Preparation of polyvinylidene fluoride-*co*-hexafluoropropylene-based polymer gel electrolyte and its performance evaluation for application in EDLCs

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Abstract. Polymer gel electrolyte (PGE) film is prepared by incorporating polyvinylidene fluoride-*co*-hexafluoropropylene (PVDF-HFP) as polymer, ethylene carbonate (EC)-propylene carbonate (PC) as plasticizers and tetraethylammonium tetrafluoroborate (TEABF₄) as salt using solution cast technique. By varying weight percentages of EC-PC-TEABF₄ into a host polymer, different samples of PGE were prepared, and the concentration of EC-PC-TEABF₄ was optimized for maximum conductivity, and stability of the prepared film. The maximum ionic conductivity of the order of $4.9 \times 10^{-3} \text{ S cm}^{-1}$ was determined for 80 wt% of [EC-PC (1:1 v/v)-TEABF₄ (1.0 M)]. From the conductivity as a function of temperature, activation energy E_a was calculated and it is about 0.06 eV. Overall, the amorphous structure was confirmed by X-ray diffraction analysis. Dielectric and impedance spectroscopic analysis was also carried out to understand the electrical behaviour of electrolyte using modified Debye's function. An ionic character of prepared electrolyte was confirmed from DC polarization method. The ionic transference number of 0.91 was calculated from the data while the electrical potential stability window was found to be 3.8 V. The electrical performance of prepared PGE was examined by fabricating electrical double-layer capacitor (EDLC). In a supercapacitor, commercially procured activated carbon electrodes were employed. The specific capacitance of EDLC cell is found to be $\sim 60 \text{ mF cm}^{-2}$, and equivalent single-electrode capacitance is about 39 F g^{-1} .

Keywords. Polymer gel electrolyte; dielectric studies; XRD; electrical double-layer capacitor.

1. Introduction

Polymer-based gel electrolytes play a major role in the application of electrochemical devices such as supercapacitors, batteries etc. [1–4]. Usually, the different compositions of salt, polymer and plasticizer have been explored for an electrolyte system to improve the performance of electrochemical devices [5,6]. In recent years, polymer gel electrolytes (PGEs) have attracted global attention due to their better electrochemical performance [1–6]. The formation of materials is based on the liquid electrolyte, for example, a solution of lithium perchlorate (LiClO₄) in ethylene carbonate (EC), magnesium perchlorate (MgClO₄) in EC-propylene carbonate (PC) etc., immobilization in the host polymers such as polyvinylidene fluoride-*co*-hexafluoropropylene (PVDF-HFP), polymethyl methacrylate (PMMA) and polyvinyl alcohol (PVA) etc. [7–10]. Gel electrolytes are preferred as they reduce the leakage compared with the liquid electrolyte systems and also give better performance relative to the device using liquid electrolytes. They provide better electrode–electrolyte interfacial contact in an electrochemical cell. In PGE systems, electrical conductivity enhances an addition of liquid electrolyte and

approximately, it is of the order of $\sim 10^{-3} \text{ S cm}^{-1}$ due to the mobilization of salt ions in polymer matrix. Further, the addition of plasticizers such as EC and PC in polymer electrolyte increases the mechanical stability as well as conductivity [11].

Currently, electrochemical double-layer capacitors (EDLCs) find wide applications due to higher power density, rapid charging/discharging and long cyclic stability [12,13]. For improvement of EDLCs performance, efforts to improve the conductivity and mechanical stability of electrolyte systems are made. Further, the performance of EDLC is improved by adopting electrode materials having particles with higher specific surface area (table 5) [12–17].

In this research study, we have prepared PGE and it has been optimized for better conductivity and good mechanical stability. The electrical characteristics of PGE such as ionic conductivity, temperature-dependent conductivity, dielectric behaviour, have been examined using impedance spectroscopy. Modified Debye's function has been employed to analyse the dielectric and impedance of the prepared electrolyte. Ionic transport studies and electrical potential window of the cell: stainless steel (SS)||PVDF-HFP+EC-PC-tetraethylammonium tetrafluoroborate (TEABF₄)||stainless

steel (SS) have been carried out. The frequency-dependent conductivity has been analysed by using Jonscher's power law. The electrical performance of prepared electrolyte has been probed by fabrication of EDLC with commercially procured activated charcoal (AC) electrode material. The performance of electrical double-layer capacitor cell: AC||PVDF-HFP+EC-PC-TEABF₄||AC have been analysed using impedance spectroscopy, cyclic voltammetry (CV) and charge–discharge techniques.

2. Materials and methods

2.1 Preparation of electrolytes

For the preparation of PGE, PVDF-HFP (Sigma-Aldrich) (average molecular weight = 4,00,000) as a polymer, TEABF₄ (Alfa Aesar) as an ionic salt, PC (Loba Chemie) and EC (Sigma-Aldrich) as plasticizers and acetonitrile (Merck) as an intermediate solvent were used without any further treatment.

Firstly, liquid electrolyte was prepared adding TEABF₄ salt in binary solution of EC: PC (1:1 v/v). The conductivity of prepared electrolyte was optimized as a function of concentration of TEABF₄ salt. The highest conductivity was obtained for 1.0 M concentration of salt [18]. The PGE containing the liquid electrolyte was prepared. To prepare the PGE, polymer PVDF-HFP was separately dissolved in acetonitrile at 60°C with continuous stirring for 4 h till a uniform viscous solution is obtained. A uniformly thin film was obtained by pouring gel into a Petri dish and allowing slow evaporation at room temperature. The PGE systems having different concentrations of liquid electrolyte were prepared and the conductivity at room temperature was measured. Further, the mechanical stability of the prepared PGE was also monitored. The combination of PVDF-HFP (20 wt%) and EC-PC-TEABF₄ (80 wt%) was found having highest conductivity and good mechanical stability among the combinations of PVDF-HFP and EC-PC-TEABF₄ to form the PGE.

2.2 Preparation of electrode

The electrode material was prepared from the commercially procured AC. Initially, the PVDF-HFP was added into acetone and heated at 60°C with constant stirring for 2 h followed by addition of AC surface area (721 m² g⁻¹), the PVDF-HFP and activated carbon was taken into ratio of 1:9 (wt%). The prepared slurry was coated on the graphite sheet (area 0.25 cm² and thickness 25 µm) which was used as a current collector. The prepared electrode was kept in the oven at 70°C for 8–10 h for drying.

3. Instrumentation

For electrical properties measurements, LCR Hi-TESTER (3522–50, Hioki, Japan) 10 mV AC signal in a range of frequency between 1 Hz and 100 kHz was used to measure the impedance of the specimen. XRD-6000 Shimadzu Japan X-ray diffractometer was used for structural studies. Fourier transform infrared (FTIR) spectra were recorded using a Shimadzu 8400S FTIR spectrophotometer in the range 400–4000 cm⁻¹ employing KBr pellets as a standard. For analysis of supercapacitor parameters, CHI 608C, CH Instrument, USA was used.

4. Results and discussion

4.1 X-ray diffraction (XRD)

The XRD study has been used to understand the morphology of synthesized PGE. Figure 1 shows the XRD pattern of (a) pure PVDF-HFP and (b) optimized PGE. Figure 1a of pure PVDF-HFP shows predominant broad peaks at 2θ = 20° and 38° corresponding to the (020) and (021) crystalline peaks of PVDF-HFP [19,20]. The presence of broad peaks indicates semi-crystalline nature of polymer in which crystalline regions are mixed with the amorphous phase. Figure 1b shows the effect of blending of polymer with liquid electrolyte EC-PC-TEABF₄. The disappearance of peak at 2θ = 38° and further broadening of existing peak at 2θ = 20° confirms the complete blending of liquid electrolyte with the polymer PVDF-HFP at a molecular level in PGE. It further indicates an increase in amorphosity, which explains enhanced ionic conductivity of the PGE system. The enhancement in conductivity can be attributed to the availability of more space for ionic movement.

Figure 1. XRD pattern of (a) pure PVDF-HFP and (b) [PVDF-HFP (20 wt%)+EC-PC (1:1 v/v)-TEABF₄ (1.0 M) (80 wt%)].

4.2 FTIR spectroscopy analysis

FTIR spectral investigations are very useful for the determination of functional groups and to confirm the structure. FTIR spectra of the host polymer PVDF-HFP and PGE, mix of polymer and liquid electrolyte with plasticizers [PVDF-HFP+EC-PC+TEABF₄], are separately shown in figure 2a and b, respectively. This comparison enables the understanding of effect of complexation in polymer + salt and plasticizer.

FTIR spectra of host polymer PVDF-HFP, shown in figure 2a, vibrational peaks are observed at 421, 605, 674, 720, 737, 771, 874, 1017, 1083, 1380, 2852, 2923, 2981 and 3024 cm⁻¹. The identified peaks at 605, 674, 720, 737, 771 cm⁻¹ typically confirms the semi-crystalline nature of PVDF-HFP with lots of free space which is occupied by liquid electrolyte. These peaks decrease in intensity on addition of liquid electrolyte (EC-PC+TEABF₄), which further show increase in amorphous behaviour of synthesized PGEs [21]. This enhanced amorphous nature of PGE gives more free volume for the movement of ions, hence the increased mobility. This is responsible for the expanded ionic conductivity of the PGE.

A broad peak observed at 1640 cm⁻¹ comprising of few weak peaks can be correlated with -CH=CF skeletal breathing of PVDF-HFP polymer. The C-H stretching vibrational modes, in the range 2852–3024 cm⁻¹, are not much affected by incorporation of liquid electrolyte into polymer metrics. In figure 2b, FTIR spectra of PGE (mix of PVDF-HFP+EC-PC+TEABF₄) yield peaks at 720, 778, 1079, 1127, 1171, 1395, 1485, 1643 cm⁻¹. The vibration groups at 1079 and 1643 cm⁻¹ are characteristic modes of TEABF₄ and related to B-F asymmetric stretching of ionic inorganic salts [22]. These peaks show the presence of BF₄⁻ ions in the PGE.

Figure 2. FTIR spectra of (a) pure PVDF-HFP and (b) [PVDF-HFP (20 wt%)+EC-PC (1:1 v/v)-TEABF₄ (1.0 M) (80 wt%)].

4.3 Room temperature ionic conductivity

Ionic conductivity of the prepared electrolyte was extracted from the impedance spectra. The conductivity was calculated by relation $\sigma = t/R_b A$, where t is the thickness of the electrolyte, R_b the bulk resistance obtained from the real vs. imaginary impedance plot and A is the area of the electrode. To determine the composition, the conductivity of the prepared PGE for the concentration of EC-PC-TEABF₄ has been performed. In addition, the mechanical stability of the film was also tested. Figure 3 shows the variation of conductivity as a function of weight ratio of EC-PC-TEABF₄. The conductivity of the host polymer PVDF-HFP, which is of the order of 10⁻¹⁰ S cm⁻¹, increases on addition of the liquid electrolyte system [EC-PC-TEABF₄] that has conductivity approximately 10⁻² S cm⁻¹ for 1.0 M concentration of TEABF₄ [18]. The conductivity of PGE system exhibits maxima at 80 wt% concentration of EC-PC-TEABF₄. Further, for an optimized concentration, mechanical stability of the film relative to the other prepared film appears better. Conductivity is enhanced due to the dissociation of salt ions TEA⁺ and BF₄⁻ in PGE system. In an amorphous PVDF-HFP, the polymer chain assists the movement of dissociated ions resulting in higher ionic conductivity [18,20]. The conductivity at room temperature, 295 K, for an optimized system [PVDF-HFP (20 wt%)+EC-PC-TEABF₄ (80 wt%)] is approximately 4.0 × 10⁻³ S cm⁻¹, which makes prepared PGE a good candidate for application in EDLCs.

4.4 Temperature dependence of conductivity

For understanding the thermal stability of the optimized PGE, the conductivity at various temperatures has been carried out and provided in figure 4. This increase in conductivity may be associated with an increase in the mobility of polymer

Figure 3. Room temperature ionic conductivity of PGE as a function of liquid electrolyte concentration.

Figure 4. Variation of ionic conductivity of optimized [PVDF-HFP (20 wt%)+EC-PC (1:1 v/v)-TEABF₄ (1.0 M) (80 wt%)] as a function of temperature.

chains. The conductivity variation can be approximated by the Arrhenius equation:

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right) \quad (1)$$

where σ is the temperature-dependent conductivity, σ_0 the pre-exponential factor, E_a the activation energy and k is the Boltzmann constant.

The activation energy of 0.06 eV was calculated from the slope. Within the 60°C difference, the conductivity changes by approximately the magnitude of 10. This shows that synthesized PGE has potential application in electrochemical devices for a substantially wider temperature range.

4.5 Dielectric constant

The study of dielectric properties is related to storage and dissipation of electric energy in materials. The dissipation in various electronic and optical devices can be understood if the dielectric behaviour of materials is known.

Dielectric properties of optimized PGE are analysed by complex dielectric constant (ϵ^*), which is described by the following relation:

$$\epsilon^* = \epsilon' - j\epsilon'' \quad (2)$$

where $j = \sqrt{-1}$ and ϵ' is the real part and ϵ'' the imaginary part of the dielectric constant. Figure 5a and b shows the frequency dependence of real and imaginary part of dielectric constant at different temperatures. From figure 5a, it is clearly seen that dielectric constant decreases with increasing frequency due to the electrical relaxation process [23]. Higher value of dielectric constant at lower frequency is due to

the ionic, space charge and the orientation polarization effect [24,25]. In the low-frequency region, the value of dielectric constant increases with increasing temperature; this may be associated with the generation of thermal charge carriers [26]. At high frequencies, all the curves approach each other. Fast periodic reversal of electric field freezes oriental contribution to dielectric constant and makes it independent of temperature.

Experimental data were fitted using modified Debye's function which is described by relation:

$$\epsilon' = \epsilon'_\infty + (\epsilon'_0 - \epsilon'_\infty) / \left[1 + (\omega\tau)^{2(1-\alpha')} \right] \quad (3)$$

where ϵ' is the real part of dielectric constant, ϵ'_∞ the dielectric constant at higher frequency, ϵ'_0 the dielectric constant at lower frequency, $\omega = 2\pi f$ is the angular frequency, f the applied frequency, τ the mean relaxation time and α' is the spreading factor of actual relaxation time about the mean value. The fitted curve is shown in figure 5c. Experimental data are matching very well with calculated values which confirm the validity of modified Debye's function.

Figure 5b shows that the dielectric loss, related to ϵ'' , is very high at low frequency due to free charge migration within the material. It is clear from the figure that dielectric loss decreases with increase of frequency and finally reaches a constant value at high frequency.

4.6 Conductivity spectra

AC conductivity plot as a function of frequency at different temperatures is shown in figure 6a. Basically, all PGE systems show similar behaviour for ac conductivity plot. In figure 6a, distinct regions are observed. At low frequency, dispersion region is observed because of the interfacial polarization effect at the electrode–electrolyte interface. In general, the conductivity is extracted from the cole–cole plot high-frequency region. The high-frequency region is fitted to a semicircle and the intercepts on real axis give resistance value. However, the impedance measurements have been carried out in the frequency between 1 Hz and 100 kHz [27,28]. In a plot of Z as a function of frequency, a plateau region indicates DC equivalent resistance. The dispersion is observed in high-frequency region. In both the cases, extracted DC equivalent resistance is approximately identical.

The AC conductivity is analysed by universal Joshers' power law:

$$\sigma(\omega) = \sigma_{dc} + A\omega^n \quad (4)$$

where σ_{dc} is the DC conductivity, A the pre-exponential constant, n the power-law exponent with limit $0 < n < 1$. Using equation (4), experimental data was fitted and the DC conductivity (σ_{DC}), the power-law exponent (n) and pre-exponential constant (A) were evaluated. These parameters are given in table 1 and fitted curve is shown in figure 6b.

Figure 5. Variation of dielectric constant (a) real part and (b) imaginary part optimized [PVDF-HFP (20 wt%)+EC-PC (1:1 v/v)-TEABF₄ (1.0 M) (80 wt%)] as a function of frequencies at various temperatures. (c) Fitted curve of dielectric constant by using modified Debye's function.

4.7 Ionic transference number

For measurement of the ionic transference number (t_{ion}) of PGE systems, we used a DC polarization technique [29]. A DC voltage (0–1 V) is applied and current vs. time plot is observed in the DC polarization technique. The value of t_{ion} is evaluated by

$$t_{ion} = \frac{i_T - i_e}{i_T}, \quad (5)$$

where i_T and i_e are the total and the electronic current, respectively. Figure 7 indicates the current vs. time plot and the calculated value of ionic transference number from equation (5) is equal to 0.91 which is closer to 1. This indicates predominant ionic conduction.

Table 1. Fitted parameters of Jonscher's power law.

Temperature (K)	$\sigma_0 \times 10^{-3} (\text{S cm}^{-1})$	$A (\text{S cm}^{-1} \text{ rad}^{-n} \text{ S}^n)$	n
303	1.9	0.00004	0.412
313	3.8	8.8179E-6	0.424
323	5.0	3.6792E-7	0.690
333	7.1	9.0517E-7	0.634

I_t is the measured current at $t = 0$ s, and I_e the measured current at t_{max} s.

4.8 Electrochemical potential window stability

Electrochemical potential stability is one of the important merits of the PGE system and hence it needs to be determined. For optimized polymer electrolyte system, we

Figure 6. (a) Variation of ionic conductivity as a function of frequency for [PVDF-HFP (20 wt%)+EC-PC (1:1 v/v)-TEABF₄ (1.0 M) (80 wt%)] at various temperatures. (b) Fitted curve of Jonsher's power law.

measured the electrochemical potential stability behaviour from CV technique using cell: SS||[PVDF-HFP (20 wt%)+EC-PC-TEABF₄ (80 wt%)]||SS. The electrochemical window, which is a measure of the safe voltage limit, is about 3.8 V and it is good enough for any potential application such as supercapacitors. Figure 8 shows the current vs. potential plot and indicates the value of potential stability.

4.9 EDLC analysis

The performance of cell: AC||[PVDF-HFP (20 wt%)+EC-PC-TEABF₄ (80 wt%)]||AC is analysed by various techniques such as: AC impedance spectroscopy, CV and charge-discharge technique.

4.9a Impedance spectroscopy: From impedance spectroscopy technique, we have calculated the electrical parameters such as low-frequency capacitance, bulk nature

Figure 7. DC polarization curve at room temperature 295 K as a function of time for optimized [PVDF-HFP (20 wt%)+EC-PC (1:1 v/v)-TEABF₄ (1.0 M) (80 wt%)] at 1 V signal.

of electrolyte, and charge transfer and ions aggregation at electrode–electrolyte interfaces. The capacitance of 1 and 10 mHz has been calculated by

$$C = -\frac{1}{\omega Z''} \quad (6)$$

where ω is the angular frequency, Z'' the imaginary part of the complex impedance. Figure 9a shows the impedance plot of the fabricated cell. Two distinct regions, high-frequency region with semicircle and low-frequency region showing straight line are observed in the figure. From higher-frequency

Figure 8. CV curve of optimized gel polymer electrolytes system at a scan rate of 5 mV s⁻¹ for a cell, SS||[PVDF-HFP (20 wt%)+EC-PC (1:1 v/v)-TEABF₄ (1.0 M) (80 wt%)]||SS recorded at room temperature.

Table 2. Electrical parameters of EDLC cell from impedance analysis.

R_b ($\Omega \text{ cm}^2$)	R_{ct} ($\Omega \text{ cm}^2$)	R ($\Omega \text{ cm}^2$)	10 mHz		1 mHz	
			C		C	
			(mF cm^{-2}) ^a	(F g^{-1}) ^b	(mF cm^{-2}) ^a	(F g^{-1}) ^b
16.04	2.83	70.15	42.49	28.14	526.7	32.9

^aSpecific capacitance.^bSingle-electrode capacitance. **Figure 9.** (a) Typical impedance plot of cell: AC||[(1:4) PVDF-HFP+EC-PC (1:1 v/v)+TEABF₄ (1.0 M)]||AC. (b) Simulated electrochemical impedance spectra at 1 mHz of an EDLC cell experimental plot (blue) and simulated plot (red) at room temperature with equivalent circuit model.

semicircle, the value of the bulk resistance (R_b) and charge transfer resistance (R_{ct}) can be calculated. The straight line in the low-frequency region is due to Warburg impedance and indicates a large number of ion aggregation between electrode–electrolyte interfaces which form the electric double layer [29,30]. The calculated parameters are given in table 2.

Table 3. Simulated parameters obtained from impedance plot.

R_b ($\Omega \text{ cm}^2$)	R_{ct} ($\Omega \text{ cm}^2$)	C (μF)	α
16.2	2.39	1.163	0.45

An equivalent circuit that can describe the observed impedance response of the EDLC is provided as an inset in figure 9b. The experimental and equivalent circuit fitted data is shown in figure 9b. All the parameters in the given equivalent circuit have been kept free for fitting. The calculated values of these parameters are provided in table 3. Warburg impedance element Z_w is calculated by

$$Z_w = R_w \coth \left[\frac{(I\omega T_w)^{WP}}{(I\omega T_w)^{WP}} \right] \quad (7)$$

where R_w is the limiting diffusion resistance and $T_w = 2L/D$, where L is the diffusion length, D the diffusion coefficient and exponent W_P varies in range between 0 and 1.

4.9b CV studies: From CV studies, the specific capacitance is evaluated by the following relation:

$$C = \frac{i}{s} \quad (8)$$

where i is the current and s the scan rate. Figure 10a shows the CV characteristics plot at different scan rates. From the figure a rectangular shape is observed and the absence of redox peaks indicates the non-faradic processes; thus the presence of homogeneous and ideal polarized double layer at interfaces [30–32]. Figure 10b shows the variation of capacitance as a function of scan rate, which is almost constant except few initial scan rates. The capacitance values obtained from CV are large enough and are in good agreement with AC impedance spectroscopy and charge–discharge techniques. From equation (9), the calculated value of capacitance at 1 mV s^{-1} scan rate is found to be 60 mF cm^{-2} and is equivalent to the single electrode capacitance 39 F g^{-1} . As determined, the potential window of 3.8 V, CV curves in the range between -3.8 and 3.8 are provided as an inset in figure 10a. Some faradic reaction approximately beyond 1 V is visible. However, it has

Figure 10. (a) Cyclic voltammogram of cell: AC||[(1:4) PVDF-HFP+EC-PC (1:1 v/v)+TEABF₄ (1.0 M)]||AC at different scan rate. (b) Variation of the capacitance of cell as a function of scan rates.

Figure 11. Charge-discharge curve of cell: AC||[(1:4) PVDF-HFP+EC-PC (1:1 v/v)+TEABF₄ (1.0 M)]||AC at a current density of 1.0 mA cm⁻².

been observed that the electrolyte films suffer the damage at a higher voltage. The damage can be attributed to trapped liquid electrolytes in the film.

4.9c Charge-discharge technique: Figure 11 shows the charge-discharge profile of fabricated EDLC cells. As shown in the figure, we obtain ideal triangular profile which verifies the capacitive behaviour. This also confirms that energy storage mechanism depends upon the charge accumulation at electrode-electrolyte interface [18,30]. The discharge capacitance value from the discharge curve is calculated by the relation:

$$C_d = i \frac{\Delta t}{\Delta V} \quad (9)$$

where i is the constant current, Δt the time interval and ΔV the change of voltage. The value of capacitance obtained from equation (9) is shown in table 4. Using calculated capacitance, energy density (ED) and power density (PD) are also calculated using the formula:

$$ED = \frac{1}{2} C V^2 \quad (10)$$

$$PD = \frac{1}{2} \frac{C V^2}{\Delta t} \quad (11)$$

The value of ED and PD of EDLC cell is also tabulated in table 4.

Various factors contribute to the capacitance of EDLC cells. Ohmic loss across internal resistance, R_i , carbon morphology (surface area and porosity) and conductivity of electrolytes predominately modify the capacitance. The structure of the pores offers large surface area and they are accessible to electrolyte ions leading to the formation of interfacial ionic double layer, which results in higher capacitance (110–140 F g⁻¹ for activated carbons). Pores can be classified as micropores (0–2 nm), mesopores (2–50 nm) and macropores (>50 nm). The activated carbon that has been used in this investigation can be classified as mesopores. The relatively larger mesopores (2–50 nm) not only contribute to large surface area but also encourage improved adsorbate accessibility and ionic diffusion. It can be easily accessible by organic electrolyte ions, hence actively takes part in surface layer formation. On the contrary, micropores have high surface-area-to-volume ratio, hence contribute to high surface area. However, micropores (0–2 nm) have restricted diffusion and molecular sieve effect. Due to its small size, micropores are mostly not accessible to electrolyte ions, specifically the solvent ions (specially non-aqueous organic electrolytes) [33,34]. The capacitance decreases with smaller pore size. Further, microporous carbons have high electrolyte resistance and less electrolyte penetration, which limits their capacitance. Thus, mesoporous carbons are commercially favoured (for organic electrolytes) for effective pore accessibility. In table 5, the conductivity of

Table 4. Typical charge–discharge characteristics of EDLC cell at current density of 1 mA cm^{-2} .

Current density (mA cm^{-2})	$R_i (\Omega \text{ cm}^2)$	Discharge capacitance, C_d		Working voltage (V) (V)	Energy density (Wh kg^{-1})	Power density (kW kg^{-1})
		(mF cm^{-2}) ^a	(F g^{-1}) ^b			
1	16.9	38.7	22.4	1	3.1	1.6

^aOverall capacitance of the cell.^bSingle electrodes specific capacitance of the cell.**Table 5.** Typical values of double-layer capacitance of carbonaceous material [32].

Carbonaceous materials	Electrolyte	Capacitance	BET area ($\text{m}^2 \text{ g}^{-1}$)
Activated carbons	10% NaCl	19 μF	~ 1200
Carbon black	1 M H_2SO_4 , 31 wt% KOH	8 μF , 10 μF	80–230
Carbon fibre cloth	0.51 M Et_4NBF_4 :PC	7 μF	~ 1630
<i>Graphite</i>			
Basal plane	0.9 N NaF	3 μF	Highly oriented
Edge plane		50–70 μF	pyrolytic graphite
Graphite powders	10% NaCl	35 μF	~ 4
Graphite cloth	0.17 N NaCl	10.7 μF	~ 630
Glassy carbon	0.9 N NaF	$\sim 13 \mu\text{F}$	~ 900
Carbon aerogel	4 M KOH	23 μF	~ 650
Chemically treated AC	PVDF(HFP)-[EDiMIM][BF ₄]-PC-Mg(ClO ₄) ₂	395.8 F g^{-1}	~ 1515
Activated carbon	($8.4 \times 10^{-3} \text{ S cm}^{-1}$) [34]	4.4 F g^{-1}	~ 721
Activated carbon	[PVDF-HFP+EC-PC-TEABF ₄ + ZnO (12 wt%)] ($6.3 \times 10^{-3} \text{ S cm}^{-1}$) [33]	26 F g^{-1}	~ 721
Activated carbon	{PVDF(HFP)-BMIMCl-EC-PC-TEABF ₄ } ($8.99 \times 10^{-3} \text{ S cm}^{-1}$) [18]	40 F g^{-1}	~ 721
Present work-activated carbon	[PVDF-HFP (20 wt%) + EC-PC-TEABF₄ (80 wt%)] ($\sim 4.0 \times 10^{-3} \text{ S cm}^{-1}$)	22.4 F g^{-1}	~ 721

separators employed in devices are approximately identical. From table 5, it can be seen that a marginal difference in the conductivity alters the capacitance value [32]. Further, if the surface area of the electrode material particles increases dramatically, capacitance of the EDLC cell also improves. Thus it can be suggested that the critical values of the surface area of the particles or pores, the interface between electrodes and separators along with good ionic conductivity of electrolytes predominately describe the electrical response of the EDLC cell.

5. Conclusion

In this study, we have prepared PGEs and optimized them [PVDF-HFP (20 wt%) + EC-PC-TEABF₄ (80 wt%)] to give a higher value of conductivity $\sim 4.0 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature. The temperature-dependence conductivity plot verifies the Arrhenius behaviour. The dielectric nature has been analysed by modified Debye's function. Jonscher's power law is used for AC conductivity measurement. Ionic transport number $t_{\text{ion}} \sim 0.91$ and potential window $\sim 3.8 \text{ V}$ show

predominant ionic conduction and good electrochemical stability of synthesized PGE. The EDCL cell was fabricated and found to show a good capacitance value by the charge–discharge technique. A fabricated EDLC cell using AC-based electrodes and optimized gel polymer electrolyte gives a capacitance value 60 mF cm^{-2} at 1 mV s^{-1} using the CV technique, which is equivalent to the single electrode capacitance 39 F g^{-1} .

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