

Quasi-solid-State Electrolytes for Low-Grade Thermal Energy Harvesting using a Cobalt Redox Couple

Abuzar Taheri,^[a] Douglas R. MacFarlane,^[b] Cristina Pozo-Gonzalo,^[a] and Jennifer M. Pringle^{*[a]}

Thermoelectrochemical cells, also known as thermocells, are electrochemical devices for the conversion of thermal energy directly into electricity. They are a promising method for harvesting low-grade waste heat from a variety of different natural and manmade 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-methoxy-

propionitrile (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 optimizing the concentration of the redox couple and the separation between the hot and cold electrodes, and the stability of the device over 25 h 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 into electricity can be achieved by using thermoelectric or thermoelectrochemical devices. Energy conversion in these technologies is based on the Seebeck effect, which yields a potential difference (ΔV) as a result of a temperature gradient (ΔT) across the device.^[1] Thermoelectrochemical cells, also known as thermocells, are an attractive technology because they can achieve higher Seebeck coefficient (S_e) than thermoelectric generators and there is the possibility to make lower costing devices. The highest reported S_e to date for inorganic thermoelectric devices is $850 \mu\text{V K}^{-1}$,^[2] this value is lower than the Seebeck coefficients reported for 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 dependent.^[3] Hold-

ing the two electrodes at different temperatures leads to a temperature gradient (ΔT) across the cell and produces a potential difference (ΔV). 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 (ΔS) of the redox reaction [Eq. (1)]:

$$S_e = \frac{\Delta V}{\Delta T} = \frac{\Delta S}{nF} \quad (1)$$

in which n is the stoichiometric number of electrons involved in the reaction and F is the Faraday constant.^[3]

For the development of efficient thermoelectrochemical cells, the Seebeck coefficient is one of the key parameters that needs to be optimized, as it dictates the open-circuit voltage that can be achieved.^[4] 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 in the redox reaction and S_e is affected by interaction between the redox ions with the solvent. For example, the entropy of transition-metal-based redox couples was studied by Weaver et al.^[5] and was shown to be dependent on both the ligand and solvent. Nevertheless, the exact relationship between different solvent parameters such as acceptance number, donor number, and polarity and the Seebeck coefficient of the redox electrolyte is still not well understood.

[a] A. Taheri, Dr. C. Pozo-Gonzalo, Prof. J. M. Pringle
ARC Centre of Excellence for Electromaterials Science
Deakin University
221 Burwood Highway
Burwood, VIC 3125 (Australia)
E-mail: jenny.pringle@deakin.edu.au

[b] Prof. Dr. D. R. MacFarlane
School of Chemistry
Monash University
Wellington Road
Clayton, VIC 3800 (Australia)

Supporting Information and the ORCID identification number(s) for the author(s) of this article can be found under:
<https://doi.org/10.1002/cssc.201800794>.

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 $^{-1}$ depending on the concentration of the redox couple.^[6] To allow the use of the $[Fe(CN)_6]^{3-/4-}$ redox couple in an ionic liquid, (BMP) $_3[Fe(CN)_6]$ (BMP = 1-butyl-1-methylpyrrolidinium) was prepared,^[7] and it gave a S_e of -1.49 mV K $^{-1}$ if dissolved in 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide ([C $_4$ mpyr][NTf $_2$]). The use of a cobalt bipyridyl redox couple in high-boiling organic solvents can also allow access to a 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) in organic solvents such as 3-methoxypropionitrile (MPN), dimethyl sulfoxide (DMSO), and ionic liquids (ILs) gives a S_e of 1.5 – 2.2 mV K $^{-1}$.^[4] The use of molecular solvents or ILs also allows operation of the thermocell with a hot electrode temperature of 130 °C, thereby achieving high power densities.^[8]

Although the high ionic conductivities of liquid electrolytes are highly advantageous for electrochemical devices, thermocells in which liquid electrolytes are used 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 summarized 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 reported the gelation and thermocell application of cobalt-based redox electrolytes, the use of which can be advantageous for achieving high S_e values. One of the unique challenges in this avenue of research is achieving a quasi-solid-state electrolyte with 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 sulfonic acid and formaldehyde) in copper sulfate solution, a quasi-solid-state electrolyte was prepared without significantly affecting S_e .^[9] In that work, only potentials were measured; full devices were not prepared.

Different quantities of cellulose (2.5–20 wt%) were 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.^[10] The optimal cellulose concentration was determined to be 5 wt%, at which an optimum balance of mechanical properties, S_e , and diffusion coefficients was achieved. This yielded thermocell power densities only 20% less than that of the liquid system.

Gelation of aqueous 0.1 M $K_{3/4}[Fe(CN)_6]^{3-/4-}$ was also investigated by using gelatine, agar agar (agarose), and poly(sodium acrylate).^[11] By addition of different quantities of these gelation agents, it was found that agar agar and poly(sodium acrylate) formed effectively gelled electrolytes. The maximum reported power densities of thermocells containing agar agar gel and poly(sodium acrylate) gel were approximately 0.13 and 0.5 mW m $^{-2}$, respectively ($=0.0003$ and 0.0012 mW m $^{-2}$ K $^{-2}$) if $\Delta T = 20$ °C ($T_{hot} = 35$ °C and $T_{cold} = 15$ °C). The agar agar gel elec-

trolyte, which had more robust mechanical properties, showed a lower current density than the poly(sodium acrylate) gel owing to the lower diffusion coefficient of the redox ions.

Polyvinyl alcohol (PVA) was used for gelation of aqueous electrolytes and for designing a wearable thermocell device.^[12] 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 the Seebeck coefficient (-1.21 and 1.02 mV K $^{-1}$, 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 $\Delta T = 10$ °C) was achieved. The maximum power density produced by this series-connected device was 0.0236 mW m $^{-2}$ K $^{-2}$ if $\Delta T = 20$ °C.

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

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, the 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, that is, in an n-type and p-type series connect,^[14] to increase power output and to enable the development of more commercially viable devices.

Prior research in the dye-sensitized solar cell (DSSC) field showed that 1.5–10 wt% polyvinylidene difluoride (PVDF) or poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP) could be used to gel $[Co(bpy)_3]^{2+/3+}[NTf_2]_{2/3}$ in MPN or acetonitrile.^[15] A small increase in the cell performance with PVDF was observed compared to that observed with the liquid electrolyte,^[15a] whereas the use of PVDF-HFP improved the long-term stability.^[15b] As our prior research achieved a S_e of 2.19 mV K $^{-1}$ for $[Co(bpy)_3]^{2+/3+}[NTf_2]_{2/3}$ in MPN,^[8] this was identified as the best redox system for developing into a quasi-solid-state electrolyte. Thus, herein we report, for the first time, the development of quasi-solid-state electrolytes for thermal energy harvesting by 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-based gel, the device performance was optimized by investigating the effect of the concentration of the redox couple and the 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 $[\text{Co}(\text{bpy})_3]^{2+/3+}[\text{NTf}_2]_{2/3}$ in MPN was sufficient to produce a quasi-solid electrolyte (Figure 1). The gel with PVDF was produced after 10 min standing at room temperature after the initial heating process at 120 °C, whereas the PVDF-HFP-based gel needed 30 min to solidify after cooling to room temperature.

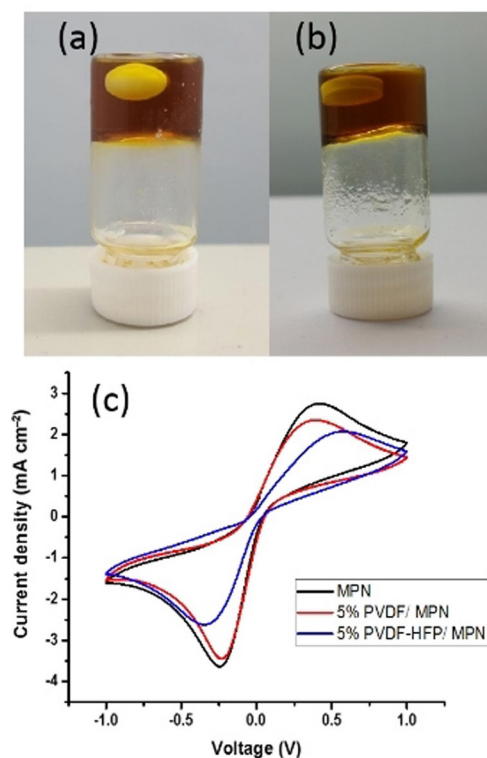


Figure 1. Quasi-solid state electrolytes containing 0.05 M $[\text{Co}(\text{bpy})_3]^{2+/3+}[\text{NTf}_2]_{2/3}$ in MPN gelled with a) 5 wt% PVDF and b) 5 wt% PVDF-HFP; c) electrochemical behavior of the redox electrolytes before and after gelation measured by using a three-electrode cell equipped with a platinum working electrode and two platinum wires as the counter and pseudoreference electrodes at a scan rate of 50 mV s⁻¹.

Analysis of the rheological properties of the PVDF- and PVDF-HFP-based electrolytes (Figures S3–S5 in the Supporting Information) confirmed that both samples were in a gel form. The PVDF gel electrolyte kept its form over a temperature range of 25 to 70 °C, and only a small decrease in the storage modulus was observed at high temperatures. However, for the PVDF-HFP gel, a sharp decrease in the storage modulus was observed at 60 °C, and differential scanning calorimetry showed that this gel had a lower melting point than the PVDF gel (Figure S6). Thus, the physical properties of the PVDF gel appear to be 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 .^[5,16] However, the addition of PVDF or PVDF-HFP to the $[\text{Co}(\text{bpy})_3]^{2+/3+}$ redox electrolyte did not significantly affect S_e (Table 1, experimental details in

Table 1. Effects of gelation of the electrolyte on the Seebeck coefficient (S_e) and the diffusion coefficient (D) at 25 °C.

Electrolyte	S_e [mV K ⁻¹]	D [10 ⁶ cm ² s ⁻¹] $[\text{Co}(\text{bpy})_3]^{2+}$	$[\text{Co}(\text{bpy})_3]^{3+}$
MPN	1.81 ± 0.03	5.00 ± 0.39	4.90 ± 0.27
5 wt% PVDF-MPN	1.80 ± 0.02	4.63 ± 0.13	4.21 ± 0.09
5 wt% PVDF-HFP-MPN	1.84 ± 0.01	4.48 ± 0.15	3.55 ± 0.25

Figure S1 in the Supporting Information). This suggests an absence of any strong interactions between the polymer chains and the redox species and, consequently, a negligible effect on the entropy change in the redox reaction. Thus, in spite of gelation of the electrolyte, the S_e of the quasi-solid-state electrolytes remains high enough to be promising for further development of the thermocells.

To maintain 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 revealed that gelation did not cause a significant decrease in the diffusion coefficient (Table 1). The diffusivity of the $[\text{Co}(\text{bpy})_3]^{3+}$ ions in the PVDF-HFP gel was a little lower than that 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.^[17]

Cyclic voltammetry (Figure 1c) showed that the redox couple in the gelled electrolytes maintained electrochemically quasireversible behavior. However, there was an increase in the peak-to-peak separation in the PVDF-HFP-based gel and a more significant decrease in the 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 relative to that in the liquid system, and this is consistent with an increase in the mass-transport resistance and a decrease in the ionic conductivity. Thus, the electrochemical characterization 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 were held at different temperatures and the power and current output were 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 electrolyte with a hot electrode temperature of 60 °C, a 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 stabilize compared to the cell with the liquid electrolyte. This was due to limited convection and mass transport in the gelled systems, and thus, much longer stabilization times (60 min at each resistance) were used to ensure steady-state measurements.

The PVDF-based gel electrolyte gave a maximum power density of 6 mW m⁻², which is better performance than the PVDF-HFP gel electrolyte (4.5 mW m⁻²). Using a liquid MPN-based electrolyte in the same cell with the same redox-couple concentration and the same ΔT resulted in a power density of approximately 48 mW m⁻². Given the similar Seebeck coefficient and a relatively small decrease in the diffusion coefficient of the 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.^[3b,6,18] Strategies to improve significantly the power output of the gelled electrolyte system by addressing some of the mass-transport limitations through cell optimization 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.^[18b]

To address the mass-transport limitation and to improve the power and current density of the cells containing the gelled electrolytes, the concentration of the redox couple and separation of the electrodes were optimized, as discussed below. The effects of polymer content, concentration of the redox couple, and electrode separation were studied by 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.

Optimization of the PVDF-based gel and thermocell design

The effect of polymer content

The amount of polymer used for gelation of the redox-active liquid electrolyte affected the mechanical properties of the resulting quasi-solid-state electrolyte, as shown in Figure 3. An amount of 2.5 wt %

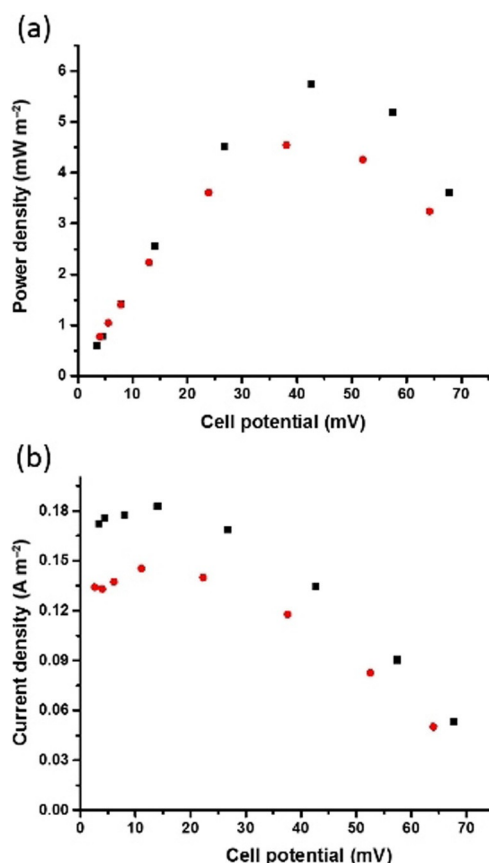


Figure 2. a) Power density and b) current density of thermocells containing gelled electrolyte: 0.05 M [Co(bpy)₃]^{2+/3+} [NTf₂]_{2/3} in MPN gelled with either 5 wt % PVDF (■) or PVDF-HFP (●); electrode separation = 1 cm, $T_{\text{cold}} = 20^{\circ}\text{C}$, $T_{\text{hot}} = 60^{\circ}\text{C}$.

was not sufficient to gel the material fully (Figure 3a), whereas upon using 15 wt % polymer a free-standing redox electrolyte was prepared (Figure 3d). To investigate the effect of the polymer content on the electrochemical properties and thermocell performance, different amounts of PVDF (2.5–15 wt %) were used for gelation of 0.05 M [Co(bpy)₃]^{2+/3+} [NTf₂]_{2/3} in MPN. Increasing the amount of polymer in the redox electrolyte steadily decreased the diffusion coefficient of the redox species (Figure 4b) as the material became progressively more solid. However, there was only a small effect on the Seebeck coefficient (Figure 4a).

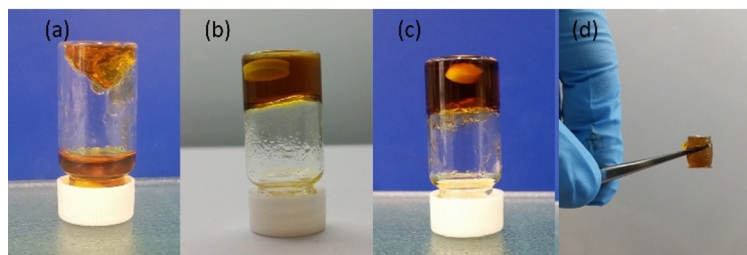


Figure 3. Polymer gel electrolytes containing different quantities of PVDF in 0.05 M [Co(bpy)₃]^{2+/3+} [NTf₂]_{2/3} in MPN: a) 2.5 wt % PVDF, b) 5 wt % PVDF, c) 7.5 wt % PVDF, and d) 15 wt % PVDF.

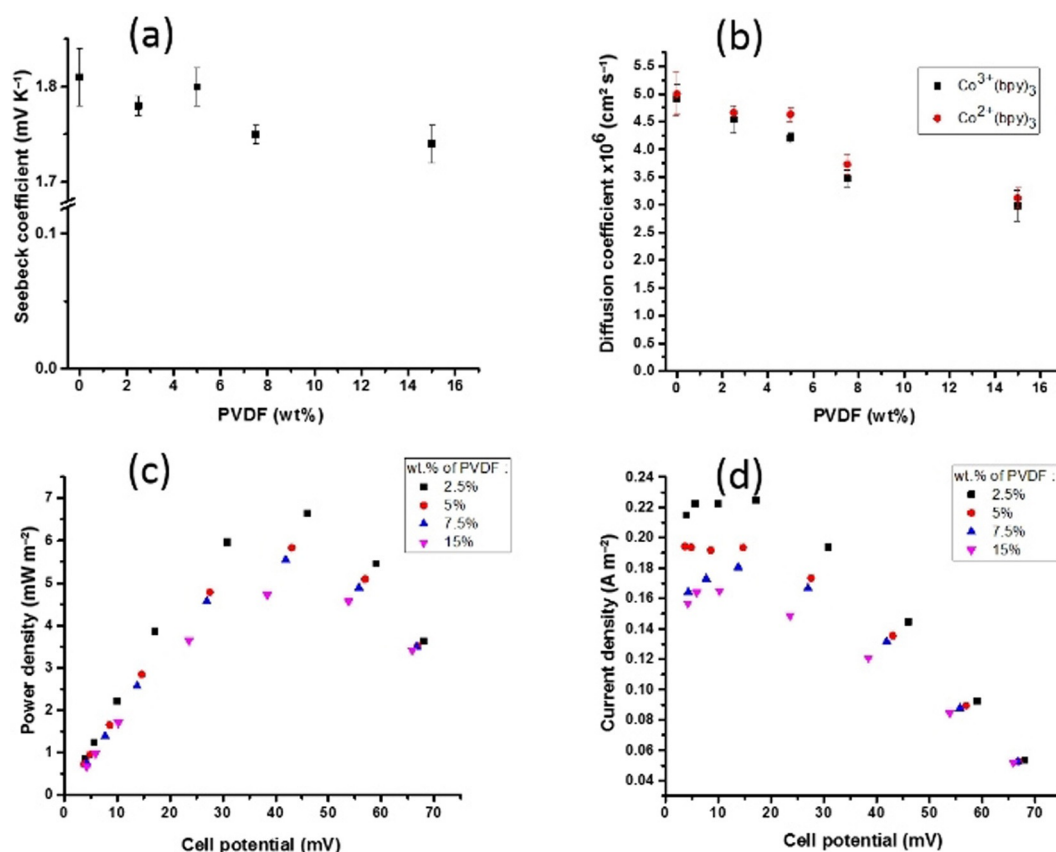


Figure 4. Effects of the PVDF content in 0.05 M $[\text{Co}(\text{bpy})_3]^{2+/3+}[\text{NTf}_2]_{2/3}$ in MPN on a) the Seebeck coefficient, b) the diffusion coefficient of the redox species, c) the power density, and d) the current density of the thermocell; electrode separation = 1 cm, $T_{\text{cold}}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

The performance of the thermocell was also dependent on the polymer content. Although the gel electrolyte with 2.5 wt% PVDF showed better cell performance, it was not sufficiently solidified to 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 was observed as a result of the lower diffusivity of the redox species.

The effect of redox-couple concentration

It was hypothesized that increasing the concentration of the 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.^[6] To study the effect of the 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 and 0.25 M in both the liquid and gelled electrolytes.

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 (Fig-

ure 5b). This was 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 thermal analysis (Figure S6), which showed that the PVDF gel with a 0.25 M redox couple had a higher melting point than the gel with a lower redox-couple concentration.

The power density of the thermocell was increased by approximately 50% from 6 to 9 mW m^{-2} by increasing the concentration of the redox couple from 0.05 to 0.1 M (Figure 5c,d). However, a higher concentration (0.25 M) of the redox couple did not improve the cell performance further, which was 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 ΔT , was concluded to be 0.1 M.

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 (ΔT) and the mass transfer across the cell. Whereas 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 ΔT that can be

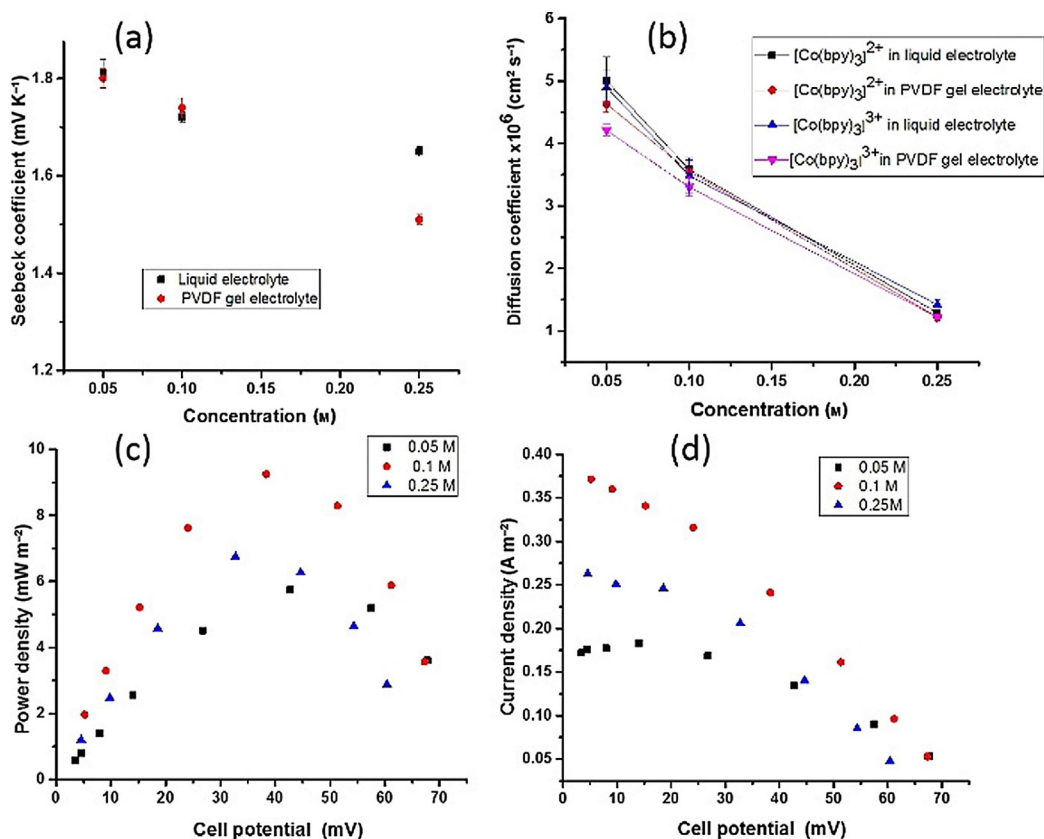


Figure 5. Effects of the concentration of the redox couple in MPN-based electrolyte before and after gelation on a) the Seebeck coefficient, b) the diffusion coefficient of the redox ions, c) the power density, and d) the current density of the thermocell containing PVDF gel electrolyte (5 wt% PVDF with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

maintained across the cell will result in a corresponding decrease in the 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 was expected to have limited thermal convection and, consequently, less heat transfer than the liquid-electrolyte-based device.

To examine this, the performance of the cell containing 5 wt% PVDF with 0.05 M $[\text{Co}(\text{bpy})_3]^{2+/3+}$ and $[\text{NTf}_2]_{2/3}$ in MPN was studied by decreasing the distance between the two electrodes from 10 mm through 5 and 2.5 mm to 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, significant improvements in the power and current density of the cell were achieved. The power density was increased from 6 to 14 mW m^{-2} ($=0.0037$ to $0.0087 \text{ mW m}^{-2} \text{ K}^{-2}$) after decreasing the electrode separation from 10 to 1 mm.

Finally, to investigate any further optimization of the cell containing the PVDF gel electrolyte, the effect of electrode separation on cell performance was studied with different concentrations of the redox couple (0.05, 0.1, and 0.25 M; Figure 6c). The same trend as that observed for the redox-couple concentration was observed for the thinner cell, as discussed above for the 10 mm cell, and the highest power density was

achieved by using the 0.1 M electrolyte. Decreasing the electrode separation from 10 to 1 mm increased the maximum power density of the cell from 9.5 to 23 mW m^{-2} ($=0.006$ to $0.0144 \text{ mW m}^{-2} \text{ K}^{-2}$). The maximum powers achieved here by using the optimized device compare well to the maximum powers of previously reported thermocells utilizing the gelled aqueous-based electrolytes discussed above. Incorporating the cells into arrays could enable a further increase in the 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 convert thermal energy continuously into electricity. Thus, 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 by using a cell with the optimized parameters identified above: electrode separation of 1 mm with 5 wt% PVDF and 0.1 M $[\text{Co}(\text{bpy})_3]^{2+/3+}$ and $[\text{NTf}_2]_{2/3}$ in MPN. The performance of this gelled electrolyte was compared with

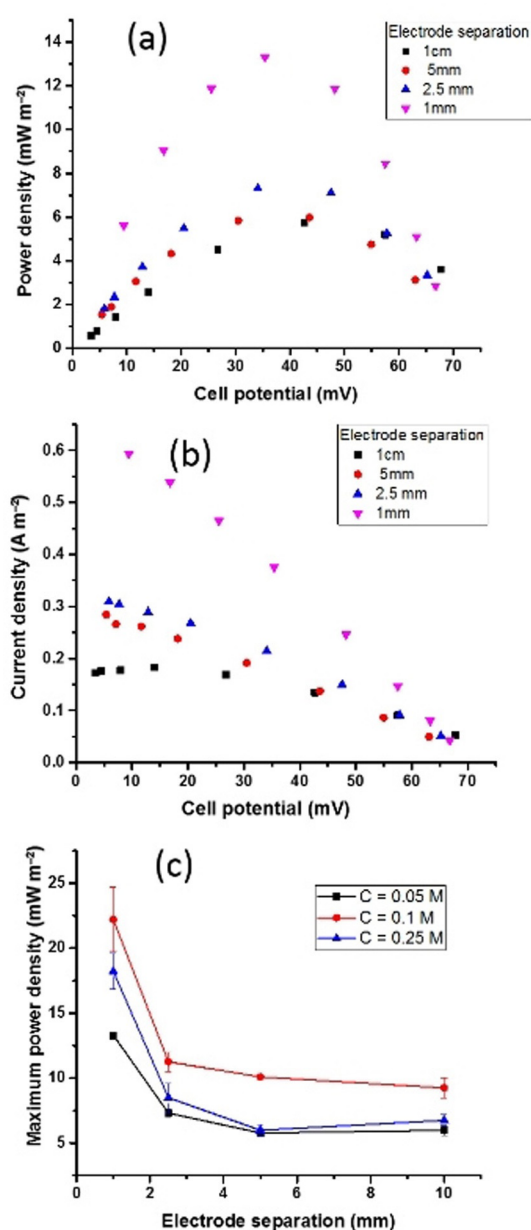


Figure 6. Effects of electrode separation on a) the power density and b) the current density of the cell by using PVDF gel electrolyte (5 wt% PVDF, 0.05 M $[\text{Co}(\text{bpy})_3]^{2+/3+}$ $[\text{NTf}_2]_{2/3}$ in MPN); $T_{\text{cold}} = 20^\circ\text{C}$, $T_{\text{hot}} = 60^\circ\text{C}$. c)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

that of the optimum liquid electrolyte device, that is, in a cell with an electrode separation of 1 cm (Figure 7).

After stabilization 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 h. Data were recorded after the usual 1 h of stabilization time. After 24 h, the thermocell with the PVDF gel electrolyte retained more than 92% of the initial performance. Some of this decrease can be attributed to further equilibration of the Soret effect, which can take many hours.^[3b] However, the open-circuit voltage, measured to be

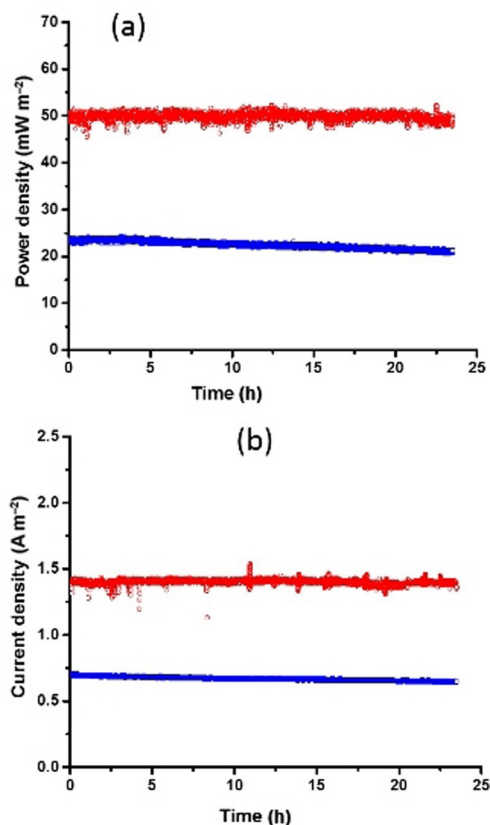


Figure 7. Operation of the thermocell over 24 h: a) power density and b) current density of the cell containing (○) liquid (0.1 M $[\text{Co}(\text{bpy})_3]^{2+/3+}$ $[\text{NTf}_2]_{2/3}$ in MPN, electrode separation = 10 mm) or (□) solid (5 wt% PVDF with 0.1 M $[\text{Co}(\text{bpy})_3]^{2+/3+}$ $[\text{NTf}_2]_{2/3}$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

70 mV before operation, remained unchanged, which also demonstrated the stability of the device.

Conclusions

The synthesis, characterization, and thermocell application of new quasi-solid-state electrolytes for thermal energy harvesting by using the $[\text{Co}(\text{bpy})_3]^{2+/3+}$ (bpy = 2,2'-bipyridyl) redox couple were reported. To the best of our knowledge, this is the first report on the gelation of non-aqueous electrolytes for thermocell technologies. The use of a cobalt redox couple in 3-methoxypropionitrile (MPN) gelled with either polyvinylidene difluoride (PVDF) or poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP) provided an opportunity to design a leak-free thermocell device utilizing a redox couple with a high, positive Seebeck coefficient (S_e). 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 increase the power output further.

The PVDF gel was concluded to be superior to PVDF-HFP as it has a higher melting point, allowed faster diffusion of the redox species, and supported higher thermocell powers. Whereas the S_e of the redox couple was not affected by gelation with the polymers, a decrease in the diffusivity of the

redox ions was observed with both types of polymers. Gelation of the electrolyte caused a decrease in the 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 the redox couple and the electrode separation the performance of the cell was significantly improved. Increasing the concentration of the redox couple to 0.1 M and decreasing the distance between the two electrodes to 1 mm allowed optimization of the cell performance; ultimately, the cell achieved a power density up to 23 mW m^{-2} ($0.0144 \text{ mW m}^{-2} \text{ K}^{-2}$) with a temperature gradient 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 by 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 synthesized as described previously,^[8] and the purity was confirmed by NMR spectroscopy.

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 a 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 a minimum amount of MPN and mixed, and then the total volume of solution was increased to 4 mL by the addition of MPN.

To prepare the gel electrolytes, the polymer powder (PVDF or PVDF-HFP) was added to the liquid electrolyte, and then the mixture was stirred at 120°C under a N_2 atmosphere for 30 min to get a clear solution. Cooling to room temperature and resting for 10 or 30 min gave the gelled electrolyte.

Characterization

The Seebeck coefficient was measured by using a non-isothermal H-cell setup, with two platinum wires as electrodes, shown in Figure S1. The potential difference was measured by using a UNI-T UT803 TRMS voltmeter.

Cyclic voltammetry (CV) was performed by using a three-electrode setup with platinum as the working electrode (1.6 mm diameter, ASL, Japan) and two platinum wires as the counter and reference electrodes and scanning between -1 and $+1$ V at a scan rate of 50 mV s^{-1} , as shown in Figure 1.

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

$$I = nFAC_0 D_0 \pi^{-1/2} t^{-1/2} \quad (2)$$

in which I [A] is the current, n is the stoichiometric number of electrons involved in the reaction, F is the Faraday constant (96485 C e^{-}

equivalent $^{-1}$), A [cm^2] is the electrode area, C_0 [mol cm^{-3}] is the concentration of the electroactive species, D_0 [$\text{cm}^2 \text{ s}^{-1}$] is the diffusion constant for the electroactive species, and t [s] is the time.

The thermocell setup used is shown in Figure S2. A Teflon cell with a 9 mm internal diameter representing the active electrode area and an 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, whereas the temperature of the hot electrode was increased by using a cartridge heater inside a copper block connected to a Manson NP-9613 DC and a regulated power supply, all controlled by the temperature controller (Novous NI020) and Pt100 temperature sensors at the hot and cold electrodes. The accuracy of both the hot and cold temperature controls was $\pm 0.1^\circ\text{C}$. The performance of the thermocell was measured by using a Bio-Logic SP-200 potentiostat. Different resistances were applied by using the Constant Load Discharge (CLD) technique, and EC-Lab (Bio-logic) software was used to collect the data. To ensure that steady-state cell performance was measured, for each applied resistance enough time (60 min) was given to allow the voltage and power outputs to become constant. Extracting data from EC-Lab software, the current and power density were calculated by using the averaged final 60 s of power and current data. The maximum power was obtained when the external resistance was 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.

Acknowledgements

The authors acknowledge funding from the Australian Research Council (ARC) through its Centre of Excellence program (CE140100012) and through the Australian Laureate Fellowship Scheme for D.R.M.

Conflict of interest

The authors declare no conflict of interest.

Keywords: cobalt • electrolyte • energy conversion • redox chemistry • thermoelectrochemical cells

- [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. Ikahara, M. Hirano, *Nat. Mater.* **2007**, *6*, 129–134.
- [3] a) B. Burrows, *J. Electrochem. Soc.* **1976**, *123*, 154–159; b) T. I. Quicken-den, Y. Mua, *J. Electrochem. Soc.* **1995**, *142*, 3985–3994.
- [4] M. Dupont, D. MacFarlane, J. Pringle, *Chem. Commun.* **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. Int. Ed.* **2016**, *55*, 12050–12053; *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.* **2016**, *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*, 1605652.
- [15] a) M. B. Achari, V. Elumalai, N. Vlachopoulos, M. Safdari, J. Gao, J. M. Gardner, L. Kloo, *Phys. Chem. Chem. Phys.* **2013**, *15*, 17419–17425; b) W. Xiang, W. Huang, U. Bach, L. Spiccia, *Chem. Commun.* **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, Houston, TX, USA, **2012**, pp. 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.

Manuscript received: April 12, 2018

Revised manuscript received: June 5, 2018

Accepted manuscript online: June 6, 2018

Version of record online: July 10, 2018