Flexible and non-volatile redox active quasi-solid state ionic liquid based electrolytes for thermal energy harvesting

Abuzar Taheri, a Douglas R. MacFarlane, b Cristina Pozo-Gonzalo a and Jennifer M. Pringle *a

a ARC Centre of Excellence for Electromaterials Science, Deakin University, 221 Burwood Highway, Burwood, VIC 3125, Australia, b School of Chemistry, Monash University, Wellington Road, Clayton, VIC 3800, Australia

Supporting information

Thermocell

In a thermocell, the temperature dependence of the electrode potential of the redox couple leads to a potential difference across the cell. In a thermocell with a redox active electrolyte containing \([\text{Co(bpy)}_3]^{2+/3+}[\text{NTf}_2]^{-2/3}\) redox couple, which has a positive Seebeck coefficient, oxidation occurs at the cold electrode, while reduction occurs at the hot electrode:

Cold electrode: \([\text{Co(bpy)}_3]^{2+} \rightarrow [\text{Co(bpy)}_3]^{3+} + e^-\)

Hot electrode: \([\text{Co(bpy)}_3]^{3+} + e^- \rightarrow [\text{Co(bpy)}_3]^{2+}\)

Experimental

Rheology measurements

A strain-controlled rheometer (Discovery HR-3 rheometer, TA Instruments) with 40 mm plate-plate geometry and 1000 μm gap was used to study of the rheological properties of the gels. Applying a frequency of 1 Hz at 25 °C, the strain sweep was performed in the range of 0.02 – 100%. The frequency sweep was performed by applying a strain of 0.1% at 25 °C, in the range of 0.1 – 20 Hz. For temperature sweep, values obtained from frequency and strain sweeps were applied. Applying a strain of 0.1% with the frequency of 1 Hz, the temperature sweep was carried out in the range of 25-70 °C, with a temperature step of 1 °C.

Dynamic mechanical analysis (DMA)

Samples with dimensions of 15 mm × 10 mm × 0.22 mm were cut from the prepared film electrolytes. Using Tensile mode in the dynamic mechanical analyzer (DMA Q800, TA Instruments), stress-strain mechanical measurements were carried out at room temperature. Stress-strain mechanical measurements were carried out with 0.01 N preload force and a frequency of 1 Hz, within the strain range of 0.01 – 100% with the strain rate of 5% per minute.

Differential scanning calorimetry (DSC)

Thermal analysis was performed using a Netzsch DSC 214 Polyma, driven by Proteus 70 software and equipped with liquid N₂ cooling system. Typically, 10-15 mg sample was put in an Al pan, sealed and cooled from room temperature to - 50 °C at 10 °C/min, and after an isothermal equilibration time of 10 min, was heated to 140 °C at the same scan rate.
Results

Rheology

Figure S1. Rheology measurements of quasi-solid state electrolytes containing 0.05 M [Co(bpy)$_3$$^{2+}$/3+][NTf$_2$]$_2$ in [C$_2$mim][NTf$_2$], gelled with either 2.5 wt% PVDF or PVDF-HFP: a) strain sweep of PVDF gel, b) strain sweep of PVDF-HFP gel, c) frequency sweep of PVDF gel, d) frequency sweep of PVDF-HFP gel and e) temperature sweep of PVDF gel, f) temperature sweep of PVDF-HFP gel

Dynamic mechanical analysis (DMA)

Stress-strain mechanical measurements show that PVDF film has higher Young’s modulus (5.19 ± 0.86 KPa) than PVDF-HFP film (7.98 ± 0.31 KPa). By increasing the strain after yield point, PVDF film loses its elasticity and finally at 75% strain breaks. The PVDF-HFP film, with lower Young’s modulus, has elastic behaviour and does not break at the higher strain, possibly as a result of lower crystallinity of the PVDF-HFP copolymer.
Figure S2. DMA measurement: tensile test and stress-strain curves of PVDF and PVDF-HFP films (18% polymer/0.05 M [Co(bpy)$_3$$^{2+/3+}$][NTf$_2$] in [C$_2$ mim][NTf$_2$]).

Thermal analysis

Figure S3. DSC thermograms (second heating cycle) of the polymer-based electrolytes

Figure S3 shows that the PVDF- based electrolytes, in either gel or film form, have higher melting points than the PVDF-HFP electrolyte. PVDF gel and PVDF film melt at temperatures above 110 °C (about 115 and 120 °C, respectively), which is promising for TEC applications. The observed peaks at around -20 °C are attributed to melting of ionic liquid in the gel. The PVDF-HFP gel and film melt at around 80 °C.