Thermoelectric conversion and electrochemical refrigeration using a coil–globule phase transition

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Thermocell generates thermoelectric voltage (ΔV) by applying a temperature difference (ΔT) between a pair of electrodes. Seebeck coefficient ($S_e = \Delta V/\Delta T$) of thermocells is known to be proportional to entropy change of the redox reaction ($S_e = \Delta S/nF$; ΔS, entropy change; n, number of electrons; F, Faraday constant).[1] Therefore, a redox system exhibiting a large ΔS can increase the S_e value and thus expected to improve its thermoelectric efficiency.

In this study, we focused on using the large ΔS released at the coil–globule phase transition of redox polymers in aqueous media. We synthesized poly(*N*-isopropyl acrylamide-*co*-*N*-(2-acrylamide ethyl-*N'*-propylviologen)[2] (noted as PNV) and evaluated the phase transition temperature by both turbidimetry and differential scanning calorimetry (DSC). The transition temperature of the dicationic form (PNV^{2+}) was 40 °C, while that of the radical cationic form (PNV^{+}) decreased to 22 °C. The ΔS of PNV^{+} at the coil–globule transition was evaluated as 0.12 kJ K^{-1} per mole of viologen unit by DSC. The S_e of $PNV^{2+/+}$ thermocell showed a drastic increase from +0.09 to +2.1 mV K^{-1}at the phase transition temperature, which corresponds to the ΔS of 0.19 kJ K^{-1} mol^{-1} and agrees with the result from the DSC analysis. Moreover, a small temperature drop was observed when the cell temperature was increased above the transition temperature (T > 25 °C, Figure 1a). This result shows the coil–globule phase transition can induce an electrochemical refrigeration (i.e., Peltier effect) (Figure 1b).

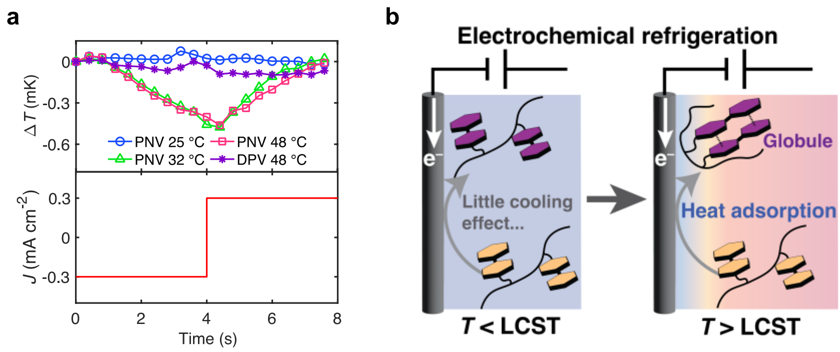

Figure 1. a) Temperature change of one of the electrodes in response to the applied current. b) A schematic showing that the coil–globule phase transition induces an electrochemical refrigeration.

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