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Ionic liquid–solid polymer electrolyte blends for supercapacitor applications

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Abstract The electrochemical, structural and photoelectrochemical properties of blend of a low-viscosity IL 1-ethyl 3-methyl imidazolium dicynamide (EMIM DCA, viscosity 17 cP) in poly(vinylidene fluoride-hexafluoropropylene) (PVdF-HFP) are presented in detail. The blending of low-viscous IL provides charge carriers with higher mobility which are significantly observed in ionic conductivity measurement. The incorporation of IL provides more amorphous region within polymer matrix which is known as a beneficial condition for conductivity enhancement and are affirmed by our DSC and XRD measurements. The fabricated supercapacitor with configuration MWCNT/PVdF-HFP +IL/MWCN shows promising results.

Keywords MWCNT · Ionic liquid · Electrochemical stability · Supercapacitor

Introduction

Ionic liquids (ILs) are proposed as one among known materials playing a dominant role in the emerging electrochemical devices market. Recent research trends prove that ILs are safe, environmentally friend and used as novel electrolytes in popular electrochemical devices available in market [1–3]. Due to its advantageous properties over other popular electrolytes it may be treated as recent hot electrolytes and worldwide IL companies are growing rapidly. In electrochemical devices such as batteries, dye sensitized solar cell (DSSC), actuators, fuel cells, supercapacitors, etc., the IL demand is increasing day by day [4–7]. The selection criteria for IL

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application in each above-mentioned devices are based on their matching physical and chemical properties. It is well known that ILs are composed of ions only and hence they play a dominant role in conductivity modulation. In supercapacitors the attainable cell voltage depends mainly on the electrolyte breakdown voltage, while the equivalent series resistance (ESR) depends on the electrode nature and electrolyte conductivity. Hence, the choice of good electrolytes plays a dominant role in developing efficient supercapacitor. The most frequent popular electrolytes are based on either aqueous electrolytes or organic solvents. Although aqueous electrolyte shows high conductivity, their narrow cell voltage, low energy density create problem while in other side the organic electrolytes have a higher breakdown voltage, but have also greater resistance than those based on aqueous solution [8, 9].

Ionic liquids (ILs) have attracted a great deal of attention due to their low vapor pressure, nonflammability, high thermal stability, good conductivity albeit the liquid natures at room temperature of most of the ILs are the biggest disadvantage [10, 11]. Therefore, to develop a solid electrolyte, one of the novel methods is to blend these ILs in a suitable polymer electrolyte matrix. It is well documented that the ionic conductivity (σ) of polymer electrolyte is closely related to viscosity (η) by the following equations:

$$\mu = q/6\pi\eta r \qquad (1)$$

and

$$\sigma = nq\mu \qquad (2)$$

where n, q and μ are defined as the number of ionic charge carriers, columbic charge and mobility of the species, respectively. Following these equations, it is clear that the mobility (μ) or ionic conductivity (σ) is inversely proportional to the viscosity (η), and hence low-viscosity IL could be a preferable material to achieve high ionic conductivity.

Good efficient electrochemical double-layer supercapacitors (EDLC) have been reported in the literature, choosing various polymer matrixes such as poly(methyl methacrylate) (PMMA), polyacrylonitrile (PAN), poly(vinyl chloride) (PVC), poly(vinyl pyrrolidone) (PVP), poly(ethylene oxide) (PEO) and poly(vinylidene fluoride) (PVDF) or poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP). Among them, poly(vinylidene fluoride-*co*-hexafluoropropylene) is widely used because of its good mechanical and electrochemical stability with respect to nonaqueous electrolyte and electrode materials [9, 10]. Keeping these things in mind the prime aim of the present communication is to check the role of low-viscosity IL (1 ethyl 3 methylimidazolium dicyanamide, EMIM DCA, viscosity 17 cP) [10] addition into polymer poly(vinylidene fluoride-hexafluoropropylene) (PVdF-HFP) matrix. Fabrication of supercapacitor comprising multiwalled carbon nanotubes (MWCNT) and IL-blent solid polymer electrolyte is presented in detail.

Experimental

IL-blent solid polymer electrolyte films were prepared as follows. PVDF-HFP (average molecular weight $M_w = 400,000$, Aldrich, USA) was dissolved in acetone by continuous stirring ($\sim$5 h) at 60 °C. The desired amount of low-viscosity IL (EMIM DCA; Sigma-Aldrich, USA) was then mixed in PVDF-HFP polymer electrolyte solutions. The viscous polymer solutions with and without IL were poured into glass petri dishes and dried under room ambient condition. These free-standing polymer electrolyte films were later dried in a vacuum. The room temperature bulk electrical conductivity, electrochemical stability and supercapacitor performance were carried out with the help of a computer-controlled CHI instrument (CH Instrument, USA) with a frequency range between 10 mHz and 100 kHz. The X-ray diffraction (XRD) patterns were recorded using an X-ray diffractometer (Rigaku D/max-2500) at a scan rate of 50 min^{-1}. The differential scanning calorimetry (DSC) was performed using a TA instrument (MDSC 2910) at 50 °C min^{-1} in a nitrogen gas atmosphere with a sample weight of $\sim$5 mg in the temperature range 120–190 °C while thermogravimetry analysis (TGA) measurement was carried out using a Perkin-Elmer Pyris-1 analyzer with a heating rate of 10 °C min^{-1} at a temperature range between 20 and 400 °C.

Multiwalled carbon nanotube (MWCNT) powder was purchased from Sigma-Aldrich., USA. For electrode fabrication fixed amount of MWCNTs, acetylene black, and poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) as binder [70:10:20 (w/w)] was mixed with mortar and pestle. Acetone was used as medium to form slurry which was coated on the graphite sheets having dimension 1×1 cm^2. Finally the prepared electrodes were vacuum-dried overnight at $\sim$100 °C before fabricating EDLC cell.

Good efficient EDLC was fabricated by sandwiching solid polymer electrolyte (SPE) between two symmetric MWCNT electrodes. The 1×1 cm^2 graphite sheet has been used as a current collector.

Results and discussions

The electrical conductivities (σ) of solid polymer electrolyte films with and without IL were measured and conductivity variation is shown in Fig. 1.

The conductivity of pure PVDF-HFP was in the range of 1.20×10^{-6} S cm^{-1} while for IL it was 25×10^{-3} S cm^{-1}. It was clear from the figure that with increasing amounts of IL (EMIM DCA), the ionic conductivity (σ) of the films is found to increase, attain a maximum and then decrease. The maximum conductivity was obtained at 250 weight % IL concentration with a conductivity (σ) value of 3.42×10^{-3} S cm^{-1}. The free-standing PVDF-HFP + 250 weight % IL–polymer electrolyte photograph is shown in Fig. 2. It was noticed that after 250 weight % IL concentration, the IL came out from the PVDF-HFP matrix.

Taking account of Eqs. 1 and 2, it was clear that the conductivity enhancement till 250 wt% could be due to more numbers of free charge carriers (n) or high

Fig. 1 Variation of ionic conductivity (σ) with amount of IL added in the IL-added solid polymer electrolyte films at 62 % relative humidity
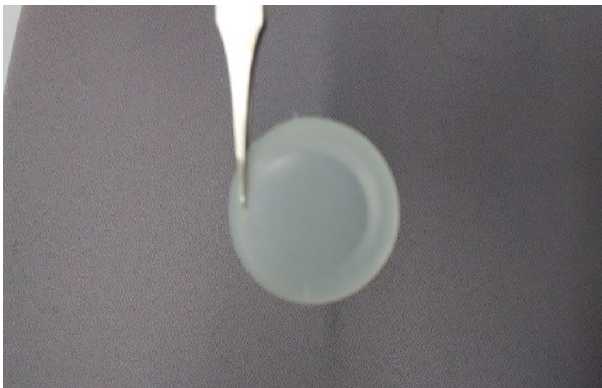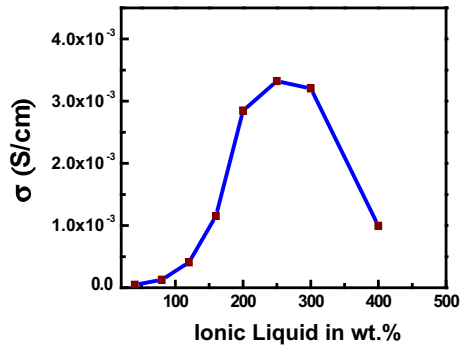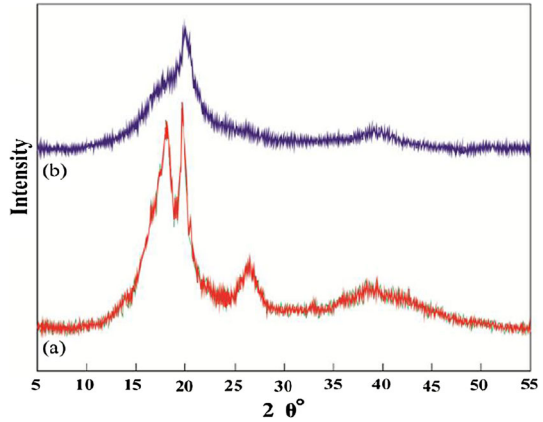

Fig. 2 Photograph of free-standing PVDF-HFP + 250 wt% IL–solid polymer electrolyte film

mobility of ions. Interestingly, using Eq. 2, it is well established that ionic conductivity (σ) is inversely proportional to viscosity (η) and hence low viscosity leads to an increase in mobility or ionic conductivity [12–14]. The dispersal of low-viscosity IL (EMIMDCA) could fulfill both the requirements stated above. Adding of low-viscosity IL could provide free charge carriers since it composed of ions only while in other side it produces a less viscous matrix within the gel matrix by suppressing crystallinity (as observed in XRD, DSC) and hence easy movement of ions, which results in an overall improvement in ionic conductivity while suppressing the ionic conductivity, in the later part, was attributed to the aggregation of charge carriers [15]. Figure 3 shows the recorded XRD patterns of the pure PVDF-HFP and PVDF-HFP + 250 weight % EMIM DCA solid polymer electrolyte films. It was clear that pure PVDF-HFP polymer matrix shows well-defined peaks at $2\Theta = 18.3°$, $20°$, $26.6°$ and $39°$ with a hollow at the base indicating the semi-crystalline nature (Fig. 3a). With the blending of low-viscosity IL, the intensity of the PVDF-HFP polymer matrix peaks decreases drastically (Fig. 3b). Additionally the peaks of the polymer electrolyte films (Fig. 3b) become broader and weaker in intensity compared with the patterns of the film without IL. The

decreasing crystallinity can result in more amorphous areas of the polymer matrix
and enhanced ionic conductivity of polymer electrolyte films. This is a well-known
ideal condition for ionic conductivity enhancement [15].

Figure 4 shows the typical DSC thermograms of the PVDF-HFP polymer and
PVDF-HFP solid polymer electrolyte blend with low-viscosity IL.

The exothermic peak observed in the temperature range 140–150 °C was
(Fig. 4a) ascribed to the melting point of PVDF-HFP [12].

The relative percentage of crystallinity (χ) of PVDF-HFP and PVDF-HFP blend
solid polymer electrolyte films was calculated using the following equation

$$\chi = \Delta H_m / \Delta H_0 \tag{3}$$

where ΔH_m is the melting enthalpy obtained from the DSC results. ΔH_0 is the
melting enthalpy of 100 % crystalline PVDF-HFP which was assumed to be
104.7 J g^{-1} [12, 16].

The evaluated values of the melting temperature (T_m), melting enthalpy (ΔH_m)
and relative percentage of crystallinity (χ) are listed in Table 1.

Fig. 4 DSC curves of *a* pure
PVDF-HFP and *b* PVDF-
HFP + 250 wt% IL-blent solid
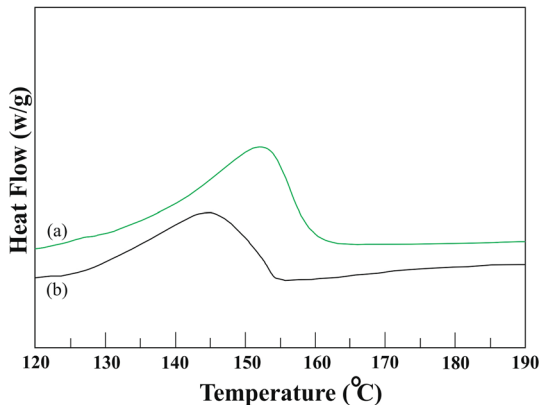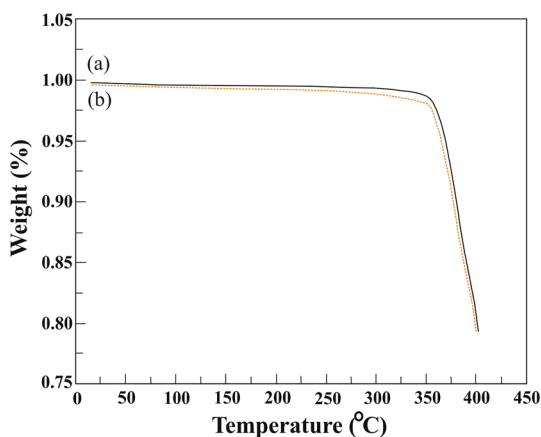polymer electrolyte films

Table 1 Melting temperature (T_m) and % crystallinity (χ) of host PVDF-HFP polymer and IL-mixed PVDF-HFP solid polymer electrolyte films

Composition (wt%)	T_m (°C)	ΔH_m (J/g)	χ (%)
PVDF-HFP	150.71	32.32	30.87
PVDF-HFP + 250 wt% IL	145.00	18.56	17.72

Fig. 5 TGA plots of *a* pure PVDF-HFP and *b* PVDF-HFP + 250 wt% IL-blent solid polymer electrolyte films

It was clear from the table and Fig. 4b that the value of melting temperature of PVDF-HFP film was found to decrease with IL mixing. It has also been observed that the melting endotherm was broadened after incorporation of the IL. Both the reduced melting temperature and the broadening of the melting endotherm supported our findings, which we have already discussed in the previous sections.

Thermal stability of the solid polymer electrolyte films with and without IL was carried out using TGA measurement and plots are shown in Fig. 5.

It is in literature that pure PVDF-HFP matrix shows high thermal decomposition temperature at around 400 °C, and incorporation of IL with polymer electrolyte lowered decomposition temperature [12, 14]. However, we could not observe significant lowering temperature phenomenon in our ionic liquid–polymer electrolyte system.

The electrochemical stability window (ESW) of IL-blent solid polymer electrolyte film was carried out using cyclic voltammetry with symmetrical stainless steel electrodes. Figure 6 shows the typical cyclic voltammograms of PVdF-HFP + 250 wt% IL film, recorded at the scan rate of 5 mV s^{-1}. The ESW of IL-blent solid ionogel electrolyte has been observed from −1. 2 to +2.3 V, which was found to be higher as compared to that for the pure IL-based electrolyte [17].

The EDLC having configuration MWCNT//PVDF-HFP + 250 wt% IL// MWCNT was fabricated and characterized using impedance spectroscopy and cyclic voltammetry techniques. The photograph of sandwich supercapacitor comprising electrodes and electrolyte is shown in Fig. 7. Due to the beneficial nature of

Fig. 6 Electrochemical stability test of PVDF-HFP + 250 wt% IL-blent solid polymer electrolyte films
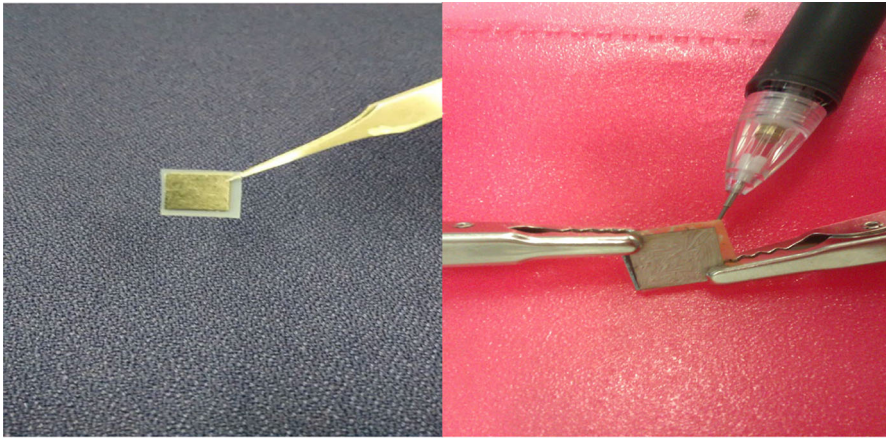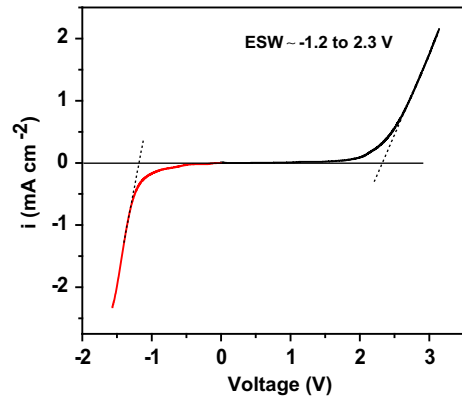

Fig. 7 Photographs of complete EDLC assembly using polymer–IL solid electrolyte

sticky polymer–IL electrolyte we do not need any other sticking materials externally.

Figure 8 shows the typical complex impedance spectra of fabricated supercapacitor. The MWCNT electrode materials with the IL-based solid polymer electrolyte shows capacitive behavior reflected by the steep rising behavior of the impedance plots in the lower frequency range observed in complex impedance spectroscopy. The various electrical parameters of EDLC were calculated at 10 mHz frequency and values are shown in Table 2.

Cyclic voltammetry (CV) is performed to explain the nature of charge storage at the individual interfaces in the anodic and cathodic regions. Figure 9 shows typical cyclic voltammograms of capacitor (mentioned above) in the potential range −0.8 to 0.8 V at 100 mV/s scan rate. The EDLC supercapacitor using symmetrical electrode and IL-blent solid polymer electrolyte shows specific capacitance of 21 F g^{-1} which was matched well by our conductivity measurement.

Fig. 8 Complex impedance
plot of supercapacitor with
configuration MWCNT//PVDF-
HFP + 250 wt% IL//MWCNT
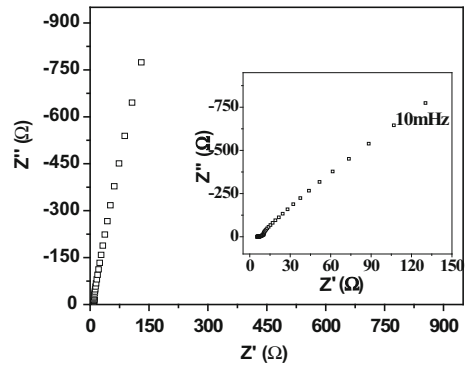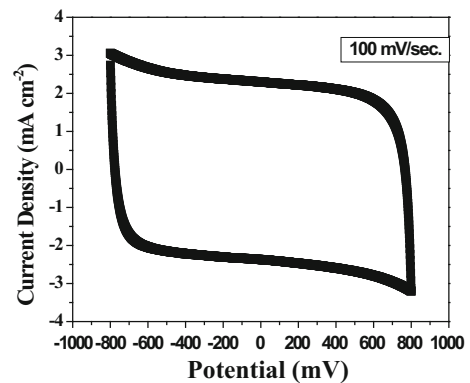at frequency range from 10 mHz
to 100 kHz

Table 2 Calculated electrical parameters of EDLC at 10 mHz frequency

R_b (Ω cm^2)	R_{ct} (Ω cm^2)	C (mF cm^{-2})	C (F g^{-1})
4.5–6.8	0.4–0.9	44	22

Fig. 9 Cyclic voltammetry
curve of supercapacitor with
configuration MWCNT//PVDF-
HFP + 250 wt% IL//MWCNT
at 100 mV/s scan rate

Conclusions

Low-viscosity IL (EMIM DCA) was dissolved in the PVDF-HFP polymer
electrolyte matrix. Incorporation of low-viscosity IL shows dual beneficial behavior
in polymer matrix. It provided additional charge carriers as it composed of ions only
while in other side; it reduced the crystallinity of host polymer and hence increased
the ionic conductivity. The crystallinity suppression was confirmed by XRD, DSC
measurements. The maximum ionic conductivity of PVDF-HFP + 250 wt% IL was
found to be 3.42×10^{-3} S cm^{-1}. The fabricated supercapacitor showing high
performance (22 mF cm^{-2}) further affirmed that these IL-blent solid polymer
electrolytes seem novel candidates for supercapacitor.

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