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Redox-Active Quasi-Solid-State Electrolytes for Thermal Energy Harvesting

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ABSTRACT: Thermochemical cells (TECs) are a promising and cost-effective approach to harvesting waste thermal energy. For the widespread uptake of this new technology and the development of flexible, leak-free devices, solidification of the redox electrolyte is key. Thus, here we report the first quasi-solid-state electrolyte incorporating the ferri/ferrocyanide redox couple within a cellulose matrix. The electrolyte with 5 wt % cellulose achieved an optimum balance of mechanical properties, Seebeck coefficients, and diffusion coefficients and supported power outputs comparable to those of the liquid electrolyte systems.

The ability to efficiently utilize low-grade waste heat (e.g., below 130 °C) from industry or natural sources could make a considerable contribution to solving imminent global environmental and energy challenges, as well as providing an autonomous power supply for a range of independent low power sensors, controls, and wearable devices.¹ Thermoelectric²⁻⁶ and thermochemical⁷⁻¹³ devices directly convert thermal energy to electricity, utilizing a range of different technologies that are in various stages of development. The most mature and commercialized technology, the thermoelectric generator (TEG), is based on the Seebeck effect of semiconductors.^{1,14,15} One emerging area of application is that of wearable devices, designed to utilize waste body heat to power small portable electronics.⁴ However, harvesting these relatively low temperature sources of waste heat using TEGs is challenging as semiconductor-based devices are typically most effective at high temperatures and with large temperature differences.

An alternative device design, the thermochemical cell (TEC), has been attracting increasing attention for low-temperature applications.^{8,9,12,16-20} This concept makes use of the change in chemical potential of a reversible redox reaction with temperature to produce a potential gradient across the device. Thus, in a TEC, the two electrodes are held at different temperatures and separated by an electrolyte containing the redox couple. The Seebeck coefficient, S_e , describes the temperature dependence of the electrochemical potential, E ; thus, $S_e = \partial E / \partial T$.

The S_e of the redox electrolyte dictates the open-circuit voltage of the thermocell. For example, a 0.4 M equimolar potassium ferri/ferrocyanide ($K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$) solution, the benchmark electrolyte for TECs, gives $S_e = -1.4$ mV per Kelvin temperature difference. In comparison, for semiconductor TEGs, the S_e is generally only on the order of 100s of $\mu V K^{-1}$. This intrinsic advantage of the TEC is one of the reasons for the increasing research interest in these devices, which includes the development of high-surface-area carbon electrodes,¹² new high Seebeck coefficient cobalt-based redox couples,^{8,18} and the use of ionic liquid (IL) electrolytes to enable higher operating temperatures.^{19,20}

An important strategy for increasing the viability of TECs is the use of solid-state redox electrolytes to eliminate electrolyte leakage and enable the development of flexible devices. These might, for example, be manufactured by reel-to-reel or other printing processes. Solidification of the electrolyte is also advantageous for achieving the maximum ΔT across the device by elimination of convection, that is, it decreases the warming of the cold electrode by heat transfer that can occur by convection through the electrolyte from the hot electrode. While a separator can be used in liquid-based TECs,^{17,21} which can assist in minimizing this heat transfer, it does not eliminate liquid leakage. For viable flexible and leak-free devices, solidification of the electrolyte must be achieved at relatively low cost and without a significant decrease in Se or power generation. Here we report the first development of a quasi-solid-state redox electrolyte for TECs, formed by optimization of a cellulose matrix. The thermal energy harvesting performance of these novel materials with varying cellulose content is discussed.

A number of possible approaches to solidification of the aqueous solution were investigated, and cellulose was chosen as the polymer matrix as it did not suffer from the problems of brittleness, water loss, and volume shrinkage that we encountered with other biphasic or hydrogel systems (e.g., gelatin or poly(vinyl alcohol) based) that were attributed to additional cross-linking of the polymer backbones by the $\text{Fe}(\text{CN})_6^{3-/4-}$ ions. Quasi-solid-state electrolytes containing the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple were prepared by first making the cellulose matrix using a procedure described in ref 22 that was modified to utilize an ionic liquid-based solvent, as described in the Supporting Information. Synthesis of the cellulose matrix was followed by loading the cellulose matrix with the aqueous redox electrolyte by solvent exchange. Following this solvent exchange procedure, the IL was present in no higher than trace levels within the electrolyte. The electrolytes developed for use in this study were thus biphasic, composed of a defined cellulose network and a redox-active aqueous phase.

As discussed below, the interconnection between the pores depends on the cellulose content. Thus, here we refer to these biphasic systems as “quasi-solid-state electrolytes” rather than “hydrogels”; while this latter term is widely used in the literature and the exact definition of a “gel” is still the subject of debate,^{23,24} the insolubility of cellulose in water even at low concentrations indicates that this is not strictly a hydrogel according to the most accepted definition. Regardless, the mechanical properties of the new electrolyte systems developed here are highly suitable for the application, varying from a “soft sponge” at 2.5 wt % to a “tough rubber” at 20 wt %, with no evidence of fluid leakage even on bending. The systems with 5–10 wt % cellulose had the best balance between strength and flexibility, ideal for flexible devices. Figure 1a shows a photograph of the electrolyte with 5 wt % cellulose.

The influence of cellulose concentration on the Seebeck coefficient was measured using a U-tube cell filled with the electrolyte, described in full in the Supporting Information, by assessing the change in open-circuit voltage upon heating one side of the cell. Introduction of the cellulose polymer network had only a minor influence on Se, as shown in Figure 1a. There is a gradual decrease in the absolute magnitude of Se, from -1.4 mV K^{-1} for the liquid (0 wt % cellulose) to -1.32 mV K^{-1} for the electrolyte with 20 wt % cellulose. The Seebeck coefficient of a redox couple is directly related to the entropy change associated with the redox reaction,²⁵ most simply represented by the difference between the molar entropies of the two halves of the redox couple, $Se = \Delta S/nF$, where n is the number of electrons transferred and F is the Faraday constant. Thus, the change in Se suggests that containment of the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple within the hydrated cellulose matrix has a slight influence on the extent of structural rearrangement of the hydration shell that occurs upon electron transfer. However, the impact of cellulose content is relatively small, and the electrolyte with 5 wt %

cellulose shows the optimum mechanical and other properties along with an Se value of -1.38 mV K^{-1} .

For the successful development of quasi-solid-state electrolytes for TECs, it is important to achieve solidification while still maintaining sufficient mass transport rates for the redox couple. Thus, to assess the impact of cellulose content on this parameter, the diffusion coefficients of the $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ ions in the electrolytes was measured by chronoamperometry and calculated using the Cottrell equation.²⁶ The change in the diffusion coefficients with respect to cellulose concentration is shown in Figure 1c. As expected, both $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ ions diffuse more slowly in the electrolytes containing higher concentrations of cellulose. This is consistent with the increased solidity as the cellulose content is raised. However, the diffusion coefficients in the 2.5 wt % cellulose system only decreased by $\sim 37\%$ compared with those in solution. Given the significant change in the physical and mechanical nature of the electrolyte at this concentration, from a liquid to a free-standing, quasi-solid-state electrolyte, the decrease in mass transport rate may be considered relatively minor. At higher cellulose content, the mass transport limitations become more significant. It is likely that ion transport is impeded in these cases by the tortuous diffusion route created by the cellulose network.

The morphology of the electrolytes was further characterized by scanning electron microscopy (SEM). The SEM images (Figure 2) reveal the microstructure of the cleaved surfaces of freeze-dried electrolytes with 5 and 20 wt % cellulose, before incorporation of the redox solution. Under lower magnification, the 5 wt % sample shows uniform porosity of the cellulose fiber network and a flat cleavage surface, while the higher magnification reveals a honeycomb-like structure and relatively uniform pore size. In contrast, the 20 wt % cellulose sample shows more substantial cellulose agglomeration and a granular surface, and the higher magnification image reveals a structure with varying pore sizes and some closed pores. These contrasting morphologies show that as the concentration of cellulose is increased, the liquid channels become more restricted or even closed and, thus, the ion transport becomes more difficult. This is consistent with the measured decrease in diffusion coefficients at higher cellulose loading. However, the open honeycomb-like structure at only 5 wt % cellulose is ideal for the properties required here: high, almost liquid-like mass transport combined with solid mechanical properties.

To assess the thermal energy harvesting performance of the different electrolytes in the TEC, they were placed in a parallel plate cell with two identical nickel foil electrodes and a spacer to keep the dimension at $30 \times 10 \times 3 \text{ mm}$. Hot and cold electrode temperatures of 35 and 20 °C were used, representing a wearable type of application. Full details of the cell design and testing procedure are given in the Supporting Information. The current and power output performance of the different devices is shown in Figure 3.

Upon incorporation of the cellulose, to form the quasi-solid-state device, there was a relatively small decrease in power output. For example, the maximum power output of the TEC with the liquid electrolyte (0 wt % cellulose) was 18 mW m^{-2} , compared to 14 mW m^{-2} for the solidified system with 5 wt % cellulose. This clearly demonstrates the promise of these solid electrolytes. Analysis of the effect of cellulose content on TEC output shows that the device performance roughly falls into two domains. The devices with 10, 15, and 20 wt % cellulose exhibit similar maximum power outputs of $6\text{--}8 \text{ mW m}^{-2}$ and have more resistive behaviour evident in their current–voltage plots. In combination with the diffusion coefficient and morphological analysis, this indicates that the currents and power output are significantly limited by the mass transport. In comparison, the devices with 2.5 and 5 wt % cellulose show higher power output and less resistance to current flow, which is consistent with the more open solid electrolyte morphology and better transport

properties. The effect of the Seebeck coefficient on TEC performance of these two electrolyte systems is also evident; the slightly higher S_e with 5 wt % cellulose, compared to 2.5%, results in a higher open-circuit voltage, and in terms of TEC power output, this more than compensates for the lower diffusion coefficient.

In conclusion, we have demonstrated the feasibility of quasi-solid-state TECs through use of cellulose-based electrolytes. Even at relatively low loadings, the cellulose polymer network can provide sufficient mechanical support to form free-standing and flexible electrolytes with no leakage. The concentration of cellulose impacts both the mechanical and transport properties of the solid electrolyte systems. Thus, the cells utilizing 5 wt % cellulose to solidify the aqueous $\text{Fe}(\text{CN})_6^{3-/4-}$ system were found to exhibit an optimum morphology and Seebeck coefficient while also allowing sufficient mass transport rates to achieve cell power outputs close to those of the liquid system.

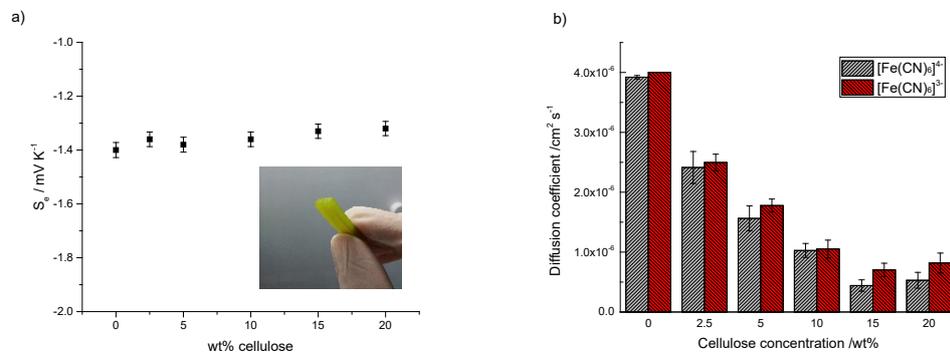


Figure 1. (a) Seebeck coefficients of the aqueous solution and the solidified electrolytes (error bars are based on the largest observed standard deviation for the different systems); the inset shows the physical appearance of the solid redox electrolyte with 5 wt % cellulose. (b) Diffusion coefficients of $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ in the solution and in the solid electrolytes at 22 °C.

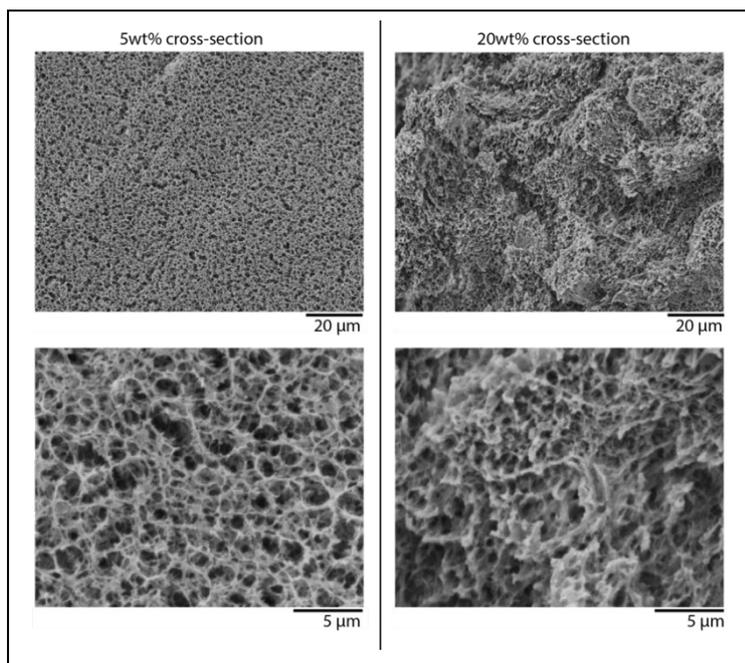


Figure 2. SEM images, at two different magnifications, of the cross sections of the quasi-solid-state electrolytes after freeze-drying, with 5 (left column) and 20 wt % (right column) cellulose.

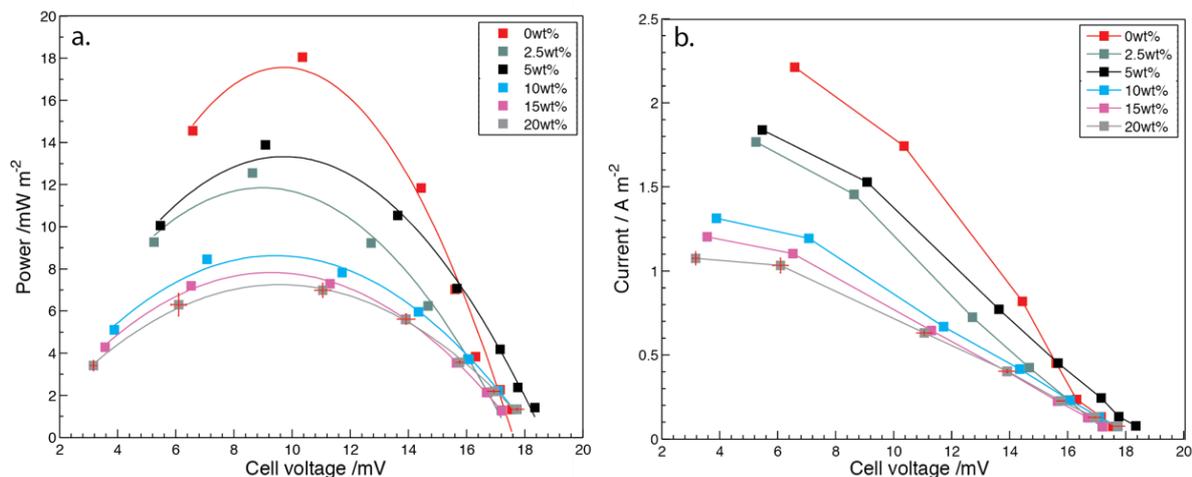


Figure 3. TEC power output using the quasi-solid-state electrolytes with different wt % cellulose concentrations: (a) power output as a function of cell voltage and (b) current output as a function of cell voltage. The hot and cold electrode temperatures were 35 and 20 °C, respectively. The typical uncertainty range is shown for the 20 wt % sample. Data for a cell with a liquid electrolyte (0 wt % cellulose) is included for comparison.

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