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Seebeck coefficients in ionic liquids –prospects for thermo-electrochemical cells†

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Measurement of Seebeck coefficients in a range of ionic liquids (ILs) suggests that these electrolytes could enable the development of thermoelectric devices to generate electrical energy from low-grade heat in the 100–150 °C range.

Low-grade heat, below 150 °C, is likely to be an important sustainable energy source in the near future.[1–3] Thermoelectric cells may be used to directly convert such thermal energy into electrical energy *via* the Seebeck effect. For many years research has focused on using thermoelectric semiconductors for this application.[3] In semiconductor-based thermocells, a voltage is generated by the free energy difference of the electrons in the metals comprising the hot and cold junctions.[4–11] The magnitude of the Seebeck effect, where a voltage is induced in response to a temperature difference between two electrodes, is described by the Seebeck coefficient:

$$S_e = \partial E(T)/\partial T$$

where $E(T)$ is the electrode potential, which is a function of the temperature, T. S_e is therefore a fundamental determining factor in the operation of a practical device. It determines the open circuit voltage that can be produced by the device at any given temperature difference.

Research on thermoelectrics extends from microtechnology and nanofabrication,[12] to hybrid tandem solar cell devices[13] and wearable thermoelectric generators for body-powered devices.[14] However, the efficiency of semiconductor thermocell systems appears to have reached its limit as a result of their relatively small S_e, which is a temperature difference typically in the order of microvolts per Kelvin.[12] On the other hand, thermo-electrochemical cells rely on the Seebeck effect created when a temperature difference between a hot electrode and a cold electrode causes a difference in the electrochemical potential of a redox couple in the equilibrium on the electrodes.[11] In these redox couple-based thermo-electrochemical cells, S_e can be as high as millivolts per Kelvin, hence these devices have attracted interest because of the higher power output they may provide.[15] They may also enable the harvesting of energy from lower grade heat sources, where the voltage generated by semiconductor devices is impractically small.

To date, research into redox couple-based thermo-electrochemical cells has been focused on aqueous media, for example, the ferrocyanide/ferricyanide redox couple in aqueous solution (Fig. 1).[3,15] One electron per iron atom reversibly exchanges producing a large reaction entropy, which, in turn, yields a large S_e (−1.4 mV K^{-1}) and a high exchange current.[3] However, aqueous electrolyte-based thermo-electrochemical cells are limited to applications where the hot electrode does not exceed 100 °C. They also require rigorous sealing to prevent evaporative losses that would eventually lead to a reduced lifetime. Thus, the development of non-volatile electrolytes would allow the advancement of longer lasting devices that may also be used in higher temperature applications. Recent work in other aspects of electrochemical devices has identified ILs as an ideal choice for such an electrolyte.[16–21]

ILs are molten salts with melting points below 100 °C.[22,23] The unique and, in some cases, tuneable properties of ILs have resulted in them being regarded as designer solvents and their applications include use as electrolytes in a wide variety of electrochemical contexts and devices[18] such as batteries,[24] fuel cells,[25–27] electrochromic devices[28] and solar cells.[29–32] ILs can also have a wide electrochemical window, in some cases spanning from −2.5 to +2.5 V *vs.* NHE, which overcomes the limitations imposed by common aqueous or organic media. In the context of thermo-electrochemical cell applications, another attractive property that some ILs exhibit is their high thermal stability, which allows them to operate without degradation at elevated temperatures (100–150 °C).[33]

IL and/or molten salt incorporation in thermo-electrochemical cells has been limited to date.[34] Chum and Osteryoung *et al.*[34] reviewed a number of publications from the 1960s and 1970s focused on the use of high temperature molten salts (T > 300 °C);

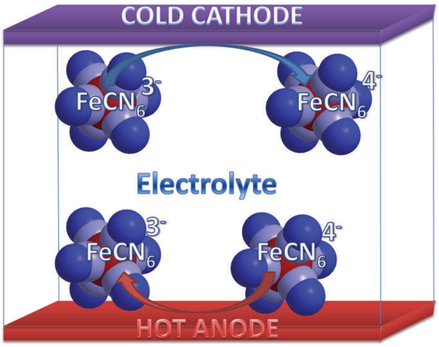

Fig. 1 A schematic of a thermo-electrochemical device.

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these systems are not appropriate for low grade heat applications that typically involve upper temperatures of around 150 °C.[34] S_e measurements in IL systems are also very limited. Migita *et al.*[19] have reported S_e measurement of some iron complexes in 1-butyl-1-methylpyrrolidinium bis(trifluoro-methanesulfonyl)-amide. However, the influence of the nature of the IL on the S_e of redox couples has not been studied to date, and such information is crucial for the development of IL-based thermo-electrochemical devices. This communication describes the measurement of the S_e for an archetypal redox couple (iodide/triiodide) in a range of ILs and shows that the nature of the IL can have a significant influence on the voltages produced.

Measurements of the S_e were performed using approximately 1 mL of IL solution of the redox couple in each of two electrode compartments, which were connected *via* a salt bridge of the same mixture. The voltage difference between the two electrodes was measured with a UNI-T UT803 high impedance voltmeter. The temperature of the cold side was controlled using a water bath and the hot side by insertion of the compartment into a brass heating block attached to a thermostat. The Pt electrodes were prepared by washing with concentrated nitric acid followed by rinsing with methanol. As a test of the electrodes in each measurement, a reading of 0.0 mV was required at zero temperature difference.

Measurement of the potential difference was taken at 30 °C intervals across various temperature ranges. The S_e was determined from the slope of a straight line fitted to the data in regions where the trend appeared to be linear. The experimental apparatus was first tested using a 0.4 M aqueous solution of $K_3Fe(CN)_6$/ $K_4Fe(CN)_6$. The S_e was determined to be −1.41 (±0.01) mV K^{-1}, consistent with literature data.[3]

Measurement of the S_e of the iodide/triiodide (I^-/I_3^-) redox couple was performed in a range of different solvents, at various concentrations, over different temperature ranges depending on the stability of the reading of potential difference. The molecular solvents were chosen for their high boiling points. The ILs were chosen for their low viscosity and to explore the influence of the nature of the cation and anion on the S_e. Descriptions of the preparation of the ionic liquids and the test solutions can be found in the electronic supplementary information (ESI).†

S_e measurements for the I^-/I_3^- redox couple, at a concentration of 0.4 M in a number of ILs, along with water and the aprotic organic solvent methylpropionitrile, are shown in Fig. 2. To assure reproducibility, trial measurements were run in triplicate and the resultant error range was found to typically be ±0.01 mV K^{-1}. Table 1 lists the S_e values and the maximum potential reached in the measurements. The ILs all showed lower S_e values than the aqueous or organic solvent, but the [C$_2$mim][BF$_4$]-based system was relatively close, achieving a maximum potential of 36.7 mV and an S_e of only half that of the aqueous system. A strong influence on the nature of the IL is evident, which is further discussed below. Future work in this area will be focused on investigating alternative redox couples that can provide a higher S_e in ILs, thereby providing advantages of low volatility and high stability of the IL in combination with a high S_e, for more efficient, longer-lasting devices.

Previous studies have found that a maximum S_e is attained at infinite dilution of the redox couple in aqueous solution, while the opposite effect exists in organic solutions.[35] Typical voltage *versus* temperature data are presented in Fig. 3, illustrating the effect of the redox couple concentration on the S_e using an IL electrolyte. S_e values of 0.26 mV K^{-1}, 0.39 mV K^{-1}, and 0.47 mV K^{-1} were obtained at 0.4M, 0.1 M, and 0.02M I^-/I_3^- concentrations, respectively, in [C$_2$mim][BF$_4$]. Hence, similar to aqueous systems, a trend of increasing S_e with decreasing concentration of the redox couple was observed. This trend was also observed in [C$_2$mim][NTf$_2$] and [P$_{4,4,4,6}$][NTf$_2$]. However, the stability of the measurement at elevated temperatures decreased with decreasing concentration of redox couple, suggesting some instability of the redox couple under these conditions.

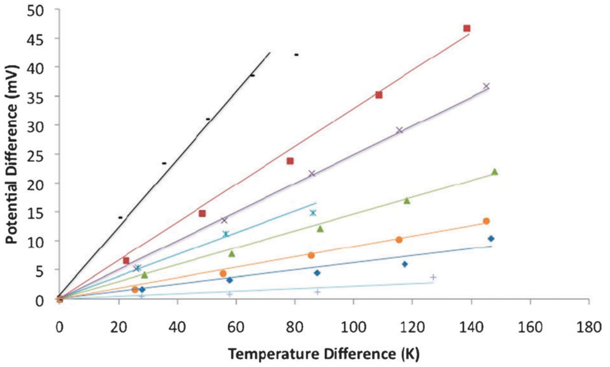

Fig. 2 Seebeck coefficients of 0.4M I^-/I_3^- in water (-), methoxy-propionitrile (■), [C$_2$mim][BF$_4$] (×), [P$_{4,4,4,6}$][NTf$_2$] (✳), [C$_2$mim][NTf$_2$] (▲), [C$_4$mpyr][NTf$_2$] (◆), [C$_2$mim][B(CN)$_4$] (●) and [P$_{2,2,2,(101)}$][NTf$_2$] (+). Measurement error was less than the data point size.

Thermodynamically, the temperature dependence of an electrode potential is related to ΔS, the reaction entropy for the redox reaction:

$$\partial E(T)/\partial T = \Delta S/nF$$

where n is the number of electrons involved in the reaction and F is Faraday's constant.[11,15] In the aqueous systems this entropy change stems, at least partly, from the solvent reorganization that takes place as a result of the change in charge occurring during the redox process. It is interesting to note that the S_e of the triiodide/iodide redox couple is positive, compared to the negative S_e of the ferro/ferricyanide redox couple. This likely stems from the increase in the number of species in the reaction $I_3^- + 2e^- \rightarrow 3I^-$, which creates a positive ΔS in this case, whereas the entropy change in the ferricyanide reduction is dominated by the negative solvent reorganisation entropy. The different S_e values in the different ILs provides insight into the influence of the nature of the IL on the entropy change in the redox reaction. It is clear that the nature of both the cation and anion influence these parameters; the four [NTf$_2$] salts give quite distinctly different values for S_e. There are probably several solvation factors at play here, since both the small and somewhat hydrogen bonding [C$_2$mim] cation and the larger and more hydrophobic [P$_{4,4,4,6}$] cation produce similarly high S_e. The use of a common [C$_2$mim] cation with different anions also results in significant differences; [C$_2$mim][BF$_4$] produces the largest S_e, while that of [C$_2$mim][B(CN)$_4$] is substantially lower.

With a decreasing concentration of the redox couple in the IL there are more solvent ions available to independently "solvate" the redox ions, thereby accentuating the differences in the solvation environment that the change in redox state creates. This is similar to the aqueous system, where the majority of the

Table 1 Seebeck coefficients and the maximum potentials obtained using a range of solvents and 0.4M I^-/I_3^-

Solvent	Seebeck coefficient (mV K^{-1})	Max. potential (mV)
Water	0.53 ± 0.04	42.2
Methylpropionitrile	0.34 ± 0.01	46.7
[C$_2$mim][BF$_4$]	0.26 ± 0.01	36.7
[P$_{4,4,4,6}$][NTf$_2$]	0.17 ± 0.01	25.4
[C$_2$mim][NTf$_2$]	0.154 ± 0.005	22.0
[C$_4$mpyr][NTf$_2$]	0.06 ± 0.01	13.4
[C$_2$mim][B(CN)$_4$]	0.094 ± 0.003	10.4
[P$_{2,2,2,(101)}$][NTf$_2$]	0.03 ± 0.01	3.7

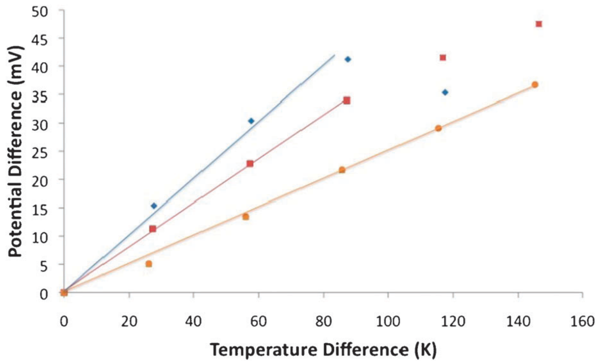

Fig. 3 The temperature dependence of the potential difference produced using [C$_2$mim][BF$_4$] with the I^-/I_3^- redox couple at 0.02 M (◆), 0.1 M (■) and 0.4 M (●) concentrations.

entropy change originates from reorientation of the aqueous solvation shell around the redox couple. In molecular solvents it is thought that this solvent reorientation is less substantial,[35] presumably scaling with the dielectric constant, but increases when there are higher concentrations of the redox couple present, possibly as a result of a subtle balance of self reorientation dynamics *versus* solute-imposed reorientation; hence the S_e increases with the redox couple concentration in those cases. The observation of increased S_e at lower concentrations of redox couple in the ILs is advantageous for the development of IL-based thermo-electrochemical devices, as it implies that only moderate solubilities may be required for the most efficient devices.

As long as the system is in equilibrium, the choice of electrode should not affect the S_e of the redox couple, as the thermodynamics of the redox couple is the governing factor.[3] The present measurements were carried out using platinum electrodes, which can limit potential industrial applications. Carbon-based electrodes, including the nanotube electrodes used by Baughman *et al.*,[3] will be investigated as potential alternatives in future work.

In conclusion, redox couple-based thermo-electrochemical cells represent an important way forward in the development of thermoelectric energy generating devices. ILs appear to be a useful option for the electrolytes in these systems due to their negligible vapour pressure, high thermal stability and non-flammable nature. These characteristics should enable the design of long-lifetime devices of this type. The S_e for a given redox couple was found to vary substantially as a function of the IL, hypothetically as a result of the solvation environment that the IL represents for the redox couple species. Further investigations into which ILs and redox couples are optimal for thermoelectric applications are underway.

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