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A novel mediator all-solid-state supercapacitor for low-temperature application

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Commercial supercapacitors (SCs) may have to be operated over a wide temperature range from -30 to 90°C However, almost all SCs including aqueous, non-aqueous, and solid-state electrolyte SCs suffer from significant performance degradation at low temperatures or adverse volatility at high temperatures. Lowering the temperature results in: 1) reduction in the degree of dissociation and, hence, reduction in the concentration of free ions and 2) increase of liquid viscosity and, hence, immobility and inaccessibility of the ions in highly porous electrodes. This is reflected by a sharp increase in the series resistance of the SC and sharp decrease of specific energy at a high specific power. Electron exchange between mediators in electrolytes at low temperatures is that the electron exchanges cause instantaneous breakdowns of electro-neutrality or electrical disturbances which will prompt and facilitate the motion or migration of charge carriers at low temperatures. As shown in Fig. 1, mediators (e.g. $K_3Fe(III)(CN)_6$ and $K_4Fe(II)(CN)_6$ in this specific case) exist in a polymer electrolyte with polymer chains, cations, and anions. At low temperatures, the chain segmental motion and diffusion of charge carriers are slow or stagnant. However, electron exchanges between the mediators may be sufficiently active, resulting in net displacements of ions in response to breakdowns of electro-neutrality. At a low concentration of mediators is not enough to form a general connectivity of electron conduction but sufficient for promoting ionic conduction in an electrolyte, this mediator-doped electrolyte can be used to make a membrane separator for a SC to have an improved performance at low temperatures.

We designed and evaluated performance characteristics of an all-solid-state supercapacitor that can operate at both low and ambient temperatures. The membrane separator is cast with a polyvinylidene fluoride/lithium trifluoromethanesulfonate polymer electrolyte doped with a low concentration of $K_3Fe(III)(CN)_6$ and $K_4Fe(II)(CN)_6$ mediators. The two identical electrodes contain carbon black and poly (ethylene oxide)/lithium perchlorate polymer electrolyte containing a high concentration of $K_3Fe(III)(CN)_6$ and $K_4Fe(II)(CN)_6$ mediators. Electrochemical measurements including electrochemical impedance spectroscopy, galvanostatic charge/discharge, and cyclic voltammetry indicate that the SC possesses good capacitance retention of 87.8% when the temperature is reduced from 20°C to -20°C. The specific energy at a specific power of 1.0 kW kg^{-1} is 28.1 Wh kg^{-1} at 20°C or 24.0 Wh kg^{-1} at -20°C (Fig. 2). Based on the experimental results, the following conclusions can be drawn:

1) Addition of the mediators to the PVDF/LiTFS membrane mitigates the reduction in its conductivity at the lower temperatures.
2) Addition of the mediators to the polymer electrolyte and PVDF/LiTFS separator also improves the shape and reversibility of the CVs for the solid-state SCs at the low operation temperature of -20°C.
3) The degree of reduction in capacitance at low temperature can be reduced by the addition of the mediators.
4) The degree of reduction in the specific power and energy at low temperature is significantly reduced by the addition of the mediators to the polymer electrolyte and separator.

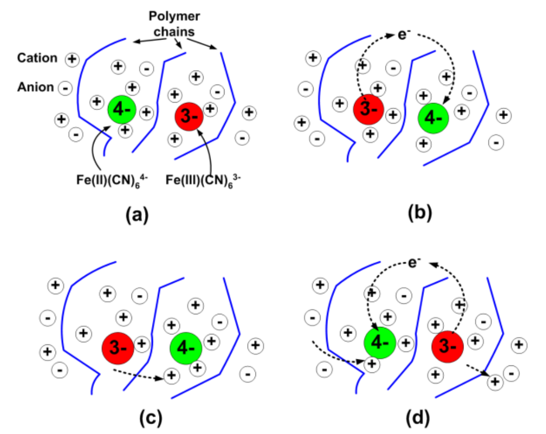

Fig. 1. Illustration of mediator-assisted ionic conduction. (a) initial state; (b) electron transfer between the mediators resulting in a breakdown of electroneutrality; (c) displacement of a cation to re-establish electroneutrality; and (d) after a reverse electron transfer cations move to the right.

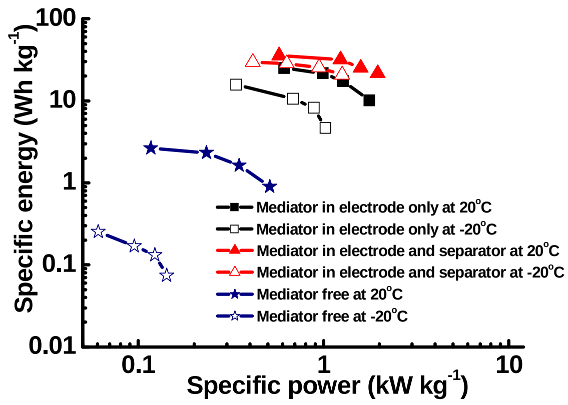

Fig. 2. Regone plots for SCs without mediator in both electrode and electrolyte, with mediators in electrode only, and with mediators in electrode and with a very low concentration of mediators in separator.