

## Electrochemistry: general discussion

Andrew Abbott, Leigh Aldous,  Natalia Borisenko, Samuel Coles, Olivier Fontaine, Jorge Daniel Gamarra Garcia, Ramesh Gardas,  Oliver Hammond,  Laurence J. Hardwick,  Paul-Henri Haumesser, Florian Hausen, Corie Horwood, Johan Jacquemin,  Robert Jones,  Erlendur Jónsson,  Abhishek Lahiri, Doug MacFarlane,  Guy Marlair, Benjamin May,  Himani Medhi, Vitor H. Paschoal, Joshua E. S. J. Reid,  Theresa Schoetz, Kazuhisa Tamura,  Morgan L. Thomas,  Shraeddha Tiwari, Betul Uralcan, Adriaan van den Bruinhorst,  Masayoshi Watanabe and James Wishart 

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**Andrew Abbott** opened a general discussion of the paper by Abhishek Lahiri: The word “anomalous” at the start of the presentation is only valid when it is put into perspective. The results are possibly unexpected compared to pure water but they are not anomalous once speciation is taken into account. Since the redox potential is governed by speciation, if you get the speciation the same then the galvanic series should also be the same. Our work has shown the relative redox potentials for metal couples in deep eutectic solvents (DESS).<sup>1</sup> Repeating the experiments in aqueous NaCl solutions produces the same galvanic series and good correlation in redox potentials.<sup>2</sup> I would certainly welcome the publication of more standard redox potentials in ionic liquids.

1 A. P. Abbott, G. Frisch, S. J. Gurman, A. R. Hillman, J. Hartley, F. Holyoak and K. S. Ryder, *Chem. Commun.*, 2011, **47**, 10031–10033.

2 J. Hartley, PhD thesis, University of Leicester, 2011.

**Abhishek Lahiri** replied: We agree with the comment that speciation governs the redox potentials of the species/metal ions. In our case we have used the word “anomalous” by considering the standard aqueous electrochemical series. In order to obtain a standard redox potential in ionic liquid, first one needs to have a standard reference electrode which can be used for all ionic liquids and won't be affected by varying the constituent ions. Also understanding the speciation in chloride/non-chloride-based ILs is not straightforward. Therefore, developing a universal galvanic series in ILs still remains a challenge.

**Leigh Aldous** asked: You talked about the conventional galvanic series, but this refers to pure metals, while you are actually forming complexes or alloys. Is this a genuine ionic liquid effect or would you see the same effect in aqueous media or organic solvents?

**Abhishek Lahiri** answered: It is indeed a clear effect of ILs on the formation of species/complexes. The formed species/complexes may be unstable and a redox reaction can be triggered even in the presence of a noble electrode (*viz.* Cu). To the best of our knowledge such effects may not occur in aqueous media (in general, hydration/hydrolysis of metal ions predominate) or in organic media (generally solvation of metal ions can take place). In aqueous electrolytes, hydrogen evolution is a concern for metal deposition, so even if you form some suitable complexes for electroless deposition, the redox potentials of metal ions need to be more positive to 0 V *vs.* normal hydrogen electrode (NHE) for the galvanic displacement process to take place. However, in ionic liquids and probably in organic solvents, hydrogen evolution will not take place and therefore it will be easier for such galvanic displacement reactions.

**Doug MacFarlane** commented: To continue the discussion on the creation of a galvanic series, this is a great idea if the metal stays active in the IL. However, the formation of interfacial layers may be an issue. These could form by intrinsic reaction of the metal with the IL or from IL contaminants. Also the active corrosion of the metal could create an additional effect.

**Abhishek Lahiri** responded: We completely agree that issues such as corrosion of the metal due to additional effects and IL contaminants will affect the galvanic displacement reaction. To develop a galvanic series, one can start with investigating chloride-based ILs (*e.g.* imidazolium chloride) and study the various complexes which can be formed with a change in the metal ion concentration. A relatively good amount of literature is available with a number of metals in chloride systems and can be extended to other metal chloride systems with Ag/AgCl(IL) as the reference electrode. As it is well known in aqueous systems that Cl can easily adsorb on the surface, one can assume that in ionic liquids with Cl<sup>-</sup> anions, the interface will be concentrated with Cl<sup>-</sup> ions and other factors such as impurities will not play a role. This can then be used as a reference point and similar studies can be performed with changing from chloride to other anionic systems.

**Doug MacFarlane** opened a general discussion of the paper by Masayoshi Watanabe: The hydronium triflate seems to be an attractive fuel cell electrolyte. Even though water could be lost into the gas stream, could this be controlled by appropriate humidification of the incoming hydrogen/air?

**Masayoshi Watanabe** answered: Thank you. One of the serious problems of the [H<sub>3</sub>O][TfO] system is the highly corrosive nature of this protic ionic liquid.

**Corie Horwood** resumed discussion of the paper by Abhishek Lahiri: Galvanic replacement is known to be a surface limited process. Sustained galvanic replacement may occur if new surface (Cu in this case) is exposed, however, bulk replacement of one metal with another is not possible by galvanic replacement. Rather than nanoplates made of Sb, it is likely that you have nanoplates made of Cu with a thin surface layer of Sb (likewise for Fe replacement of Cu).

**Abhishek Lahiri** responded: We agree that the galvanic displacement is known to be a surface phenomenon for aqueous-based electrolytes. However, it can be a sustainable process in the presence of a catalyst. In ionic liquids, it has been shown to be a sustainable process by Abbott *et al.*,<sup>1</sup> wherein Ag ions can displace copper through the pores of the Ag thin film, and Cu ions can diffuse away from the substrate. Therefore, in our case, we expect such similar phenomena to occur. Furthermore, we mentioned that the nanoplates formed are Cu<sub>2</sub>Sb and not Sb. This was confirmed by XRD. Moreover, the XPS depth profile clearly showed the presence of both Cu and Sb even after etching for longer time (50 min), which also supports that thick films were formed.

1 A. P. Abbott, S. Nandhra, S. Postlethwaite, E. L. Smith and K. S. Ryder, *Phys. Chem. Chem. Phys.*, 2007, **9**, 3735–3743.

**Guy Marlair** commented on the paper by Masayoshi Watanabe: In the presentation of the paper you presented (DOI: c7fd00132k), you have shown the thermal stability data of some ionic liquids without any indication of the heat ramp used. Indeed, it becomes more and more important to report thermal stability data with appropriate information indicating to the reader how they were obtained: now we are in need to develop predictive models, like quantitative structure–property relationship (QSPR)-type models predicting macroscopic properties from a series of descriptors calculated at the molecular level. The quality of those models highly relies on the quality and consistency of databases used to develop and validate those models. Please do precise accurately such data (e.g. heat ramp used, other useful information regarding thermal stability analysis).

**Masayoshi Watanabe** replied: As is written in the paper, the thermal property data were collected in the following way. Differential scanning calorimetry (DSC) was carried out on a Seiko Instruments DSC 220C, under a N<sub>2</sub> atmosphere, to monitor the thermal transitions. The samples were tightly sealed in aluminium pans inside a glove box, under an Ar atmosphere. The PILs were heated to 150 °C at a rate of 10 °C min<sup>-1</sup>, followed by cooling to –150 °C at a rate of 10 °C min<sup>-1</sup>, and then reheated to 150 °C at a rate of 10 °C min<sup>-1</sup>. The DSC thermograms were recorded during the reheating scans. Thermogravimetric analysis (TGA) was carried out on a Seiko Instruments thermo-gravimetry/differential thermal analyser (TG-DTA 6200) from room temperature to 450 °C at a heating rate of 10 °C min<sup>-1</sup>, under a N<sub>2</sub> atmosphere, using open aluminium pans. These conditions are the same as our previous paper.<sup>1</sup>

1 M. Shah Miran, H. Kinoshita, T. Yasuda, M. Abu Bin Hasan Susan and M. Watanabe, *Phys. Chem. Chem. Phys.*, 2012, **14**, 5178–5186.

**Guy Marlair** continued: So eventually, with the ILs tested in your work, what were the criteria used to define thermal stability performance? Was it actually a degree of initial mass loss? What is the accurate value?

**Masayoshi Watanabe** responded: Thermal stability can be defined only relatively. In the present paper, [H<sub>3</sub>O][TfO] with  $\Delta pK_a = 14$  is relatively stable up to 100 °C. However, [DBU][NTf<sub>2</sub>] with  $\Delta pK_a = 23.4$  is thermally stable up to 400 °C,

even if it is a protic ionic liquid. For fuel cell application purposes, which can be operable above 100 °C, the thermal stability of [H<sub>3</sub>O][TfO] is insufficient.

**Leigh Aldous** said: Your best electrolyte was the water-deficient [H<sub>3</sub>O][CF<sub>3</sub>SO<sub>2</sub>], but during continued usage in a fuel cell at 80 °C, the product is water. Do you know what the equilibrium state would be? Would it soak up more water, or evaporate? What would happen to the electrolyte during usage over an extended time?

**Masayoshi Watanabe** answered: Thank you for your comments. Our motivation to study protic ionic liquids as fuel cell electrolytes is to develop proton conductors that can be used at temperatures higher than 100 °C. At such temperatures, water-based proton conductors such as hydrated Nafion membranes cannot be used due to the evaporation of water, which dramatically reduces the proton conductivity. As you suggested, the cathode product of H<sub>2</sub>/O<sub>2</sub> fuel cells is water. We have not investigated in detail how the produced water affects the properties of the protic ionic liquids at temperatures higher than 100 °C. However, we have already reported that we can design water-immiscible protic ionic liquids.<sup>1</sup>

1 T. Yasuda, A. Ogawa, M. Kanno, K. Mori, K. Sakakibara and M. Watanabe, *Chem. Lett.*, 2009, **38**, 692–693.

**Joshua E. S. J. Reid** commented: In reference to the thermal stability of the DBU-derived PILs, you make the statement that the  $\Delta pK_a$  of the PILs with the DBUH<sup>+</sup> cation needs to be greater than 15 to be a highly ionic PIL, on the basis of the thermal stability of the PILs you have studied. I would be careful of making this statement, as the ionic nature of PILs is temperature sensitive. We understand now that the vaporization mechanism of PILs typically proceeds *via* a reverse proton transfer from the cation to the anion, prior to vaporization of the neutral precursor materials. It is logical that PILs with high thermal stability have stable ionic structures at these higher temperatures, thus resisting the reverse proton transfer process prior to vaporization. However the PILs with lower thermal stability do not necessarily have a reduced extent of proton transfer universally. At lower temperatures, the ionic species are more likely to exist, and in the case of DBU PILs one would expect them to exhibit highly ionic characteristics. So my comment is that you should be careful in saying that DBU-based PILs with a  $\Delta pK_a$  less than 15 is not highly ionic, as the ionic nature is highly temperature dependant. I would specify that your observed relation applies only to the temperatures you have studied.

**Masayoshi Watanabe** replied: Thank you for your important comments. Proton transfer reactions from acid to base are highly exothermic. This means that the extent of the proton transfer decreases with increasing temperature. We have reported such results previously, as shown in Fig. 1.<sup>1</sup> The change in the extent of the proton transfer with temperature becomes smaller with increasing  $\Delta pK_a$  values. So, my statement that DBU-based PILs with a  $\Delta pK_a$  less than 15 is not highly ionic is temperature dependent and would be applied to the temperatures that I have studied.

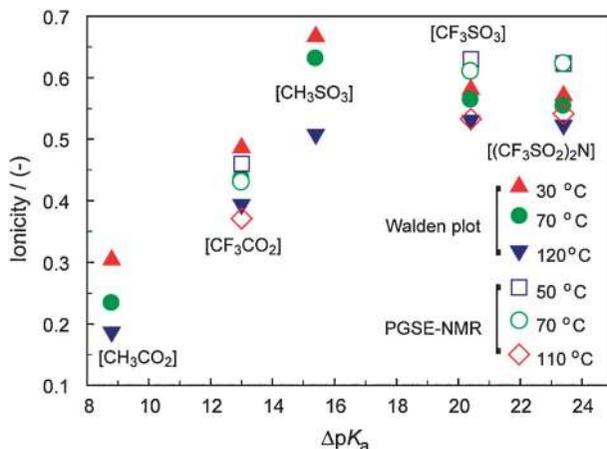


Fig. 1 Variation of ionicity with  $\Delta pK_a$  of constituent amine and acid for [DBU]-based PILs at different temperatures. (●, ▼, ▲), obtained from Walden plot and (○, □, ◇), obtained from PGSE-NMR measurement. Reproduced from ref. 1 with permission from the PCCC Owner Societies.

1 M. Shah Miran, H. Kinoshita, T. Yasuda, M. Abu Bin Hasan Susan and M. Watanabe, *Phys. Chem. Chem. Phys.*, 2012, **14**, 5178–5186.

**Joshua E. S. J. Reid** said: In this work, you looked at PILs where water was used as either the anion (as  $\text{OH}^-$  with  $\text{DBUH}^+$ ) or as the cation (as  $\text{H}_3\text{O}^+$  with  $\text{TfO}^-$ ), and you compared with your benchmark PIL, [dema][TfO]. I am curious as to what would the electrochemical properties be for equimolar mixtures of your benchmark PILs with water – have you explored this, or is there a reason not to consider water–PIL mixtures in this way?

**Masayoshi Watanabe** responded: We have not systematically studied the electrochemical properties of [dema][TfO] and water mixtures. However, it is well known that water molecules react with the surface of Pt at oxygen reduction reaction (ORR) potentials, which causes a large overpotential of the ORR. This fact is also demonstrated in this study, as shown in Fig. 8 in the paper (DOI: c7fd00132k). Therefore, I speculate that the overpotential of ORR in [dema][TfO] becomes larger with the presence of water.

**Shraeddha Tiwari** asked: It is interesting to note that the viscosity of PIL [H<sub>3</sub>O][TfO] is comparable to that reported for [dema][TfO], but the former ([H<sub>3</sub>O][TfO]) is prepared by mixing equimolar amounts of water and acid. The general perception is that water should be instrumental in reducing the viscosity and hence the PIL [H<sub>3</sub>O][TfO] is expected to have a lower viscosity. Can we reason the cause for the high viscosity (higher than expected) of [H<sub>3</sub>O][TfO]?

**Masayoshi Watanabe** responded: We do not know the reason for the higher viscosity of [H<sub>3</sub>O][TfO] compared to that of [dema][TfO]. One possible reason could be the higher molar concentration of [H<sub>3</sub>O][TfO] than [dema][TfO], as shown in Table 2 in the paper (DOI: c7fd00132k). Molar concentrations of [H<sub>3</sub>O]

[TfO] and [dema][TfO] are 9.98 and 5.41 M, respectively. Higher molar concentration means higher charge density of the liquid, which may cause the higher viscosity of  $[\text{H}_3\text{O}][\text{TfO}]$ .

**Johan Jacquemin** stated: Very interesting results and good discussion surrounding your findings. Do you think that it could be more useful to plot the self-diffusion coefficients of the ions (or ILs) vs. the Walden product instead of using the current Walden plot? In its current form, do you think that the Walden plot actually helps within the formulation of electrolytes for energy storage applications?

**Masayoshi Watanabe** responded: Thank you for your comments. We have already recognized that ionicity determined by pulsed gradient spin-echo (PGSE)-NMR and conductivity measurements is different between aprotic ionic liquids and protic ionic liquids. In the case of protic ionic liquids, the liquids consist entirely of ions, and the ionicity means how the correlated motion of ions causes the deviation from the ideal independent motion of ions. On the contrary, in the case of protic ionic liquids, especially protic ionic liquids with small  $\Delta\text{p}K_{\text{a}}$ , the liquids contain neutral species in addition to ionic species. However, we cannot distinguish by NMR between protonated base and neutral base and also proton-released anion and neutral acid, due to high proton exchange. So, we just measure the average of such charged and neutral species. In this sense, the ionicity of protic ionic liquids is similar to the magnitude of deviation of the Walden plots from the KCl ideal line.

**Leigh Aldous** returned to discussion of the paper by Abhishek Lahiri: I was slightly confused by the differences between the XPS measurements and the mass spectroscopy measurements. The mass spectroscopy measurements were very interesting for looking at the intermediates. However, both measurements were performed at 50 °C and under vacuum. Does this mean that active species and intermediates were evaporating in the XPS?

**Abhishek Lahiri** replied: Secondary fragmentation might be possible in mass spectrometry, which might not occur in XPS measurements. Furthermore, we cannot rule out the possibility of vaporization of the intermediates or further species produced by beam damage in XPS.

**Leigh Aldous** said: In your answer just now, you say you destroyed the ionic liquid in the mass spectrometry measurements, but how when you only went up to 50 °C? I assumed the mass spectrometry measurements were head space measurements.

**Abhishek Lahiri** responded: In our opinion neat IL (the fraction of the IL present in the  $\text{SbCl}_3$  in  $[\text{EmIm}]\text{TFSA}$ ) cannot be decomposed at 50 °C. However,  $\text{SbCl}_3$ - $[\text{EmIm}]\text{TFSA}$  might be decomposed under the experimental conditions. Our device is QMS.

**Kazuhisa Tamura** addressed Abhishek Lahiri and Natalia Borisenko: About Fig. 7 in your manuscript (DOI: c7fd00121e), you describe the surface process by

these AFM images. In detail, you described that dissolution occurs in (a)–(c) and electrodeposition occurs in (e) and (f). However, these AFM images except (a) look the same to me. How did you determine the surface process, *i.e.*, dissolution and electrodeposition by AFM images?

**Abhishek Lahiri** responded: The AFM images in Fig. 7 are quite different according to our observation, and Movie S1 in the paper clearly shows the changes in the Cu substrate in a dynamic mode. Therefore we do not understand how the figures look the same. In order to analyse the surface process and determine the rate of deposition and dissolution, we used line profile analysis of the images obtained at various time intervals. Fig. S1 and S2 in the paper show the changes in the height profile during the two processes. We must mention that it was extremely difficult to measure the rate of deposition as the deposition occurred both horizontally and vertically.

**Natalia Borisenko** answered: We agree that it might be difficult to distinguish between dissolution and deposition processes from only the presented AFM images (Fig. 7). Therefore, the line profile analysis of the images obtained at various time intervals was performed to determine the surface processes and the rates of deposition and dissolution (ESI, Fig. S1 and S2). Furthermore, all AFM images were combined together into a Movie (ESI, movie S1), which shows the dissolution and deposition processes more clearly.

**Kazuhisa Tamura** addressed Abhishek Lahiri and Natalia Borisenko: In your XPS experiments, you did the etching. However, in the surface conditions shown in Fig. 2 in the manuscript (DOI: c7fd00121e), many kinds of cross-sections of the surface can be exposed after etching. It is clear that when the angle between nanoplates and the substrate surface is not uniform, the etching depth is not uniform. It means that measured XPS spectra have a lot of information. How did you treat this XPS spectrum, which contains complicated information, in your analysis?

**Abhishek Lahiri** responded: The question concerns the *ex situ* analyzed XP spectra. Qualitative and quantitative information of the sample surface was obtained in a planar projection, which was covered by the analyzer lens system ( $\sim 0.3 \text{ cm}^2$ ) by neglecting shading effects. Indeed, the sputter depth achieved by etching the sample with argon ions might not be uniform over the sample surface. In addition to shading due to the random alignment of the nanoplates, the rate of etching is not uniform, and depends on the chemical and physical properties of the entities that were hit by the ion beam.

The accelerated Ar ions (at 1 keV) hit an area of almost  $1 \text{ cm}^2$ , while a sputter current of  $6 \mu\text{A}$  is achieved. In comparison to thin films, we can assume the sputter depth to be small compared to the structures shown in Fig. 2.

**Natalia Borisenko** responded: In this study, the sputtering was applied to remove the remains of the IL to get information about the “clean” surface of the electrodeposit. We agree that the incident angle of sputtering varies for differently orientated nanoplates resulting in different sputtering depths for individual nanoplates as the electrodeposit contains nanoplates, which are randomly

distributed over the surface. To overcome this, the sputtering time was significantly increased. From our experience, 10 min is usually enough to remove all the remaining IL even from randomly orientated nanoplates under sharp incident angles towards the sputter beam. In order to remove the impurities from the surface of the nanoplates the sputtering time was increased to 50 min, which is not so typical for sputtering processes.

XPS reveals if the remains of the IL and the oxides of the metals are removed from the surface or not. From our experience we know where the peaks related to the pure IL can occur and that the peaks related to Sb and Cu can be distinguished and analyzed based on the literature. Therefore, the analysis of the XPS spectra is not complicated by surface morphology of the electrodeposits.

**Robert Jones** asked: In this work  $\text{SbCl}_3$  was dissolved in the ionic liquid and the mixture was used in high vacuum.  $\text{SbCl}_3$  has a vapour pressure of 1 Torr at 50 °C. Can you comment on whether the  $\text{SbCl}_3$  will have been significantly pumped out of solution while under the high vacuum conditions of the XPS and mass spectrometry experiments?

**Abhishek Lahiri** responded:  $\text{SbCl}_3$  in the ionic liquid forms a complex to form  $[\text{SbCl}_2(\text{TFSA})_3]^{2-}$  which was shown by mass spectrometry. The complex might have a completely different vapor pressure compared to  $\text{SbCl}_3$  and therefore might have been stable under vacuum conditions in the XPS measurements.

**Florian Hausen** stated: The authors compare the performance of electroless deposited  $\text{Cu}_2\text{Sb}$  film as the anode material for Li-ion and Na-ion batteries to literature values of the same material deposited by sputtering or electrodeposition. Apart from differences in the obtained surface morphology the authors have also employed a different electrolyte, namely an ionic liquid rather than the classical organic electrolyte, for their study. My question is what the authors think is more important for the observed variation of the performance of the material in battery applications: the difference in surface morphology or the use of an ionic liquid as the electrolyte?

**Abhishek Lahiri** answered: In general it is known that ionic liquid electrolytes have a higher viscosity and lower Li ion diffusivity compared to organic electrolytes. Ideally, the nanoplate structure should have good diffusion pathways for Li ions as the surface area is much higher compared to other structures. Therefore, it appears that use of the ionic liquid electrolyte rendered a lower capacity storage compared to theoretical values.

**Paul-Henri Haumesser** queried: You measure open circuit potentials (OCP) of metals in the pure ionic liquid. However, for electroless deposition, this OCP should be measured in the electrolyte, including the metal salt (Fe or Sb). Indeed, the OCP of the deposited metal depends on this concentration (according to the Nernst law). Also, one would have expected that the OCP for Cu is not stable in such electrolytes, rising from the OCP of Cu (as measured in the pure ionic liquid) to the value of the second metal (Fe or Sb). Does the OCP stay close to the initial value because some of the Cu surface remains uncovered?

**Abhishek Lahiri** responded: The OCP measured here is ideally  $\text{Cu}/\text{Cu}^+$  and  $\text{Fe}/\text{Fe}^{2+}$  and can be taken as a redox potential in the corresponding ionic liquid *versus* Pt quasi-reference electrode. On contacting the electrodes with the electrolyte and completing the circuit, at the interface, equilibrium will be established which will involve dissolution of the metal to form the metal/metal ion interface. Regarding the second part of the question, the OCP change was monitored over a period of a few hundred seconds and within this time we did not see the OCP change towards the OCP of the second metal, which might be due to some remaining copper. It might be that the change in OCP will require more than a few hundred seconds.

**Corie Horwood** remarked: The AFM images show very little change in surface height over the course of 41 min, while the dissolution rate you calculated would suggest a significant (10–70 nm) dissolution of Cu over this time period. Is the entire surface getting lower with time? Does the Sb deposited on the Cu surface protect the Cu from dissolution?

**Abhishek Lahiri** replied: The dissolution rate was calculated from the height profile of the images with time. It was observed that the troughs at the copper surface decreased significantly with time within the first 8 min from which the dissolution rate was calculated. However, along with dissolution, deposition of Sb also takes place due to a galvanic displacement process. Therefore, one would not expect a significant change of 10–70 nm over the entire 41 min. In the second part of the question, Sb forms nanoplates which might not have covered the entire Cu surface and therefore the galvanic displacement process continues with time.

**Samuel Coles** continued discussion of the paper by Masayoshi Watanabe: In your 2014 *Physical Chemistry Chemical Physics* paper,<sup>1</sup> you define a continuum for solvate ionic liquids consisting of good and poor solvate ionic liquids, and concentrated solutions. Is the continuum you discuss here for protic ionic liquids directly analogous to that one? If so, what defines the difference between a poor solvate ionic liquid, and a concentrated solution?

1 T. Mandai, K. Yoshida, K. Ueno, K. Dokko and M. Watanabe, *Phys. Chem. Chem. Phys.*, 2014, **16**, 8761–8772.

**Masayoshi Watanabe** responded: Thank you for your comments. Poor protic ionic liquids with small  $\Delta pK_a$  are just concentrated solutions of proton transferred salts in mixtures of neutral acid and base. On the contrary, good protic ionic liquids with large  $\Delta pK_a$  consist entirely of ions, just like typical aprotic ionic liquids.

**Benjamin May** resumed discussion of the paper by Abhishek Lahiri: In Fig. 4 in your manuscript (DOI: c7fd00121e) you claim that the peaks labeled  $\text{Cu}_B$  and  $\text{Cu}_{B'}$  are due to  $\text{Cu}(\text{II})$  – I believe that this assignment is incorrect.  $\text{Cu}(\text{II})$  is distinguished from  $\text{Cu}(\text{I})$  or  $\text{Cu}(\text{0})$  by both a shift to higher binding energy (as seen here) but also an intense shake-up structure, due to the species open shell structure, covering the 940–945 eV range (see for example, ref. 1). The shake-up is missing in this case, ruling out the presence of  $\text{Cu}(\text{II})$ .

Instead, this peak may be the Sb 3s shifted to a lower binding energy. A formula of Cu<sub>2</sub>Sb should give an Sb 3s peak of a similar size to that of the peak labeled Cu<sub>B</sub>. I suggest that you research the XPS of copper/antimony alloys.

1 M. C. Biesinger, L. W. M. Lau, A. R. Gerson and R. S. C. Smart, *Appl. Surf. Sci.*, 2010, 257, 887–898.

**Abhishek Lahiri** replied: This is an interesting question, as we did not explain the absence of Cu 2p satellite features in the manuscript. One would expect a shake-up structure in the case of Cu(II). The reference by Biesinger *et al.* even described a method for quantification of Cu(0) and Cu(II) species.

In the case of CuCl<sub>2</sub> a multiplet shake-up structure is expected.<sup>1</sup> However, there are quite a few XPS investigations in the literature describing the absence of Cu 2p satellite features for CuCl<sub>2</sub> in silica and anatase<sup>2</sup> or etched by HCl to a previously oxidized Cu(110) surface.<sup>3</sup> In conclusion, Cu(II) species can't be ruled out due to missing (or weak) satellite features.

We don't agree with your suggested alternative. An Sb 3s component would give a much smaller peak compared to Cu 2p.

1 G. van der Laan, C. Westra, C. Haas and G. A. Sawatzky, *Phys. Rev. B.*, 1981, 23, 4369–4380.

2 P. A. Sermon, K. Rollins, P. N. Reyes, S. A. Lawrence, M. A. Martin Luengo and M. J. Davies, *J. Chem. Soc., Faraday Trans. 1*, 1987, 83, 1347–1353.

3 A. F. Carley, P. R. Davies, K. R. Harikumar and R. V. Jones, *Phys. Chem. Chem. Phys.*, 2009, 11, 10899–10907.

**Himani Medhi** communicated: You mentioned that Cu<sub>2</sub>Sb has been shown to be an anode material for both Li-ion and Na-ion batteries with a theoretical capacity of 323 mA h g<sup>-1</sup>. What is the theoretical method employed to evaluate the capacity of a battery? It should be mentioned.

**Abhishek Lahiri** communicated in reply: It was determined using Faraday's law considering the following equation: 3Li + Cu<sub>2</sub>Sb → Li<sub>3</sub>Sb + 2Cu.

**Himani Medhi** also communicated: The authors do not analyze the amount of Fe and Sb deposited on Cu by XRF and SEM EDS analysis. This will provide information about the amount of reacted Fe and Sb with Cu.

**Abhishek Lahiri** communicated in reply: The main focus of the study was to deposit Sb and Fe from the employed ILs, and we observed electroless deposition of these metals. Furthermore, we intended to study only the feasibility of the process but not quantifying the amount of deposited material.

**Theresa Schoetz** opened a general discussion of the paper by Olivier Fontaine: Does the redox reaction of the biredox species take place on the surface of the porous electrode or also in the pores? If there is a reaction, does the biredox species remain partially trapped in the pores? Do ionic species cause a change in the electrode surface?

**Olivier Fontaine** replied: Due to the size of the biredox ions (about 4 nm), it is impossible for them to penetrate in the microporosity (<2 nm). The first adsorbed layer is composed of the ions of the electrolyte (*i.e.* BMI and TFSI) that bring pure

capacitive storage. Then, in the second layer (in pores that are large enough), biredox molecules can be adsorbed. In addition to their capacitive effect, these molecules can exchange electrons with the carbon surface, resulting in a faradaic effect that increases the overall capacitance. The very interesting feature of this biredox concept is that ions indeed remain trapped in the pores. This is proved by measurements of the self-discharge of our devices that are similar with or without the biredox ionic liquid.

To comment on the latter question on the surface, it can be noticed that in supercapacitors the adsorption/desorption of ions is purely electrostatic and no surface change occurs for tens of thousands of cycles. That is why, contrary to batteries, in which electrode structural changes are involved in electrochemical processes, supercapacitors are very stable and can be charged/discharged for almost an infinite time. This remains true when more complex ions, like biredox ions, are used. It can be mentioned that fading of capacitance with the number of cycles is sometimes observed when tailored molecules are used, but it is due to chemical stability of these molecules and not to carbon surface alteration. However, a careful choice of carbon (for example PICA activated carbon) leads to very stable behavior. On the other hand, previous work in our group and the present article give evidences that the type of carbon (that we could call the “surface”) play a major role towards the performance. This is explained by differences in pore size and distribution (for activated carbons), tortuosity (in the case of carbon onions), or the absence of porosity (glassy carbon) for example.

**Doug MacFarlane** asked: Could you think of this as a battery rather than a capacitor? The CVs look quite redox-like but the discharge is double layer capacitor-like, *i.e.* a voltage that decreases steadily in time. Why is that?

**Olivier Fontaine** responded: This is a very interesting question. On one hand classical batteries are characterized by clear redox peaks on the CV (often with high peak separation) and a plateau at constant potential (Nernst) during galvanostatic experiments. Faradaic reactions involve phase change, and the kinetics are a diffusion-limited process. On the other hand, pure electrostatic capacitors (electrochemical double layer capacitors, EDLCs) are characterized by a rectangular CV, and the potential varies linearly with time during galvanostatic charging/discharging. Adsorption does not involve phase change, and the kinetics are indicative of a surface-controlled electrochemical process. In between, there are the pseudocapacitors that are so-called because their electrochemical behavior is the same as for EDLCs. Moreover the charge storage mechanism does not involve phase change. However, in this kind of material, storage does not any more involve reversible ion adsorption but rather a continuous change in oxidation state (or even intercalation and a change in oxidation state). The most famous pseudocapacitor materials are  $\text{MnO}_2$  and  $\text{RuO}_2$ .

The notion of pseudocapacitors is still controversial in the literature and lots of papers claiming pseudocapacitance that are in fact pure batteries are often published. Anyway this is not really the debate herein, and the question was “how to qualify” a device using a biredox electrolyte. Looking at the galvanostatic behavior there is no real doubt that it behaves more like a pseudocapacitor than like a battery. This is mainly due to the benefit of fast kinetics (dynamics of the liquid state). However, electronic transfer from a molecule in solution to the solid

electrode is a very new concept for energy storage. In a pseudocapacitor, redox reactions involve structural modifications of the electrodes. In our case charge storage arises from electron transfer between the electrode and the “solution” (molecule in solution).”

We cannot propose a special word for now, but obviously, we present here a new kind of electrochemical energy storage device.

**Joshua E. S. J. Reid** opened a general discussion of the paper by Andrew P. Abbott: This is very nice experimental work on a very challenging task in the characterisation of solvents in general. You had looked specifically at Brønsted acidity of the systems in this work (DOI: c7fd00153c), can you draw any parallels between these observations in your work with other studies of hydrogen bond acidity? I believe these two properties are similar but not the same, so I am keen to understand the differences you have observed between the two.

**Andrew Abbott** answered: In terms of the hydrogen bond acidity I presume you are referring to the work of Abraham *et al.*<sup>1</sup> There has not, to my knowledge, been any work using this approach with ionic liquids or deep eutectic solvents although the Kamlet and Taft parameters for hydrogen bond donor and acceptor properties have been widely applied to these types of liquids. Based on a limited data set that we have for pH and hydrogen bond donor number,<sup>2</sup> there does not appear to be a direct correlation between these two parameters, which is not necessarily surprising.

1 M. H. Abraham, P. L. Grellier, D. V. Prior, P. P. Duce, J. J. Morris and P. J. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1989, 699–711.

2 R. C. Harris, PhD thesis, University of Leicester, 2008.

**Joshua E. S. J. Reid** added: With the work you have done, did you observe any peculiar deviations from trends that could be attributed to preferential solvation interactions between the ILs studied and bromophenol blue?

**Andrew Abbott** responded: There is a slight solvatochromic shift (about 10 nm) that occurs between the indicator dissolved in water and that dissolved in the DES. Measuring the shift as a function of water content shows a gradual change showing that there is not a significant preferential partitioning of the indicator into either phase.

**James Wishart** returned to discussion of the paper by Olivier Fontaine: In order to fit your self-discharge kinetics you made some assumptions about the diffusion constants based on literature values for redox-active solutes. In the present case the redox-active species are attached to ionic groups, so the diffusion rates would be expected to be substantially slower. Would it help to experimentally determine the diffusion constants in the bulk using PGSE-NMR, also for both redox states of the redox-active groups (including the dianions and dications)? I realize that this is only part of the problem because diffusion of these species in the confined spaces of the electrodes is another, more difficult issue to address.

**Olivier Fontaine** responded: As it is mentioned in the question/comment, the diffusion coefficient was first chosen according to typical literature values for similar media. Then these coefficients were adjusted to fit our experimental electrochemical data obtained from self-discharge tests.

It is indeed interesting to use NMR to determine diffusion coefficients and we already performed it in our group for other projects. In general we confirm experimental with numerical simulations. The next part of the project looking at the “fundamental understanding” aspect is to develop protocols to perform *in situ* NMR, EQCM (microbalance) and SECM (electrochemical microscopy). Considering the complexity of both porous carbon and liquid media, it is a very challenging project that requires many efforts. Elucidating the diffusion dynamics of redox charged molecules in such complex media will definitely have a huge impact for future development of this project.

**Oliver Hammond** continued discussion of the paper by Andrew P. Abbott: I have a question about the two-phase, water-in-DES microemulsion that you describe in your paper using dynamic light scattering (DLS). Following your earlier paper which hinted at separate water-rich regions using NMR,<sup>1</sup> we have done a series of experiments using isotope-variation small-angle neutron scattering (SANS) and neutron total scattering, and small-angle X-ray scattering (SAXS) using lab sources, synchrotrons and neutron facilities. Your DLS results are at odds with our measurements as we have consistently failed to see any large length-scale, long time-scale nanostructured aggregates in the small-angle region for various DES systems and water contents. However, we do see a variance on the level of the intermolecular solvent structure interactions ( $1 \leq q \leq 2 \text{ \AA}^{-1}$ ). Our models therefore suggest there is some water–water “cluster” formation where water is preferably structured around choline, but these clusters seem to be extremely transient in nature, and rarely greater than a few molecular widths in size.<sup>2</sup> The formation of such transient nanoscale clusters would explain the high water self-diffusivity observed in your earlier NMR works, without the formation of large “pools”. Please can you comment on this?

1 C. D'Agostino, L. F. Gladden, M. D. Mantle, A. P. Abbott, E. I. Ahmed, A. Y. M. Al-Murshedi and R. C. Harris, *Phys. Chem. Chem. Phys.*, 2015, **17**, 15297–15304.

2 O. S. Hammond, D. T. Bowron and K. J. Edler, *Angew. Chem., Int. Ed.*, 2017, **56**, 9782–9785.

**Andrew Abbott** replied: I agree that the two sets of data appear to be at odds, however the DLS data are very reproducible and potentially our two techniques are demonstrating phenomena that occur on different length- and time-scales. It is quite clear from bulk diffusional measurements that there are species which move as if they are in a viscous environment and others that move as if in a less-viscous medium in the same way as occurs in micellar solutions. Self diffusion coefficients also show species which move as if they are in media of different viscosity, and the time-scales of these experiments suggest regions which are more than a few molecular dimensions. I think we can agree that the systems are not homogeneous and the extent of the heterogeneity is a topic that needs to be investigated using a variety of techniques.

**Leigh Aldous** opened a general discussion of the paper by Laurence J. Hardwick: You have done a really nice study looking at the two cations and their effect upon the reduced anion, but how significant is the anion, given that it is still 50% of the system?

**Laurence J. Hardwick** responded: We do have unpublished data on a family of anions and we see that the Lewis basicity of superoxide can be tuned further with the choice of anion. The observed effect is smaller (*i.e.* shift in Raman bands of superoxide) than changing what was observed by changing the cation.

**Leigh Aldous** asked: So you want the superoxide to interact with the cation, but to do that it has to compete with the anion; is that correct?

**Laurence J. Hardwick** answered: Yes, we would want the superoxide to initially interact with the cation so that it can be transported away from the electrode surface. As the anion and cation are fairly dissociated we do not expect too much competition. From the data presented we show the trifluorosulfonylimide (TFSI) anion either undergoes confrontational exchange or is expelled from the surface as a function of potential. Band intensities associated with the triethylsulfonium (TES) cation mirror the appearance and removal of the superoxide, suggesting that they are interacting closely at the interface. Tetraalkylammonium cations (TAA<sup>+</sup>) have been shown to form ion pairs with superoxide.

**Leigh Aldous** commented: I guess now you have to “go through the mirror” and focus upon the anion, in particular after introducing lithium to the system. Does this mean your ideal system is an ionic liquid cation that can strongly interact with the superoxide anion, and an ionic liquid anion that can strongly interact with the lithium cation, but also the ionic liquid anion and cation will not strongly interact with each other?

**Laurence J. Hardwick** replied: Indeed, now we have to observe how these effects play out in the presence of lithium cations and this is planned further work. Spectroscopically this will be more challenging as we will then precipitate out lithium peroxide (Li<sub>2</sub>O<sub>2</sub>) on the electrode surface and we will have to capture the Raman signal of the superoxide intermediate before this happens.

As you state in your question, yes the ideal ionic liquid for lithium -oxygen batteries should therefore have a cation that can strongly interact with the superoxide anion, and an ionic liquid anion that can strongly interact with the lithium cation, but also the ionic liquid anion and cation will not strongly interact with each other. This should have the effect that the intermediates should be fairly soluble and be able to have a significant capacity, *i.e.* significant formation of a Li<sub>2</sub>O<sub>2</sub> layer on the electrode. Whether we can find or design an ionic liquid to do all this is another question, but our Raman studies provide some spectral evidence to point us in the right direction.

**Betul Uralcan** resumed discussion of the paper by Olivier Fontaine: I was wondering if you could show/compare the CVs at higher scan rates (20–50 mV s<sup>-1</sup>) for the neat BMImTFSI and biredox ILs in BMImTFSI?

**Olivier Fontaine** answered: Very interestingly, power capabilities are the same for 0.5 M biredox IL in BMI TFSI and for neat BMI TFSI. Of course, rate capabilities for ionic liquid-based devices are not as good compared to aqueous devices but this trend was expected. In a previous article,<sup>1</sup> power and rate capabilities were deeply investigated and detailed information (including CVs that are required in the question) can be found.

1 E. Mourad, L. Coustan, P. Lannelongue, D. Zigah, A. Mehdi, A. Vioux, S. A. Freunberger, F. Favier and O. Fontaine, *Nat. Mater.*, 2017, **16**, 446–453.

**Ramesh Gardas** returned to discussion of the paper by Andrew P. Abbott: Can homogeneous mixtures of DESs in organic solvent can be considered as binary mixtures (solvent + DES) or ternary (solvent + HBD + HBA) or quaternary (if the DES contains a significant amount of water)?

**Andrew Abbott** responded: You are right that the phase behaviour in binary and ternary mixtures can be complex. We have done dynamic light scattering measurements with both ILs and DESs with organic solvent and these do appear to form non-homogeneous systems. The extent to which a system will be homogeneous or heterogeneous will depend upon the solute's ability to hydrogen bond compared to the ability of the hydrogen bond donor in the DES. The only work we have carried out in this area is with the solvent extraction of solutes from different polarities from alkanes. This shows that the partition coefficient is dependent upon the surface tension of the DES and the ability of the solute to hydrogen bond. More details can be found in ref. 1.

1 A. P. Abbott, A. Y. M. Al-Murshedi, O. A. O. Alshammari, R. C. Harris, J. H. Kareem, I. B. Qader and K. Ryder, *Fluid Phase Equilib.*, 2017, **448**, 99–104.

**Ramesh Gardas** added: How different will dissociation constants for organic solvent be in a homogeneous mixture of HBD and HBA, compared to those in DESs (formed from the same HBD and HBA)?

**Andrew Abbott** answered: This is not something that we have studied but it would be interesting to measure them. We have calculated the enthalpy of hydrogen bonding using calorimetry,<sup>1</sup> and this same method could be used to perform the measurements you are suggesting.

1 A. P. Abbott, A. Y. M. Al-Murshedi, O. A. O. Alshammari, R. C. Harris, J. H. Kareem, I. B. Qader and K. Ryder, *Fluid Phase Equilib.*, 2017, **448**, 99–104.

**Guy Marlair** continued discussion of the paper by Laurence J. Hardwick: I thank you very much for this interesting talk, about energy cells based on Li metal/oxygen. My question is again about the safety issues of such future(?) battery technologies. We know that technical challenges are still significant with this emerging chemistry. With regard to the safety of electrochemical energy storage systems (batteries), we have moved to a new safety paradigm while we quit conventional ones (lead acid, Cd/Ni, even NiMH, *etc.*), all using aqueous electrolytes, and for which the main safety issue is potentially uncontrolled hydrogen release during short circuit events or charging processes, to promote Li-ion based systems making use of non-aqueous systems (*e.g.* mixture of flammable organic

carbonates and Li salt) where the root safety issue is known as the so-called thermal runaway potential, possibly leading to gassing, fires and explosion.

With a new move to Li-O<sub>2</sub> or Li-air systems, how would you rate comparatively the remaining safety challenges that will have to be solved with such a significantly energy density intensified cell? I know the answer is not necessarily easy.

**Laurence J. Hardwick** replied: Safety remains the number one concern for new battery technologies. For the lithium-air battery the main known safety concern is the lithium metal anode. The safety issues of working with lithium metal have been well known for 30 years during the initial commercialisation of rechargeable lithium metal batteries (which were subsequently withdrawn from the market). On cycling, lithium dendrites form on the lithium metal, eventually growing through the separator and causing a short circuit with the cathode, leading to thermal runaway.

Getting lithium metal to work safely is another massive scientific challenge (on top of understanding the reactions of oxygen at the cathode side). Certainly the presence of dissolved oxygen or air in the electrolyte will exasperate the situation if there is a safety failure, as there is a ready supply of oxidant (oxygen) and fuel (organic solvent) in the cell.

**Leigh Aldous** resumed discussion of the paper by Olivier Fontaine: You have functionalised your ionic liquid with anthraquinone. Anthraquinone is well known to have two 1-electron reduction processes in ionic liquid and aprotic media. I notice you only have one reduction peak in your data, and have assigned this to a single 2-electron process. Can you please comment on this?

**Olivier Fontaine** responded: The electrochemistry of anthraquinone in ionic liquid has been intensively studied by Compton *et al.*,<sup>1</sup> and they show that the presence of 2 peaks is not always observed. We didn't further investigate this peak shape behavior because it was not really in the scope of this study. However, we can comment on this. First, we are used to performing cyclic voltammetry experiments in our lab, and indeed, with glassy carbon and anthraquinone molecules in solution two peaks (overlapped) can be observed. In the case of activated porous carbon electrodes, it is in fact not very surprising that only one large peak appears. With this type of electrode, there are so many different environments for the redox molecules, that it is very unlikely that they all react at the exact same potential. This explains why two peaks are not observed for the oxidation/reduction of anthraquinone.

1 S. Ernst, L. Aldous and R. G. Compton, *Chem. Phys. Lett.*, 2011, **511**, 461–465.

**Doug MacFarlane** returned to discussion of the paper by Andrew P. Abbott: Regarding the glass reference electrode, I know you've accounted for the junction potentials. It appears that it is relatively constant across the systems studied. However, recalling the theory that junction potentials in aqueous solution result from differences in conductivity (though I am not certain that this applies for ionic liquid), how applicable would your approach be to very low conductivity ionic liquids?

**Andrew Abbott** replied: The liquid junction potential (LJP) will depend upon the difference in mobility between the ions in the two phases (water and IL). The LJP at the interface will be controlled by the slowest moving ion. The reason that many LJPs are similar is because the size of the cations are roughly constant in ILs. The mobility of the cation is probably not paramount as the interface is not a hard liquid–liquid interface in a glass frit, but a gradation from an aqueous solution to an IL. It is probably the fact that the charge carrier changes from a quaternary ammonium cation to a proton that causes the largest change in the ionic mobility and hence the LJP.

**Adriaan van den Bruinhorst** remarked: As a follow-up to the question asked by Oliver Hammond, did you study the stability of the observed micro-emulsions? Did you observe any agglomeration of the droplets over time right after mixing (seconds/minutes), or long term (days)?

**Andrew Abbott** answered: The samples were mixed using a magnetic stirrer and left for several hours to reach equilibrium. They were filtered to remove any solid particulates and left again to reach equilibrium. The particle sizes obtained were reproducible. They did not appear to differ significantly if they were left for up to 1 day.

**Adriaan van den Bruinhorst** continued: As a follow-up to my previous question, did you evaluate the droplet size after different mixing procedures? For instance, ultrasonic mixing *versus* magnetic stirring? If there is a difference, this might give more information about how quickly smaller droplets agglomerate and a stable emulsion is obtained.

**Andrew Abbott** responded: When the water is added to the DES it initially forms a separate layer due to differences in density. The liquids can be easily homogenised with mechanical stirring to produce a transparent liquid. We did not try ultrasonic mixing. It is an interesting idea and we should try that.

**Leigh Aldous** asked: Did you see any evidence of your triflic acid protonating the chloride? I expect entropy would help drive breaking up the chloride–glycerol complex.

**Andrew Abbott** answered: Assuming the triflic acid is fully dissociated then the proton must interact with the best base in the liquid, which will be the chloride anions. The conjugate acid could be HCl or  $\text{H}_2\text{Cl}^+$ .

**Leigh Aldous** added: Are you able to comment on metal chloride-based deep eutectic solvents? Would they be stable in the presence of strong acids?

**Andrew Abbott** replied: There is no real issue with the stability of the metal based eutectics with strong acids. With relatively weak carboxylic acids such as oxalic and citric acid then these are good complexing agents and may cause some of the metals to precipitate. The metal-based liquids are not particularly stable to strong bases as this may again change speciation.

**Vitor H. Paschoal** continued discussion of the paper by Laurence J. Hardwick: In Fig. 6 of your manuscript (DOI: c7fd00170c) the Raman spectra are shown over the whole range under four different conditions. Considering the region between 600–650 wavenumbers we can observe a clear change in the bands, which are associated with specific cation conformations. Did you try to track the change of the conformation?

**Laurence J. Hardwick** responded: Indeed the bands in the range of 600–700  $\text{cm}^{-1}$  are seen to change in shape and intensity with respect to the potential. We agree that these may arise from conformational changes of TES at the electrode surface, as we have seen previously.<sup>1</sup> We did not in this study focus on tracking the specific cation conformations as we had oxygen present in the electrolyte. However, we do have data in oxygen-free ionic liquids and we are presently analysing these data sets in order to focus on the behaviour of ionic liquid anion and cations, under potential control.

1 I. M. Aldous and L. J. Hardwick, *J. Phys. Chem. Lett.*, 2014, 5, 3924–3930.

**Andrew Abbott** returned to discussion of the paper by Olivier Fontaine: A question asked why a  $\text{Ag}/\text{AgCl}/\text{Cl}^-$  reference electrode was not used in ionic liquids and the answer is that most silver salts are too soluble. Instead it was suggested that the  $\text{Ag}/\text{Ag}^+$  electrode was used. This has a silver wire in a solution of 0.1  $\text{mol dm}^{-3}$  silver salt (usually chloride or nitrate) in the appropriate ionic liquid which is separated from the test solution using a glass frit. Some groups describe the silver wire in an ionic liquid (pseudo reference electrode) as  $\text{Ag}/\text{Ag}^+$  but this is wrong. For a full review of suitable reference electrodes in ionic liquid refer to the article by MacFarlane in *Electrodeposition from Ionic Liquids*.<sup>1</sup> The reference potentials can be related to standard redox potentials.<sup>2</sup>

1 D. R. MacFarlane, in *Electrodeposition from Ionic Liquids*, ed. F. Endres, A. P. Abbott and D. R. MacFarlane, 2nd edn, Wiley-VCH, 2017, pp. 408–423.

2 A. P. Abbott, G. Frisch, H. Garrett and J. Hartley, *Chem. Commun.*, 2011, 47, 11876–11878.

**Olivier Fontaine** answered: Thank you for the comment and the reference. This first question/comment is very interesting and raises an important point which is: “what reference electrode should I use in ionic liquids?” In this study, we used a silver wire on which an  $\text{AgCl}$  paste has been coated. This coated wire is directly immersed in the electrolyte. The coating is very stable and allows reproducing measurements with largely acceptable precision regarding our investigations. In our lab we are used to incorporating classical redox probes (ferrocene or ferrocene methanol) that always comforts us about the reliability of our reference ( $\text{Ag}/\text{AgCl}$ ).

To feed the discussion, it should be mentioned that a recent article<sup>1</sup> concludes that both ferrocene and hexacyanoferrate do not represent a universally usable internal redox probe standard for ionic liquids. The authors claim that the choice of internal redox standard remains a decision that has to be made individually for every series of experiments.

1 N. Frenzel, J. Hartley and G. Frisch, *Phys. Chem. Chem. Phys.*, 2017, 19, 28841–28852.

**Corie Horwood** said: To allow the reproduction or comparison to your results, could you elaborate on the reference electrode used in this work? Please include how the reference electrode was prepared, and what is the potential with respect to a common redox couple such as ferrocene.

**Olivier Fontaine** replied: I invite you to refer to the answer to the previous question.

**Erlendur Jónsson** resumed discussion of the paper by Laurence J. Hardwick: Could you comment on how stable is the superoxide in the systems under study? Do you see any decomposition due to the superoxide?

**Laurence J. Hardwick** answered: The superoxide is relatively stable compared to other known radical species. However its stability is not at the level required to maintain electrolyte and electrode stability for long term battery use.

In the ionic liquids we have examined we do not observe any decomposition from superoxide attack. The reason for this is that these particular ionic liquids have been pre-selected due to their expected stability, and electrochemical analysis by us and others have shown them to be stable, *i.e.* they do not have functional groups that are susceptible to nucleophilic attack from the superoxide.

We have previously monitored the reaction of superoxide with carbon electrode surfaces leading to the formation of lithium carbonate ( $\text{Li}_2\text{CO}_3$ ).<sup>1</sup>

<sup>1</sup> T. A. Galloway, L. Cabo-Fernandez, I. M. Aldous, F. Braga and L. J. Hardwick, *Faraday Discuss.*, 2017, DOI: 10.1039/c7fd00151g.

**Johan Jacquemin** commented: People have worked for a long time with ionic liquids as electrolytes for energy storage applications. There are still several issues to be solved related to their safety, cost, transport properties, stability and interaction with electrode materials. What are your recommendations to move from fundamental studies to large scale practical applications involving ILs in batteries, supercapacitors and fuel cells?

**Andrew Abbott** responded: I think that the first important factor to understand is that there is not just one energy storage application, and the aim to achieve the highest energy density is not necessarily the only goal. There will be some applications where safety and cost are paramount where zinc will be a useful electrode material. Other applications may benefit from some of the lower cost aluminium systems which are coming through. In terms of cost and sustainability I think these are two systems which show promise. Lithium-based cells and supercapacitors will naturally have a segment of the market and new, low-cost, stable electrolytes will need to be developed. Whether they are pure ionic liquids or hybrids does not really matter. It is their performance which is paramount.

**Laurence J. Hardwick** answered: What will drive the uptake of ionic liquids in batteries and supercapacitors will be that the ionic liquid can clearly be demonstrated to offer a step change in performance either in energy stored, safety or operational temperature range. What we heard from this conference was

a blurring of the concept of using just a pure ionic liquid in these devices. I think initially ionic liquids may find themselves used as an “additive” into a conventional organic electrolyte blend. This goes some way to answer your question that larger scale research could focus on ionic liquids as the minor component to be demonstrated to have a beneficial effect.

**Olivier Fontaine** responded: We work on green synthesis with low cost ionic liquids. We think that this is essential to go towards large scale practical applications.

Also, it should be mentioned that the price of ionic liquids is subject to industrial production. We encourage all academic groups to be in close relationships with chemical industries (Solvay, Solvionic for example) that give us wise advice of what could be realistic in energy storage devices and what is not even feasible for upscale.

It is also important to remember that real devices (supercapacitors) use dense packing of electrodes and separators which implies quite a small amount of electrolyte.

**Abhishek Lahiri** returned to discussion of the paper by Laurence J. Hardwick: It has been shown that porous gold is a good ORR catalyst as well as a good SERS substrate. Have you thought of using a porous gold electrode for *in situ* Raman studies? Do you think it would give the same surface effect as the rough gold substrate used for this study?

**Laurence J. Hardwick** replied: Yes we have considered using porous gold for these studies. In principle the substrate should provide a surface enhanced Raman surface. Nanoporous gold can be created by a dealloying method, in which the silver from a silver–gold alloy is dissolved in nitric acid. However the films we have made have been very fragile and difficult to use as electrodes in our present Raman cell setup. They generally disintegrate unless they are kept upon a polymer support, so for practical reasons we have remained using an electrochemically roughened planar gold electrode for our SERS studies.

**Johan Jacquemin** continued discussion of the paper by Olivier Fontaine: Very good and interesting results demonstrating good capacitance of the tested supercapacitors using biredox ILs. How do these values compare with classical performances reported in the literature? To boost these capacitance values you may need to select another type of electrode material, in which case, what sort of materials are you investigating at the moment?

**Olivier Fontaine** replied: This is a very good remark and of course, the nature of the electrolyte and nature of the interface between carbon and the electrolyte is a key point for future optimization of the devices.

First, to answer the question, when using classical porous carbon used in the literature and industry, our concept leads to a two to three time improvement of capacitance. However, due to the complexity of this new system and the huge work performed on the chemistry and electrochemistry of biredox molecules, carbon electrodes (that are the only suitable material that can be considered) have not been optimized yet, but previous work on different carbons confirms it.<sup>1</sup>

Even if not fully understood, it has been known for years now that porous structures impact the electrochemical performance of devices and that porosity should be optimized for all molecules that are considered. Building these home-made desired carbons with controlled porosity is very challenging but this is something we are considering for future works (*via* national and international collaborations). We also investigate tailoring new molecules in order to enhance the performance of our devices.

1 E. Mourad, L. Coustan, P. Lannelongue, D. Zigah, A. Mehdi, A. Vioux, S. A. Freunberger, F. Favier and O. Fontaine, *Nat. Mater.*, 2017, **16**, 446–453.

**Jorge Daniel Gamarra Garcia** continued discussion of the paper by Andrew P. Abbott: Even at low concentrations of water (5%), you report relatively large domains of water. How do you expect them to respond to applied potentials? At what point do you think we are dealing with an aqueous double layer surrounded by an ionic bulk?

**Andrew Abbott** answered: We have carried out voltammetry as a function of water content for solutions of ferricyanide, ferric chloride and iodide to try to see whether species partition into different phases. There does appear to be some anomalous behaviour for ferric chloride above 20 wt% water where we think a change in speciation occurs. The most striking change appears to be for the iodide/iodine couple which goes from a hydrophilic to a hydrophobic species. Voltammetry at low water content shows the expected reversible redox behaviour but increasing the water content above 40 wt% the voltammogram shows evidence of the iodine changing phase and depositing on the electrode, which would be the case for an aqueous solution in contact with the electrode. We take this to be evidence that the double layer is changing its structure but only after a relatively high water content is added. This is something that we hope to show more clearly in the near future.

**Laurence J. Hardwick** returned to discussion of the paper by Olivier Fontaine: Very interesting and very nice study. Do you include the mass of the biredox additive in your specific capacitance per gram ( $F\ g^{-1}$ ) plot (Fig. 2, DOI: c7fd00174f)? To add to this, what is the likely impact of the mass of the biredox additive at the capacitor cell level?

**Olivier Fontaine** responded: To answer the question, no the mass of the biredox ionic liquid was not taken into account to estimate the capacitance. They are rather normalized to the mass of active carbon used to formulate the electrode. On one hand, of course standard procedures should be used to harmonize all literature data. On the other hand, as answered in previous questions, this is a new kind of electrochemical energy storage concept and no standards have been established yet. However, in this study experiments were performed in one-compartment, three-electrode electrochemical cells, and normalization by the mass of the biredox ionic liquid wouldn't be so relevant. In future development, we are going to "upscale" this biredox concept (Pouch cell) and, in this case, the mass of all components (current collectors, electrodes, electrolyte (including

biredox molecules) and separator) will be taken into account so that capacitances and energy and power densities with accurate meaning will be provided.

**Laurence J. Hardwick** said: Instead of putting in a biredox molecule, what would be the effect on the capacitance of just adding into the electrolyte either anthraquinone (AQ) or 2,2,6,6-tetramethylpiperidiny-1-oxyl (TEMPO)?

**Olivier Fontaine** replied: The solubility of anthraquinone in BMImTFSI is  $2 \times 10^{-3}$  M and the solubility of TEMPO is 7 M in BMImTFSI whereas we can solubilize 0.5 M of a biredox molecule in BMImTFSI. The biredox molecules permit to increase the concentration of redox species in the ionic liquid especially for the anthraquinone. Then, the biredox is made of an ion and a redox molecule. The ion permits to change the dynamics of the molecule. Instead of only migration, there is diffusion and migration of the species. The size also changes. All these different characteristics induce different electrochemical mechanisms and permit to obtain better performance. Another very interesting feature and maybe the most important is that this molecular configuration in which the redox center is covalently attached to a charged ion permits to avoid self-discharge of the device. Indeed ions are adsorbed and then remain in the double layer. In fact, if redox molecules are used “alone” in solution, as soon as they are oxidized/reduced they migrate towards the counter electrode to be reduced/oxidized, giving rise to the so-called “redox shuttle” effect. This effect leads to quick self-discharge and such devices can be practically used.

**Morgan L. Thomas** returned to discussion of the paper by Laurence J. Hardwick by communicating: The substrate (working electrode) employed in this work is a roughened gold surface, giving a strong SERS signal. The interfacial liquid structure and superoxide binding mode are presumably quite different depending on the type of surface. Do you have in mind a strategy to extrapolate the findings reported here, and indeed later the findings in the presence of Li cation, to the ORR occurring on other types of working electrode, in particular carbon? In other words, how can the results of this interesting study be used more generally for greater understanding of lithium–air batteries?

**Laurence J. Hardwick** communicated in reply: Yes, we have been working on the Shell Isolated Nanoparticles for Enhanced Raman Spectroscopy (SHINERS) method, which allows us to do surface enhanced Raman on any electrode substrate and we have monitored the oxygen reduction reaction on platinum, palladium and various carbon surfaces using this technique.

Please see some recently published work.<sup>1,2</sup> We plan to continue our studies on ionic liquids using the SHINERS method we have implemented previously on using organic solvents on carbon electrodes, so that we can see if the trends still hold on more practical electrode materials.

1 T. A. Galloway, L. Cabo-Fernandez, I. M. Aldous, F. Braga and L. J. Hardwick, *Faraday Discuss.*, 2017, DOI: 10.1039/c7fd00151g.

2 T. Galloway and L. J. Hardwick, *J. Phys. Chem. Lett.*, 2016, 7, 2119–2124.