



PVDF-HFP and 1-ethyl-3-methylimidazolium thiocyanate-doped polymer electrolyte for efficient supercapacitors

High Performance Polymers
1–7

© The Author(s) 2018

Reprints and permission:

sagepub.co.uk/journalsPermissions.nav

DOI: 10.1177/0954008318772009

journals.sagepub.com/home/hip



Pankaj Tuhania¹, Pramod K Singh¹, B Bhattacharya^{1,2}, Pawan S Dhapola^{1,3},
Shivani Yadav¹, PK Shukla⁴ and Meenal Gupta¹

Abstract

The sole aim of the present article is to develop an ionic liquid (IL)-doped solid polymer electrolyte for an electrochemical double-layer capacitor (EDLC). A solution cast technique was adopted to develop a solid polymer electrolyte of poly (vinylidene fluoride-co-hexafluoropropylene) as host polymer and low-viscosity IL (1-ethyl-3-methylimidazolium thiocyanate) as dopant. Electrochemical impedance spectroscopy measurement showed a six orders of magnitude enhancement in conductivity (σ) by IL doping. A linear sweep voltammetric investigation of the electrolyte films exhibited a good electrochemical stability window of 3.6 V. Polarized optical microscopy of the synthesized films revealed a reduction in crystallinity by IL doping. Infrared spectroscopy further affirms the composite nature of the film. The maximum conductivity value of 2.65 mS/cm is obtained for 80% of the ionic-doped system. Using maximum conductivity film and porous carbon-based electrodes, we have developed EDLCs that show a specific capacitance value of 2.36 F/g.

Keywords

Polymer electrolyte, conductivity, supercapacitor

Introduction

In recent years, material science has been more widely recognized as a specific and distinct field of science and engineering. Additionally, it involves the discovery and design of new materials and investigation of the relationships that exist between structure and properties of materials. Solid materials are basically grouped into three basic classifications—metals, ceramics, and polymers. Each material has their own properties and device application. Polymers are large molecules made by a repeating pattern of building blocks called monomer. Those monomers can be simple—just an atom, two or three, or might be complicated ring-shaped structures. These are not as stiff or as strong as the other material types.^{1–4} In general, they are relatively inert in nature and can sustain in nearly all types of environments. Owing to the fact that the polymer electrolyte has useful properties such as ease of fabrication, moldability, thin film formation, and high conductivity, it is frequently used in electrochemical devices such as electrochromic display devices, fuel cells, batteries, solar cell, and supercapacitors.^{5–8} Supercapacitors have high power

density (10 kW/kg), longer lifetime in comparison with batteries and have very high energy density with respect to conventional capacitors. According to the charge storage mechanism, supercapacitors are grouped into pseudo capacitors, electrochemical double-layer capacitors (EDLCs) and hybrid capacitors.^{9–11} The electrolyte is one of the most important parts of a supercapacitor. It plays an equally vital role in the performance of the supercapacitor and one of the most influencing factors of the electrolyte is its ionic

¹ Material Research Laboratory, School of Basic Sciences and Research, Sharda University, Greater Noida, Uttar Pradesh, India

² MMV, Department of Physics, Banaras Hindu University, Varanasi, Uttar Pradesh, India

³ Nano Science and Nano Technology Center, Department of Chemistry, Kumaun University, Nainital, Uttarakhand, India

⁴ Department of Applied Physics, I.T.S Engineering College, Greater Noida, Uttar Pradesh, India

Corresponding author:

Meenal Gupta, Material Research Laboratory, School of Basic Sciences and Research, Sharda University, Greater Noida, Uttar Pradesh, India.

Email: meenal.gupta@sharda.ac.in

conductivity. Electrolytes are substances containing free ions. In the supercapacitor, the electrolyte contributes to the formation of an electric double layer in EDLCs and it also participates in charge storage (e.g. reversible redox reactions in pseudo capacitors).^{12–15}

The best known ion conducting electrolytes are either liquid electrolytes or gel electrolytes. However, both these electrolytes fail to provide stability and long lifetime, besides the liquid nature itself has many known disadvantages such as evaporation, encapsulation, corrosions, and degradation. The use of polymer electrolytes can overcome the problems mentioned above. Polymer electrolytes are substances containing ionic species dissolved in a polymer host. In the last few years, a variety of solid polymer electrolytes have been developed using different host polymers such as Poly(ethylene oxide) (PEO), Poly(vinyl alcohol) (PVA), Polyvinylpyrrolidone (PVP), doped with ionic salt, plasticizers, and ionic liquids (ILs).^{14–16}

ILs are molten salts at low temperature or at room temperature and are known as solely salts with melting point below 100°C. ILs recently got attention because of their wide electrochemical potential window, thermal stability, negligible volatility, nonflammability, and possibility of a large combination of cations and anions.^{17–26} The use of polymer electrolyte systems doped with thiocyanate based ionic liquids have been already demonstrated by different research groups.^{27–33}

In the present work, we have developed a low-viscosity IL-doped solid polymer electrolyte and used the highest conductivity samples to fabricate an EDLC.

Experimental details

Materials used

Used polymer poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and ionic liquid (1-ethyl-3-methylimidazolium thiocyanate) were purchased from Sigma-Aldrich, USA, while sodium iodide (NaI) and other solvents were purchased from Qualikems Fine Chem Pvt. Ltd., Vadodara, Gujarat, India.

Electrolyte preparation

Pure and IL-doped electrolyte films were prepared using the solution casting technique. Initially, PVDF-HFP was dissolved in acetone using magnetic stirrer for 2 h. In the prepared solution, a directly chosen amount of IL was mixed to maintain its desired ratio (by wt) in PVDF-HFP films to prepare IL-doped films. Again, the mixture was kept on magnetic stirrer for the whole night to make a homogenous viscous solution of polymer-IL. Finally, the prepared solution was kept for drying in polypropylene petri dishes at room temperature, followed by vacuum drying to remove the remaining traces of acetone (if any).

After drying, we could achieve freestanding films of pure PVDF-HFP and IL-doped films. First, we characterized the films via doing their conductivity measurements, electrochemical stability window (ESW) measurements, optical microscopy, and Fourier transform infrared (FTIR) spectroscopy. Finally, we prepared a supercapacitor (EDLC) using the maximum conductivity IL-doped film as electrolyte material.

Supercapacitor fabrication

To fabricate the EDLC, we have used a $1 \times 1 \text{ cm}^2$ graphite sheet as current collector. Approximately, 1 mg of fresh paste of porous carbon (derived from corn starch) is well coated on the current collector. To prepare the paste, corn starch-derived carbon was mixed with binder (PVDF-HFP) in the ratio of 80:20 wt%. The electrodes were prepared via coating the porous carbon paste on the graphite sheet.^{2,3} Uniformly coated graphite sheets were then kept at 80°C for overnight before using as electrode. Maximum conductivity IL-doped film was sandwiched between these thoroughly cleaned electrodes to perform cyclic voltammetry (CV) and low-frequency impedance spectroscopy to check its specific capacitance (C_{sp}). Electrochemical impedance spectroscopy was used to measure the capacitive nature of the prepared sample.

Result and discussion

Conductivity measurement

The ionic conductivity of the ionic liquid-doped polymer electrolyte (ILDPE) was carried out using a CH Instruments workstation (model 604D; Austin, Texas, USA). We have used two stainless steel (SS) electrodes and sandwiched freestanding polymer electrolyte films in-between SS electrodes. The ionic conductivity of the samples was calculated using the following formula

$$\sigma_{dc} = 1/R_b \cdot L/A \quad (1)$$

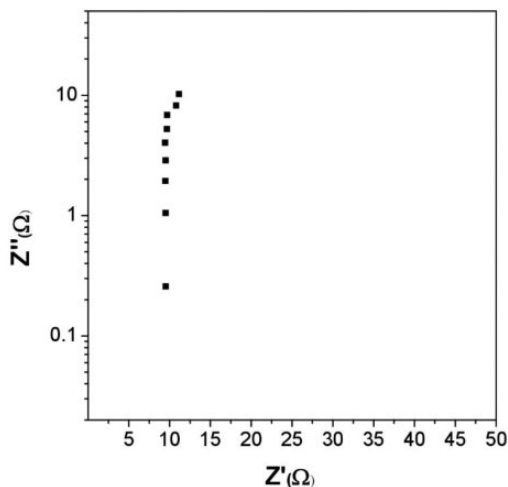
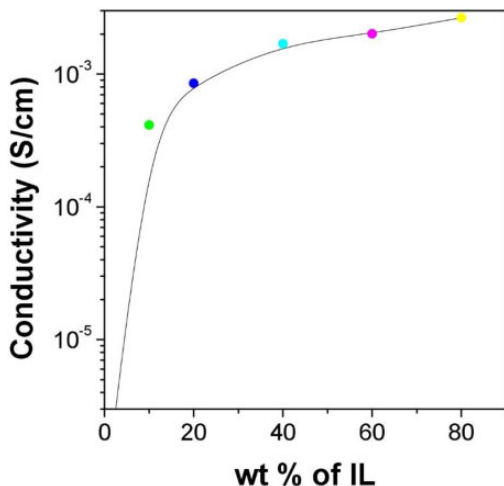
where σ_{dc} is the dc ionic conductivity, R_b is bulk resistance, L is the thickness of the film, and A is the area of cross section of the sample.

The conductivity values evaluated using equation (1) are listed in Table 1. The bulk resistance (R_b) of the films were obtained using Cole–Cole plots. One typical Cole–Cole plot (for maximum conductivity ILDPE film) is shown in Figure 1. The variation in ionic conductivity of the synthesized electrolyte films as a function of IL concentration is shown in Figure 2. It is clear from Figure 2 (and Table 1) that on addition of IL into the PVDF-HFP polymer matrix, the σ_{dc} value increases sharply, which is due to the enhancement in the number of charge carriers as IL is composed of cations (imidazolium) and anions (thiocyanate). The conductivity of the polymer host was $5.74 \times 10^{-9} \text{ S/cm}$ and on doping with IL, the conductivity values

Table 1. Conductivity with an increased amount of IL concentration in pure polymer and ILDPE films.

Composition (wt% of IL)	Conductivity (S/cm)
0	5.74×10^{-9}
10	4.12×10^{-4}
20	8.53×10^{-4}
40	1.69×10^{-3}
60	2.01×10^{-3}
80	2.65×10^{-3}

IL: ionic liquid; ILDPE: ionic liquid-doped polymer electrolyte.

**Figure 1.** Cole-Cole plot of the maximum conductivity ILDPE film. ILDPE: ionic liquid-doped polymer electrolyte.**Figure 2.** Ionic conductivity versus wt% of IL in pure and ILDPE films. IL: ionic liquid; ILDPE: ionic liquid-doped polymer electrolyte.

increase sharply and reach maximum (2.65×10^{-3} S/cm) for 80 wt% IL concentration. The freestanding electrolyte films could not be obtained beyond this concentration. The sharp

Table 2. Dielectric constant with an increase in IL concentration in ILDPE films at three frequencies.

wt% of IL	10^4 Hz	10^5 Hz	10^6 Hz
0	157.00	134.00	107.03
10	267871.11	165227.47	93992.78
20	657488.82	453047.77	277388.97
40	1688750.00	1110700.00	851942.64
60	3239170.00	1534680.00	1205520.00
80	4313210.00	2183330.00	1752920.00

IL: ionic liquid; ILDPE: ionic liquid-doped polymer electrolyte.

increase in conductivity (six orders of magnitude) is mainly due to the availability of free cations and anions upon doping with IL. As the amount of IL incorporated into the polymer matrix is increased, the value of n increases and hence conductivity increases according to the general relation for conductivity given by

$$\sigma = n \cdot q \cdot \mu \quad (2)$$

where n is the concentration of charge carriers (here cations and anions), q is the charge on ions, and μ is the mobility.

Dielectric measurement

The dielectric response has been explored to further elaborate on the ionic conductivity behavior of electrolyte films. We have evaluated the dielectric constant of ILDPE films at three different frequencies (viz., 10^4 , 10^5 , and 10^6 Hz) and the values are listed in Table 2. At lower frequency (10^4 Hz), the dielectric constant is found to increase with an increase in IL concentration and follow a similar pattern as we have observed in conductivity data. A similar trend has been observed for 10^5 Hz and 10^6 Hz frequencies, but with an order of magnitude lower change in the values.

Figure 3 depicts the variation in the dielectric constant of ILDPE films for different IL concentration at three different frequencies (viz., 10^4 , 10^5 , and 10^6 Hz). It is clear that as we increase the IL concentration in the polymer matrix, the dielectric constant value increases. This is due to the increase in charge carrier concentration on increasing the amount of IL in electrolyte films. The variation in dielectric constant follows a similar trend that was observed in conductivity behavior.

Electrochemical stability window

The linear sweep voltammetric (LSV) response was recorded to estimate the ESW of ILDPE films. Figure 4 displays the linear sweep voltammogram recorded for maximum conductivity ILDPE electrolyte film from -3.0 to 3.0 V. For LSV measurement, the ILDPE was sandwiched between two SS electrodes and the measurement was

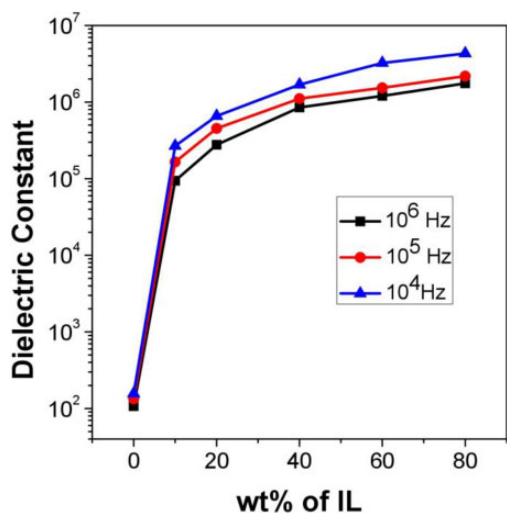


Figure 3. Variation in dielectric constant for different ILDP films (wt% of IL in host polymer) at three different frequencies. ILDP: ionic liquid-doped polymer electrolyte.

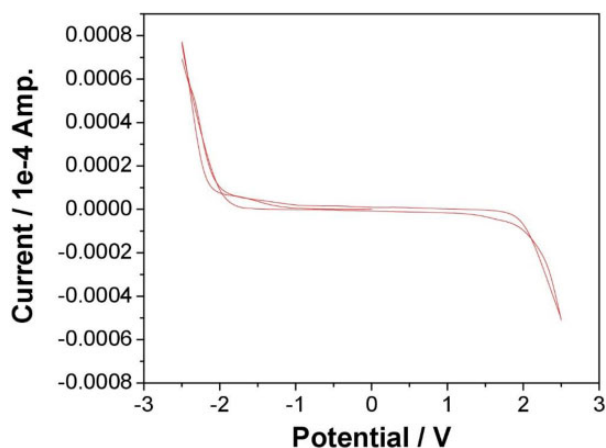


Figure 4. LSV of the maximum conductivity ILDP film. LSV: linear sweep voltammetry; ILDP: ionic liquid-doped polymer electrolyte.

carried out using the CH Instruments workstation. It can be seen that no faradic peak appears in the voltage range approximately from -1.8 V to $+1.8$ V range. Thus, the ILDP film shows ESW of approximately 3.6 V, which is enough to use it as a novel solid electrolyte for EDLC application.

Optical measurements

Optical micrographs of the electrolyte films have been recorded using a polarized optical microscope (POM) (Motic-model no. BA310 Pol, Carlsbad, California, USA) at $40\times$ magnifications to see the effect of IL doping on polymer texture. The optical micrographs of pure PVDF-HFP and the maximum conductivity ILDP film are

shown in Figure 5. The pure polymer film exhibits smooth and dense morphology. The scratches observed on the surface of the films are a replica of scratches on the inner surface of the petri dish used for the synthesis of films. On the other hand, the micrographs of the ILDP film show an interesting morphology with a reduction in crystallinity (dark portion). It is well known that an increase in the amorphous nature leads to better segmental mobility and hence high ionic conductivity of the electrolyte films. The observed texture of the ILDP film using POM is thus in agreement with the conductivity response.

FTIR spectroscopy

Fourier transform infrared (FTIR) spectroscopy of the synthesized samples was carried out using a CARY 630 (Agilent Technologies, USA) spectrophotometer to investigate the IL-polymer interaction. Figure 6 shows the FTIR spectra of pure polymer, IL, and maximum conductivity ILDP film. The FTIR spectra of PVDF-HFP films (Figure 6(a)) show prominent peaks at 484 cm^{-1} , 528 cm^{-1} , 762 cm^{-1} , 839 cm^{-1} , 879 cm^{-1} , and 976 cm^{-1} . The peaks at 528 cm^{-1} and 976 cm^{-1} are assigned to nonpolar trans-gauche-trans-gauche (TGTG') conformation (i.e. an α -phase) of the semicrystalline PVDF-HFP. The peak at 484 cm^{-1} is due to an intermediate polar TTTGTTG' conformation (γ -phase), which occurs when the polymer is moderately stressed. The band at 762 cm^{-1} is assigned to the α -phase. Further, the bands at 839 cm^{-1} and 879 cm^{-1} are assigned to the amorphous phase of the polymer.

In case of IL 1-Ethyl-3-methylimidazolium thiocyanate (EMImSCN), the FTIR spectra (Figure 6(c)) exhibit peaks related to both thiocyanate anion and imidazolium cation. The peaks at 3166 cm^{-1} and 2892 cm^{-1} are due to the stretching of C-H and antisymmetric CH_3 stretching, respectively, while peaks at 1462 cm^{-1} , 1432 cm^{-1} , 1172 cm^{-1} , and 912 cm^{-1} , respectively, correspond to anti-symmetric bending of CH_3 , symmetric bending of CH_3 , stretching of $\text{CH}_3\text{-N}$, and out of plane stretching of H-C bond.²⁵ The peaks at 2058 cm^{-1} , 1600 cm^{-1} , 620 cm^{-1} , and 600 cm^{-1} are ascribed to the absorption of thiocyanate (SCN^-), CN stretching, C-S stretching, and stretching vibration of S-CN bond, respectively.

It is noticed that the IR spectra of ionic liquid-doped PVDF-HFP film (Fig. 6b) contain almost all the peaks related with polymer (PVDF-HFP) or IL with a moderate change in intensity which affirms the composite nature of ILDP films. Similar findings have been also reported earlier by our group.¹²

Fabrication and performance of EDLC

We have successfully fabricated laboratory-scale EDLC using the optimized IL-doped polymer electrolyte.^{2,14,17}

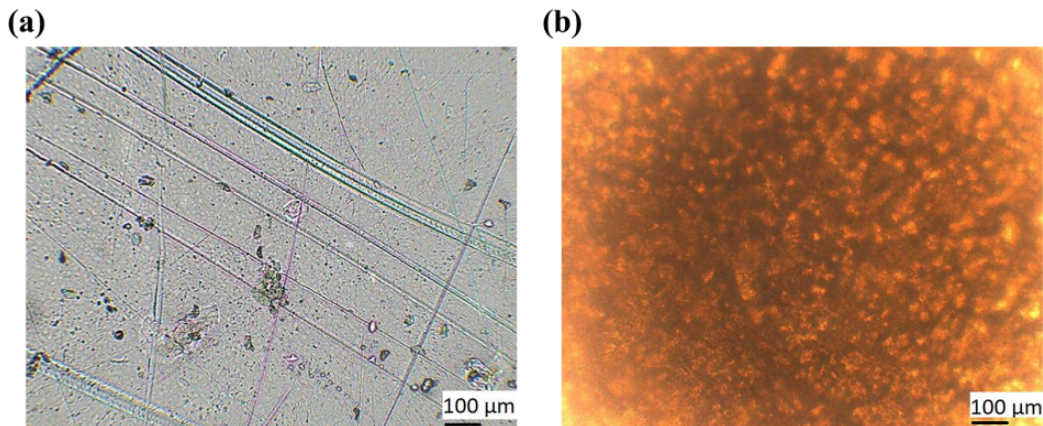


Figure 5. POM of (a) pure PVDF-HFP matrix and (b) maximum conductivity ILDPE film at magnification 40 \times . POM: polarized optical microscopy; PVDF-HFP: polymer poly(vinylidene fluoride-co-hexafluoropropylene); ILDPE: ionic liquid-doped polymer electrolyte.

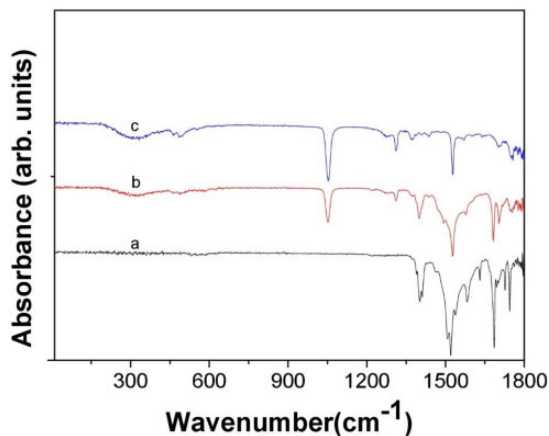


Figure 6. FTIR spectra of (a) pure PVDF-HFP, (b) maximum conductivity ILDPE, and (c) pure IL. FTIR: Fourier transform infrared spectroscopy; PVDF-HFP: polymer poly(vinylidene fluoride-co-hexafluoropropylene); ILDPE: ionic liquid-doped polymer electrolyte; IL: ionic liquid.



Figure 7. Photograph of EDLC fabricated using the ILDPE film as the electrolyte and corn starch-derived porous carbon as high surface area electrodes. EDLC: electrochemical double-layer capacitor; ILDPE: ionic liquid-doped polymer electrolyte.

To develop an EDLC, we have sandwiched the electrolyte film between the two electrodes made of corn starch-derived porous carbon synthesized in our laboratory.²⁶

To fabricate the EDLC, we have used a $1 \times 1 \text{ cm}^2$ graphite sheet as current collector. Approximately, 1 mg of freshly prepared paste of porous carbon (derived from corn starch) is well coated on the current collector and kept at 100°C in an oven overnight. The maximum conductivity ILDPE film was sandwiched between the two symmetric porous carbon-based electrodes to obtain the EDLC. A photograph displaying the complete geometry of the EDLC is shown in Figure 7.

We have performed low-frequency electrochemical impedance spectroscopy and CV of the EDLC. The C_{sp} was evaluated from the cyclic voltammogram using the following expression

$$C = i/s \quad (3)$$

where s is the scan rate and i is total current.

The cyclic voltammogram of an ideal capacitor shows a perfect rectangular shape, and the deviation from the rectangular shape is observed for real capacitors, which is represented as a series combination of internal resistance R and ideal capacitance C .⁶ Figure 8 shows the cyclic voltammogram of the EDLC fabricated as explained above. The voltammogram exhibits a well-known hysteresis-type loop which is typical of a supercapacitor.⁶ The C_{sp} value evaluated using equation (3) is 2.36 F/g.

The C_{sp} value of the EDLC was also evaluated using low-frequency impedance spectroscopy data using the following expression

$$C = -1/\omega Z'' \quad (4)$$

where Z'' is imaginary part of impedance at the lowest frequency (Figure 9). This value of capacitance was then used to calculate C_{sp} . The C_{sp} of the EDLC estimated from

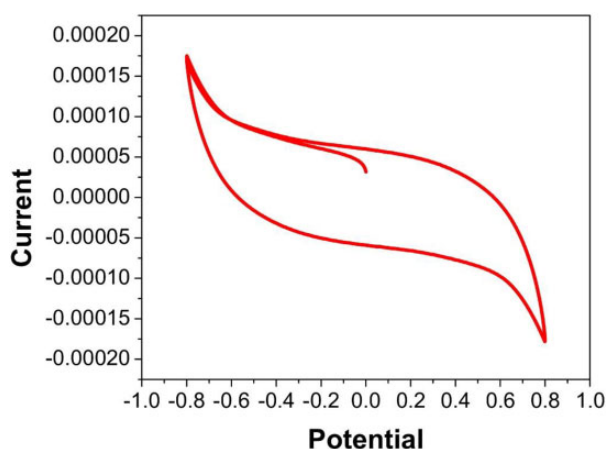


Figure 8. Cyclic voltammogram of EDLC fabricated using the maximum conductivity ILDPE film and recorded at a scan rate 0.05 mV/s. EDLC: electrochemical double-layer capacitor; ILDPE: ionic liquid-doped polymer electrolyte.

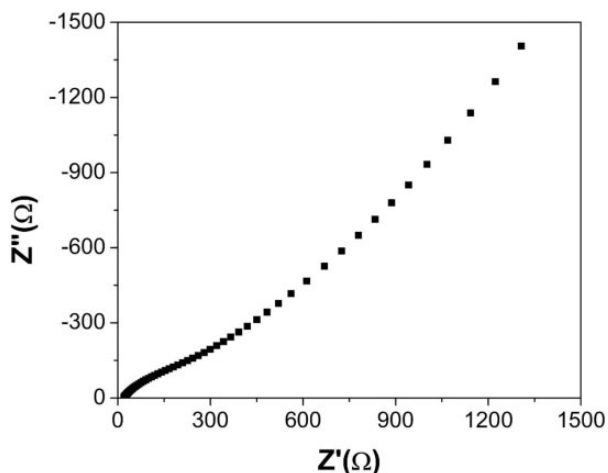


Figure 9. Low-frequency impedance spectra of EDLC containing maximum conductivity ILDPE film as electrolyte. EDLC: electrochemical double-layer capacitor; ILDPE: ionic liquid-doped polymer electrolyte.

the impedance data was 2.26 F/g, which matches well with the value obtained from CV data.

Conclusion

High conductivity ILDPE films have been synthesized using the solution cast technique and used in the EDLC. Impedance spectroscopy of ILDPE exhibits a six orders of magnitude enhancement in the conductivity of the host polymer by IL doping. The dielectric response supports the conductivity behavior of electrolyte films. LSV shows good ESW of 3.6 V. A POM study showed the texture of electrolyte films with reduced crystallinity. IR spectroscopy affirms the composite nature of ILDPE films. The EDLC fabricated using the maximum conductivity film (80

wt% IL) and corn starch-derived porous carbon electrodes showed a C_{sp} of 2.36 F/g.

Declaration of Conflicting Interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

The author(s) disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: This work was supported by research-oriented funds given by Sharda University. One of the authors, Meenal Gupta, thanks Ministry of Micro, Small & Medium Enterprises (MSME) for providing research grant to carry out the research work.

References

1. Bhattacharya B, Nagarale RK and Singh PK. Effect of sodium-mixed anion doping in PEO-based polymer electrolytes. *High Perform Polym* 2010; **22**: 498–512.
2. Singh R, Singh PK, Tomar SK and Bhattacharya B. Synthesis, characterization, and dye-sensitized solar cell fabrication using solid biopolymer electrolyte membranes. *High Perform Polym* 2015; **28**: 47–54.
3. Pandey GP, Kumar Y and Hashmi SA. Ionic liquid incorporated polymer electrolytes for supercapacitor application. *Indian J Chem* 2010; **49**: 743–751.
4. Singh PK, Nagarale RK, Pandey SP, et al. Present status of solid state photoelectrochemical solar cells and dye sensitized solar cells using PEO-based polymer electrolytes. *Adv Nat Sci: Nanosci Nanotechnol* 2011; **2**: 023002.
5. Beidaghi M, Wang Z, Gu L, et al. Electrostatic spray deposition of graphene nanoplatelets for high-power thin-film supercapacitor electrodes. *J Solid State Electrochem* 2012; **16**: 3341–3348.
6. Hashmi SA. Supercapacitor: an emerging power source. *Sci Lett* 2004; **27**: 27–46.
7. Wang KP and Teng H. Structural feature and double-layer capacitive performance of porous carbon powder derived from polyacrylonitrile-based carbon fiber. *J Electrochem Soc* 2007; **154**: 993–998.
8. Singh PK, Kim KW and Rhee HW. Development and characterization of ionic liquid doped solid polymer electrolyte membranes for better efficiency. *Synthetic Met* 2009; **159**: 1538–1541.
9. Masarapu C, Zeng HF, Hung KH, et al. Effect of temperature on the capacitance of carbon nanotube supercapacitors. *ACS Nano* 2009; **3**: 2199–2206.
10. Singh MK, Suleman M, Kumar Y, et al. A novel configuration of electrical double layer capacitor with plastic crystal based gel polymer electrolyte and graphene nano-platelets as electrodes: a high rate performance. *Energy* 2015; **80**: 465–473.

11. Karandikar PB, Talange DB, Mhaskar UP, et al. Development, modeling and characterization of aqueous metal oxide based supercapacitor. *Energy* 2012; **40**: 131–138.
12. Singh PK, Jadhav NA, Mishra SK, et al. Application of ionic liquid doped solid polymer electrolyte. *Ionics* 2010; **16**: 645–648.
13. Mahmood N, Zhang C, Yin H, et al. Graphene-based nanocomposites for energy storage and conversion in lithium batteries, supercapacitors and fuel cells. *J Mater Chem* 2014; **2**: 15–32.
14. Pandey GP, Hashmi SA and Kumar Y. Multiwalled carbon nanotube electrodes for all solid state electrical double layer capacitors with ionic liquid based gel polymer electrolyte. *J Electrochem Soc* 2010; **157**: 105–114.
15. Wang Y, Song Y and Xia Y. Electrochemical capacitors: mechanism, materials, systems, characterization and applications. *Chem Soc Rev* 2016; **45**: 5925–5950.
16. Choi BG, Chang SJ, Kang HW, et al. High performance of a solid-state flexible asymmetric supercapacitor based on graphene films. *Nanoscale* 2012; **4**: 4983–4988.
17. Pandey GP and Hashmi SA. Performance of solid-state supercapacitors with ionic liquid 1-ethyl-3-methylimidazolium tris(pentafluoroethyl) trifluorophosphate based gel polymer electrolyte and modified MWCNT electrodes. *Electrochim Acta* 2013; **105**: 333–341.
18. Emmenegger C, Mauron P, Sudan P, et al. Investigation of electrochemical double-layer (EDLC) capacitors electrodes based on carbon nanotubes and activated carbon materials. *J Power Sources* 2003; **124**: 321–329.
19. Girija TC and Sangaranarayanan MV. Analysis of polyaniline-based nickel electrodes for electrochemical supercapacitors. *J Power Sources* 2006; **156**: 705–711.
20. Stoller MD, Park S, Zhu Y, et al. Graphene-based ultracapacitors. *Nano Lett* 2008; **8**: 3498–3502.
21. Tamilarasan P and Ramaprabhu S. Graphene based all-solid-state supercapacitors with ionic liquid incorporated polyacrylonitrile electrolyte. *Energy* 2013; **51**: 374–381.
22. Lu W, Henry K, Turchi C, et al. Incorporating ionic liquid electrolytes into polymer gels for solid-state ultracapacitors. *J Electrochem Soc* 2008; **155**: 361–367.
23. Liew CW, Ramesh S and Arof AK. Good prospect of ionic liquid based-poly(vinyl alcohol) polymer electrolytes for supercapacitors with excellent electrical, electrochemical and thermal properties. *Int J Hydrog Energy* 2014; **39**: 2953–2963.
24. Dong K, Liu X, Dong H, et al. Multiscale studies on ionic liquids. *Chem Rev* 2017; **117**: A–BH.
25. Singh PK, Bhattacharya B, Nagarale RK, et al. Synthesis, characterization and application of biopolymer-ionic liquid composite membranes. *Synthetic Metals* 2010; **160**: 139–142.
26. Pang L, Zou B, Zou Y, et al. A new route for the fabrication of corn starch-based porous carbon as electrochemical supercapacitor electrode material. *Colloids Surf A Physicochem Eng Aspects* 2016; **504**: 26–33.
27. Karuppasamy K, Reddy PA, Srinivas G, et al. Electrochemical and cycling performances of novel nonafluorobutanesulfonate (nonaflate) ionic liquid based ternary gel polymer electrolyte membranes for rechargeable lithium ion batteries. *J Memb Sci* 2016; **514**: 350–357.
28. Karuppasamy K, Kim HS, Kim D, et al. An enhanced electrochemical and cycling properties of novel boronic Ionic liquid based ternary gel polymer electrolytes for rechargeable Li/LiCoO₂ cells. *Sci Rep* 2017; **7**: 11614–11.
29. Karuppasamy K, Reddy PA, Srinivas G, et al. An efficient way to achieve high ionic conductivity and electrochemical stability of safer nonaflate anion-based ionic liquid gel polymer electrolytes (ILGPEs) for rechargeable lithium ion batteries. *J Solid State Electrochem* 2017; **21**: 1145–1155.
30. Karuppasamy K, Prasanna K, Kim D, et al. Headway in rhodanide anion based ternary gel polymer electrolytes (TILGPEs) for applications in rechargeable lithium ion batteries: an efficient route to achieve high electrochemical and cycling performances. *RSC Adv* 2017; **7**: 19211–19222.
31. Liew CW, Ramesh S and Arof AK. Investigation of ionic liquid-based poly (vinyl alcohol) proton conductor for electrochemical double-layer capacitor. *High Perform Polym* 2014; **26**: 632–636.
32. Woo HJ, Liew CW, Majid SR, et al. Poly(ϵ -caprolactone)-based polymer electrolyte for electrical double-layer capacitors. *High Perform Polym* 2014; **26**: 637–640.
33. Singh R, Bhattacharya B, Gupta M, et al. Electrical and structural properties of ionic liquid doped polymer gel electrolyte for dual energy storage devices. *Int J Hydrog Energy* 2017; **42**: 14602–14607.