

# Quasi-solid state electrolytes for low-grade thermal energy harvesting using a cobalt redox couple

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**Abstract:** Thermoelectrochemical cells, also known as thermocells, are electrochemical devices for the conversion of thermal energy directly to electricity. They are a promising method for harvesting low-grade waste heat from a variety of different natural and man-made sources. The development of solid or quasi-solid state electrolytes for thermocells could address the possible leakage problems of liquid electrolytes and make this technology more applicable for wearable devices. Here we report the gelation of an organic solvent-based electrolyte system containing a redox couple, for application in thermocell technologies. The effect of gelation of the liquid electrolyte, comprising a cobalt bipyridyl redox couple dissolved in 3-methoxypropionitrile (MPN), on the performance of thermocells was investigated. Polyvinylidene difluoride (PVDF) and poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP) were used for gelation of the electrolyte, and the influence of the different polymers on the mechanical properties was studied. The Seebeck coefficient and diffusivity of the cobalt redox couple were measured in both liquid and gelled electrolytes and the effect of gelation on the thermocell performance is reported. Finally, the cell performance was further improved by optimising the redox couple concentration and the separation between the hot and cold electrode, and the stability of the device over 25 hours of operation is demonstrated.

## Introduction

Harvesting the waste thermal energy produced in industry, by geothermal sources, body heat and so forth, is a promising method of clean energy production. The direct conversion of this thermal energy to electricity can be achieved using thermoelectric or thermoelectrochemical devices. Energy conversion in these technologies is based on the Seebeck effect, which yields a potential difference ( $\Delta V$ ) as a result of a temperature gradient ( $\Delta T$ ) across the device.<sup>[1]</sup> Thermoelectrochemical cells, also known as thermocells, are an attractive technology because of the higher Seebeck coefficient,  $S_e$ , that can be achieved compared to thermoelectric generators, and the possibility of making lower cost devices. The highest reported  $S_e$  to-date for inorganic thermoelectric devices is 850  $\mu V/K$ ,<sup>[2]</sup> which is lower than most thermoelectrochemical systems.

A thermoelectrochemical cell comprises two inert electrodes and a redox couple dissolved in an electrolyte, the electrochemical potential of which is temperature dependant.<sup>[3]</sup> Holding the two

electrodes at different temperatures leads to a temperature gradient ( $\Delta T$ ) across the cell and produces a potential difference ( $\Delta V$ ). The open-circuit potential across the cell is directly dependent on the  $S_e$  of the redox couple, which is dependent on the entropy change ( $\Delta S$ ) of the redox reaction:

$$S_e = \frac{\Delta V}{\Delta T} = \frac{\Delta S}{nF} \quad \text{Eq 1}$$

where,  $n$  is the stoichiometric number of electrons involved in the reaction, and  $F$  = Faraday's constant.<sup>[3]</sup>

For the development of efficient thermoelectrochemical cells, the Seebeck coefficient is one of the key parameters that needs to be optimised as this dictates the open circuit voltage that can be achieved.<sup>[4]</sup> Also extremely important is achieving sufficient rates of transport of the redox couple through the electrolyte to avoid significant mass transport resistance. Thus, in the development of new quasi-solid state electrolytes for thermocells both of these parameters need to be considered.

The Seebeck coefficient of a redox electrolyte depends on both the nature of the redox couple and the solvent used. The partial molar entropy of redox ions, and consequently the entropy change of the redox reaction and  $S_e$ , is affected by interaction between the redox ions with solvent. For example, the entropy of transition metal-based redox couples has been studied by Weaver et al.<sup>[5]</sup> and shown to be dependent on both ligand and solvent. Nevertheless, the exact relationship between different solvent parameters such as acceptance number, donor number, polarity etc. and the Seebeck coefficient of the redox electrolyte is still not well understood.

The  $K_{3/4}[Fe(CN)_6]^{3-/4-}$  redox couple in water has the highest reported  $S_e$  known for aqueous systems with values between -1.43 and -1.77 mV/K depending on the concentration of redox couple.<sup>[6]</sup> To allow the use of the  $[Fe(CN)_6]^{3-/4-}$  redox couple in an ionic liquid,  $(BMP)_3[Fe(CN)_6]$  has been prepared (where  $BMP$  = 1-butyl-1-methylpyrrolidinium)<sup>[7]</sup>, which gave an  $S_e$  of -1.49 mV/K when dissolved in 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide ( $[C_4mpyr][NTf_2]$ ). Using a cobalt bipyridyl redox couple in high-boiling organic solvents can also allow access to high  $S_e$  and higher temperatures of operation. For example, the  $[Co(bpy)_3]^{2+/3+}[NTf_2]_{2/3}$  redox couple ( $bpy$  = 2,2'-bipyridyl,  $NTf_2$  = bis(trifluoromethanesulfonyl)amide) in organic solvents such as 3-methoxypropionitrile (MPN), dimethyl sulfoxide (DMSO) or ionic liquids, gives  $S_e$  of 1.5–2.2 mV/K.<sup>[4]</sup> The use of molecular solvents or ILs also allowed operation of the thermocell with a hot electrode temperature of 130 °C, thereby achieving high power densities.<sup>[8]</sup>

While the high ionic conductivities of liquid electrolytes is highly advantageous for electrochemical devices, their application in thermocells may suffer from leakage problems. This can be addressed through solidification of the electrolytes, which is an avenue of thermocell research that has not yet been widely studied. As summarised below, there are only a few prior publications that report the development of polymer-based thermocell electrolytes. To the best of our knowledge, no one has

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reported the gelation and thermocell application of the cobalt-based redox electrolytes that are advantageous for achieving a high  $S_e$ . One of the unique challenges in this avenue of research is achieving a quasi-solid state electrolyte with the mechanical properties sufficient to prevent solvent leakage while still enabling sufficient transport of the redox couple, and there is a paucity of prior reports on such redox active gelled systems.

The polymer-based electrolytes reported for thermocell systems have thus far been limited to aqueous electrolytes. For example, by soaking a Nepton CR-51 membrane (a condensation polymer of phenol sulphonic acid and formaldehyde) in copper sulphate solution, a quasi-solid state electrolyte was prepared without significantly affecting  $S_e$ .<sup>[9]</sup> In that work, only potentials were measured – full devices were not prepared.

Different quantities of cellulose (2.5 - 20 wt%) have been used to prepare insoluble cellulose-based matrixes in water, which were then immersed in an aqueous  $K_{3/4}[Fe(CN)_6]^{3-/4-}$  redox electrolyte to produce quasi-solid-state electrolytes.<sup>[10]</sup> The optimal cellulose concentration was determined to be 5 wt%, achieving an optimum balance of mechanical properties,  $S_e$  and diffusion coefficients. This yielded thermocell power densities only 20% percent less than that of the liquid system.

Gelation of aqueous 0.1 M  $K_{3/4}[Fe(CN)_6]^{3-/4-}$  has also been investigated using gelatine, agar agar (agarose) and poly(sodium acrylate).<sup>[11]</sup> By addition of different quantities of these gelation agents, it was found that agar agar and poly(sodium acrylate) form effectively gelled electrolytes. The maximum reported power density of the thermocell containing agar agar gel or poly(sodium acrylate) gel was approximately 0.13 mW/m<sup>2</sup> and 0.5 mW/m<sup>2</sup> respectively ( $= 0.0003$  and  $0.0012$  mW/m<sup>2</sup>K<sup>2</sup>), when  $\Delta T = 20$  ( $T_{hot} = 35$  °C and  $T_{cold} = 15$  °C). The agar agar gel electrolyte, which had more robust mechanical properties, showed a lower current density compared to the poly(sodium acrylate) gel due to the lower diffusion coefficient of the redox ions.

Polyvinyl alcohol (PVA) has been used for gelation of aqueous electrolytes and for designing a wearable thermocell device.<sup>[12]</sup> Using two different iron-based redox couples ( $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$  and  $FeCl_2/FeCl_3$ ) with opposite signs of Seebeck coefficient ( $-1.21$  and  $1.02$  mV/K, respectively), and connecting the thermocells with the gelled electrolytes in series (equivalent to n-type and p-type semiconductors in thermoelectric generators), a large potential difference (23 mV with a  $\Delta T = 10$  °C) was achieved. The maximum power density produced by this series-connected device was  $0.0236$  mW/m<sup>2</sup>K<sup>2</sup> when  $\Delta T = 20$  °C.

Finally, in a different kind of thermoelectrochemical device concept, Ag<sup>+</sup>-substituted polymers of Nafion and polystyrene-sulfonate (PSSA), have been used to prepare unipolar ion-conducting, solid-state polymers for thermocells. These polymer systems do not contain a redox couple and instead are based on the combination of two different polyelectrolytes with opposite signs of their intrinsic Seebeck coefficients. The powers were  $\sim 6 \times 10^{-13}$  W for a 4 °C temperature gradient.<sup>[13]</sup>

However, the use of aqueous electrolytes, either in liquid or gel form, limits application of the thermocell to harvesting waste heat at temperatures below the boiling point of water. The feasibility for higher temperature applications could be improved by gelling high-boiling, non-aqueous electrolytes, such as MPN. Further,

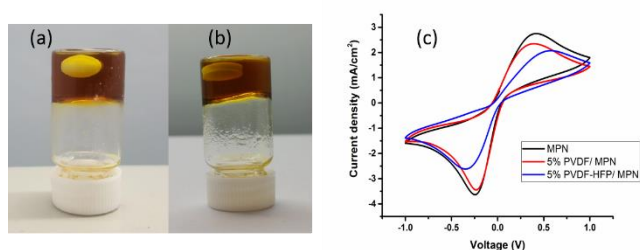
use of the  $[Co(bpy)_3]^{2+/3+}$  redox couple in a quasi-solid state electrolyte could allow access to higher Seebeck coefficients. For the  $Co(bpy)_3$  based electrolytes that have a positive Seebeck coefficient, they could also be used in combination with a redox electrolyte with a negative  $S_e$  to make thermocell arrays, i.e. in an n-type and p-type series connect,<sup>[14]</sup> to increase power output and enable the development of more commercially viable devices.

Prior research in the dye-sensitised solar cell (DSSC) field has shown that 1.5 - 10 wt% polyvinylidene difluoride (PVDF) or poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP) can be used to gel  $[Co(bpy)_3]^{2+/3+}[NTf_2]_{2/3}$  in MPN or acetonitrile.<sup>[15]</sup> A small increase in the cell performance with PVDF was observed compared to the liquid electrolyte,<sup>[15a]</sup> while using PVDF-HFP improved the long-term stability.<sup>[15b]</sup> As our prior research achieved an  $S_e$  of 2.19 mV/K for  $[Co(bpy)_3]^{2+/3+}[NTf_2]_{2/3}$  in MPN,<sup>[8]</sup> this was identified as the best redox system for developing into a quasi-solid state electrolyte. Thus, here we report, for the first time, the development of quasi-solid state electrolytes for thermal energy harvesting using the  $Co(bpy)_3^{2+/3+}$  couple. We compare the effect of using PVDF and PVDF-HFP for solidification of this redox electrolyte, and the influence of gelation on the Seebeck coefficient, diffusion coefficient and thermocell performance. For the PVDF-based gel, which was concluded to be superior to the PVDF-HFP, the device performance was optimised by investigating the effect of redox couple concentration and cell design.

## Results and Discussion

### Comparison of PVDF and PVDF-HFP gels

The addition of a minimum amount of 5 wt% PVDF or PVDF-HFP to 0.05 M  $[Co(bpy)_3]^{2+/3+}[NTf_2]_{2/3}$  in MPN is sufficient to produce a quasi-solid electrolyte (Figure 1). The gel with PVDF was produced after 10 minutes standing at room temperature after the initial heating process at 120 °C, while the PVDF-HFP-based gel needed 30 minutes to solidify after cooling to room temperature.



**Figure 1.** Quasi-solid state electrolytes containing 0.05 M  $[Co(bpy)_3]^{2+/3+}[NTf_2]_{2/3}$  in MPN, gelled with a) 5 wt% PVDF, b) 5 wt% PVDF-HFP, c) the electrochemical behaviour of the redox electrolytes before and after gelation, measured using a three-electrode cell equipped with a platinum working electrode and two platinum wires as counter and pseudo reference electrodes, at a scan rate of 50 mV/s.

Analysis of the rheological properties of the PVDF and PVDF-HFP based electrolytes (Figure S3-S5) confirms that both samples are in a gel form. The PVDF gel electrolyte kept its form over a

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temperature range of 25–70 °C, with only a small decrease in storage modulus observed at high temperature. However, for the PVDF-HFP gel a sharp decrease in storage modulus is observed at 60 °C, and the DSC shows a lower melting point compared to the PVDF gel (Figure S6). Thus, the physical properties of the PVDF gel appear to be the more promising for use in thermocells at elevated temperatures.

### Seebeck coefficient and Diffusion coefficient

The Seebeck coefficient ( $S_e$ ) of the redox couple plays an important role in the performance of a thermocell and can be strongly affected by the nature of the solvent. Solvent interaction with the redox ions affects the entropy and free energy of the ions, and consequently the  $S_e$ .<sup>[5, 16]</sup> However, the addition of PVDF or PVDF-HFP to the  $[\text{Co}(\text{bpy})_3]^{2+/3+}$  redox electrolyte does not significantly affect  $S_e$  (Table 1, experimental details in supporting information figure). This suggests an absence of any strong interactions between the polymer chains and the redox species, and consequently negligible effect on the entropy change of the redox reaction. Thus, in spite of gelation of electrolyte, the  $S_e$  of the quasi-solid state electrolytes remains high enough to be promising for further development of the thermocells.

**Table 1.** The effect of gelation of the electrolyte on the Seebeck coefficient, and the diffusion coefficient at 25 °C.

Electrolyte	Seebeck coefficient [mV/K]	Diffusion coefficient [ $\text{D} \times 10^6 \text{ cm}^2/\text{s}$ ]	
		$[\text{Co}(\text{bpy})_3]^{2+}$	$[\text{Co}(\text{bpy})_3]^{3+}$
MPN	$1.81 \pm 0.03$	$5.00 \pm 0.39$	$4.90 \pm 0.27$
5wt% PVDF-MPN	$1.80 \pm 0.02$	$4.63 \pm 0.13$	$4.21 \pm 0.09$
5wt% PVDF-HFP-MPN	$1.84 \pm 0.01$	$4.48 \pm 0.15$	$3.55 \pm 0.25$

In order to maintain the thermocell operation, the redox couple needs to move from one electrode to the other. This can be driven by three phenomena: diffusion, migration and convection. Using chronoamperometry to investigate the effect of gelation on the diffusivity of the redox couple reveals that gelation does not cause a significant decrease in diffusion coefficient (Table 1). The diffusivity of the  $[\text{Co}(\text{bpy})_3]^{3+}$  ions in the PVDF-HFP gel is a little lower than in the PVDF gel. This may be a result of more interactions between the  $[\text{Co}(\text{bpy})_3]^{3+}$  cations and the polar groups on the PVDF-HFP polymer, as reported in PVDF-HFP gel electrolytes containing lithium or sodium ions.<sup>[17]</sup>

Cyclic voltammetry (Figure 1c) shows that the redox couple in the gelled electrolytes maintain electrochemically quasi-reversible behaviour. However, there is an increase in peak-peak separation in the PVDF-HFP based gel and a more significant decrease in current after gelation in this system. This is consistent with a larger increase in mass transfer resistance, indicated by the lower diffusion coefficient. The peak-to-peak potential separation in the PVDF-HFP system is also increased compared to the liquid system, consistent with an increase in the mass transport resistance and decrease in ionic conductivity. Thus, the electrochemical characterisation supports the conclusion that the

PVDF-based gel is the more promising, and that the important characteristics of the redox electrolyte are maintained upon gelation.

### Thermocell performance

To study the performance of a thermocell, the two electrodes are held at different temperatures and the power and current output are measured across a range of applied external resistances. Full details of the cell testing are given in the supporting information. The characteristics of the thermocell containing either the PVDF or PVDF-HFP redox electrolytes, with a hot electrode temperature of 60 °C and cold electrode temperature of 20 °C and an electrode separation of 1 cm, are shown in Figure 2. Upon applying each resistance, the potential and current slowly decreased and took a lot longer to stabilise compared to the cell with the liquid electrolyte. This is due to the limited convection and mass transport in the gelled systems, and thus much longer stabilization times (60 minutes at each resistance) was used to ensure steady-state measurements.

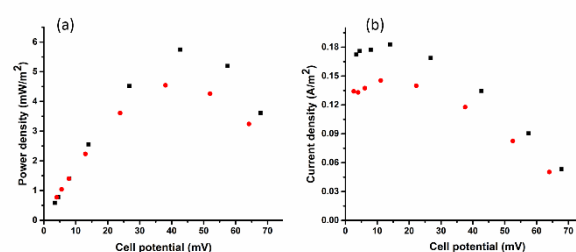


Figure 2. (a) Power density and (b) current density of thermocells containing gelled electrolyte: 0.05 M  $[\text{Co}(\text{bpy})_3]^{2+/3+}[\text{NTf}_2]_{2/3}$  in MPN gelled with either 5wt% PVDF (■) or PVDF-HFP (●), electrode separation = 1 cm,  $T_{\text{cold}} = 20$  °C,  $T_{\text{hot}} = 60$  °C.

The PVDF-based gel electrolyte gives a maximum 6 mW/m<sup>2</sup> power density, which is better performance than the PVDF-HFP gel electrolyte (4.5 mW/m<sup>2</sup>). Using a liquid MPN-based electrolyte in the same cell, with the same redox couple concentration and the same  $\Delta T$ , produced ~48 mW/m<sup>2</sup>. Given the similar Seebeck coefficient and a relatively small decrease in diffusion coefficient of redox ions after gelation of the liquid electrolytes (Table 1), the drop in thermocell power and current density with the gel electrolytes is thought to be primarily a result of limiting the convection in the cell, which decreases mass transport.<sup>[3b, 6, 18]</sup> Strategies to significantly improve the power output of the gelled electrolyte system, by addressing some of the mass transport limitations through cell optimisation, are discussed below. The drop in current density that is evident at low cell potentials (<10 mV) in the gelled electrolytes (Figure 2b) also suggests a mass transfer limitation. This is in agreement with previously reported analytical models that suggest that thermocell power density can be as much as eight times larger as a result of mass transport through natural convection.<sup>[18b]</sup>

To address the mass transport limitation, and improve the power and current density of the cells containing the gelled electrolytes, the concentration of redox couple and electrode separation were optimised, as discussed below. The effect of polymer content, concentration of redox couple and electrode separation was



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studied using the PVDF gel electrolyte because, as discussed above, this had better performance than PVDF-HFP in the thermocell, a higher melting point and better electrochemical characteristics.

### Optimisation of the PVDF-based gel and thermocell design

#### a) The effect of polymer content

The amount of polymer used for gelation of the redox-active liquid electrolyte affects the mechanical property of the resulting quasi-solid state electrolyte, as shown in Figure 3. 2.5 wt% is not sufficient to fully gel the material (Figure 3 a), whereas with 15 wt% polymer a free standing redox electrolyte can be prepared (Figure 3 d). To investigate the effect of polymer content on the electrochemical properties and thermocell performance, different amounts of PVDF (2.5–15 wt%) were used for gelation of the 0.05 M  $[\text{Co}(\text{bpy})_3]^{2+/3+}[\text{NTf}_2]_{2/3}$  in MPN. Increasing the amount of polymer in the redox electrolyte steadily decreases the diffusion coefficient of the redox species (Figure 4b) as the material becomes progressively more solid. However, there is only a small effect on the Seebeck coefficient (Figure 4a).

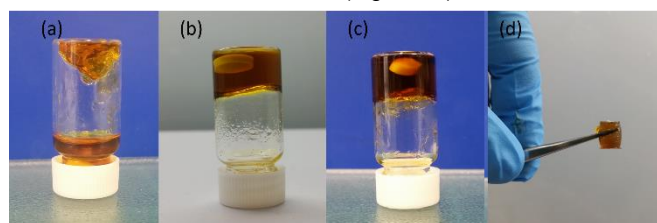


Figure 3. Polymer gel electrolytes containing different quantities of PVDF, in 0.05 M  $[\text{Co}(\text{bpy})_3]^{2+/3+}[\text{NTf}_2]_{2/3}$  in MPN, a) 2.5 wt%, b) 5 wt%, c) 7.5 wt% and d) 15 wt%.

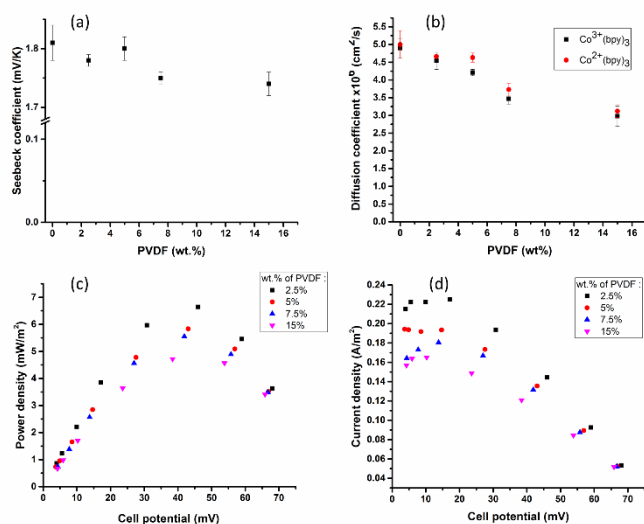


Figure 4. The effect of PVDF content in 0.05 M  $[\text{Co}(\text{bpy})_3]^{2+/3+}[\text{NTf}_2]_{2/3}$  in MPN on (a) the Seebeck coefficient, (b) the diffusion coefficient of the redox species, (c) the power density and (d) the current density of the thermocell (electrode separation = 1 cm,  $T_{\text{cold}} = 20^\circ\text{C}$ ,  $T_{\text{hot}} = 60^\circ\text{C}$ ).

The performance of the thermocell is also dependent on the polymer content. Although the gel electrolyte with 2.5 wt% PVDF showed better cell performance, it is not sufficiently solidified to

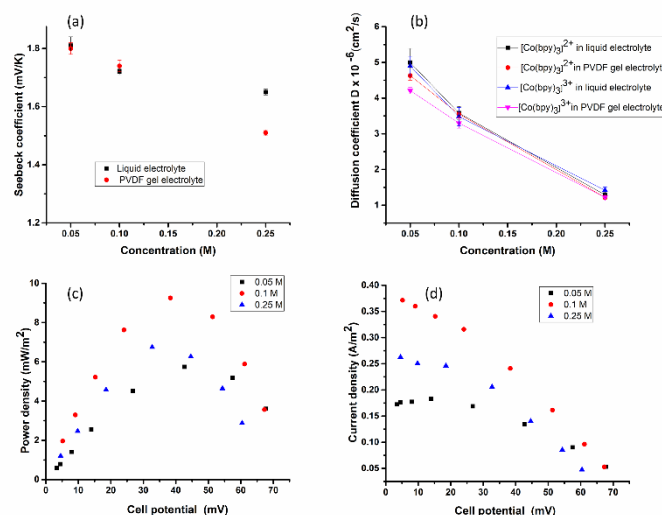


Figure 5. The effect of concentration of redox couple in MPN-based electrolyte before and after gelation on (a) Seebeck coefficient and (b) diffusion coefficient of redox ions, (c) power density and (d) current density of the thermocell containing PVDF gel electrolyte (5 wt% PVDF with 0.05, 0.1 or 0.25 M  $[\text{Co}(\text{bpy})_3]^{2+/3+}[\text{NTf}_2]_{2/3}$  in MPN, electrode separation = 1 cm,  $T_{\text{cold}} = 20^\circ\text{C}$ ,  $T_{\text{hot}} = 60^\circ\text{C}$ ).

eliminate leakage problems (Figure 3a). Thus, considering the power output of the cell and the physical properties of the electrolytes, 5 wt% PVDF was concluded to be optimum. Increasing the amount of polymer to 15 wt% gave a free standing polymer electrolyte, but a decrease in the power output of the cell, as a result of the lower diffusivity of the redox species.

#### b) The effect of redox couple concentration

It was hypothesised that increasing the concentration of redox species in the gelled electrolytes could help to address the mass transfer limitations. However, the trade-off in this approach is that the  $S_e$  of a redox couple is commonly inversely related to the concentration in the electrolyte, and would thus decrease at higher concentrations.<sup>[6]</sup> To study the effect of redox couple concentration on  $S_e$ , diffusion coefficient and cell performance, the concentration of  $[\text{Co}(\text{bpy})_3]^{2+/3+}[\text{NTf}_2]_{2/3}$  in MPN was varied between 0.05 M and 0.25 M in both the liquid and gelled electrolyte.

Increasing the concentration of the redox couple led to a decrease in  $S_e$  (Figure 5a) and also had a detrimental effect on the diffusivity in both the liquid and gelled electrolytes (Figure 5b). This is attributed to an increase in the viscosity of the liquid and increased solidification of the gel at higher redox couple concentrations. This is supported by the thermal analysis (Figure S6), which shows that the PVDF gel with 0.25 M redox couple has a higher melting point than the gel with lower redox couple concentration.

The power density of the thermocell was increased by ~50% from 6 to 9 mW/m<sup>2</sup>, by increasing the concentration of redox couple from 0.05 M to 0.1 M (Figure 5c and d). However, a higher concentration (0.25 M) of redox couple did not improve the cell performance further, which is attributed to the smaller  $S_e$  and

lower diffusion coefficient of the redox species at the higher concentration. Thus, the optimum redox couple concentration for the PVDF electrolyte, with this cell design and  $\Delta T$ , was concluded to be 0.1 M.

### c) The effect of thermocell electrode separation

The separation distance between the electrodes in the thermocell can affect the performance by influencing both the temperature gradient,  $\Delta T$ , and the mass transfer across the cell. While a smaller electrode separation can be desirable for improving the mass transfer of redox species between the two electrodes, it can have the disadvantage of increasing the heat transfer across the cell, particularly in thermally conductive liquid electrolyte systems. Any decrease in the  $\Delta T$  that can be maintained across the cell will result in a corresponding decrease in power output. However, it was proposed that the performance of the thermocell containing the PVDF gel electrolyte could be improved by decreasing the distance between the two electrodes as this cell is expected to have limited thermal convection and, consequently, less heat transfer compared to the liquid-electrolyte based device.

To examine this, the performance of the cell containing 5 wt% PVDF with 0.05 M  $[\text{Co}(\text{bpy})_3]^{2+/3+}[\text{NTf}_2]_{2/3}$  in MPN was studied by decreasing the distance between the two electrodes from 10 mm to 5 mm, 2.5 mm and 1 mm (Figure 6a, b). A consistent open circuit voltage in the cell with the gelled electrolyte, even with an electrode separation of 1 mm, indicated that a consistent temperature gradient could be maintained across the cell. By decreasing the distance between the two electrodes, a significant improvement in power and current density of cell was achieved. The power density was increased from 6 to 14  $\text{mW}/\text{m}^2$  ( $= 0.0037$  to  $0.0087 \text{ mW}/\text{m}^2\text{K}^2$ ) after decreasing the electrode separation from 10 to 1 mm.

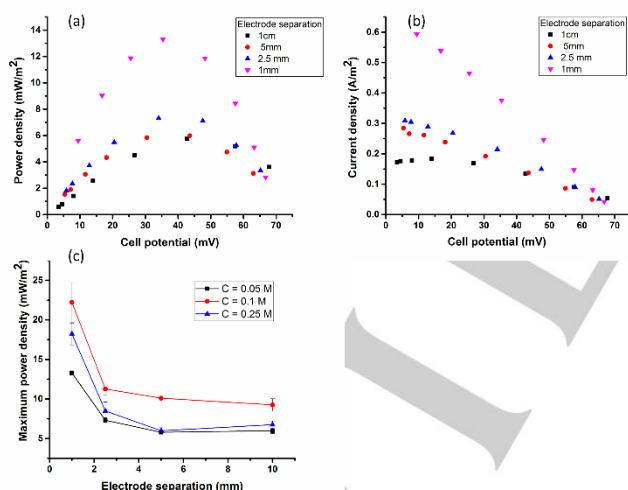


Figure 6. The effect of electrode separation on the (a) power and (b) current density of the cell using PVDF gel electrolyte (5 wt% PVDF, 0.05 M  $[\text{Co}(\text{bpy})_3]^{2+/3+}[\text{NTf}_2]_{2/3}$  in MPN,  $T_{\text{cold}} = 20^\circ\text{C}$ ,  $T_{\text{hot}} = 60^\circ\text{C}$ ), (c) the effect of concentration of redox couple and electrode separation on the maximum power density of the cell (5 wt% PVDF with 0.05, 0.1 or 0.25 M  $[\text{Co}(\text{bpy})_3]^{2+/3+}[\text{NTf}_2]_{2/3}$  in MPN),  $T_{\text{cold}} = 20^\circ\text{C}$ ,  $T_{\text{hot}} = 60^\circ\text{C}$ .

Finally, to investigate any further optimisation of the cell containing the PVDF gel electrolyte, the effect of electrode separation on cell performance was studied with different concentrations of redox couple (0.05, 0.1 and 0.25 M, Figure 6c). The same trend with redox couple concentration is observed for the thinner cell as is discussed above for the 10 mm cell, with the highest power density achieved using the 0.1 M electrolyte. Decreasing the electrode separation from 10 to 1 mm increased the maximum power density of cell from 9.5 to 23  $\text{mW}/\text{m}^2$  ( $= 0.006$  to  $0.0144 \text{ mW}/\text{m}^2\text{K}^2$ ). The maximum powers achieved here using the optimised device compare well to previously reported thermocells utilising gelled aqueous-based electrolytes discussed above. Incorporating the cells into arrays could enable further increases in power output.

### Extended operation of the PVDF-based thermocell

The thermocell technology relies on the presence of a temperature gradient between the two electrodes to continuously convert thermal energy to electricity. In other words, a thermocell is an energy conversion device that does not discharge in the way that a battery does - it should be able to operate continuously as long as there is a temperature gradient across the cell. However, any decomposition of the electrodes or electrolyte upon long-term operation would negatively affect the device performance. To assess this, longer-term testing of the PVDF gel electrolytes was performed using a cell with the optimised parameters identified above: electrode separation of 1 mm, with 5 wt % PVDF and 0.1 M  $[\text{Co}(\text{bpy})_3]^{2+/3+}[\text{NTf}_2]_{2/3}$  in MPN. The performance of this gelled electrolyte was compared with that of the optimum liquid electrolyte device, i.e. in a cell with electrode separation of 1 cm (Figure 7).

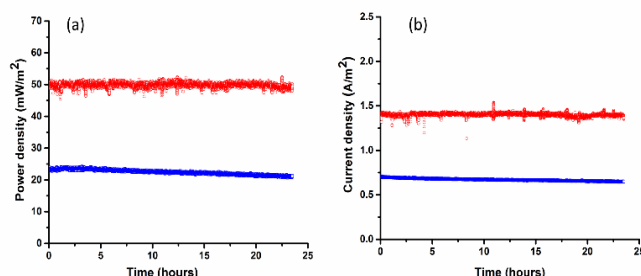


Figure 7. Operation of the thermocell over 24 hours: (a) power density and (b) current density of the cell containing: (○) liquid (0.1 M  $[\text{Co}(\text{bpy})_3]^{2+/3+}[\text{NTf}_2]_{2/3}$  in MPN, electrode separation = 10 mm), or (□) solid (5 wt% PVDF with 0.1 M  $[\text{Co}(\text{bpy})_3]^{2+/3+}[\text{NTf}_2]_{2/3}$  in MPN, electrode separation = 1 mm).  $T_{\text{cold}} = 20^\circ\text{C}$ ,  $T_{\text{hot}} = 60^\circ\text{C}$ .

After stabilisation of the temperature, the external resistance corresponding to that for which the cell had previously shown the maximum power density (Figure 6) was applied, and the experiment was run for 24 hours. Data was recorded after the usual 1 hour of stabilisation time. After 24 hours, the thermocell with the PVDF-gel electrolyte retained more than 92% of the initial performance. Some of this decrease is attributed to further equilibration of the Soret effect, which can take many hours.<sup>[3b]</sup> However, the open circuit voltage, measured to be 70 mV before

operation, remained unchanged, which also demonstrates the stability of the device.

## Conclusions

The synthesis, characterisation and thermocell application of new quasi-solid state electrolytes for thermal energy harvesting using the  $[\text{Co}(\text{bpy})_3]^{2+/3+}$  redox couple are reported. To the best of our knowledge, this is the first report on the gelation of non-aqueous electrolytes for thermocell technologies. Use of a cobalt redox couple in MPN gelled with either PVDF or PVDF-HFP provides an opportunity to design a leak-free thermocell device utilising a high, positive Seebeck coefficient redox couple. This quasi-solid state electrolyte could be used in a thermocell array, in combination with a gel containing the  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  redox couple or other negative  $S_e$  couples, to further increase the power output.

The PVDF gel was concluded to be superior to PVDF-HFP as it has a higher melting point, allows faster diffusion of the redox species and supported higher thermocell powers. While the  $S_e$  of the redox couple was not affected by gelation with the polymers, a decrease in diffusivity of the redox ions was observed with both types of polymer. Gelation of the electrolyte caused a decrease in power density of the cell, which was attributed to limited mass transport as a result of suppressed thermal convection. However, by optimizing the concentration of redox couple and the electrode separation, the performance of the cell was significantly improved. Increasing the concentration of redox couple to 0.1 M, and decreasing the distance between the two electrodes to 1 mm, allowed optimisation of the cell performance and achieved up to 23 mW/m<sup>2</sup> (0.0144 mW/m<sup>2</sup>K<sup>2</sup>) power density with a  $\Delta T$  of 40 °C. The development of quasi-solid state electrolytes is important for flexible thermocell devices and is also cost effective as it allows harvesting of the same size of temperature gradient using less electrolyte.

## Experimental Section

### Materials

Polyvinylidene difluoride (PVDF) powder (KF850,  $M_w = 3 \times 10^5$  from Kureha Chemicals, Japan) and poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP) powder ( $M_w = 3.13 \times 10^5$  from Solvay, Belgium) were used as received. The redox couple  $[\text{Co}(\text{bpy})_3][\text{NTf}_2]_2/[\text{Co}(\text{bpy})_3][\text{NTf}_2]_3$  was synthesised as described previously,<sup>[9]</sup> and the purity confirmed by NMR.

Liquid electrolytes were prepared by dissolving equimolar amounts of  $[\text{Co}(\text{bpy})_3][\text{NTf}_2]_2$  and  $[\text{Co}(\text{bpy})_3][\text{NTf}_2]_3$  in MPN. For example, to prepare 0.05 M solution of  $[\text{Co}(\text{bpy})_3]^{2+/3+}[\text{NTf}_2]_{2/3}$  in MPN,  $[\text{Co}(\text{bpy})_3][\text{NTf}_2]_2$  (217 mg, 0.2 mmol) and  $[\text{Co}(\text{bpy})_3][\text{NTf}_2]_3$  (273 mg, 0.2 mmol) were dissolved in the minimum amount of MPN, mixed, and then the total volume of solution was increased to 4 ml by addition of MPN.

To prepare the gel electrolytes, polymer powder (PVDF or PVDF-HFP) was added to the liquid electrolyte and then the mixture was stirred at 120 °C under N<sub>2</sub> for 30 minutes to get a clear solution. Cooling to room temperature and resting for 10 or 30 minutes gave the gelled electrolyte.

### Characterisation

The Seebeck coefficient was measured using a non-isothermal H-cell setup, with two platinum wires as electrodes, shown in Figure S1. The potential difference was measured using a UNI-T UT803 TRMS voltmeter. Cyclic voltammetry (CV) was performed using a three-electrode set-up using platinum as the working electrode (1.6 mm diameter, ASL, Japan) and two platinum wires as counter and reference electrodes, scanning between -1 V and +1 V at scan rates of 50 mV/s shown in Figure 1.

Chronoamperometry was used to measure the diffusivity of the  $[\text{Co}(\text{bpy})_3]^{2+/3+}$  ions.<sup>[19]</sup> The diffusion coefficient was calculated using the Cottrell equation (Eq. 2), measured by applying  $\pm 1$  V potential for 10 seconds.

$$I = nFAC_0D_0\pi^{-1/2}t^{-1/2} \quad \text{Eq. 2}$$

Where  $I$  is current (A),  $n$  is the stoichiometric number of electrons involved in the reaction,  $F$  is Faraday's constant (96,485 C/equivalent),  $A$  is electrode area (cm<sup>2</sup>),  $C_0$  is concentration of electroactive species (mol/cm<sup>3</sup>),  $D_0$  is diffusion constant for electroactive species (cm<sup>2</sup>/s) and  $t$  is time (s).

The thermocell setup used is shown in Figure S2. A Teflon cell with a 9 mm internal diameter representing the active electrode area, and electrode spacing of 10, 5, 2.5 or 1 mm, equipped with two platinum disks (18 mm diameter), was used. The temperature of the cold electrode was kept constant using a TE Technology cold plate cooler CP-031, while the temperature of the hot electrode was increased using a cartridge heater inside a copper block, connected to a Manson NP-9613 DC and regulated power supply, all controlled by the temperature controller (Novous NI020) and Pt100 temperature sensors at the hot and cold electrodes. The accuracy of the both hot and cold temperature control was  $\pm 0.1$  °C. The performance of the thermocell was measured using a Bio-Logic SP-200 potentiostat. Different resistances were applied using the Constant Load Discharge (CLD) technique, and EC-Lab (Bio-logic) software was used to collect the data. In order to ensure that steady state cell performance was measured, for each applied resistance enough time (60 minutes) was given to allow the voltage and power output to become constant. Extracting data from EC-Lab software, the current and power density was calculated using the averaged final 60 seconds of power and current data. The maximum power is obtained when the external resistance is equal to the internal resistance. The maximum power density was determined by plotting the power density as a function of the cell voltage, as shown in Figures 2, 4 and 5.

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- [1] A. J. DeBethune, T. S. Licht, N. Swendeman, *J. Electrochem. Soc.* **1959**, *106*, 616-625.
- [2] H. Ohta, S. Kim, Y. Mune, T. Mizoguchi, K. Nomura, S. Ohta, T. Nomura, Y. Nakanishi, Y. Ikuhara, M. Hirano, *Nat. Mater.* **2007**, *6*, 129-134.
- [3] a) B. Burrows, *J. Electrochem. Soc.* **1976**, *123*, 154-159; b) T. I. Quickenden, Y. Mua, *J. Electrochem. Soc.* **1995**, *142*, 3985-3994.
- [4] M. Dupont, D. MacFarlane, J. Pringle, *Chem. Comm.* **2017**, *53*, 6288-6302.
- [5] a) E. L. Yee, R. J. Cave, K. L. Guyer, P. D. Tyma, M. J. Weaver, *J. Am. Chem. Soc.* **1979**, *101*, 1131-1137; b) S. Sahami, M. J. Weaver, *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *122*, 155-170; c) S. Sahami, M. J. Weaver, *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *124*, 35-51.

- [6] T. J. Kang, S. Fang, M. E. Kozlov, C. S. Haines, N. Li, Y. H. Kim, Y. Chen, R. H. Baughman, *Adv. Funct. Mater.* **2012**, *22*, 477-489.
- [7] a) Y. Yamato, Y. Katayama, T. Miura, *J. Electrochem. Soc.* **2013**, *160*, H309-H314; b) T. Migita, N. Tachikawa, Y. Katayama, T. Miura, *Electrochemistry* **2009**, *77*, 639-641.
- [8] T. J. Abraham, D. R. MacFarlane, J. M. Pringle, *Energy Environ. Sci.* **2013**, *6*, 2639-2645.
- [9] W. T. Grubb, *Nature* **1958**, *181*, 338-339.
- [10] L. Jin, G. W. Greene, D. R. MacFarlane, J. M. Pringle, *ACS Energy Lett.* **2016**, *1*, 654-658.
- [11] J. Wu, J. J. Black, L. Aldous, *Electrochim. Acta* **2017**, *225*, 482-492.
- [12] P. Yang, K. Liu, Q. Chen, X. Mo, Y. Zhou, S. Li, G. Feng, J. Zhou, *Angew. Chem.* **2016**, *128*, 12229-12232.
- [13] W. B. Chang, C. M. Evans, B. C. Popere, B. M. Russ, J. Liu, J. Newman, R. A. Segalman, *ACS Macro Lett.* **2015**, *5*, 94-98.
- [14] L. Zhang, T. Kim, N. Li, T. J. Kang, J. Chen, J. M. Pringle, M. Zhang, A. H. Kazim, S. Fang, C. Haines, *Adv. Mater.* **2017**, *29*.
- [15] a) M. B. Achari, V. Elumalai, N. Vlachopoulos, M. Safdari, J. Gao, J. M. Gardner, L. Klöo, *Phys. Chem. Chem. Phys.* **2013**, *15*, 17419-17425; b) W. Xiang, W. Huang, U. Bach, L. Spiccia, *Chem. Comm.* **2013**, *49*, 8997-8999.
- [16] P. A. Lay, N. S. McAlpine, J. T. Hupp, M. J. Weaver, A. M. Sargeson, *Inorg. Chem.* **1990**, *29*, 4322-4328.
- [17] a) Y. Saito, H. Kataoka, C. Capiglia, H. Yamamoto, *J. Phys. Chem. B* **2000**, *104*, 2189-2192; b) M. Noor, M. Buraidah, M. Careem, S. Majid, A. Arof, *Electrochim. Acta* **2014**, *121*, 159-167.
- [18] a) C.-H. Lin, A. Gunawan, P. E. Phelan, D. A. Buttry, V. Mujica, R. A. Taylor, R. Prasher, in *ASME 2012 International Mechanical Engineering Congress and Exposition*, American Society of Mechanical Engineers **2012**, 541-547; b) P. F. Salazar, S. Kumar, B. A. Cola, *J. Appl. Electrochem.* **2014**, *44*, 325-336; c) A. Gunawan, H. Li, C.-H. Lin, D. A. Buttry, V. Mujica, R. A. Taylor, R. S. Prasher, P. E. Phelan, *Int. J. Heat Mass Transfer* **2014**, *78*, 423-434; d) T. Quickenden, Y. Mua, *J. Electrochem. Soc.* **1995**, *142*, 3652-3659.
- [19] G. Denuault, M. V. Mirkin, A. J. Bard, *J. Electroanal. Chem. Interfacial Electrochem.* **1991**, *308*, 27-38.