Supporting Information

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

Liyu Jin,† + George W. Greene,† Douglas R. MacFarlane, ‡ and Jennifer M. Pringle†*

† Deakin University, Geelong, Australia, ARC Centre of Excellence for Electromaterials Science, Institute for Frontier Materials. email: jenny.pringle@deakin.edu.au

‡ School of Chemistry, Monash University, Clayton, VIC 3800, Australia, ARC Centre of Excellence for Electromaterials Science.

† Current affiliation: Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK

Electrolyte preparation

The redox active quasi-solid state electrolytes were prepared by the following procedure\(^1\): 1) A known amount of cellulose powder (microcrystalline powder, purchased from Sigma-Aldrich) was mixed with the ionic liquid 1-ethyl-3-methylimidazolium diethylphosphate ([C\(_2\)mim][DEP], purchased from Merck, purity ≥ 98.0 %) at room temperature, to prepare slurries with 2.5, 5, 10, 15, 20 wt% of cellulose. 2) The homogeneous slurries were poured into a rectangular aluminium mold (30 x 10 x 3 mm), which was then placed in a furnace preheated to 100 °C. 4) The molds were kept at 100 °C for an hour and then cooled to room temperature in air. 5) The resultant solids were immersed in distilled water to leach out the [C\(_2\)mim][DEP]. 6) The resultant white solid materials were further leached with a 0.4 M equal-molar potassium ferri/ferrocyanide (K\(_3\)[Fe(CN)\(_6\)]/K\(_4\)[Fe(CN)\(_6\)]\) solution
for 24 hours, during which time the solution was refreshed twice. 7) The quasi-solid state electrolytes loaded with the redox couple were stored in the redox electrolyte solution ready for use.

**Seebeck coefficient measurements**

The Seebeck coefficients of the electrolytes were measured using the same general experimental procedure reported previously.\(^2\)\(^3\) However, in this case, platinum (Pt) wire electrodes were inserted into two identical solid electrolytes that were placed in two vials half filled with 0.4 M K\(_3\)[Fe(CN)\(_6\)]/K\(_4\)[Fe(CN)\(_6\)] solution. The solution did not make contact with the Pt wire electrodes but acted as a buffer to ensure that the redox concentration in the solids remained at 0.4 M and to ensure uniform heating/cooling of the solid electrolytes. The setup is shown in Figure S1. One side was then heated and the other side cooled, using a temperature controlled brass block with cartridge heater, and iced water, respectively. Note that for optimum power generation, it is the absolute size of \(S_e\) that is important rather than the sign.

![Figure S1: the U-tube setup for measurement of the Seebeck coefficient of the solid electrolyte electrolytes.](image)

**Diffusion coefficient measurements**

The same three-electrode electrochemical cell was used for the cyclic voltammetry (below) and diffusion coefficient measurements. The working and quasi-reference electrodes were Pt wires. These were inserted into solid electrolytes half-immersed in the 0.4 M redox solution, as described above. Only the counter electrode (Pt wire) was in direct contact with the solution, to minimise ohmic drop.

The diffusion coefficients of the redox species were measured using a chronoamperometry method based on the Cottrell equation,\(^4\) as shown below:
\[ I = \frac{nFA\sqrt{Dc}}{\sqrt{\pi t}} \]

where \( n \) is the number of electrons, \( F \) is Faraday's constant, \( A \) is the surface area of the working electrode, \( c \) is the concentration of the electroactive species and \( D \) is the diffusion coefficient to be measured. To use the Cottrell equation, the current-time response (\( I(t) \)) over 10 seconds was monitored by chronoamperometry (CA) using a variable multiple potentiostat (VMP3, Bio-logic) controlled by EC-Lab (10.44) software. The initial potential was set to the CV peak potential, determined by the prior CV tests. Depending on the redox species of interest, either the oxidation or a reduction peak potential of the CV was used (e.g. to measure the diffusion coefficient of \( \text{Fe(CN}_6\text{)}^{3-} \), the reduction peak potential was used). Each measurement was repeated three times for each redox species in different solid electrolytes to obtain the sample standard deviations. The data were plotted as current versus square root of time (\( \sqrt{t} \)) and fitted using EC-Lab.

The surface area of the working electrode (a thin Pt wire with fixed surface area masked by epoxy) was measured as follows: 1) A three-electrode electrochemical cell consisted of a working electrode (a standard planar Pt electrode with known surface area), a counter electrode and a quasi-reference electrode (both were Pt wires) placed in the 0.4 M \( \text{K}_3[\text{Fe(CN)}_6] / \text{K}_4[\text{Fe(CN)}_6] \) redox solution. A CA measurement was run for both halves of the redox couple and the diffusion coefficient (\( D_1 \)) was obtained by applying the Cottrell Equation. 2) The same CA measurement was run using the same electrochemical cell and the same redox solution as in step 1, but by replacing the standard working electrode by the masked Pt wire. The apparent diffusion coefficient (\( D_2 \)) was calculated assuming the surface area of the working electrode stayed the same. 3) The surface area of the masked Pt wire was then calculated by scaling the surface area of the standard electrode by a factor of \( \frac{\sqrt{D_2}}{\sqrt{D_1}} \).

**Cyclic voltammetry**

The same three-electrode electrochemical cell was used for both cyclic voltammetry (Figure S2) and diffusion coefficient measurements of the different electrolytes. The working, counter and quasi-reference electrodes were Pt wires. The CVs were conducted using a potentiostat (VMP3, Bio-Logic) controlled by EC-Lab (10.44) software with a scan rate of 50 mV/s.
Figure S2. Cyclic voltammograms of 0.4 M $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ solution and of the quasi-solid state electrolytes, at scan rate 50 mV s$^{-1}$, with different wt% cellulose concentrations.

**Scanning electron microscopy**

Scanning electron microscopy (SEM) images were taken on the freeze-dried cellulose-based solids prior to incorporation of the redox solution. The samples were first quenched with liquid nitrogen, quickly transferred into a freeze-dryer (CT-100, Heto), and freeze dried at – 40 °C for 24 hours. The dried samples were then sputter-coated with a thin layer of gold (about 30 nm) for imaging. The SEM (JEOL JCM-5000 NeoScope Benchtop) images were taken under 5 kV accelerating voltage.

**Thermoelectrochemical cell (TEC) testing**

Analysis of TEC performance was conducted using the apparatus shown in Figure S3, where the cell is placed between heating and cooling blocks. The cooling block was a cold plate cooler (CP-031, TETechnology Inc.) connected to a temperature controller (TC-48-20, TETechnology Inc.). The heating block was made of brass, with three cartridge heaters embedded that were controlled by a PID controller. For both the cold and hot temperature control, the accuracy was ±0.1 °C.
The solid electrolyte was fitted into a plastic cell frame (Figure S4.a) with inner cavity dimensions of $(30 \times 10 \times 3 \text{ mm})$. The two exposed surfaces of the electrolyte were covered by nickel foil electrodes (thickness of $0.03 \text{ mm}$, MTI Corp., Figure S4.b). Two G-clamps were used to ensure that good contact was achieved between the electrodes, the electrolyte and the temperature control blocks.

The TEC performance was assessed using a Potentiostat (SP-200, Bio-logic) using the **Constant Load Discharge (CLD)** technique. The test discharges the cells using a series of external loads and then calculates the maximum power output. There were 7 different resistances used per test, which were the same for each electrolyte system: $800$, $400$, $200$, $100$, $60$, $20$ and $10 \text{ Ohm}$. Each discharge step was set to $10 \text{ mins}$. Prior to testing, the cell was kept at open circuit for $30 \text{ minutes}$ to ensure that the hot and cold temperatures had stabilised. All the tests were conducted at the temperature difference of $15.0 ^\circ \text{C}$, achieved using a hot block set temperature of $35.0 ^\circ \text{C}$ and Peltier cooler setting of $20.0 ^\circ \text{C}$. The data were collected using EC-Lab (10.44, Bio-logic).
software. The raw data were further processed and plotted by Matlab (R2013a, MathWorks).

References