficiency for biomass pretreatment, we synthesized a series of tertiary amine based ILs from aromatic aldehydes derived from lignin and hemicellulose, the major byproducts of lignocellulosic biofuel production. A comprehensive analysis of extractable cell wall carbohydrates and sugar yields from switchgrass and switchgrass pretreated with tertiary amine based ILs derived from vanillin ([Van][H₂PO₄]), *p*-anisaldehyde ([*p*-AnisEt₂NH][H₂PO₄]) and furfural ([FurEt₂NH][H₂PO₄]) confirmed their effectiveness for biomass pretreatment. The amounts of sugar released by enzymatic hydrolysis of the cellulose present in switchgrass was comparable to that obtained after pretreatment with 1-ethyl-3-methylimidazolium acetate ([C₂C₁im][OAc]). Enzymatic saccharification with [FurEt₂NH][H₂PO₄] and [*p*-AnisEt₂NH][H₂PO₄] provided 90% and 96% of total possible glucose and 70% and 76% of total possible xylose, respectively, after biomass pretreatment. Computationally, [Van][H₂PO₄] showed the lowest net basicity, and poor lignin removal efficiency and low sugar yields were observed experimentally. We found that [FurEt₂NH][H₂PO₄] and [*p*-AnisEt₂NH][H₂PO₄] had higher *b* values and higher net basicity than [C₂C₁im][OAc]. Though [FurEt₂NH][H₂PO₄] and [*p*-AnisEt₂NH][H₂PO₄] were slightly less effective towards lignin removal, sugar yields from SG pretreated with these compounds were nearly equivalent to yields from SG pretreated with [C₂C₁im][OAc]. Glycome profiling experiments suggest that the biomass derived ILs [FurEt₂NH][H₂PO₄] and [*p*-AnisEt₂NH][H₂PO₄] act on plant cell walls in a mechanism distinct from [C₂C₁im][OAc], and studies are underway to understand these process implications in terms of lignin and hemicellulose depolymerization and IL recycling. These results indicate that biomass derived renewable ILs are very effective in pretreating biomass, and establish an important foundation for the further study of these unique compounds in other industrial applications^[3]. Our concept of deriving ILs from lignocellulosic biomass shows significant potential for the realization of a “closed-loop” process for future lignocellulosic biorefineries, and has far-reaching economic impacts for other IL based process technology currently using ILs synthesized from non-renewable sources.

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How Does Structure Influence Translational and Rotational Dynamics in ILs?

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In ionic liquids, local structure and local energetics are interconnected.

For a probe that is small enough to sense this, regions with excess charge are also regions that are stiff and with interactions that are normally stronger. Structural heterogeneity is therefore directly associated with heterogeneity in interactions. During this talk I will discuss the effect of this energetic heterogeneity on different dynamical processes including OH rotations of water and alcohols as well as translation in the case of charged and neutral solutes^{1,2,3,4}.

Of particular interest is the question of whether energetic heterogeneities affect translations and rotations in a similar fashion. Do stiff and soft solvent environments slow down or speed up rotations and translations concomitantly or are these motions decoupled⁴? Our findings appear to indicate that both types of motion are coupled. Stiff environments result in translational cages and in restricted rotations as highlighted in Figure 1 below.

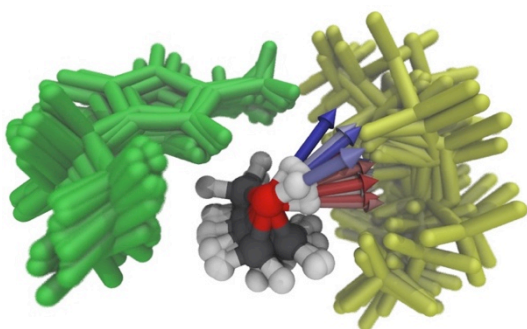


Figure 1. Energetic heterogeneities result in hindered rotations of alcohol OH bonds in stiff ionic liquid solvent environments.

Furthermore both rotations and translations in soft liquid regions appear to be governed by a viscosity significantly lower than the bulk value.

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Prediction of thermodynamic and transport properties of ionic liquids from multi-scale calculations

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Figure 1. Comparison of accuracy of the SCS-IL-MP2 method for large clusters of ILs with the benchmark method, CCSD(T).

Recently in our group we have developed a modification of the second order Moller-Plesset Perturbation Theory method, MP2, to predict interaction energies in ionic liquid (IL) ion pairs within

chemical accuracy.¹ The new method, termed SCS-IL-MP2, scales the same- and opposite-spin component of the MP2 correlation energy with the advantage of excluding time-consuming counterpoise correction that takes into account basis set superposition error as a result of incomplete basis sets used. SCS-IL-MP2 has been successfully applied to studying large clusters of ionic liquids with unprecedented accuracy (see Figure 1).² The maximum error < 4 kJ mol⁻¹ is observed in clusters of 4 ion pairs for 15 types of ionic liquids. The developed SCS-IL-MP2 method has been recently generalized to work equally well for ionic liquids and intermolecular complexes among neutral molecules, spanning a wide range of interaction types from strong hydrogen bonding to weak van der Waals interactions. This finding further reinforces the . Combined with the Fragment Molecular orbital (FMO) approach,³ the SCS-IL-MP2 method has allowed us to study multi-scale clusters of ionic liquids *from first principles* with high accuracy, not available before for these semi-Coulombic systems. When performed on massively parallel computers the combination of the FMO and SCS-IL-MP2 methods may approach linear scaling with cluster size of up to 32 ion pairs.

Recently our group have also studied the correlation of interaction energy and its components with thermodynamic (such as melting point) and transport (such as viscosity and conductivity) properties of imidazolium- and pyrrolidinium based approaches. It has been established that dispersion interactions not only are important in ionic liquids but also govern trends in their melting points by correlation the ratio of total interaction energy to its dispersion component with experimentally measured melting points.⁴ This approach has been recently expanded for larger clusters of imidazolium- and pyrrolidinium-based ionic liquids consisting of 2 ion pairs, whose energetic components are calculated with the newly developed SCS-IL-MP2 method. Generalized trends between the dispersion component and experimental melting points as well as transport properties have been established, thus paving the way towards a universal approach for the prediction of physicochemical properties of ionic liquids from multi-scale calculations.

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Ionic liquids from theoretical considerations

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In order to develop more efficient procedures in energy applications, the quest for alternative reaction media for different materials became of crucial importance. Ionic liquids (ILs) possess many unique properties making them a promising material class. Utilizing state of the art theoretical methods, such as molecular dynamics (MD) simulations and ab initio calculations [1], helps understanding these liquids on the atomic level. By examining the fundamental interactions, the solvents' nanostructure and the complex behavior with different materials can be explored more accurately. The side chain aggregation of ILs, i.e. microheterogeneity, showed a significant effect with respect to gas absorption [2]. Within our program TRAVIS, we present alternative ways to obtain dipole moments and thus spectroscopic information, as well as new analysis tools such as domain analysis and structure factor tool [3]. Applying these tools to a newly suggested mixture from alkyl- and fluoroalkylimidazolium ILs, the formation of a tri-phillic nano-system [4] is seen. As shown by Schulz and coworkers [5] and many others, the formation and morphology of nanoparticles within highly structured ILs is affected by the choice of the IL, e.g., the side chain or the anion can play a role [6]. In order to shed light on this behavior, the interactions with the ILs are investigated and results are being presented. Mixtures of ionic liquids with and of molecular liquids [7] are also in the scope of this talk.

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Structure of Ionic Liquid - Solid Interfaces Predicted using Fast Quantum Chemistry

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The density functional tight binding (DFTB) method is a 2-centred, extended Hückel approximation to density functional theory (DFT). As such, it can describe chemical systems with near quantum chemical accuracy, but at a fraction of the cost of full DFT. In this talk I will present our applications of DFTB in the context of bulk and interfacial ionic liquid systems, and demonstrate that it is a promising candidate for developing future multi-scale simulation methodologies for ionic liquids. I will outline the performance of DFTB in predicting energetic and bulk structural aspects of protic ionic liquids [1]. I will also present DFTB-based molecular dynamics simulations of alkylammonium nitrate [2] and imidazolium bis(trifluoromethane)sulfonamide [3] ionic liquids adsorbed on graphitic substrates, and demonstrate the origins of their 3-dimensional nanostructures. By adding a static dipole field to the DFTB Hamiltonian, the structural response of these interfaces to electric fields can also be simulated. I will present how this can be used to explain structural origins of tribotronic phenomena [4].

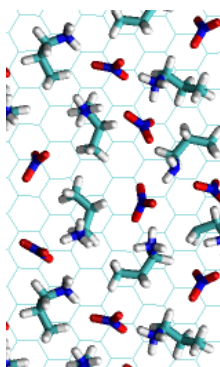
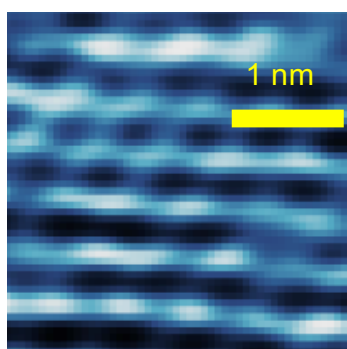
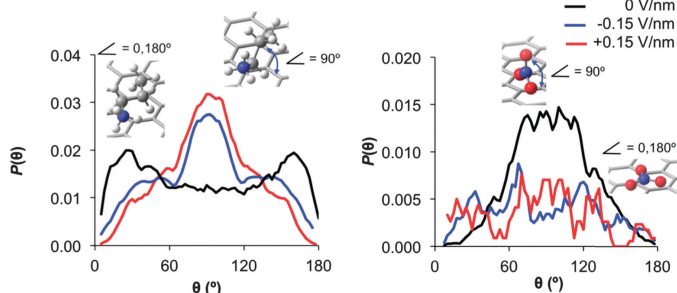


Figure 1. Structure of propylammonium nitrate - graphite interface obtained using AM-AFM experiments (top left) and DFTB/MD simulations (top right), and the response of this interface to the application of positive and negative electric fields (bottom).

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On the activity of carbene catalysts in ionic liquid solvents

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Since ionic liquids are often applied as solvents for catalysis, the changes in the activity of reagents and substrates in these substances is of crucial importance. The differences in activities can serve as a basis for designing ionic liquids for certain synthetic goals, to achieve the desired reactivity with optimal rate and selectivity. Recently, we have pointed out based on ab initio molecular dynamics simulations that the reactivity of N-heterocyclic carbenes in ionic liquids is highly dependent on the hydrogen bonding nature of both the anion and the cation, due to the competition between the anion and the carbene for the hydrogen bond donor sites of the cation [1]. Accordingly, by altering the ionic liquid, the activity, and possibly the selectivity of the carbene can be tuned to the given process. This theory has been proven experimentally in a subsequent electrochemical study [2].

Besides hydrogen bonding, however, other interactions, and the long range ordering effects might also be influential in this matter, such as the segregation of polar and non-polar domains in certain ionic liquids. To understand this kind of behavior, the very time consuming ab initio molecular dynamics simulations could not be utilized, and a molecular mechanical force field had to be developed that allows the investigation of required large systems, and long time scales [3]. The obtained model describes the strength and directionality of the hydrogen bonding properties of the imidazol-2-ylidene molecule, which enabled to discover a peculiar dynamic behavior for these molecules in hydrogen bond donor solvents [3].

In this contribution the effects of the ionic liquid's structure on the hydrogen bonding and the connected activity of the carbene are explored in details, depending on the head group and the side chain length of the ions, as well as the effect of mixtures. We believe that the knowledge gathered here reach beyond the direct applications of these systems, and the presented influence of the ionic liquid's structure on (material) synthesis with nucleophilic/hydrogen bond acceptor catalysts can be considered as a case study for a general and potentially beneficial way to steer reactions.

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Quantum Chemical investigation into the structure and properties of Deep Eutectic Solvents

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Deep eutectic solvents (DES) are a class of ionic solvents formed by mixing an inorganic salt and a hydrogen bond donor. At a specific mixture composition (known as the eutectic point) the melting point undergoes a temperature depression compared to the pure components. This temperature depression give DESs properties analogous to ionic liquids (ILs) e.g non-flammability and wide electrochemical window, while being relatively cheap, environmentally friendly, and simple to produce.¹ The archetypal DES is a 1:2 mole ratio mixture of choline chloride (m.p. 302 °C) and urea (m.p. 133 °C), which has a melting point of 22 °C when dry.² I will present quantum chemical molecular dynamics (QM/MD) simulations to elucidate the structure of this DES, and for the first time, reveal the structure in choline chloride- ethylene glycol and glycerol DES. These simulations demonstrate a direct inverse correlation between the melting point depression and the arrangement of the choline chloride charge centers in these liquids. A correlation between the hydrogen bond density and rheological properties, such as viscosity, is also observed. These simulations establish for the first time structure-property relationships in choline chloride deep eutectic solvents.

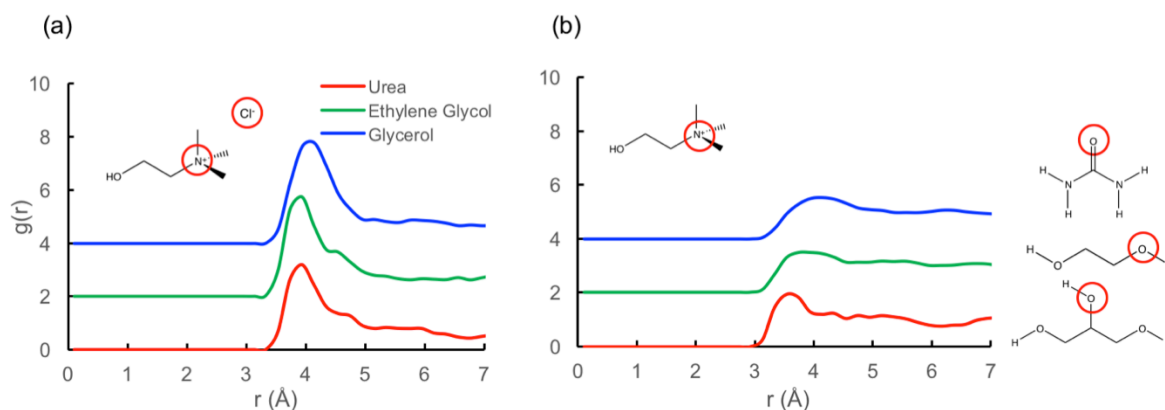


Figure 1. Radial distribution functions at 298 K for (a) choline charge group - chloride interaction and (b) choline charge group - hydrogen bond donor oxygen interactions for the ChCl:urea, ChCl:ethylene glycol and ChCl:glycerol DES, obtained from DFTB3-D/MD simulations.

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Magnetic Resonance as a Probe of Dynamics and Associations in Lithium or Sodium-Containing Ionic Liquid Electrolytes

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Ionic liquids show huge potential as electrolyte materials for lithium or sodium-based electrochemical devices due to their low volatility, high conductivity, and tailorable properties. Our group is developing novel ILs that can dissolve relatively high amounts of lithium or sodium salts, and is using a very broad range of experimental methods to characterise them. Chief among these methods is nuclear magnetic resonance (NMR) spectroscopy, which can be used to directly measure molecular diffusion, quantify dynamic modes over a broad range of timescales, and even probe ionic associations [1]. I will discuss a number of NMR techniques (pulsed field gradients, relaxation measurements, and heteronuclear Overhauser effect spectroscopy), providing some background on how they work and what information they can provide in the context of ILs. Each method will be illustrated with some recent results obtained in our lab from novel lithium or sodium containing IL electrolytes [2].

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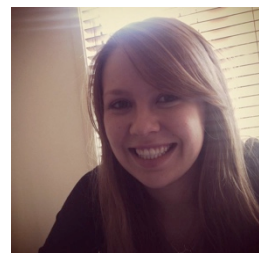
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Effect of an ionic liquid solvent on an S_NAr reaction of a heteroaromatic system

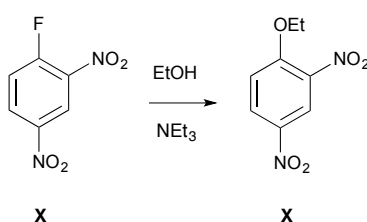
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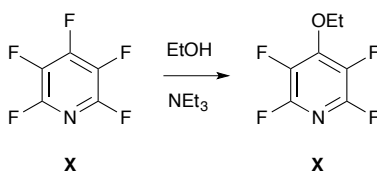


Ionic liquids can affect the reaction outcome of a range of organic processes.^[1] In particular, the ethanolysis of 1-fluoro-2,4-dinitrobenzene **1** (Scheme 1), a nucleophilic aromatic substitution (S_NAr) process, occurs with an increase in the rate constant when an ionic liquid solvent is used.^[2] It is of interest to extend this work to other reactions proceeding through an S_NAr mechanism.



Scheme 1. The S_NAr reaction between 1-fluoro-2,4-dinitrobenzene **X** and ethanol.^[2]

2,3,4,5,6-Pentafluoropyridine **3** is a useful precursor for a range of molecules of interest to the life science and materials industries, due to the ease of nucleophilic substitution.^[3] There is preference for reaction at the 4-position of pyridine **3**^[3-4] and the electron poor nature of the heterocycle makes a good comparison to the previously mentioned reaction (Scheme 1).



Scheme 2. The S_NAr reaction between 2,3,4,5,6-pentafluoropyridine **3** and ethanol.

This project focuses on the influence of an ionic liquid solvent on the reaction described above (Scheme 2) and describes the kinetic analyses of the reaction with both a molecular solvent, ethanol and the ionic liquid 1-butyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide.

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Ionic liquid solvent effects on simple pericyclic rearrangements

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Pericyclic processes, which include the well-known Diels-Alder cycloaddition, are concerted reactions that proceed through a cyclic transition state;¹ they are used extensively in organic synthesis.² Ionic liquid solvent effects on these processes are quite complex, with a variety of factors proposed to contribute to the observed changes in the rate constant.³ These factors include, but are not limited to, the following a) hydrogen bonding interactions;⁴ b) stabilization of incipient charges in the transition state;⁴ c) compression of species along the reaction coordinate;⁵ and d) enhanced solvent-solute friction due to micro-viscosity effects.⁶ Given this range of factors, it was of interest to investigate very simple pericyclic processes, so that the microscopic origin of the changes in the rate constant observed in an ionic liquid solvent could be better understood. The effect of the ionic liquid **5** and a number of molecular solvents on the rate constant of the Cope and Claisen rearrangements (Figure 1) was examined. Comparison of the obtained rate data with a number of solvent parameters provided some interesting insight on underlying causes of the observed changes in the rate constant for each case.

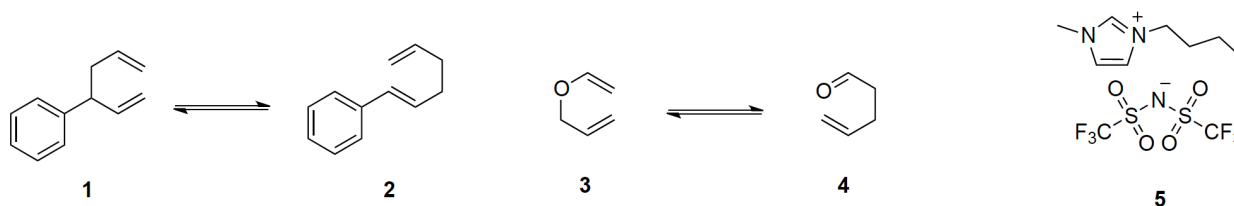


Figure 1. The Cope rearrangement of the 3-phenyl-1,5-hexadiene **1** to the product **2**, and the Claisen rearrangement of allyl vinyl ether **3** to the product **4**. Each reaction was examined in benzene, ethanol, acetonitrile and the ionic liquid [Bmim][N(CF₃SO₂)₂] **5**.

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Amino Acid Ionic Liquids Derived from the Triaminocyclopropenium Cation

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Chiral ionic liquids (CILs) are becoming an increasingly important class of IL. Amino acids are effective and excellent starting materials for the preparation of functional CILs: they come from the “chiral pool”, can contain a variety of functional groups and, due to their resemblance to biochemical substrates, amino acid-derived ILs (AAILs) have excellent potential for biodegradability. AAILs have also been shown to have excellent CO₂ absorption and membrane transport properties. These factors, along with their low volatility, relatively low cost, ready availability and promising recyclability and/or biodegradability, make them extremely interesting from a green chemistry viewpoint.

We introduced the triaminocyclopropenium (TAC) cation as a new class of IL in 2011 [1]. Despite the steric strain of the three-membered ring, these cations are remarkably unreactive: They are stable in boiling water and we have reported that the NTf₂[−] salts can have thermal decomposition onset temperatures above 400 °C. We have even been observed weak dicationic dimers in the solid state structures of unsolvated TAC halide salts [2].

Here we will present work on the synthesis and properties of AAILs derived from TAC cations (Figure 1) in which not only were monocations synthesized, but also zwitterions and a variety of novel dicationic AAILs, such as shown in Figure 2.

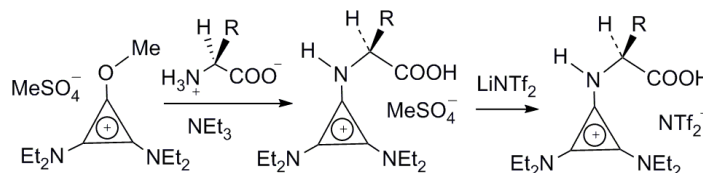


Figure 1. Synthesis of AAILs based on TAC cations.

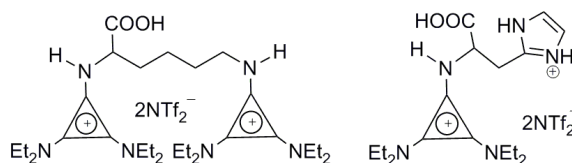


Figure 2. Dicationic AAILs based on TAC cations.

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The Electrochemical Behaviour of Toxic Gases in Ionic Liquids

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The need to detect toxic gases and explosives is increasing, in part, due to the rapid development of various emerging economies. The expansion in the number of industrial processes results in the increased likelihood of exposure to toxic gases for the personnel who work in close proximity where these gases may be released. There is thus a need to develop low-cost, portable sensors that can detect and quantify toxic gases. Many commercial amperometric gas sensors (AGSs) contain a liquid electrolyte (e.g. $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$) that can dry out quickly, particularly in very hot and dry environments. In 2006, Compton's group¹ suggested that room temperature ionic liquids (RTILs) could replace conventional solvents in AGSs, and proposed a microelectrode membrane-free device as a result of the low-volatility of RTILs. Much research has gone into understanding the fundamental electrochemical behaviour of gases in RTILs (e.g. electron counts, reaction mechanisms, diffusion coefficients, solubilities), which is important information that needs to be understood before RTILs can be used in AGSs. However, there is still a huge gap in the knowledge concerning the analytical behaviour (detection limits, sensitivities etc.) i.e. can electrochemical sensors with RTIL solvents detect toxic gases at or below their long-term exposure limits?

In this talk, the recent developments from our lab concerning detecting toxic gases in ionic liquids will be discussed. The four toxic gases are: ammonia, chlorine, methylamine and hydrogen chloride, with long-term exposure limits (8 hours over 5 days) of 25, 1, 10 and 5 ppm, respectively. The electrochemical behaviour of oxygen gas will also be discussed. We have employed microelectrodes, along with low-cost planar electrode devices such as screen-printed electrodes (SPEs) and thin-film electrodes (TFEs) as sensing surfaces. The results show that, for the most part, sensors incorporating RTILs with low-cost planar devices are highly feasible for toxic gas detection. A couple of exceptions were noted: (1) chlorine detection, where a 1ppm limit of detection was not achieved in RTILs,^[2] and (2) HCl detection, where a chemical reaction with hexafluorophosphate and tetrafluoroborate anions was observed, forming HF.^[3] The sensing of oxygen on SPEs in imidazolium RTILs also showed unusual behaviour, but this was dramatically improved by simple mechanical polishing of the screen-printed surface.^[4] In addition to gas behaviour, the electrochemical behaviour of the explosive compound 2,4,6-trinitrotoluene (TNT) in RTILs will also be briefly discussed.

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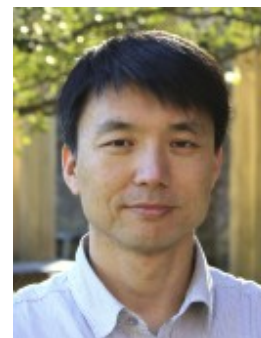
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Salt-On-A-Chip: Miniaturised Ionic Liquid Gas Sensors

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Ionic liquids have demonstrated applications in many fields of chemistry, ranging from electrochemistry, sensors, organic synthesis to biological applications. However, most of these applications suffer from one intrinsic drawback: high viscosity of ILs, which leads to poor mass transport in ILs, limiting their performance and applications in wider areas.

We address the problem by developing miniaturised ionic liquid systems.¹ The miniaturisation of ILs to the micro and nano scale brings enhanced mass transport rate of dissolved molecules and significantly improved efficiency over macro systems. Miniaturised systems have gained significant popularity and offer advantages such as material conservation, fast response or reaction time, and high product yield.² Nevertheless, to fully exploit micro- to nano-scale chemistry, solvent evaporation and lack of reproducibility are major challenges. Using non-volatile ionic liquids can effectively solve the problem of solvent evaporation and offer new opportunities.

I show in this presentation our recent progress on microcontact printing of extremely small ionic liquid drops and microstructures on a chip surface and using them as “membrane-less” and “spill-less” gas sensor arrays. I will also show our approaches for enhancing the performances of the gas sensors using functionalised ionic liquids and magnetic nanoparticles.³ The results suggest that miniaturised ionic liquid systems can provide a versatile platform for novel applications of ionic liquids.

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Investigating microscopic interactions to explain ionic liquid effects in bimolecular nucleophilic substitution processes

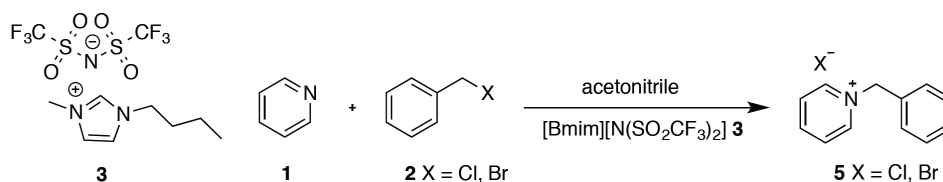
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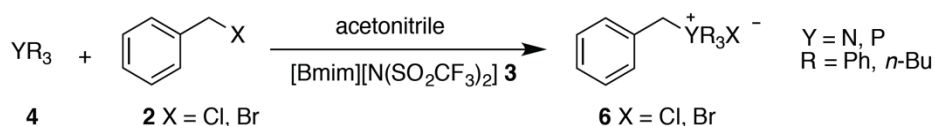


Ionic liquids have the potential to alter reaction outcome compared to that of molecular solvents.¹ For example, in the bimolecular nucleophilic substitution reaction between pyridine **1** and a benzyl halide **2** (Scheme 1), a rate enhancement was observed in the presence of the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide [Bmim][N(CF₃SO₂)₂] **3**.^{2, 3} This solvent effect was driven by an entropic benefit due to interactions between the lone pair of pyridine **1** and the cation of the salt **3**.⁴



Scheme 1. Menshutkin reaction between pyridine **1** and each of the benzyl halides **2**.²⁻⁵

Currently there is a general understanding of how varying the constituent ions of ionic liquids affects the ionic liquid-nucleophile interaction, allowing increased solvent control of reaction outcome.⁵ However, it is not understood how altering the nucleophilic heteroatom will affect this cation-nucleophile interaction and hence reaction outcome (Scheme 2).



Scheme 2. Menshutkin reaction between group 15 nucleophiles **4** and benzyl halides **2**

A variety of group 15 nucleophiles were considered, with the effect of changing the proportion of the salt **3** present in the reaction mixture on the rate constant of the reaction examined, as well as temperature dependent kinetic studies in order to elucidate the thermodynamic origins of these effects. The interactions causing the observed ionic liquid solvent effects were investigated through variation of the substituents on the nucleophile and the stereoelectronics of the electrophiles.

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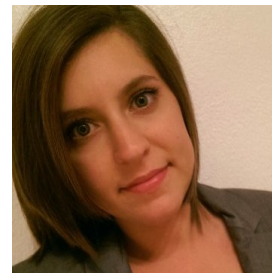
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High Energy XPS: Sulfur as probe of depth

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We recently reported the first X-ray photoelectron spectroscopy (XPS) data for a range of functionalised guanidinium based systems.[1] XPS is an established surface analysis technique where binding energies (BEs) obtained from ionic liquid solutions can help identifying the main interactions occurring between the ionic liquid solvent and the solute. It can also be used to investigate the nature of the molecular interactions within ions, providing both elemental and chemical information. The measured binding energies for this class of ILs were compared with other nitrogen cation families and main differences addressed.

Additionally, we replaced one of the nitrogen atoms in the guanidinium moiety by another element, sulfur. Interesting comparisons with NMR were acknowledged and discussed providing another route of interest. Having an element with a higher photoemission orbital provides a great opportunity to study the depth profile of these materials using a higher energy X-ray source. Previous depth profiling studies upon ionic liquid systems have frequently used ARXPS, with few examples of ERXPS.[2][3] With ERXPS, no geometry change to the sample is required, as is the case for angle-resolved XPS (ARXPS), thus enabling repeated analysis of a consistently level surface thereby minimising error caused by physical shifting of the sample. Higher energy core orbitals can be probed, such as S 1s, elucidating further information concerning ionic liquid electronic environments, which is imperative to understanding ionic liquids at a molecular level.

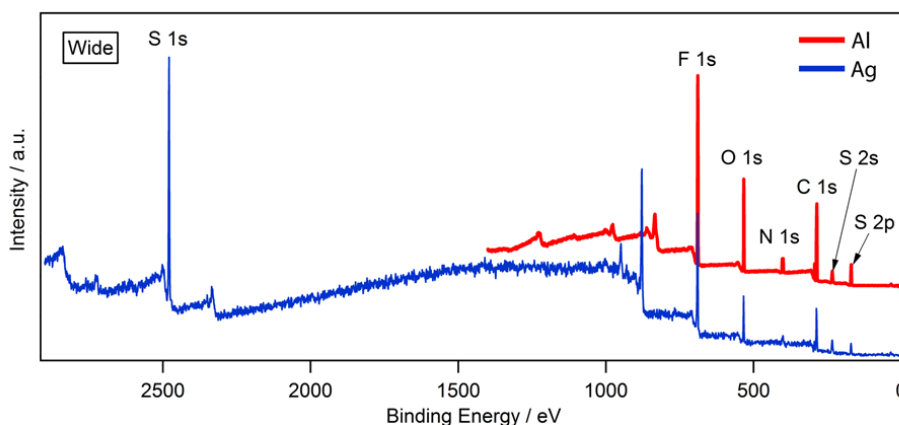


Figure 1. XPS spectra for [C₁C₁Im][NTf₂] using Al Kα (hν = 1486.6 eV) X-ray source (red) and Ag Lα' (hν = 2984.6 eV) X-ray source (blue)

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Ionic Liquids at Heterogeneous Interfaces

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Ionic liquids (ILs) have remarkable properties including vanishingly low vapor-pressures, are non-flammable, and have wide thermal and electrochemical stability windows that make them ideal for several applications, including electrolytes in supercapacitors and lubricants. Our interest is to understand the interfacial behavior of ILs, also under nanoconfinement. Several studies have demonstrated the layered structure of ILs in nanoconfinement. The confined ions resist being “squeezed out” when surfaces are compressed, with the result that an IL film remains between the surfaces up to high pressures, thus preventing direct contact between the surfaces, also under shear, which aids in reducing friction.

Laboratory studies have mainly focused on atomically flat and chemically homogeneous substrates, i.e. on ideal surfaces, to understand underlying mechanisms. In our current work we are exploring the influence of nanoscale heterogeneities on ionic-liquid interfacial properties. Such heterogeneities can be composed of contamination, roughness or chemical surface groups. The strong molecular interactions still facilitate self-assembly of ILs on the surfaces, but they reveal new aspects of the IL behavior. We address diverse fundamental questions about the interfacial IL structure and the response to shear in the presence of heterogeneities. Further, these studies are of relevance to extend studies performed on ideal systems to real applications.

Ionic Liquids as Anti-Wear Lubricant Additives

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If an improved anti-wear additive for lubricants can be discovered then the use of lower viscosity oils would lead to improved efficiencies. For instance, it has been estimated that if automotive oil viscosity could be lowered by 25%, fuel savings of up to 8% could be achieved [1]. Ionic liquids (ILs) have the potential to be this type of new anti-wear additive, however the miscibility of ILs in base oils has proven to be limited, particularly in the non-polar oils such as mineral oil [2]. Our group has been investigating ionic liquids as anti-wear additives in base oils and here present a summary of the current state of this field of research as well as our efforts in the area, particularly in developing phosphorus-free anti-wear additives for engine oils.

The very limited range of phosphonium ILs that are fully miscible in non-polar base oils contain phosphorus on both the anion and cation. Since phosphorus poisons the catalytic convertor in modern exhaust systems, lubricant manufacturers are looking to reduce its presence in oils. As a first step towards phosphorus free anti-wear additives, we have investigated ionic liquids similar to the phosphonium phosphates, but having either a phosphorus-free cation or anion.

Two quaternary ammonium phosphates (N_{66614})(DEPH) and (N_{8888})(DEPH) and a phosphonium silyl-sulfonate (P_{66614})(SSi) were compared to a phosphonium phosphate (P_{66614})(DEPH) and a traditional zinc dithiophosphate (ZDDP) as anti-wear additives in mineral oil. The change from a phosphonium to a quaternary ammonium cation drastically reduced the miscibility, while the change to a smaller sulphur and silicon containing anion also resulted in limited miscibility. For the wear test conditions used here none of the ionic liquids outperformed the ZDDP except the (P_{66614})(DEPH) at a relatively high loading of 0.10 mol.kg^{-1} (approximately 8 wt%). At a more moderate loading of $0.025 \text{ mol.kg}^{-1}$ the (P_{66614})(SSi) was the best performing ionic liquid by a significant amount, reducing the wear to 44% of the neat mineral oil, while the ZDDP reduced the wear to 25% of the mineral oils value. Electron microscopy and energy dispersive X-ray spectroscopy showed that the presence of a silicon containing tribofilm was responsible for this protective behaviour.

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Molecular additives control friction in Ionic Liquids

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The use of ionic liquids (ILs) to lubricate electrical contacts is an intriguing prospect since the magnitude of friction can be tuned by judicious selection of ions with appropriate molecular structure.[1] alternatively, it is possible to control friction via chemical additives in pure ionic liquids.[2, 3] Colloid probe friction force microscopy (FFM) has been used to study the lubricity of propylammonium nitrate (PAN) mixed with n-alkanols confined between sliding silica and mica surfaces. Mixtures of PAN with butanol, hexanol, octanol and dodecanol were investigated for various n-alkanol volume fractions to elucidate the effect of n-alkanol hydrocarbon chain length and concentration on shear forces. For all n-alkanols friction decreases with n-alkanol vol%. The trends in friction reduction with n-alkanol vol% do not correlate with changes in the bulk phase viscosity or the near surface nanostructure, and colloid probe atomic force microscope (AFM) fluid dynamic measurements showed that none of the mixtures shear thin. Thus, the reduction in friction is attributed to the n-alkanol disrupting solvophobic interactions between boundary layer propylammonium ions adsorbed to the mica and near surface liquid layers. Poly(ethylene oxide) (PEO) has been used to study the effects of a dissolved macromolecule. The adsorbed layer conformation and lubricity of 35, 100, and 300 kDa PEO adsorbed to ionic liquid–silica interfaces from 0.01 wt % solutions have been investigated using colloid probe atomic force microscopy. The ILs used were propylammonium nitrate (PAN) and 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]), which are protic and aprotic ILs, respectively. Normal force curves reveal steric interactions consistent with adsorbed polymer layers which are best fit using the mushroom model. Friction measurements show that the adsorbed polymer layer markedly reduces friction compared to surfaces sliding in the pure ILs and that lubricity increases with polymer length. When polymer is adsorbed to the sliding surfaces, friction is controlled by the creation and disruption of intermolecular interactions between entangled chains and the dragging of polymer chains through the interpenetration region.

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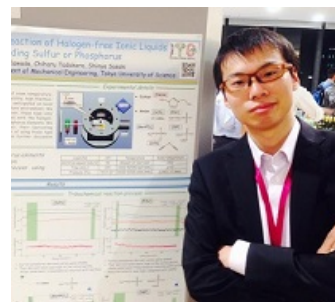
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Relationship between tribo-decomposition and friction property of cyano-based ionic liquids

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Ionic liquids are expected to be used as new base oil and/or additives because of their unusual properties. Many evaluations about friction property of fluorine-containing ionic liquids have been carried out for the last 15 years. But, fluorine in the ionic liquids have possibilities to cause corrosion of metallic materials by generation of metallic fluoride and generation of HF from hydrolysis [1]. Thus, research object shifts to fluorine-free ionic liquids. In this study, we investigated the friction property of fluorine-free ionic liquids. In addition, we discussed the friction reduction mechanism of ionic liquids by using a quadrupole-mass-spectrometer. In this paper, we express the friction property of fluorine-free ionic liquids.

The friction property of four types of ionic liquids ($[\text{C}_2\text{mim}][\text{N}(\text{CN})_2]$, $[\text{C}_4\text{mpyr}][\text{N}(\text{CN})_2]$, $[\text{C}_2\text{mim}][\text{B}(\text{CN})_4]$, and $[\text{C}_4\text{mpyr}][\text{B}(\text{CN})_4]$) on AISI 52100 surface were investigated using ball-on-disk type friction tester. The friction test were performed at a normal load of 4.5 N, with a sliding speed of 52.3 mm/s, for 2 hour.

Figure 1 show the friction coefficient behavior of each ionic liquid. Figure 2 show the average of friction coefficient of the last 5 minutes and the wear diameter of the ball specimen for each ionic liquid. It is interesting result that $[\text{C}_4\text{mpyr}]$ cation take immediate friction coefficient reduction effect. However, Eventual friction coefficient of $[\text{C}_2\text{mim}][\text{N}(\text{CN})_2]$, $[\text{C}_4\text{mpyr}][\text{N}(\text{CN})_2]$, and $[\text{C}_4\text{mpyr}][\text{B}(\text{CN})_4]$ exhibited almost same value. On the other hand, about wear diameter, each ionic liquid exhibited different value. From these results, the eventual value of friction coefficient depend on the kind of anion. Expression of the friction coefficient reduction effect depend on the kind of cation. The wear diameter depend on both of ions.

In the presentation, we discuss the tribo-decomposition process of these ionic liquids.

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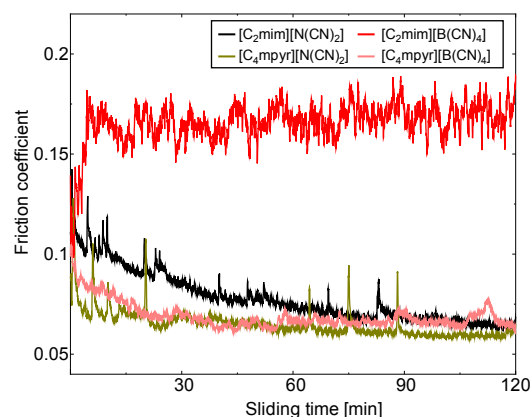


Figure 1. Friction coefficient

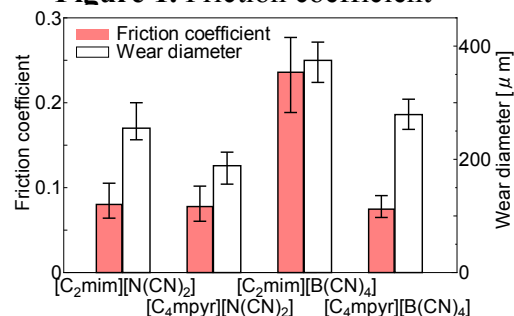
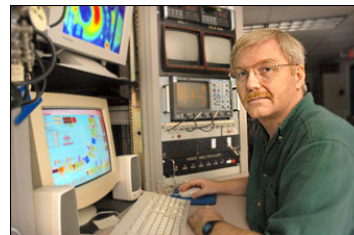


Figure 2. Average of friction coefficient and wear diameter

Durable and effective ionic liquids for a sustainable nuclear fuel cycle

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Ionic liquids attract the interest of researchers and industry due to their remarkable properties and many applications in the fields of energy and technology, [1] including as a potential medium for recycling spent nuclear fuel in support of sustainable nuclear energy. This huge task calls for the development of new technologies that are more efficient and less polluting. The special characteristics of ionic liquids provide an opportunity to reinvent reprocessing systems. The success of ionic liquids in this role depends on their effectiveness in the separation of actinides from fission products and also on the survivability of IL-based systems under the burden of ionizing radiation. We explore aspects of ionic liquid radiation chemistry to elucidate their degradation pathways and investigate how radiolysis interferes with the separation process in order to create innovative, effective and durable IL-based separations systems. [2] We have found several classes of ions that are resistant to ionizing radiation and some examples will be presented. [3] We employ mid-infrared transient absorption detection to specifically identify transient species by their vibrational characteristics. [4] For example, we observed the formation of acetaldehyde and vinyl alcohol during pulse radiolysis of choline NTf₂ (Fig. 1). [5] This work and use of the LEAF Facility of the BNL Accelerator Center for Energy Research were supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences, under contracts DE-SC0012704 (BNL) and DE-AC02-06CH11357 (ANL).

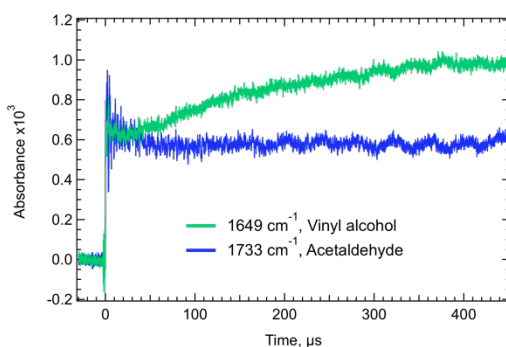


Figure 1. IR detection of molecular radiolysis products in choline NTf₂ by means of their characteristic C=C (VA) and C=O (Ace) stretching frequencies. [5]

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Change the heteroatom, change the outcome ...

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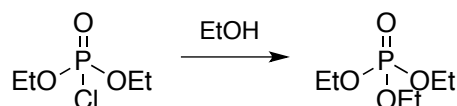
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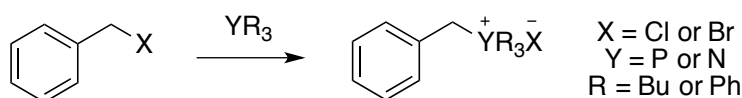


Our group has been developing a predictive framework for ionic liquid solvent effects on organic processes, based on understanding the microscopic interactions present in solutions.[1,2] We have demonstrated this for simple systems and can now identify whether an ionic liquid could beneficially affect reaction outcome, which ionic liquid would be most effective and in what proportion in the reaction mixture.[2]

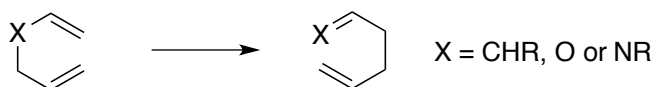
Of interest is to extend this predictive framework to a wider range of substrates and determine the extent to which the structure of the reagents is important in determining the ionic liquid solvent effects. This presentation will cover our efforts towards this, particularly looking at ionic liquid effects on nucleophilic substitution reactions at phosphorus centres (Scheme 1),[3] the effect of changing the heteroatom in bimolecular nucleophilic substitution processes (Scheme 2)[4] and the importance of charge development on solvent effects in pericyclic processes (Scheme 3).[5]



Scheme 1. Reaction of diethyl chlorophosphate with ethanol ($S_N2@P$ mechanism).



Scheme 2. Reaction of trialkyl / triaryl group 15 compounds with benzyl halides (S_N2 mechanism).



Scheme 3. Pericyclic rearrangement processes (concerted mechanism).

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Ionic Liquids at the Interface with Nanomaterials

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Several aspects of nanoscience and nanotechnology involve the use of liquids in contact with nanomaterials, for example as solvents for the dispersion, preparation and chemical modification of nano-objects, as media for transport through nanopores, or as electrolytes in energy-storage devices. In order to understand and control matter at the nanometer level we need an improved understanding of the properties of the fluid media, which do not behave as a simple continuum at these scales, and also of the interfaces. We need to describe in detail the molecular interactions between the fluids and the nanomaterials, an area where important progress can be made.

This presentation will focus on ionic liquids as media to dissolve different kinds of nanoscale objects. Ionic liquids interact through Coulomb and van der Waals forces (including hydrogen bonds), and form organized phases that are heterogeneous at the nanometer scale. Among the nanomaterials of interest are 2D-layered solids in which covalently bonded sheets with thickness of one or a few atoms are held together by van der Waals forces. Examples are graphene or molybdenum disulfide. In these materials the inter-layer forces are of a similar nature as those present in liquids. Another class of materials are biopolymers such as cellulose.

Some of the challenges these systems pose are: i) the heterogeneous structure of the ionic liquids matches the size of the nano-objects leading to solvation effects that are not present in simple molecular liquids; ii) the interactions at play are of different nature, depending on the presence of extended π -systems on carbon nanomaterials leading to polarization effects, or a tight network of H-bonds in cellulose. iii) most often different classes of atomistic model are used to represent the liquid phase and the materials, and so the fluid-solid interactions necessary for molecular simulation studies are not sufficiently well known.

The final aim of this study is to improve our understanding of the physical chemistry of systems containing liquids and nanomaterials, enabling the rational design of solvent systems.

An Efficient Trans-esterification of Cellulose in Ionic Liquid and its Application to Carbon Fiber Reinforced Plastic

Ryohei Kakuchi, Makoto Yamaguchi, Rina Hoshino, Shiori Suzuki, Kenji Takada,

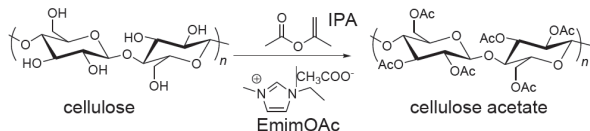
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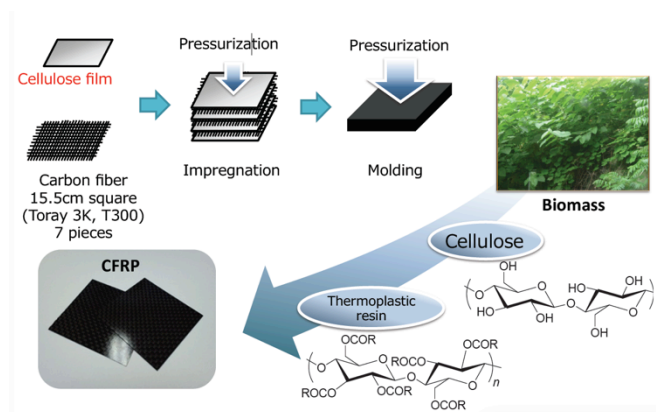


Because of the limited solubility and reactivity of cellulose, chemical modification of cellulose has been extremely difficult for long years. We recently found that, in 1-ethyl-3-methylimidazolium acetate (EmimOAc), trans-esterification of cellulose can proceed very efficiently and rapidly. The reaction performed at 80 °C (Scheme 1) for 30 to 120 min. The structures of products have been confirmed by ¹H NMR and ¹³C NMR. In these reactions we tentatively assigned carben that can be produced from EmimOAc as an activating reagent.



Scheme 1. Schematic representation of the transesterification reaction of cellulose and formation of cellulose acetate in EmimOAc with EmimOAc as a solvent and an activating reagent.

We used the cellulose derivative as thermoplastic resin in a carbon fiber reinforced plastic (CFRP). A strategy of the present work is that we want to make a CFRP from a wood as a composite resin (Scheme 2). Detail will be present at meeting.



Scheme 2. Production of CFRP from woody biomass as a source of thermoplastic resin. We used Toray 3K, T300 as a carbon fiber. CFRP was made from 8 pieces of cellulose films and 7 pieces carbon fibers. Impregnation was done at 280 °C at 2 MPa followed by molding was done at 220 °C at 20 MPa.

Acknowledgement

This research was promoted by COI program "Construction of next-generation infrastructure using innovative materials ~Realization of a safe and secure society that can coexist with the Earth for centuries~ supported by MEXT and JST. This study was also supported in part by an Advanced Low Carbon Technology Research and Development Program (ALCA) of the JST and the Cross-ministerial Strategic Innovation Promotion Program (SIP) from the JST.

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Probing the Dynamics of Ionic Liquids with NMR

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The unique properties (e.g., high ionic conductivity and wide range of solubility) of ionic liquids stem from their structure and molecular dynamics. To develop more useful ionic liquids we need a deeper understanding of the connections between the structure, dynamics and properties. Such knowledge would lead to more appropriate choices of cations and anions to achieve desired physical properties.

Most anions and cations used in ionic liquids contain NMR sensitive nuclei. NMR can probe the translational and reorientational dynamics of the individual species in ionic liquid systems non-invasively. Pulsed gradient spin-echo (PGSE) NMR diffusion measurements [1] provide information on translational motion (and thus hydrodynamic size) and NMR relaxation measurements provide information on reorientational dynamics. While electrophoretic NMR (eNMR) measurements can provide information on electrophoretic mobilities [2]. In many cases it is possible to measure multiple species simultaneously since in general the NMR measurements retain spectroscopic information.

This talk will consider these NMR techniques and will be illustrated with data from ILs such as EMIMTCM and related systems [3-5].

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Role of the Solvophobic Effect in Protein-Ionic Liquid Interactions

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Biological applications which utilise enzymes, or other proteins, require the tertiary structure of the protein to be retained. However, many proteins readily undergo aggregation or denaturation when outside their native environment, and/or over longer timescales. The stability of proteins in solvents other than water is usually considered unappealing due to an assumption that the protein will be insoluble or denatured. However, a few solvents, such as glycerol, dilute alcohols and some ionic liquids have been shown to have protein stabilising properties.

Previously we have developed extensive structure-property relationships between the chemical structures and mesostructures of non-aqueous solvents and the solvophobic effect experienced by amphiphiles for molecular solvents [1] and protic ionic liquids [2]. Here we have extended this to develop a greater understanding of what solvent features are important for protein stability. We have utilised a series of small polar non-aqueous molecular solvents and protic ionic liquids consisting of the four acid-base combinations of ethyl- and ethanolammonium cations paired with formate or nitrate anions. Solutions were prepared of these solvents combined with water, and with added formate or nitrate for the ionic liquids to explore a broad range of pH effects. For this initial work egg white lysozyme (HEWL) was used. These solvent systems enabled us to explore the effect of pH, solvent concentration, solvent cohesive energy density and polarity towards protein stability. The activity of the lysozyme was assessed based on its lytic activity towards *Micrococcus lysodieticus* using UV-Vis spectroscopy. The secondary and tertiary structures of the lysozyme were determined using small angle X-Ray scattering (SAXS) and IR spectroscopy. At low non-aqueous solvent concentrations (high water proportions), the presence of solvents and salts generally maintained lysozyme in its native structure, and enhanced its activity. Due to the presence of a net surface charge on lysozyme, electrostatic interactions in PIL-water systems and salts solutions enhanced lysozyme activity more than the specific hydrogen-bond interactions present in non-ionic molecular solvents. At higher solvent concentrations (lower water proportions), solvents with a propensity to exhibit the solvophobic effect, analogous to the hydrophobic effect in water, retained lysozyme native conformation and activity. This solvophobic effect was particularly observed for solvents which contained hydroxyl moieties.

This work extends our understanding of protein stability in a wide variety of solvent environments, and has enabled structure-property relationships to be developed for a protein in concentrated molecular solvent and protic ionic liquid solvent systems. This work has the potential to lead to the development of tailored solvent systems to optimise protein stability.

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Prospects of Room-Temperature Ionic Liquids

~Road to Novel Nano-Heterogeneity Engineering~

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Nano-confinement of water (“water pocket”) in room-temperature ionic liquid (RTIL) was experimentally proved by a complementary use of small angle X-ray and neutron scattering [1]. The size of the water pocket was estimated to be 2 ~ 3 nm. By simulations, size distribution of the water pocket is found to almost monodisperse. The water pocket is loosely packed and size-tunable in the RTIL, [C₄mim][NO₃]. It is found that formation of water pocket depends on molecular interaction between cation and water. Hydrogen bonding water of the water pocket is different from that of bulk water [2]. The water pocket is modified by nanodomains in the RTILs. With respect to a dynamic property of the water pocket, NMR experiments provide the significant evidence [3]. Quite slow H/D exchange in the RTILs-water mixtures suggests that lifetime of the water pocket is long as we expect.

We performed simultaneous X-ray diffraction and DSC measurements to determine the solid states in [C₄mim][NO₃]-D₂O system [4]. At 70 < x < 94 mol% D₂O, crystal [C₄mim][NO₃] and crystal ice were suppressed at -100 °C. Enthalpy difference (ΔH) is plotted on the water concentration (Fig. 1). Obviously, amorphous appeared discontinuously. Below 70 mol%, crystal [C₄mim][NO₃] was formed without crystal ice. On the other hand, crystal ice occurred above 94 mol%. The discrete region of ΔH almost coincides with that of the water pocket at room temperature.

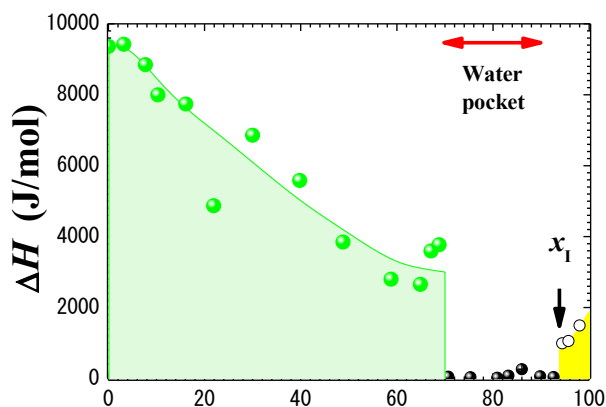


Figure 1. Water concentration dependence of enthalpy.

The water pocket-assisted amorphous ice at the water-rich region (70 < x < 90 mol%) could be utilized for cryopreservation. The cryopreservation is one of representative ideas of application of the water pocket. Loosely packed and nm-sized confinement of water pocket has long lifetime, and is flexible. Nanoheterogeneity engineering of a loosely packed and flexible confinement is likely to become an important stream of nanoscience in the future.

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Hydrogen Bubbles-Assisted Electrodeposition of Metal Nanoparticles from Protic Ionic Liquids for Electrocatalysis

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Fuel cells have been considered as promising energy storage and conversion devices thanks to their high energy density, high conversion efficiency and low pollutant emission^[1]. Nevertheless, the sluggish oxygen reduction reaction (ORR) remains one of the problems to be addressed in order to make fuel cells commercially viable. To address it, using electrocatalysts to increase the reactions kinetics is essential. The activity of electrocatalysts is strongly influenced by their structure and active surface area^[2]. Nano-structured materials have high surface area and accordingly increased catalytic activity. The low interfacial tension in ionic liquids makes them easy to adapt to other phases and results in high nucleation rates and generally smaller nanoparticles^[3].

Hydrogen evolution is usually considered to be detrimental to electrodeposition. Here we show an approach for electrodeposition of metallic nanoparticle catalysts from protic ionic liquids using hydrogen bubbles as spacers to prevent the nanoparticles from aggregation. Electrochemical behavior of silver, palladium and nickel in a protic ionic liquid, ethylammonium nitrate (EAN), is studied. The electrocatalytic activity of the deposited nanoparticles towards ORR is studied in alkaline media. It was found that enhanced ORR performance can be achieved using these metallic catalysts with smaller particle size and large electrochemical active surface areas.

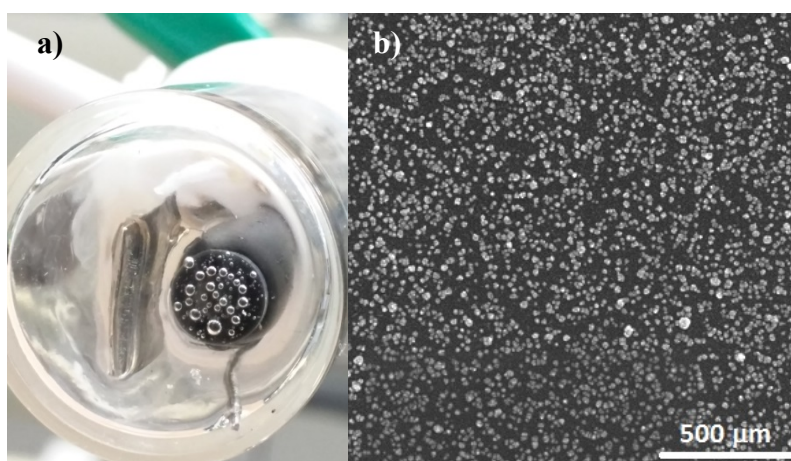


Figure 1. a) Hydrogen bubbles on the electrode surface during the electrodeposition process in EAN, b) Ni electrodeposited by hydrogen dynamic template

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Solid fuels to liquids via ionic liquid pre-treatment

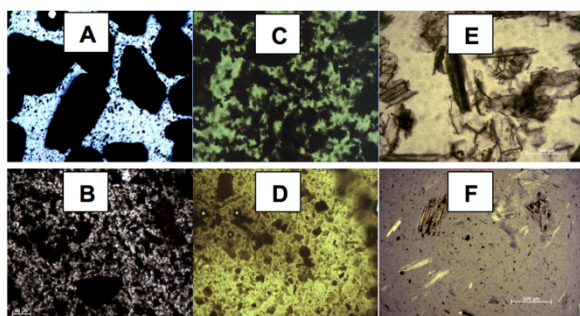
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The conversion of solid fuels to liquids has been investigated extensively in scientific literature [1-4]. A number of liquefaction processes exist in order to convert solid fuels to valuable liquids, however they require immense temperature and pressures in order to achieve this. Solvent pre-treatments are commonly employed to reduce the energy required to convert solid fuels to liquids, however conventional solvents can be expensive, have high vapour pressures and can be toxic [5, 6]. Ionic liquids are a diverse group of green solvents which have generally been shown to have remarkable physical and chemical properties including high thermal and electrochemical stabilities, low vapour pressures and, critically for this work, the capacity to solubilize a diverse range of materials. In this study, four ionic liquids; 1-butylpyridinium chloride [Bpyd][Cl], 1-ethyl-3-methylimidazolium dicyanamide [Emim][DCA], 1-butyl-3-methylimidazolium chloride [Bmim][Cl] and 1-butyl-3-methylimidazolium tricyanomethanide [Bmim][TCM] were used in a low temperature treatment process for three types of solid fuels; bituminous coal, lignite and biomass. Initial investigations have shown the ability of the chosen ionic liquids to solubilize each of the different types of solid fuel to different extents. Most effective of the ionic liquids studied was [Bmim][Cl] which was found to swell and solubilize both biomass and lignite samples and fragment bituminous coal. Characterization of the solid fuels and the liquids extracted were completed via FTIR, TGA and optical microscopy (presented in Figure 1). Changes to the pyrolysis



characteristic after all ionic liquid treatments was apparent in conjunction with a decrease in oxygenated functional groups prevalence in the solid samples examined. These findings are promising in reducing energy requirements for the conversion of solid fuels to liquids, which may then be refined to liquid fuels or valuable chemicals as appropriate.

Figure 1. Micrographs of (a) bituminous coal mixed with water and (b) bituminous coal after treatment with [Bmim][Cl] at 20x magnification, (c) lignite mixed with water and (d) lignite after treatment with [Bmim][Cl] at 20x magnification; (e) biomass mixed with water and (f) biomass after treatment with [Bmim][Cl] at 10x magnification.

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Revisiting Cellulosic carbon fibres: Can ionic liquids improve things???

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Cellulose as a carbon fibre, CF, precursor dates back to the work done by Edison in 1901 converting cellulose into carbon filaments for his electric light bulb. Indeed in the 60's the process was commercialized. However the process was slow required high heating temperatures and the fibres had relatively poor mechanical properties, irregular cross sections and low carbon yield. The cellulosic precursor used in the 60's was a textile grade regenerated fibre termed viscose. As the use of CF composites expands beyond aerospace applications and towards automotive and other high volume applications interest in cellulose as a precursor has been reignited. This is largely due to the economic and ecological benefits coupled with advances in regenerated technical grade cellulosic fibres which include the ability to process cellulose using ionic liquids. In this talk we will discuss our recent research on cellulosic carbon fibres.

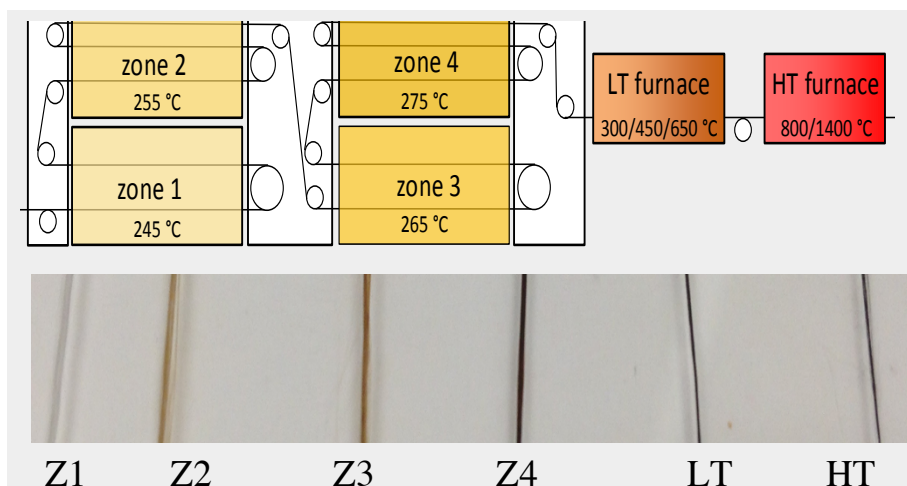


Figure 1. Scheme showing a typical carbon fibre line equipped with multiple ovens and furnaces and the related changes in fibre colour as the white fibre (precursor) changes through shades of brown towards being a black fibre (carbon fibre).

Carbon dioxide as an anti-solvent for biomass processing with concentrated aqueous hydroxide solutions

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CO₂ in the form of dry ice was employed as an antisolvent in the pretreatment of rice husks using concentrated hydroxide solutions. The pretreatment produced digested rice husks, which produced excellent glucose yield by enzymatic saccharification, and dissolved silica, which was effectively recovered by CO₂ (97% of the total silica, 89% purity). The CO₂-neutralized hydroxide solutions can be reactivated with Ca(OH)₂ and their efficiency retained for many rounds of pretreatment.

A Structural Study of Protic Ionic Liquids in Biomass Dissolution

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Lignocellulosic biomass is a renewable source of fuel and fine chemicals. Although naturally abundant, it is heterogeneous and recalcitrant to treatment. Recent studies show the potential of protic ionic liquids (PILs) for lignin extraction.^{1,2} However, the solubility selectivity at the atomic level is still a mystery. Our study describes the bulk structure of a model PIL, pyrrolidinium acetate, with a dissolved model lignin residue, guaiacol. Using neutron diffraction combined with empirical potential structure refinement (Figure 1), our study provides an atomic resolution picture of liquid structure. We reveal how PILs solubilise lignin-type residues (Figure 2), and how solvent structure is affected. While electrostatic forces dominate the solvent structure, hydrogen bonding and packing efficiency are key factors to consider for lignin dissolution. Local interactions can influence overall solvent performance. A structural understanding will facilitate the pre-treatment of biomass, and therefore, is a key step towards a commercially viable bio-refinery process.

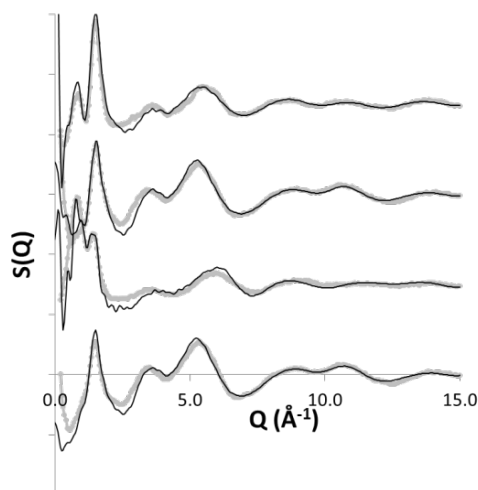


Figure 1. Neutron diffraction (grey) and simulation fitted (black) structure factors $S(q)$ with four isotopic substitutions.

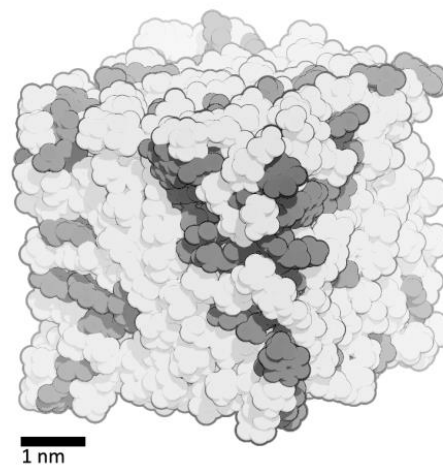


Figure 2. A snapshot of the fitted bulk structure of guaiacol (black) dissolved in pyrrolidinium acetate (white).

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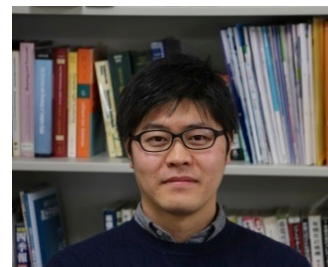
Glyme-Li Salt Molten Complexes: Classification into Ionic Liquids and Use as Electrolyte in Lithium-Sulfur Batteries

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Certain equimolar mixtures of oligoether solvents (glymes) and certain Li salts (LiX) yield low melting salt complexes, abbreviated as [Li(glyme)]X.¹ If the glyme-Li salt complexes consist of these independent complex [Li(glyme)]⁺ cations and their counter anions in the molten state, they together form the essence of an IL, and therefore can fall into a new subclass of ionic liquids, “solvate (or chelate) ILs”.² Given the similarity in composition between highly concentrated electrolyte solutions and the solvate ILs, an interesting question arises; can a sharp boundary be drawn between them? The interplay between the ion-ion and ion-solvent interactions is essential in discussing the differences between these two concentrated liquids. To study factors that divide the concentrated electrolyte solutions into these two liquid states, we investigated the effects of solvent (ligand) species and counter anions on the structures and properties of a series of glyme-Li salt molten mixtures, and discuss whether a given mixture belongs to the solvate ionic liquid or not.³⁻⁵ Appropriate combination of LiX and the glymes showed IL-like behavior, and thereby they were classified as solvate ILs. In contrast, uncoordinated glyme molecules were present more or less in other mixtures, which were regarded as ordinal concentrated solutions. We also studied battery performance using the glyme-Li salt molten complexes as electrolyte for lithium-sulfur (Li-S) batteries. The electrolyte properties depending on the ionic structure correlated with the cell performance.⁶ Moreover, dissolution of lithium polysulfides (i.e., reaction intermediates of the sulfur cathode) into the electrolyte, which is a serious issue facing practical application of Li-S cells, was greatly suppressed in the solvate ILs. Therefore, stable charge-discharge with high Coulombic efficiency was achieved with the solvate IL electrolytes.

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Exploration of the physical properties of new solvate ionic liquids

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New solvate ionic liquids (ILs) have been recognized for their use in improving rechargeable lithium-ion batteries¹, consisting of equimolar mixture of either tri- or tetraglyme (G3 or G4) and lithium *bis*(trifluoromethanesulfonylimide) (LiTFSI) and are identified as either G3 TFSI or G4 TFSI respectively. Little is known of their physico-chemical characteristics, especially in relation to synthetic chemistry. A series of analytical methods are explored to determine the Kamlet-Taft Parameters (G3 TFSI: $\alpha = 1.32$, $\beta = 0.41$, $\pi^* = 0.938$, $ET(30) = 64.02$, $E_T^N = 1.028$; G4 TFSI: $\alpha = 1.35$, $\beta = 0.37$, $\pi^* = 0.904$, $ET(30) = 64.18$, $E_T^N = 1.033$) and the Guttmann Acceptor Numbers (AN)(G3 TFSI: AN = 26.5; G4 TFSI: AN= 26.5) of these solvate ILs. This information was then used as an indicator of potentially suitable synthetic transformations.

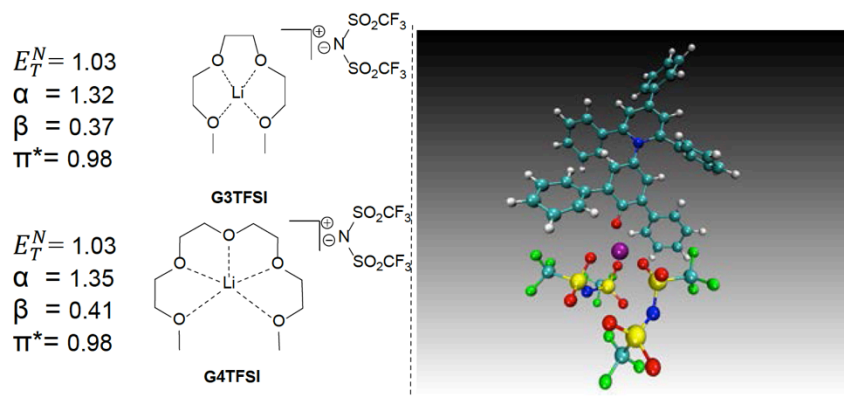


Figure 1. Exposition of G3 and G4 TFSI physical parameters and the molecular dynamics of the Lithium moiety interacting with Reichardt's Dye.

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Thermoelectrochemistry of Lithium Glyme Solvate Ionic Liquids

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Current devices to harvest heat have significant limitations, and typically consist of intricate mechanical systems. Thermoelectrochemistry is a simple, scalable technique for the direct electrochemical conversion of thermal energy into useful electricity. It is driven by the entropy change associated with a redox process, resulting in a temperature dependence of the electrode potential.[1,2] A temperature difference across two electrodes can, therefore, be converted into electricity using chemistry; such systems are ideal for harvesting low-grade heat that would otherwise go to waste.

The thermoelectrochemical properties of lithium-glyme based solvate ionic liquids have been investigated[3] using mixtures of lithium bis(trifluoromethylsulfonyl)imide (Li[NTf₂]) in tetraethylene glycol dimethyl ether (tetraglyme, G4). The process is entropically driven by the formation of a lithium glyme complex on the cold electrode accompanied by the release of an electron, and the release of the lithium from the complex at the hot electrode accompanied by the capture of an electron and deposition of lithium on the hot electrode (as shown in Figure 1).

A wide range of other solvate ionic liquids are known. Further investigation was therefore performed on a wider range of glymes (monoglyme, diglyme, triglyme), as well as tetrahydrofuran (THF). The entropy change in THF was concentration-independent, whereas the process in the glymes displayed significant differences between the dilute electrolyte and ‘super-concentrated’ solvate ionic liquid systems. The reasons behind this will be discussed.

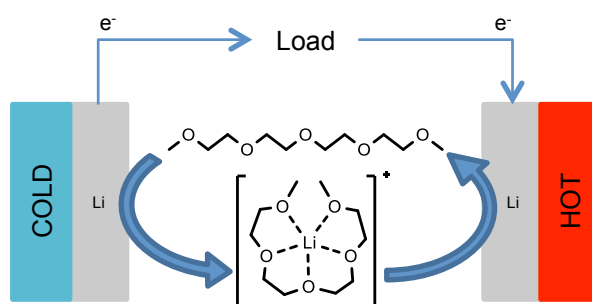


Figure 1. Schematic of a lithium-G4 thermoelectrochemical cell.

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Solvate Ionic Liquids as a Solvent for Organic Transformations

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The recent report of solvate ionic liquids (SILs) by Watanabe *et al.*¹ has spurred a huge amount of work in the area of lithium ion batteries, energy storage, lubricants and their nanostructure.² An area which has been left unchecked is the suitability of SILs as solvents for organic chemistry. The preparation of these solvate ILs attracts no synthetic challenges, simple dissolution of Li[NTf₂] in either tri- or tetraglyme yields the ionic liquids, G3TFSI or G4TFSI, respectively, within a few hours (Figure 1). Additionally, they possess various attractive attributes for organic chemists: (i) they are aprotic; (ii) they remain as liquids at low temperatures (e.g. 0 °C). Their resemblance to 5M lithium perchlorate in diethyl ether (5M LPDE) makes reactions carried out in that solvent obvious for comparison. This talk will cover our recent work into the application of SILs (G3TFSI and G4TFSI) as reaction media for organic chemical reactions and comparisons to molecular solvents, other ionic liquids, and 5M LPDE (Figure 1).³ We hope to highlight the advantages in using these ionic liquids and ease with which these SILs can be used as solvents.

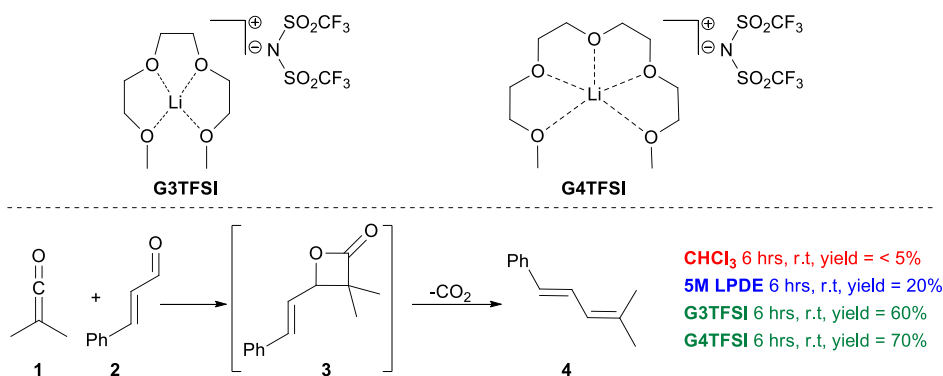


Figure 1. Simplified structures of G3/G4TFSI and a typical organic transformations using SILs as replacement for organic solvents.

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Ionic Liquids vs Salty Water for Biomass Processing

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Biomass is an abundant and poorly utilised resource. It has been deliberately burnt for energy for almost a million years, and one goal of modern chemistry is to harness its energy and chemicals in a more efficient, all-encompassing manner (the ‘biorefinery’ concept). However, hundreds of millions of years of evolution has rendered many forms of biomass (bio)chemically robust.

Certain **ionic liquids (ILs)** possess the ability to act as (almost) non-derivatising near-universal solvents for a wide range of lignocellulosic biomasses, spanning from soft and hard woods to rice husks, bagasse, nut shells, chilli, *etc.*[1,2] With weight percentage solubility values exceeding 50% for lignin and cellulose in ILs,[3,4] and with complicated biomass samples dissolving relatively intact either at room temperature or within minutes at elevated temperatures, comparable solvents for biomass processing do not exist... or do they?

Since the 1930’s, it’s been known that aqueous solutions of quaternary ammonium hydroxides (*i.e.* aqueous electrolytes, or ‘**salty water**’) can dissolve large quantities of cellulose at room temperature.[5] By the 1970’s they were largely forgotten, but are now being investigated again, including for whole biomass processing.[6]

This talk will summarise some of our investigations into biomass processing using ionic liquids, and how they compare against a wide range of aqueous hydroxide solutions.

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Understanding the Influence of Key Ionic Liquid Properties on the Hydrolytic Activity of *Bacillus lentus* subtilisin (BLS) and *Thermomyces lanuginosus* lipase (TTL)

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Ionic liquids (ILs), as solvents with a vast range of physicochemical properties, have been used for stabilizing and activating enzymes in recent times. However, due to the wide range of combinations of anion and cation, IL properties vary significantly. The key properties of ILs related to enzyme performances have not been well studied yet. This work follows up the previous work on understanding the correlation of physicochemical properties of numerous ILs and *Thermomyces lanuginosus* lipase (TTL) [1], and these key IL properties were further applied on another hydrolase *Bacillus lentus* subtilisin (BLS). Thus both of the hydrolytic activity of two commercial hydrolases in IL systems were investigated. A number of ILs based on primary, tertiary and quaternary ammonium cations coupled with mesylate and propionate anions were used as the media. We correlated the enzyme activity of with various key properties of ILs and IL-water mixtures, including ion concentration, water activity (a_w), kosmotropicity, hydrogen bond basicity (β) and pH. The ion concentration was associated with a_w , while the molar ratio of water/IL 5:1 where the $a_w = \sim 0.6$ was found to be the threshold for assured enzyme activity. Triethylammonium mesylate was the best IL owing to its kosmotropicity and ideal intrinsic β . The pH of the IL-water mixtures is a key parameter related to the conformational change and surface charge of enzymes. We demonstrated the pH effect of IL-water mixtures can be overcome by buffering, and the buffered system showed the greatest activity.

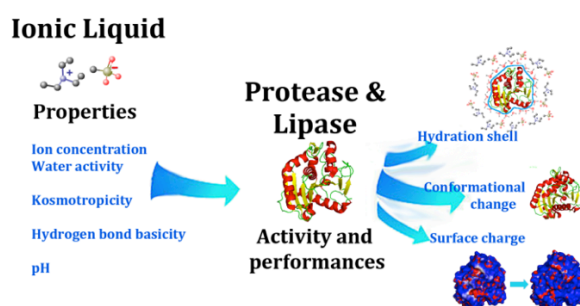


Figure 1. For ionic liquids and ionic liquid water mixtures, it is investigated various key IL properties the ion concentration, water activity, kosmotropicity, hydrogen bond basicity, and pH impact the hydrolytic activity of both *Bacillus lentus* subtilisin and *Thermomyces lanuginosus* lipase. Maximum enhancement of the enzyme activity is found in buffered triethylammonium mesylate water mixture.

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Fractionation of lignin through the use of ionic liquids

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Ionic liquids consist of essentially unsolvated anions and cations.¹ This results in unique solvation properties such as their ability to dissolve relatively large quantities of biomass intact, compared to molecular solvents.² Ionic liquids have also been shown to be capable of changing reaction outcomes when compared to molecular solvents.³

Previous work⁴ has identified ionic liquids that are suitable for the dissolution of lignin from biomass. One of these ionic liquids [Bpyr][OTf] has been examined in an effort to modify the reactivity of a range of different lignin model compounds [Fig. 1]. The ultimate goal of such studies is to develop a method for the controlled cleavage of lignin to a range of aromatic feedstock chemicals, such as phenols.

Initial work identified that the ionic liquid used here enabled the ether cleavage of a range of model compounds; these reactions did not progress in any molecular solvent examined. The selectivity of the reactions was greater in the model compounds containing two ether functionalities than predicted based on simpler substrates. Molecular dynamics simulations are being performed in order to explain this.

Studies are also underway using [Bpyr][OTf] to directly fractionate wood flour under microwave irradiation. Under these conditions, wood has been converted to a small series of compounds that have been identified using mass spectroscopy. Optimisation and recyclability studies are underway, yarr matey.

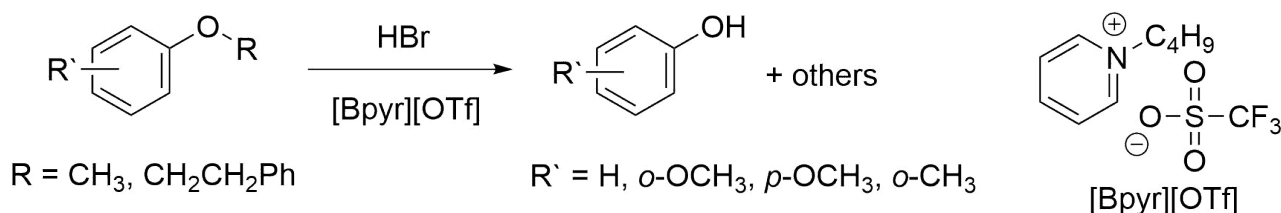


Figure 1. By performing the reaction seen here in an ionic liquid ([Bpyr][OTf]), both the rate of reaction and selectivity of the two different ethers in the same molecule changed.

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Spontaneous Exfoliation of Graphene into Ionic Liquid Solution

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Graphene is a two-dimensional sheet of hexagonally arranged carbon atoms which has recently generated intense scientific interest.¹ However, scalable isolation of this material has proven problematic; all reported methods of graphene exfoliation require energy,² while the reverse process – aggregation of single or few layer graphene sheets – occurs spontaneously in most solvents. This makes producing, and especially storing, graphene in economic quantities challenging. Here, we report that the ILs 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMIm TFMS) and 1-ethyl-3-methylimidazolium acetate (EMIm Ac) can facilitate the *spontaneous* conversion of highly-ordered pyrolytic graphite (HOPG) to graphene under ambient conditions. Specifically, in-situ amplitude modulated – atomic force microscopy (AM-AFM) is used to observe the exfoliation of graphene from the HOPG interface with molecular resolution. Our findings show the first evidence of *spontaneous graphene formation* in any system, and provide insight into the exfoliation mechanism.

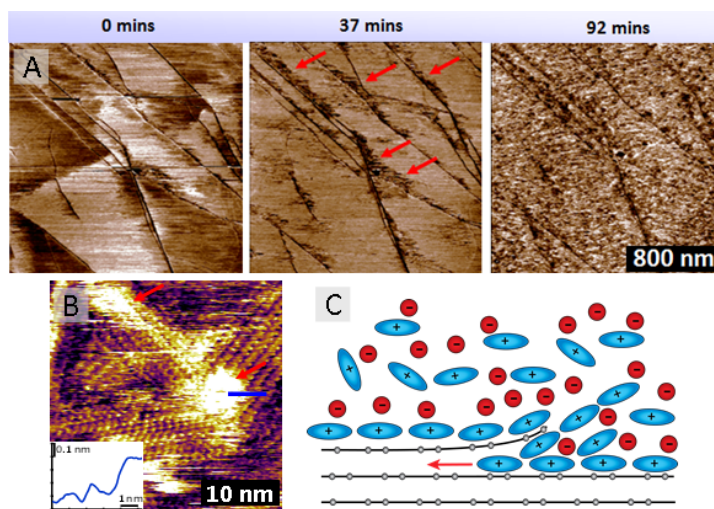


Figure 1. A) 2 $\mu\text{m} \times 2 \mu\text{m}$ AM-AFM phase images monitoring the HOPG surface exfoliating over time when in contact with IL (time indicated above images). B) 30 nm \times 30 nm AM-AFM height image of the IL– HOPG interface revealing the position of surface adsorbed cations around exfoliating graphitic flakes. C) Cartoon representation of the exfoliation mechanism.

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CO₂ Capture and Electrochemical Conversion using Super Basic Ionic Liquids



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Since the industrial revolution the harnessing of fossil fuels by combustion for energy and transportation has seen atmospheric levels of CO₂ steadily rise. As well as being a greenhouse gas, CO₂ can be considered C1 building block for the production of fuels or chemicals. Electrochemical reduction provides a route to achieve these transformations owing to the potential to reduce CO₂ at high efficiencies and selectivity. The main issues to be overcome are the thermodynamic stability of the CO₂ and the slow kinetics of the processes in general. Ionic liquids have been shown to be effective in promoting this electrochemical reduction^{1,2} and in this presentation, the use of reactive super basic ionic liquids are discussed with respect to CO₂ capture and utilization.

A range of ionic liquids consisting of the trihexyltetradecylphosphonium ([P₆₆₆₁₄]⁺) cation paired with a superbasic anions have been synthesised and evaluated for CO₂ capture and utilisation. The CO₂ absorbance performance of these ILs has been compared under dry and wet conditions. Depending on the anion structure, different effects of the water were observed. For example, in the case of ionic liquids presenting equimolar CO₂ uptake under dry conditions, e.g. benzimidazole and 1,2,4 triazolidine trihexyltetradecylphosphonium ([P₆₆₆₁₄][124Triz]) based ionic liquids, only small reductions were observed in their CO₂ uptake under wet conditions from >1 to 0.89 or 0.88, respectively. In contrast, a positive effect of the presence of water on CO₂ uptake was observed in the case of [P₆₆₆₁₄][123Triz]. The effects of the presence or the absence of water on CO₂ and ILs interactions were evaluated using ¹H and ¹³C NMR spectroscopy and ab initio calculations.³ These results showed that, in general, the CO₂ competes effectively with H₂O for absorption. Moreover, the ability to repeatedly capture and release the CO₂ under wet conditions has been also demonstrated, using [P₆₆₆₁₄][124Triz], for example, without significant reduction in its CO₂ capacity after 6 cycles. The enhanced sorption is associated with chemical binding of the CO₂ with the anion.

Using [P₆₆₆₁₄][124Triz] CO₂ has been shown to be reduced on Ag, Au and Pt electrodes to produce formate and syngas.⁴ Two reaction pathways were found to exist at -0.9 V and -1.9 V. Formate is formed in increased quantities at -0.9 V over -1.9 V on both electrode surfaces with Faradaic efficiencies of ca. 50 %. The production of CO is higher on Au and Ag electrodes than Pt electrodes for both electrolysis potentials of -0.9 and -1.9 V. The production of hydrogen, only observed at -1.9 V, is ca. 3 times higher on Pt electrodes compared with Au and higher still on Ag, enabling the ratio of CO:H₂ in the syngas mixture to be influenced by electrode choice. The reduction of physically bound CO₂ is shown to occur at similar potentials on Ag and Au electrodes to those reported for ILs that only physically absorb CO₂ albeit at lower Faradaic efficiencies

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Ionic Liquids of Superior Thermal Stability

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It is now apparent that ionic liquids (ILs), as commonly formulated, do not have an especially high degree of long-term high-temperature stability.¹ Rather, while short-term stability (minutes to perhaps hours) at temperatures $\geq 300^\circ\text{C}$ is often observed, ILs with stability at such temperatures for days, weeks, or longer have proven to be elusive quarry. However, we recently showed that ionic liquids incorporating the Tf_2N^- anion and select tetraarylphosphonium (TAP) cations can manifest thermal stabilities far superior to salts of typical dialkylimidazolium-, quaternary ammonium, or tetralkylphosphonium cations likewise paired with Tf_2N^- or other anions.² (Figure 1a) Indeed, insofar as we could determine, several of the salts we described were the most thermally stable organic-ion ionic liquids/molten salts reported thus far.

Here we describe the extension of our studies to include three additional cation types (Figure 1b) which yield Tf_2N^- salts of equal or even greater long-term stability. We discuss our hypothesis as to the basis for the thermal durability of these ILs, and the impact on their stability that certain types of structural modifications have. We will also discuss several other elements of the chemistry of these compounds, including strategies for driving down the melting points of these types of salts (salts of the respective ‘parent’ cations tend to melt at $T > 100^\circ\text{C}$) without compromising their high-T stability, and the formation of mixed ILs in which the cations are one of the present organic species paired with an alkali metal (Li^+ - Cs^+).

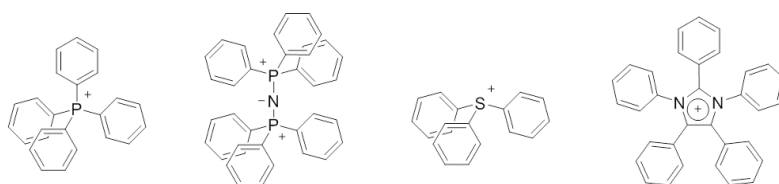
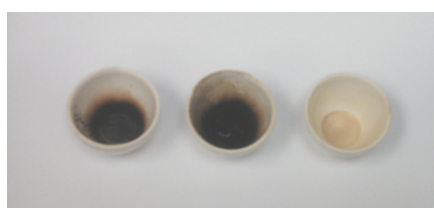


Figure 1a (left). The results of heating (*l-r*) [EMIM] Tf_2N , $[\text{C}_1\text{C}_4\text{Pyrr}]\text{Tf}_2\text{N}$, and $[\text{Ph}_4\text{P}]\text{Tf}_2\text{N}$ at 300°C for 96 h in air. The familiar ILs have been reduced to ash, while $[\text{Ph}_4\text{P}]\text{Tf}_2\text{N}$ is unchanged. **1b** (right). General structures of four basic cation types we have found to have superb degrees of long-term high temperature aerobic stability.

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Control of Self-assembly of Block Copolymers in Ionic liquids for Advanced Materials

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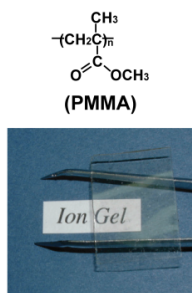
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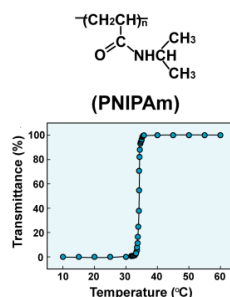
Ionic liquids (ILs) have attractive properties as solvents and additives for macromolecules, such as tunable solvation properties, negligible volatility, and high ionic conductivity [1, 2]. We have discovered that ILs exhibit a variety of solubility toward polymers [1, 2] (**Fig. 1**). For instance, in 1-ethyl-2-methyl-imidazolium bis(trifluoromethanesulfonyl)amide ([C₂mim][NTf₂]), poly(methyl methacrylate) (PMMA) is completely compatible, which makes the formation of new polymer gels (“ion gels”) possible [3-5]. Conventional polymer gels contain volatile liquids, which sometimes limits their utility in open atmosphere, under reduced pressure, or at high temperatures. If task-specific properties are designed for ionic liquids and matrix polymers, the ion gels can offer innovative polymeric materials [6-8]. In contrast to completely compatible systems, certain polymers in ionic liquids exhibit phase separation by temperature change. Poly(*N*-isopropyl acrylamide) (PNIPAm) exhibits UCST phase behavior in [C₂mim][NTf₂] [9] (**Fig. 1**). On the other hand, poly(benzyl methacrylate) (PBnMA) and related polymers show LCST phase behavior in [C₂mim][NTf₂] [10-12] (**Fig. 1**). Certain polyethers were also found to exhibit LCST behaviors [14, 14]. These systems are successfully developed to produce thermo-responsive polymer gels with a volume phase transition using [C₂mim][NTf₂] as a solvent. The UCST (LCST) polymer gels were swollen in the IL at higher (lower) temperatures and shrunken at lower (higher) temperatures than the phase separation temperature in a reversible manner, respectively [9, 10]. Light stimuli can also induce a large phase separation temperature change for photo-responsive PBnMA and PNIPAm copolymers [15-18]. In my talk, I would like to focus on block copolymers consisting of these polymer segments with different solubility, and also on the temperature and photo induced self-assembly changes in ILs [19-24].

Macromolecules in Ionic Liquids

(a) Compatible System



(b) UCST-type



(c) LCST-type

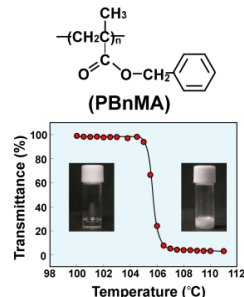


Fig. 1 Variety of solubility of different polymers in [C₂mim][NTf₂].

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Structural effect of glyme-Li salt solvate ionic liquids on the conformation of poly(ethylene oxide)

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Abstract

The conformation of 36 kDa polyethylene oxide (PEO) dissolved in four glyme-Li⁺ solvate ionic liquids (SILs) has been investigated by small angle neutron scattering (SANS) and rheology as a function of concentration and compared to a previously studied SIL. The solvent quality of a SIL for PEO can be tuned by changing the glyme length and anion type. Thermogravimetric analysis (TGA) reveals that PEO is dissolved in the SILs through Li⁺ – PEO coordinate bonds. All SILs (lithium triglyme bis(trifluoromethanesulfonyl)amide ([Li(G3)]TFSI), lithium tetraglyme bis(pentafluoroethanesulfonyl)-amide ([Li(G4)]BETI), lithium tetraglyme perchlorate ([Li(G4)]ClO₄) and [Li(G4)]TFSI) are found to be moderately good solvents for PEO but solvent quality decreases in the order [Li(G4)]TFSI ~ [Li(G4)]BETI > [Li(G4)]ClO₄ > [Li(G3)]TFSI due to decreased availability of Li⁺ for PEO coordination. For the same glyme length, the solvent qualities of SILs with TFSI⁻ and BETI⁻ anions ([Li(G4)]TFSI and [Li(G4)]BETI) are very similar because they weakly coordinate with Li⁺, which facilitates Li⁺ – PEO interactions. [Li(G4)]ClO₄ presents a poorer solvent environment for PEO than [Li(G4)]BETI because ClO₄⁻ binds more strongly to Li⁺ and thereby hinders interactions with PEO. [Li(G3)]TFSI is the poorest PEO solvent of these SILs because G3 binds more strongly to Li⁺ than G4. Rheological and radius of gyration (R_g) data as a function of PEO concentration show that the PEO overlap concentrations, c^* and c^{**} , are similar in the four SILs.

Vesicle Formation in Protic Ionic Liquids and Deep Eutectic Solvents

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The discovery of water on Mars has renewed interest in the search for alien life. However, the search for extra-terrestrial life should not be constrained by terrestrial limitations i.e. the presence of liquid water. Compartmentalization is a key feature to prebiotic life and can be excellently modeled by vesicles. Self-assembly of vesicles in non-aqueous environments such as ionic liquids and deep eutectic solvents provides evidence that life could exist without water.

Polarising optical microscopy has demonstrated that vesicles and other lamellar structures can spontaneously self-assemble in non-aqueous solvents. This confirms that water is not unique as a self-assembly solvent, and also that hydrogen bonding is not required for self-assembly to occur.

Small angle neutron scattering and differential scanning calorimetry were used to characterize these vesicles and demonstrated that phospholipid tail length influenced vesicle properties (e.g. bilayer thickness and chain melting temperature) in the same way in ionic liquids as it does in water, further confirming that the same processes can occur without water.

This research demonstrates the very real possibility of water-free, synthetic, life-forms, and also significantly broadens the ‘goldilocks zone’. That is, the range of planetary orbits that could potentially support life based on their environmental conditions (e.g. temperature).

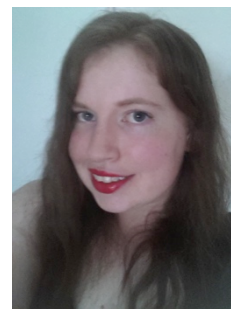
Metal Ion Adsorption at the Ionic Liquid–Mica Interface

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Mica has been employed in many studies of ionic liquid (IL) interfaces on account of its atomic smoothness and well defined surface properties. However, until now it has been unclear whether ions dissolved in ILs can compete with the IL cation and adsorb to mica charge sites. In this work amplitude modulated atomic force microscopy (AM-AFM) has been used to probe metal ion adsorption at the interface of mica with propylammonium nitrate (PAN), a room temperature IL. Lithium, sodium, potassium, magnesium and calcium nitrate salts were added to PAN at a concentration of ~ 60 mM. Aluminum nitrate was also investigated, but at only 5 mM because its solubility in PAN is much lower. The AM-AFM images obtained when the metal ions were present are strikingly different to that of pure PAN, indicating that the ions compete effectively with the propylammonium cation and adsorb to negatively charged sites on the mica surface despite their much lower concentration (Figure 1). This is a consequence of electrostatic attractions between the mica charge sites and the metal ions being significantly stronger than for the propylammonium cation; compared to the metal ions the propylammonium charged group is relatively constrained sterically. A distinct honeycomb pattern is noted for the PAN + Al^{3+} system, less obviously for the divalent ions and not at all for monovalent ions. This difference is attributed to the strength of electrostatic interactions between metal ions and mica charge sites increasing with the ion charge, which means that divalent and (particularly) trivalent ions are located more precisely above the charged sites of the mica lattice. The images obtained allow important distinctions between metal ion adsorption at mica – water and mica – PAN interfaces to be made.

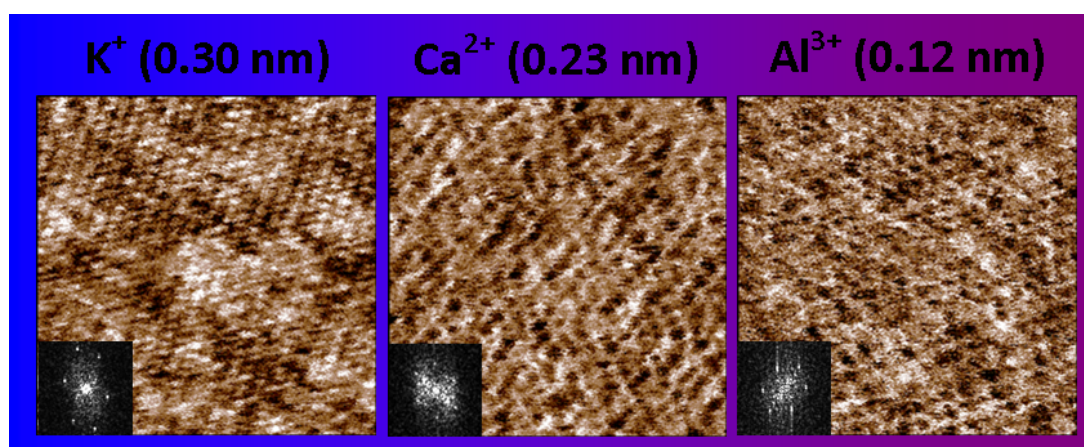


Figure 1. 10×10 nm AM-AFM phase images of a mica interface with solutions of (left) KNO_3 in PAN, (middle) $\text{Ca}(\text{NO}_3)_2$ in PAN and (right) $\text{Al}(\text{NO}_3)_3$ in PAN

Alkoxy-ammonium based ionic liquid electrolytes for reversible metal batteries

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Rechargeable Metal batteries based on zinc and magnesium are currently of interest since they could play a key role in emerging large-scale energy storage applications. However, achieving good rechargeability of such metal batteries requires significant further research and development effort. Room Temperature Ionic liquids (RTILs) offer a number of ideal thermal and physical properties as potential electrolytes for large-scale energy storage applications and thus, can help increase the practicality of such electrochemical devices. Here we report the synthesis and application of a novel quaternary tri-alkoxy ammonium bis(trifluoromethylsulfonyl)amide based RTIL i.e. $[N_{2(20201)(20201)(20201)}][NTf_2]$ (**IL1**) designed to interact and solubilize metal ions such as Zn^{2+} and Mg^{2+} , in order to aid the electrochemical reversibility of the metal. In the case of zinc, the presence of 2.5 wt.% water reduces the activation barrier required to deposit zinc and assists stable charge/discharge zinc cycling at a current density of 0.1 mA/cm² over 750 cycles (**Figure 1a**) [1]. Preliminary work also demonstrates magnesium reduction/re-oxidation from **IL1** (**Figure 1b**), however the source of magnesium salt such as the $[BH_4]^-$ ion is vital for the electrochemical reversibility of the metal ion [2].

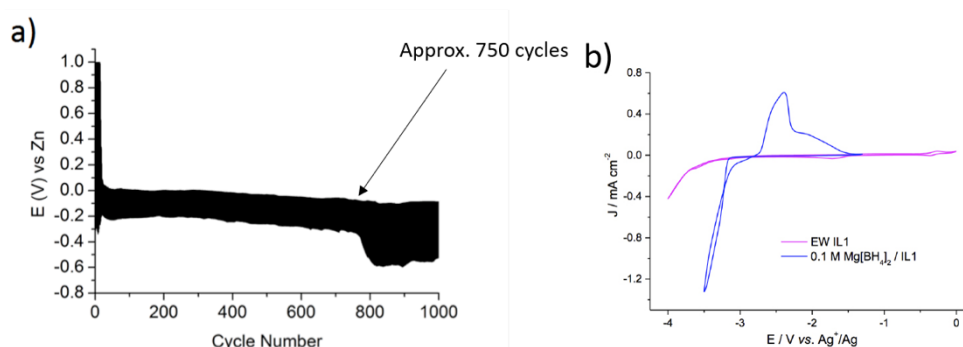


Figure 1. a) Charge/Discharge of $[0.1M Zn(NTf_2)_2 \text{ in } \mathbf{IL1}] + 2.5 \text{ wt. \% } H_2O$ over 1000 cycles vs. Zn^{2+}/Zn (working electrode: Glassy carbon) ; b) Electrochemical window (EW) of **IL1** (pink) vs. Ag^+/Ag of and CV of 0.1 M $Mg[BH_4]_2/\mathbf{IL1}$ (blue).

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Effect of zwitterions on electrochemical properties of ionic liquids

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Lithium-ion batteries (LIBs) have been widely used in power devices. For further expanding usage of LIBs, improving safety and energy density are required. We have focused on zwitterions, which have positive charge and negative charge in the same molecule [1,2]. Lithium-ion transport was improved by adding a zwitterion to polymer gel electrolytes [3]. Recently, we found that adding a small amount of zwitterion improved not only the electrochemical stability of oligo-ether electrolytes up to about 5 V [4] but also the charge-discharge cycle stability of cells with oligo-ether electrolytes [5].

In this study, we investigated the effect of zwitterions on electrochemical properties of ionic liquid (IL) electrolytes. *N*-Methyl-*N*-propylpyrrolidinium bis(fluorosulfonyl)amide (P13FSA)/lithium bis(trifluorosulfonyl)amide (LiTFSA) composites with 5 wt% zwitterion, 3-(1-butylpyrrolidinium)propane-1-sulfonate (Bpyps), were prepared. The electrochemical window of P13FSA/LiTFSA/Bpyps was 0-5.4 V vs. Li/Li⁺, which was almost identical to that of P13FSA/LiTFSA. Lilelectrolyte/LiCoO₂ cells containing IL electrolytes with Bpyps exhibited high capacities in the cut-off voltage range of 3.0-4.6 V even after 50 cycles. The increase in interfacial resistance between the electrolyte and the cathode with cycles was suppressed. In the cyclic voltammograms of cells employing a graphite electrode, current peaks corresponding to the intercalation/deintercalation of lithium ions were observed in the case of IL electrolytes containing Bpyps. Further, graphite/electrolyte/Li cells containing P13FSA/LiTFSA/Bpyps exhibited stable charge/discharge cycle behaviour over 50 cycles.

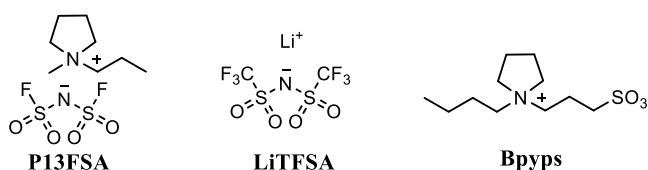


Figure 1. Chemical structures of electrolyte materials.

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Ionic liquids as electrolytes for Lithium Batteries

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The search for high energy density—safer batteries has more to do with the battery electrolytes than the electrode materials[1]. Ionic liquids have good thermal stability and wider electrochemical potential window which makes them potential candidates for safe batteries with significant energy density[2]. Apart from their attractive features, employing ionic liquids in batteries at room temperatures is limited by their viscosity which in turn limits the conductivity of lithium ions by these electrolytes. Though the addition of lithium salts helps in appreciable ionic conductivity, performances were not quite comparable with conventional battery electrolytes. Efforts have been made to reduce the viscosity of ionic liquids by mixing them with the alkyl carbonate solvents[3,4]. In this work, we have studied the effect of ionic liquid - mixed carbonate electrolytes (Hybrid Electrolytes) for lithium batteries. The synergistic effects brought by these electrolytes were compared with the conventional electrolytes as well as the pure ionic liquid by testing them versus lithium metal. The effect of ionic liquid addition to the electrolytes with respect to the thermal decomposition temperatures were tested by thermogravimetric analysis. The electrochemical performance of hybrid electrolytes was tested and compared with conventional battery electrolytes at 20°C on commercial battery cathodes. Post surface analysis of the electrochemically cycled cathodes reveals that the ionic liquids form a surface layer on the cathodes which helps in stabilizing the electrode electrolyte interface for better battery performance[4].

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Pushing the Boundaries and Breaking the Shackles of “Ionic Liquids”

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There has been a decade of discussion and debate about what is, and what is not, an “ionic liquid”. Ultimately, such definitions, and restrictions, can be limiting to innovation. This talk will highlight a number of areas where liquids comprised mostly of ions have important applications at low(ish) temperatures, but in ways that might normally fall outside our traditional definitions. Lets break these shackles!

For example, there are a number of applications in the electrodeposition¹ and biomass dissolution² areas where the ideal operating temperature of the process is well above 100°C and, while it is convenient that the media be liquid at ambient temperatures, it is certainly not a requirement. In these applications, tailoring the salt chemistry for the application becomes more important than tailoring it to lower the melting point. On the other hand, in the field of phase change materials tailoring the melting point and enthalpy of fusion are precisely the key issues and some very important thermal energy storage applications are emerging in the 100 – 200°C region of temperature.³ Higher application temperatures also very importantly open up a wider range of possible organic-inorganic salt mixtures.⁴

In another significant dimension, a large number of papers are revealing optimum application properties in the “mixture domain” that lies between pure ionic liquids and traditional salt solutions. Exactly what to call this domain and where its boundaries lie are largely immaterial if the properties are usefully superior to either extreme. Recent thermocell research from Pringle’s group⁵ and Li battery work from Mitra’s group⁶ are good examples of this.

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Poster Abstracts

Identifying ionic liquid effects on an S_N1 process

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Ionic liquids have been shown to affect reaction outcomes differently to molecular solvents.¹ Extensive efforts have been made to explore these effects and the microscopic interactions that cause them, particularly for S_N2 reactions.² Comparatively few studies have investigated these effects in unimolecular reactions, often due to slow reaction rates and competing side reactions.

Previous work on the solvolysis of the chloride **1** in methanol showed that on addition of the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][N(SO₂CF₃)₂], **3**) there was an initial increase in the rate constant of the reaction, followed by a steady decrease as the proportion of salt **3** in the reaction mixture was increased (Figure 1).³ These changes were attributed to competing enthalpic and entropic contributions as a result of the ionic liquid stabilising, and ordering about, the transition state.⁴

Of interest is how increasing the extent of charge delocalisation in the transition state for an S_N1 process, such as in the reaction between bromide **4** and 3-chloropyridine **5**, changes ionic liquid solvent effects. This work will discuss the changes in terms of the importance of the proportion of ionic liquid in the reaction mixture (Figure 2) and the microscopic origins of rate changes,⁵ along with the potential to control these effects through rational choice of the ionic liquid solvent.

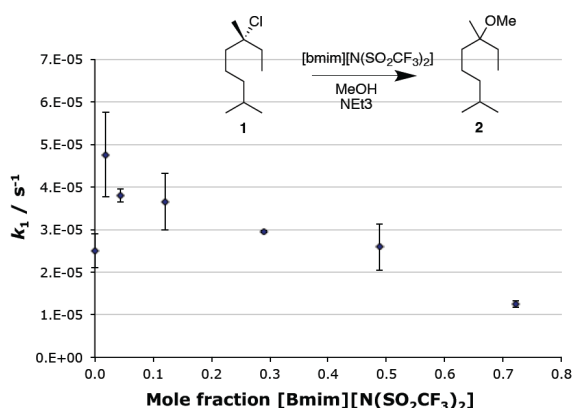


Figure 1: Variation of the rate constant with proportion of salt **3** in the reaction mixture for solvolysis of **1** in methanol

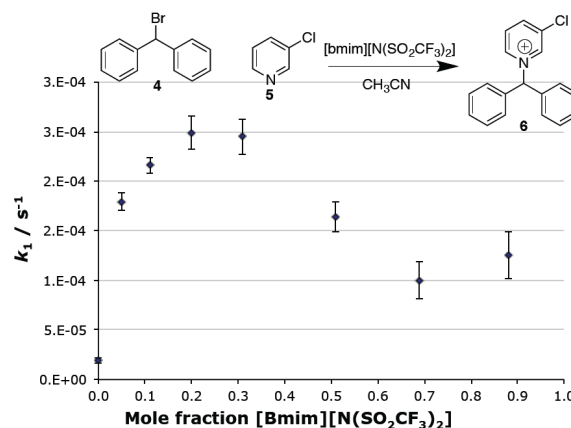


Figure 2: Variation in the rate constant with proportion of salt **3** in the reaction mixture between species **4** and **5**

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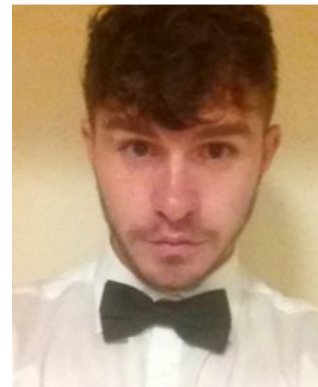
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The Investigation and Characterisation of Amino Acid/ Ionic Liquids Gels

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The purpose of this research was initially intended to further advance the development of keratin dissolution using ionic liquids (ILs). Due to unexpected results, the purpose of the project was taken on a tangent and resulted in the investigation and characterisation of IL gels being the main area of focus. Several prominent Amino Acids (Arginine, Aspartic Acid, Glutamic Acid, Lysine) based in the keratin structure underwent dissolution in several ILs, yielding mixtures; that upon investigation resemble IL gels. This research intends to explore the nature of these gels by fully characterising them through various analytical techniques, exploring possible functions and gain an insight into the interactions between the Amino Acids and the ILs.

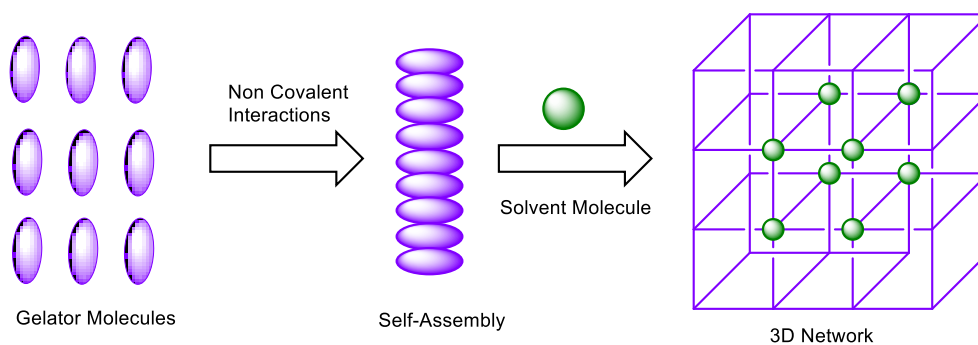


Figure 1. Schematic representation of the formation of gels.

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XPS of PEG-ylated Ionic Liquids: The Informed Design of Active Materials for Metals Extraction

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X-ray photoelectron spectroscopy (XPS) is an established and commonly applied surface analysis technique that provides structural and chemical information for non-volatile materials.

Surface chemistry and interfacial investigation has long dominated the field of XPS, however with its growing popularity, XPS is now being applied to a wide range of softer samples with increasing structural complexity. Our group has utilised XPS and related photoemission based experiments to investigate Ionic liquids (ILs) and IL based systems on an atomistic level. These techniques yield detailed information that can aid in the design of more efficient catalysts and processes, particularly those that occur at interfaces or discontinuities. XPS can give a unique insight into basic processes within liquid samples including inter-ion interaction and solvent-solute interactions that can tune processes in a very subtle way.

Here we give details of a new area of investigation within our group. We will present first XPS data for a range of functionalised PEG-ylated systems that have been designed to act as active extraction media for the refining and removal of metals, particularly heavy metals that can have significant biological activity. We will show a new peak-fitting model which allows the direct comparison to more common cation sets including dialkyl-imidazolium, pyrrolidinium and quaternary ammonium based systems. The measured binding energies (BEs) of the N and C components are presented and notable variations discussed. The principle aim of this study is the construction of a structure/property matrix that will allow the SMART selection of a specific IL-based mixture system for the dissolution and removal of problematic metals including Cr, Cd and Pb.

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Ionic Liquid-Based Microarray CO₂ Sensors

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The detection of CO₂ has been well appreciated due to their significant influence to the human society. They have played an important role in various industry and applications, such as in the fields of clinical medicine, food industry and pollution monitoring from the environmental perspective^[1]. Therefore, a considerable number of research interests have been concentrated on the development of robust and reliable CO₂ sensors^[2-4].

This work focused towards the development of IL-based microarrays electrode sensor for electrochemical detection of CO₂. Initially, the electrochemical behavior of CO₂ in aprotic ionic liquid, 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ([BMPY][NTf₂]) will be studied by using cyclic voltammetry. The construction of the microarrays sensor will be achieved by using microcontact printing of ILs, followed by investigations on their respective electrochemical CO₂ sensing performance in comparison to conventional macro IL-based sensor. The studies suggested that the use of IL-based microarrays electrode is able to improve the sensitivity, the response time and the overall performance of the CO₂ sensors.

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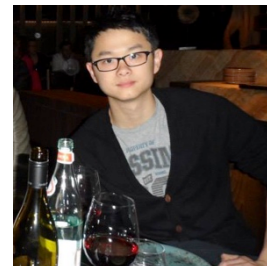
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Microcontact Printing of Thiol-Functionalised Ionic Liquids for “Membrane-less” and “Spill-less” Gas Sensors

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Lab-on-a-chip systems have gained significant interest for both chemical synthesis and assays at the micro-to-nano-scale with a unique set of benefits. However, solvent volatility represents one of the major hurdles to the reliability and reproducibility of the lab-on-a-chip devices for large scale applications. Here we demonstrate a strategy of combining non-volatile and functionalized ionic liquids with microcontact printing for fabrication of “wall-less” microreactors and microfluidics with high reproducibility and high throughput. A range of thiol-functionalized ionic liquids have been synthesized and used as inks for microcontact printing of ionic liquid microdroplets arrays onto gold chips. The covalent bonds formed between the thiol-functionalized ionic liquids and the gold substrate offer enhanced stability of the ionic liquid microdroplets, compared to conventional non-functionalised ionic liquids, and these microdroplets remain stable in a range of non-polar and polar solvents, including water. We further demonstrate the use of these open ionic liquid microarrays for fabrication of “membrane-less” and “spill-less” gas sensors with enhanced reproducibility and robustness. Ionic liquid-based microarray and microfluidics fabricated using the described microcontact printing may provide a versatile platform for a diverse number of applications at scale.

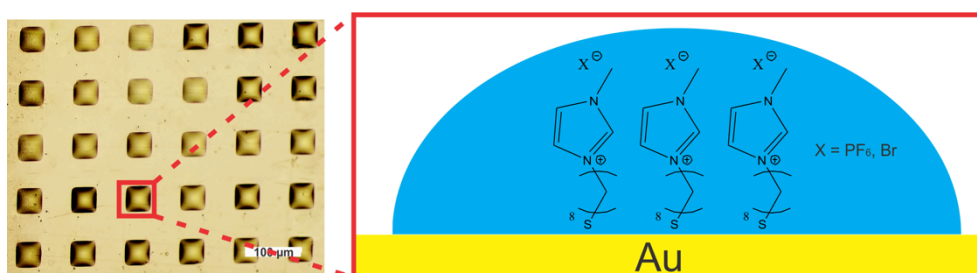


Figure 1. Micrograph of Thiol-functionalized ionic liquid micropatterned with the size of 50 μm fabricated via microcontact printing. The inset shows the illustration of the thiol-functionalised ionic liquid microdroplets.

Studies of motions and interactions of molecules in ionic liquid electrolytes by nuclear magnetic resonance

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In the last couple of decades, ionic liquids have been recognized as potential new electrolytes. Thanks to their unique properties, ILs are currently used for a wide range of applications, for example their conductivity and Li diffusion properties make them very good candidates for applications linked to electrochemistry, such as electrolytes in batteries.

However, the molecular interactions and motions in ILs are still not fully understood. The main goal of this research project is to study the molecular dynamics and ionic interactions in a series of Li-containing phosphonium TFSI and FSI based ionic liquids by NMR, primarily using pulsed field gradient diffusion measurements and T1 measurements but also using the nuclear Overhauser effect (NOE). These experiments carried out at different temperatures and lithium concentrations will help us to better understand the ionic transport properties and intermolecular interactions respectively, which will help with the design of new IL electrolytes with improved properties.

Direct esterification and Separation of Biomass Components with Ionic Liquid catalysts

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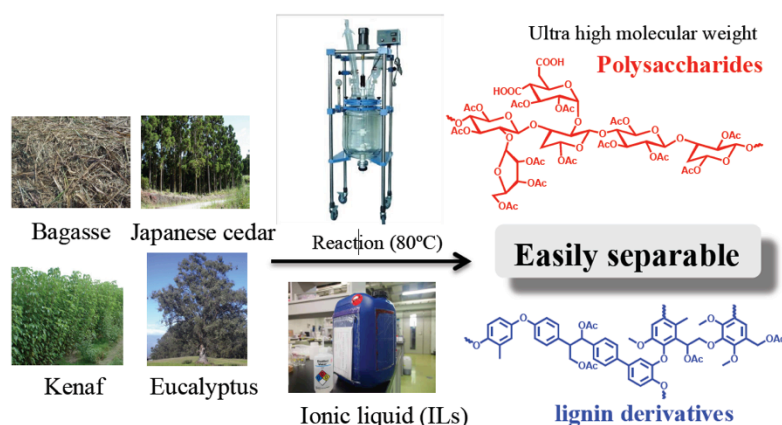
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For many decades, we've relied on fossilized organic matters, but the CO₂ produced during combustion of fossil resources is causing a significant climate change. This has led to a growing interest in renewable technologies to replace the fossil sources of carbon. One of these technologies is the conversion of biomass to fuels and chemicals in the so-called 'Integrated Biorefinery'.

Lignocellulosic biomass is the most abundant plant material on our planet, and its utilisation as a biofuel feedstock is likely to provide much higher CO₂ emission savings. Lignocellulosic materials are potentially valuable sources of both aromatic compounds *via* the lignin component and sugars from the cellulose and hemicellulose components. Reported studies of biomass application were economically and thermodynamically disadvantageous for the utilization of biomass, due to the ultimate structural complexity of the lignocellulose as depicted.

Herein, now a new biomass application, to provide a method for a direct chemical modification and separation of the polysaccharide and lignin from the lignocelluloses with ionic liquid (ILs) are proposed (Scheme 1). In specific cases, organic transformation reactions in ILs were revealed to undergo with ILs as both a solvent and catalyst. In this presentation, we describe 1) a direct esterification of raw biomass with ILs as a catalyst, and 2) subsequent separation of polysaccharides and lignin derivatives by using the differences of their solubility in organic solvents.



Scheme 1. Schematic representation of this work

Acknowledgment

This research was promoted by COI program "Construction of next-generation infrastructure using innovative materials ~Realization of a safe and secure society that can coexist with the Earth for centuries~ supported by MEXT and JST. This study was also supported in part by an Advanced Low Carbon Technology Research and Development Program (ALCA) of the JST and the Cross-ministerial Strategic Innovation Promotion Program (SIP) from the JST.

The performance of a room temperature ionic liquid based electrolyte for reversible magnesium electrochemistry

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Abstract: The utilization of new energy source from sun, wind, and nuclear, is motivating the development of rechargeable storage devices. Although the commercial lithium batteries have been realized for decades, magnesium batteries are found an competitive alternative regarding to the low costing, high volumetric capacity and most important the safety property. One of the main challenges in magnesium electrochemistry study is to achieve reversible deposition and dissolution of magnesium over many cycles. Thus a suitable non-flammable and non-volatile electrolyte that can electrochemically recharge magnesium is of special interest. Room temperature ionic liquids with wide electrochemistry window are known for their non-volatile nature, high thermal stability as well as non-flammability, which make them good choices to serve as the solvent in the electrochemistry study. In our work, the cycling of magnesium was achieved in a mixture of $\text{Mg}[\text{BH}_4]_2$ in a tri-alkoxy ammonium based room temperature ionic liquid ($[\text{N}_{2(20201)(20201)(20201)}][\text{NTf}_2]$, **IL1**) as shown in **Figure 1**. The XRD result from the $\text{Mg}[\text{BH}_4]_2/\text{IL1}$ electrolyte was assigned to typical magnesium metal planes, indicating the reduction process was attributed to the Mg^{2+}/Mg . It was elucidated by the DFT computation study that the co-ordination of Mg^{2+} with BH_4^- played the primary role for the deposition and dissolution of magnesium in the cycling process.^[1]

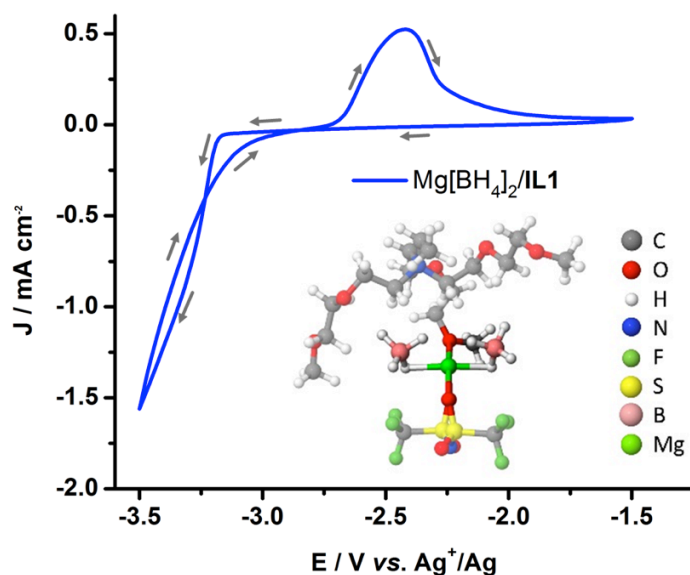


Figure 1. CV cycling in the electrolyte of $\text{Mg}[\text{BH}_4]_2/\text{IL1}$ and the counterparts of $\text{Mg}[\text{BH}_4]_2/\text{IL1}$ $[\text{N}_{2(20201)(20201)(20201)}][\text{NTf}_2]$.

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Ammonium-based Ionic Liquids as Anti-Wear Lubricant Additives

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Ionic liquids were first investigated as lubricants in 2001.¹ Ionic liquids have attractive features that make them useful for tribological applications, including negligible vapour pressure, non-flammability and high thermal stability. Zinc dialkyldithiophosphates (ZDDPs) are commercially used as anti-wear lubricant additives in engine oils, however they impair the environment indirectly by poisoning the automotive gas catalyst components. There is an urgent need to replace ZDDPs with environmentally friendly lubricant additives. Previous work in our group has shown that certain ILs are soluble in mineral oil.²

Here we report the synthesis of two quaternary ammonium phosphate ionic liquids [N₈₈₈₈]DEPH and [N₆₆₆₁₄]DEPH (**Figure 1**) and investigation of their use as lubricants. We compare the tribological properties of [N₈₈₈₈]DEPH and [N₆₆₆₁₄]DEPH with [P₈₈₈₈]DEPH and [P₆₆₆₁₄]DEPH,³ respectively, when mixed with mineral oil.

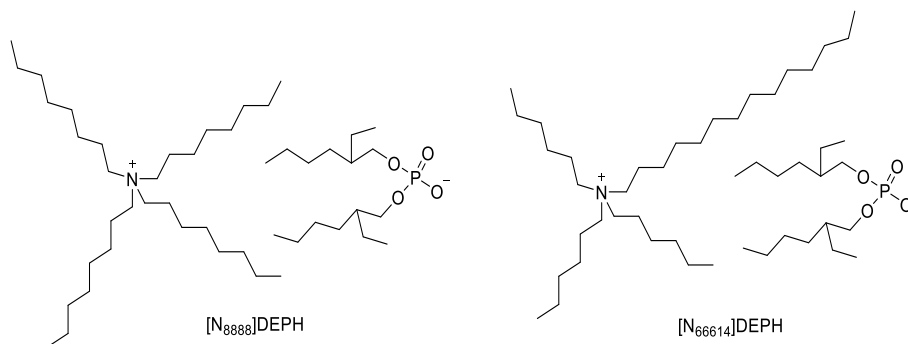


Figure 1. Structures of Ionic Liquids tetraoctylammonium bis(2-ethylhexyl)phosphate (left) and tetradecyltriethylhexylammonium bis(2-ethylhexyl)phosphate (right) investigated for use as lubricants.

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The Electrochemical Behaviour of Trinitrotoluene (TNT) in

Room temperature Ionic Liquids (RTILs)

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The detection of TNT is of utmost importance due to its phenomenal power and capability to cause immense destruction and malicious injury to living beings. There are several methods that are used for explosives detection but these methods are not always as portable or low-cost as electrochemical sensors. Thin film electrodes (TFEs) are a new type of miniaturised sensing surface where the working, counter and reference electrodes are printed on a planar substrate, exhibiting portable capabilities. The benefits of using RTILs as the solvent are their non-volatile properties and high thermal stability¹ – ideal for explosives sensing especially in hot and dry environments. In this work, three reduction peaks were observed in voltammetry in all eight RTILs, likely corresponding to the reduction processes of each one of the three nitro groups on TNT. Electrochemical studies determined that for all RTILs, reduction peak I was likely to be chemically reversible whereas peak II and III were likely to be chemically irreversible. In addition, it was found that the electrochemical behaviour of TNT can vary, depending on the RTIL employed (resistive behaviour, broadened peaks, potential differences etc.). Potential-step chronoamperometry was conducted to calculate diffusion coefficients of TNT in RTILs, reportedly for the first time. Furthermore, TNT was observed to behave in accordance with the Stokes-Einstein relationship, associated with diffusional behaviour of a ‘stick’ mechanism. The electrochemical reduction mechanism of TNT was found to likely occur via an EC₂ mechanism. This involved the formation of an electrochemically generated red solid, consistent with that reported by Forzani *et al.*², where dimerisation of the TNT radical likely forms an azo or azoxy compound. The understanding of the electrochemical reduction mechanism of TNT in RTILs gained in this study will drive toward the development of explosives sensing applications.

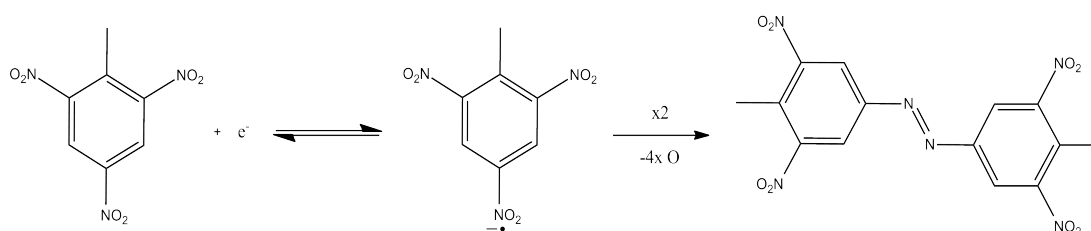


Figure 1. Proposed scheme of the EC₂ mechanism of TNT reduction, forming one of the possible electrogenerated azo products

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Pretreatment of Lignocellulosic Biomass Using Ionic Liquid

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Effective management of lignocellulosic waste is one the biggest challenges in various plant based industries all over the world. Lignocellulosic biomass is rich in sugars and lignin. In order to obtain industrial value products from the lignocellulosic biomass, enzymatic hydrolysis is preferred over other harsher methods of depolymerization, such as acid treatment, as it is more environmental benign and economical processes [1]. Lignocellulose is a highly complex and heterogeneous structure which causes significant hindrance towards enzymatic hydrolysis. This recalcitrance can be overcome by treating the biomass by certain methods in order to increase the accessibility of enzymes [2][3][4]. Recently ionic liquids (ILs) have emerged as potential solvents for the biomass pretreatment because of their various properties such as high thermal stability, low volatility and high solvation characteristics [5]. In order to understand the interaction mechanisms and effects of ionic liquid pretreatment, a detailed study was undertaken. In this study an aprotic ionic liquid 1-ethyl-3-methylimidazolium acetate was used for the pretreatment of castor stalk (CS) under different conditions. The pretreated biomass was then enzymatically hydrolyzed using commercial cellulase enzyme. The result reveal that the IL pretreatment resulted in the partial removal of lignin from the lignin-carbohydrate complex, and the pretreated CS was enzymatically more digestible in contrast to untreated CS. The surface morphological studies confirmed the disruption of the highly crystalline structure of the lignocellulosic biomass into more amorphous structure upon IL pretreatment. Fermentation of the sugars, obtained upon hydrolysis of IL pretreated CS, resulted in high yields of ethanol, which can be used as biofuel.

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Nanostructure of Lithium-Glyme Solvate Ionic Liquids at Charged Graphite Electrode Interfaces

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The solid-liquid interfacial nanostructure of lithium-glyme based solvate ionic liquids (SILs) on graphite electrodes has been studied using atomic force microscopy (AFM). SILs are salts comprised of a bulky anion and a ligand bound metal cation that are liquid at less than 100°C¹. Their high ionic conductivity and non-flammability make them excellent candidates for safer and more efficient lithium-ion battery electrolytes²⁻⁴. In this study the interfacial structure of SILs comprised of monoglyme (G1), triglyme (G3) and tetraglyme (G4) mixed with lithium bis(trifluoromethylsulfonyl)amide (LiTFSI) is investigated at the charged graphite interface using AFM force curves. It is shown on graphite that applying negative potential to the surface increased the rigidity of the interfacial structure of the SILs studied whereas application of a positive potential causes a structural rearrangement. The effect of changing the glyme length is also investigated. Li(G3)TFSI shows a stronger interfacial structure than Li(G4)TFSI due to the longer tetraglyme providing increased flexibility. The shorter monoglyme, which has a lower lithium solvation strength than the longer glymes shows weaker interfacial structure due to the presence of unsolvated glyme. This research further enables the understanding of the link between chemical structure and

interfacial structure to better enable tailoring of properties useful for electrolyte applications.

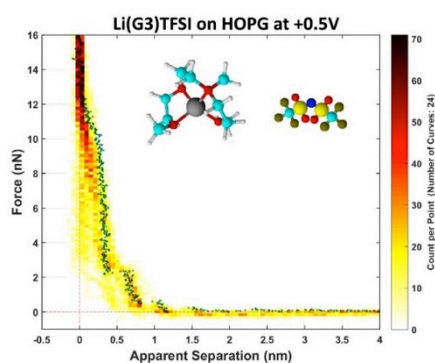


Figure 1. Overlay of histogram and representative force curve for Li(G3)TFSI on HOPG at a surface potential of +0.5V

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Understanding NO₂ Adsorption in Deep Eutectic Solvents using Quantum Chemistry

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Deep eutectic solvents (DES) are a class of liquids analogous to ionic liquids, formed by mixing an inorganic salt and a hydrogen bond donor. DES exhibit many properties that are similar to ionic liquids, such as low vapour pressure, high thermal stability and electrical conductivity. Moreover, DES have a high adsorption capacity for atmospheric pollutants, such as CO₂ and SO₂. These properties, combined with lower cost, has driven much recent research into gas-adsorption using DES.[1-3] However, to date the adsorption of NO₂ in DES has not been investigated. I will present density functional theory calculations that establish the structure and interactions between NO₂ and DES formed between choline chloride and urea, thiourea, 1-methyl urea and 1,3-dimethyl urea. These calculations show that, in each liquid, NO₂ adsorbs primarily via interaction with the hydrogen bond donor, and that the strength of this interaction is thiourea (strongest) > urea > 1-methyl urea > 1,3-dimethyl urea (weakest). We use reduced density gradient analysis[4] to demonstrate that hydrogen bonding is the primary mechanism of interaction between NO₂ and the DES, while van der Waals interactions and charge-dipole interactions are secondary in nature.

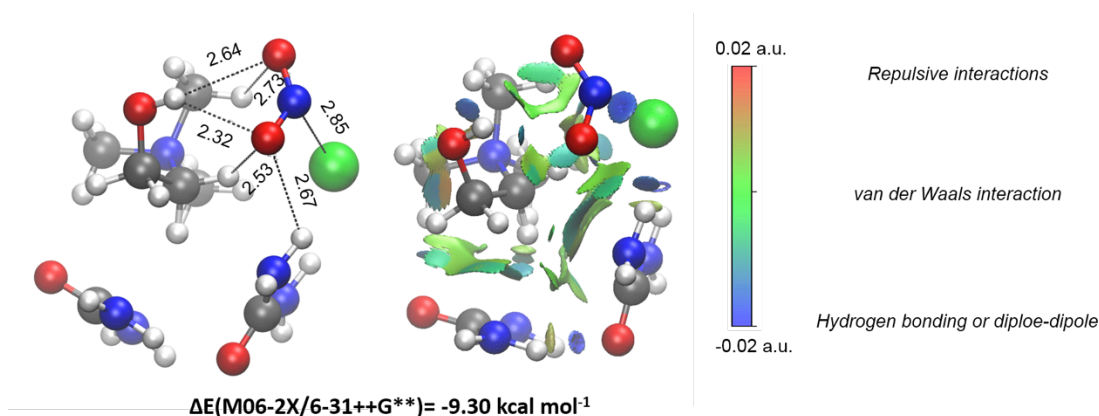


Figure 1. M06-2X/6-311G++G** - optimised structure of NO₂ + choline chloride urea DES. Gradient isosurfaces ($s = 0.35$ a.u.) are coloured on a blue–green–red scale according to values of $\text{sign}(\lambda_2)\rho$, ranging from -0.02 to 0.02 a.u.

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Low Temperature Ionic Liquid Pre-treatment for Lignite

Conversion

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Lignites make up a significant portion of Australia's coal reserves; however, their high moisture content, low calorific value and high ash yield limit their applications industrially. Due to these factors, research has been carried out on the upgradation, liquefaction and conversion of lignites [1-5]. Solvent treatments are commonly employed to break apart and extract components of lignites in order to generate liquid fuels or valuable chemicals. However, conventional solvents can be costly, have high vapour pressures and are toxic [6, 7]. Ionic liquids (ILs) are room temperature molten salts that have remarkable physical and chemical properties, including high thermal and electrochemical stabilities, and low vapour pressure. In this study, two lignite samples were treated with 1-butylpyridinium chloride ([Bpyd][Cl]), 1-ethyl-3-methylimidazolium dicyanamide ([Emim][DCA]), 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]) and 1-butyl-3-methylimidazolium tricyanomethanide ([Bmim][TCM]) at 100 °C for 3 hr.

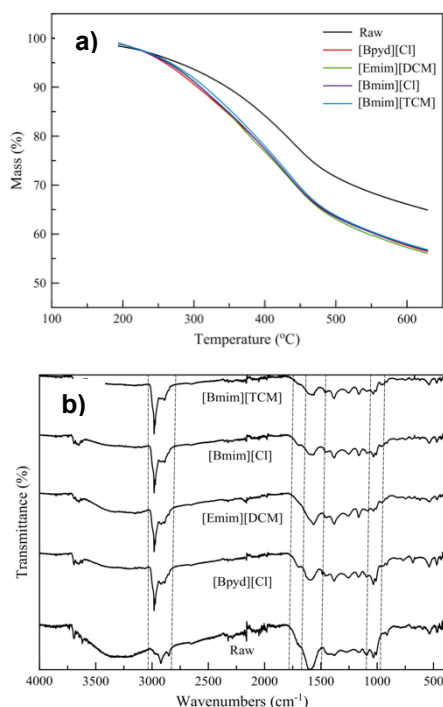


Figure 1. TG profiles (a), and FTIR spectra (b) of raw and IL-treated lignite samples.

Microscopy revealed fragmentation and swelling occurred in the treated lignite samples; especially those treated by [Bmim][Cl]. Pyrolysis studies revealed that the treated lignites had lower devolatilisation temperatures than the untreated lignite (Fig. 1a). Fourier Transform Infrared (FTIR) Analysis indicated that all of the IL-treated lignites had a higher proportion of short chain aliphatic hydrocarbons (Fig. 1b). Additionally, FTIR revealed a significant decrease in the presence of COOH and CO groups for lignites treated with [Emim][DCM]. These results indicate the potential of ILs to be applied in the conversion of lignites to chemicals and liquid fuels.

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XPS of nitrogen-based ILs: Cation impact on the electronic environment of the anion

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X-ray photoelectron spectroscopy (XPS) is an established and commonly applied surface analysis technique that provides structural and chemical information for non-volatile materials.[1]

Surface chemistry and interfacial investigations of solid samples have long dominated the field of XPS, however with its growing popularity, XPS is now being applied to a wide range of softer samples with increasing structural complexity. Our group has utilised XPS and related photoemission based experiments to investigate Ionic liquids (ILs) and IL based systems on an atomistic level. These techniques yield detailed information that can aid in the design of more efficient catalysts and processes, particularly those that occur at interfaces or discontinuities. XPS can give a unique insight into basic processes within liquid samples including inter-ion interaction and solvent-solute interactions that can tune processes in a very subtle way.[2][3]

This poster will give details of a new area of investigation within our group. We will present first XPS data for a range of functionalised guanidinium based systems, we will show a new peak fitting model which allows the direct comparison to more common cation sets including dialkyl-imidazolium, pyrrolidinium, quaternary ammonium and pyridinium based systems. The measured binding energies (BEs) of the N and C components are presented and notable variations discussed. The principle aim of this study is the construction of a structure/property matrix that will allow the SMART selection of a specific IL-based mixture system for the dissolution and processing of biomolecules of interest.

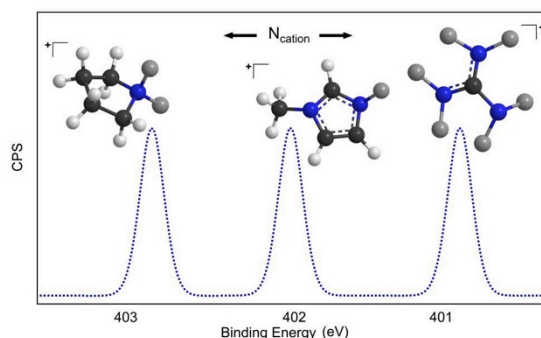


Figure 1. Comparison between the N_{cation} 1s Binding Energies for pyrrolidinium, imidazolium and guanidinium ionic liquids

References

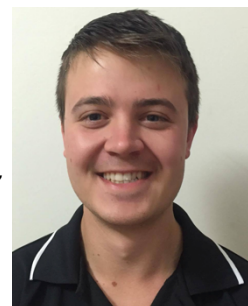
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Gold Extraction using Protic Ionic Liquid Mixtures

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Gold is a precious commodity, however the main industrial process for its extraction currently, gold cyanidation, has several drawbacks primarily relating to the toxicity of the cyanide reagent¹. In an effort to replace this reagent, thereby reducing the risk of the leaching practise, several other options, including inorganics² and ionic liquids³, have been investigated. With the recent advent of less expensive ionic liquids and their suitable properties such as chemical stability, large electrochemical window, solvating action, non-flammability, non-volatility and designable functionality, it is proposed that these chemicals could provide an ideal system for less hazardous gold leaching with improved total recovery than the current gold cyanidation process. We plan to extend earlier work⁴ in the exploration of suitable ionic liquids and mixtures thereof, to undertake this task. In this report, we plan to demonstrate the oxidative and complexing capability of protic ionic liquid mixtures with respect to the leaching of gold from a mineral ore.

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Nanotribology Study of Ionic liquids as Lubricant Additives for Alumina Surfaces

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The nanotribological performance of ionic liquids as lubricant additives to a model base oil has been investigated using atomic force microscopy (AFM) at an alumina surface. The pure ionic liquid, trihexyltetradecylphosphonium bis(2-ethylhexyl)phosphate, is a much more effective lubricant in comparison to the model base oil, hexadecane, for alumina surfaces. For ionic liquid/oil mixtures, when the ionic liquid concentration is equal or above 2 mol%, the ionic liquid mixture can effectively lubricate alumina equivalent to the pure ionic liquid due to the formation of a robust boundary layer separating the solid surfaces. The cost restrictive nature of ionic liquids makes this application of ionic liquids as additives to lubricants viable to a wider range of applications.

Ion dynamics in a mixed-cation alkoxy-ammonium ionic liquid electrolyte for sodium device applications

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ILs have established themselves as a class of compounds that can be tailored to a vast number of applications. We present the ion dynamics in this novel sodium-containing IL based on an ether-functionalised quaternary ammonium cation and bis(trifluoromethanesulfonyl)amide [NTf₂] anion with various concentrations of Na. The IL has been characterised using thermal analysis, ionic conductivity, diffusion and NMR relaxation measurements. The IL has been specifically designed with the intent to dissolve high concentrations of Na (over 2 mol kg⁻¹), as high concentration ILs have been shown to improve ion transport, conductivity and demonstrate high rate charge/discharge characteristics upon device cycling.¹

Consistent with other studies, the conductivity and diffusion measurements show the overall ionic mobility decreases with increasing salt content, however, there is also evidence for considerable ion dynamics below the glass transition temperature for the highest Na concentrations. NMR relaxation measurements also provide evidence for correlated dynamics between the ether-functionalised cation and Na cation, possibly with the latter species acting as cross-links between multiple ammonium cations.²

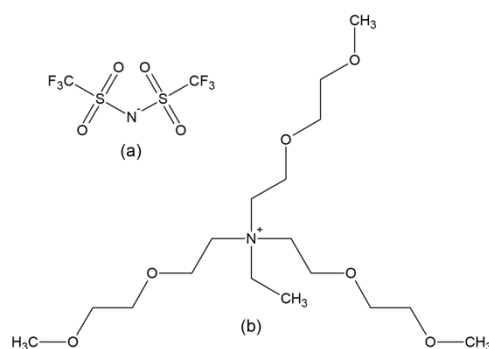


Figure 1.0. Structure of (a) the NTf₂ anion and (b) ether-functionalised quaternary ammonium cation.

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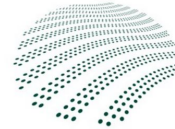
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