

Pmma Complexed With CH_3COOLi And Incorporated Along Emimtfsi For Edlc Application

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Abstract:

Polymer electrolytes based on PMMA (60 wt %): CH_3COOLi (40 wt %) : EMIMTFSI (0, 0.5, 1 wt %) are developed using technique called solution casting. Effect of ionic liquid EMIMTFSI (0, 0.5, 1 wt %) on PMMA (60 wt %): CH_3COOLi (40 wt %) polymer electrolytes confirmed through XRD studies, where peaks are totally suppressed and broadened due to complexation between the materials. FTIR showed the arising of new peaks and shifting of peaks due to molecular interaction of various functional groups. A.C impedance analysis revealed highest conductivity for PMMA (60 wt %): CH_3COOLi (40 wt %) : EMIMTFSI (1 wt %) as $3.4 \times 10^{-4} \text{ S/cm}$. The presence of double layer found from CV analysis C_{spec} value attained as 7 F/g, power density value is obtained as 750 W kg^{-1} and Energy density value is 0.8 W h kg^{-1} . Present work revealed that by incorporating EMIMTFSI (1-ethyl-methylimidazolium bis(trifluoromethylsulfonyl)imide) in polymer electrolyte complexes given best results and could be best promising candidate for fabrication of EDLC application.

Key words: Polymer electrolyte, Ionic liquid, conductivity, super capacitor.

1. Introduction:

“EDLC’s” are class of super capacitors have been considered as outstanding alternative power sources as they hold quick faradaic reaction like batteries. EDLC’s have many special features like non-toxicity, easy to fabricate, long cyclability, high power density. In EDLC’s have two identical electrodes, when salt is added into electrolyte it develops negatively charged ions (anions) and positively charged ions (cations)[1]. As voltage is applied cations attracts towards negative electrode and anions will attracts towards positive electrode. At negative electrode of EDLC over the charging time electric field generated, which attracts the cations and repels anions other way

opposing activity occurs near the positive electrode. So, charge is stored in the form of double layer at the electrode-electrolyte interface [2]. Where there is an electrostatic attraction among ions of the electrolyte to surface electrons attached to electrode [3]. From previous studies majority of the EDLC's are subjected to liquid electrolytes (LE's) like propylene carbonate PC-TEABF₄, PC-LiClO₄ and aqueous solutions like KOH, H₂SO₄, and KCL. The EDLC's related to LE's dealing with many disadvantages like corrosion, leakage of electrolyte, self-discharge, massive size [4]. In order to reduce the complications LE's substituted by solid polymer electrolytes SPE's). This idea involved to fabricate solid state EDLC using polymer electrolytes (PE's) [5]. Recent years there is a huge demand for the PE's expansion for their significant characteristics over the liquid electrolytes. Considering PE's are adaptable with the electrodes also they acquire leak free behaviour, elasticity nature, firmly moulds to desirable shape. Polymer electrolytes are utilized in electrochromic devices like EDLC and lithium ion batteries [6]. There are many polymer electrolytes reported on EDLC application like PEO-MgTf₂-LiTf-EMITf [7], PVdF-EC-PC-TEABF₄ [8], PEO-NH₄BF₄-SiO₂-DMA-EC-PC [9]. As these gel polymer electrolytes (GPE's) consists of both characteristics solid polymer electrolytes and liquid electrolytes offers flexibility and also enhances conductivity also adaptable among electrode and electrolyte medium, provides large electrochemical potential window [10]. From the published work PMMA:CH₃COOLi [11] GPE's reported as best result for PMMA:CH₃COOLi (60:40wt%) combination. Additionally, we are incorporating ionic liquid (IL) EMIMTFSI (1-ethyl-methylimidazolium bis(trifluoromethylsulfonyl)imide) to strengthen the features of GPE's. In IL's pairing between organic/inorganic anions and organic cations takes place and these are stable as liquid form upto 100°C. In presence of liquid nature these are easily miscible with other substances [12]. Ionic liquids named as green solvents as resist towards moisture and non-reactive to air also they exhibits non-volatility, high conductivity large electrochemical window. When it comes to structural changes, presence of polar groups helps for cationic movements in polymer-salt matrix [13]. The compatibility of IL "EMIMTFSI" with polymer-salt matrix (PMMA:CH₃COOLi) can be studied further.

2. Experimental:

2.1 Materials:

Poly(methyl methacrylate) (PMMA) of molecular weight $12 \times 10^5 \text{ g mol}^{-1}$, Lithium acetate (CH₃COOLi), (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) EMIMTFSI were purchased from sigma Aldrich, (DMF) Dimethyl formamide as solvent.

2.2 Preparation of polymer electrolyte:

PMMA used as host polymer and CH_3COOLi used as salt and to enhance the properties EMIMTFSI (1ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) is incorporated for the development of PE's. The combination of PMMA: CH_3COOLi (60:40) polymer electrolyte kept for stirring for 48 hours and additionally we have incorporated EMIMTFSI (0, 0.5, 1 wt %) for further improvement of results. After continuous stirring the homogeneous mixture is collected in polypropylene dishes and dried without any solvent traces to get transparent and flexible films.

2.2 Characterization:

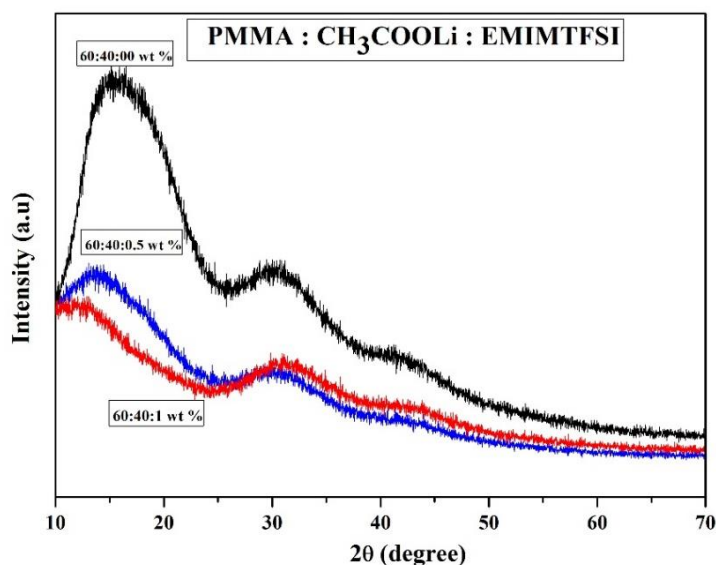
The prepared polymer electrolyte films examined using different characterization techniques. XRD analysis studied using PANalytical EMPYREAN diffractometer with $\text{Cu K } \alpha$ ($\lambda=1.5405 \text{ \AA}$) radiation between 10° to 80° . FTIR studies are conducted using JASCO spectrometer. A.C. impedance analysis, dielectric analysis studied by HIOKI 3525-50 LCR HITESTER from 500HZ to 3MHZ. CV analysis, Charge-discharge characteristics examined from metrohm electrochemical work station.

3. Results and discussion:

3.1 XRD studies:

XRD analysis explores the details for the structure of the material. Depending on the material the structure differs as semi crystalline or amorphous [14]. If the material is semi crystalline the sharp peaks are arises, if the material is amorphous broad peaks takes place [15]. Fig. 1 reveals the XRD studies for polymer electrolyte films (PMMA 60 wt %) : (CH_3COOLi 40 wt %) : EMIMTFSI (00, 0.5, 1 wt %). and 2θ varies from 10° to 80° .

Fig. 1 XRD Spectra for PMMA (60 wt %) : CH_3COOLi (40 wt %) : EMIMTFSI (0, 0.5, 1 wt %) polymer electrolyte films



From graph it reveals that for films (PMMA 60 wt %), (CH₃COOLi 40 wt %): EMIMTFSI (00 wt %) concentration of salt attains some effect, this indicates peaks are nearly blunt at some angles (2θ)~15°, 30°, 42°. By increasing ionic liquid ratio PMMA: CH₃COOLi:EMIMTFSI (60:40:0.5, 1 wt %) the peaks are completely broadened and shifted towards higher angle side which reveals that there is an effect of ionic liquid EMIMTFSI.

3.2 FTIR Analysis:

FTIR spectra is recorded in transmittance mode to make PE's (60 wt %): CH₃COOLi (40 wt %): EMIMTFSI (0, 0.5, 1 wt %) from 400 to 4000 (cm⁻¹). From the Fig. 2 represents the existence of various functional groups also bending and stretching vibrations are taken place on account of molecules interaction in PE's [16].

Fig. 2 FTIR Spectra for PMMA (60 wt %): CH₃COOLi (40 wt %) : EMIMTFSI (0, 0.5, 1 wt %) polymer electrolyte films.

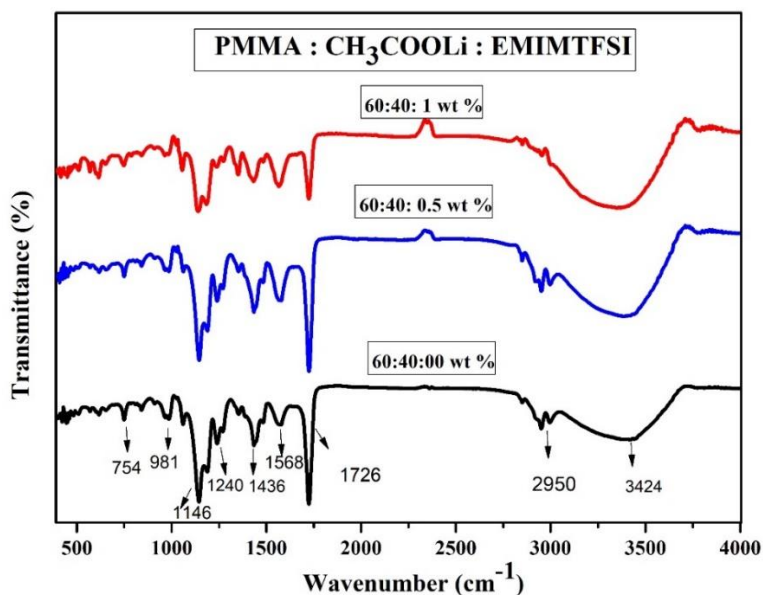
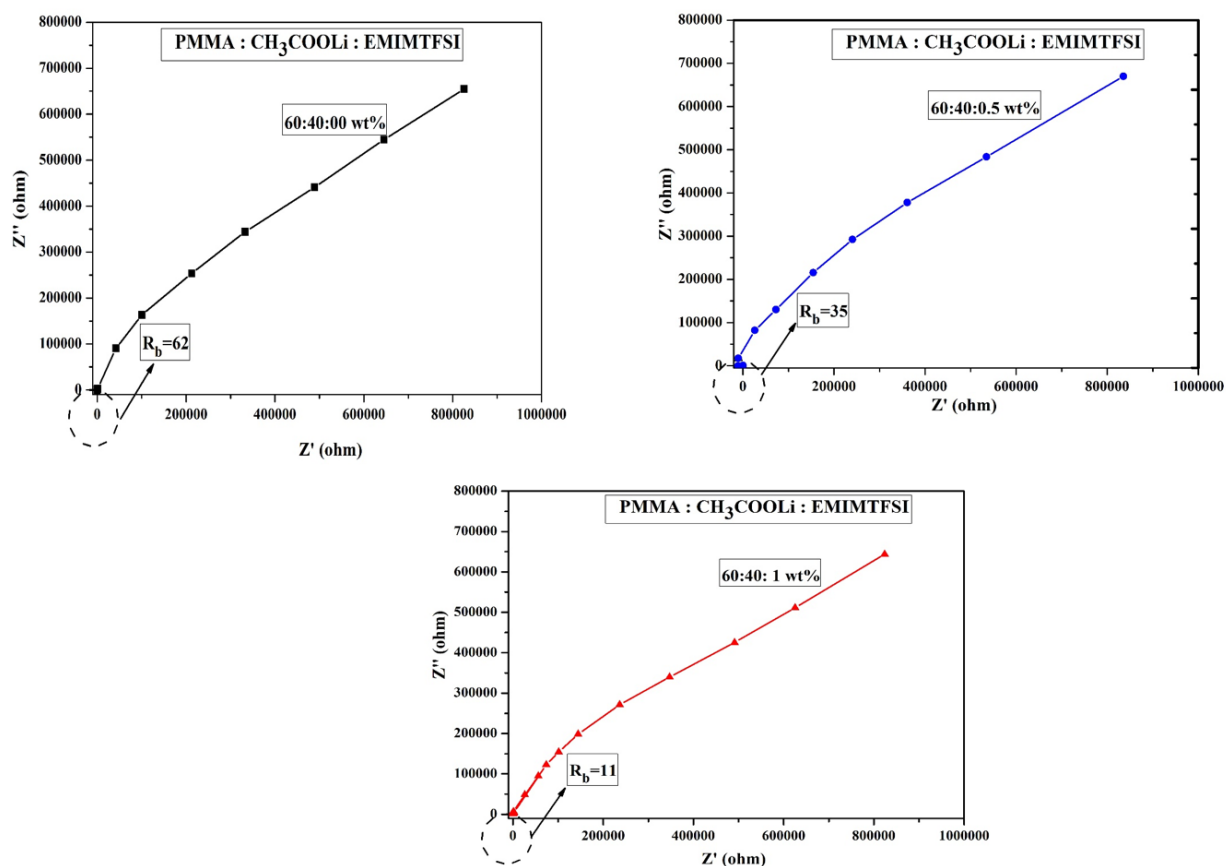


Fig.2 represents PE's of PMMA (60 wt %): CH₃COOLi (40 wt %): EMIMTFSI (0, 0.5, 1 wt %) FTIR spectra recorded for different absorption peaks for wave number regions (cm⁻¹). The absorption peaks are observed at 754 (cm⁻¹) due to -CH- bending vibrations. The absorption peak at 981 (cm⁻¹) is due to O-H bending vibrations. The absorption peak is recorded at 1146 (cm⁻¹) due to vibration of C-O hydroxyl group. The absorption observed at 1240 (cm⁻¹) due to C-O stretching vibration. Absorption peak at 1436 (cm⁻¹) due to O-H bending vibration. Absorption peak at 1568 (cm⁻¹) due to C=C ring stretching. The absorption peak at 1726 (cm⁻¹) is due to C=O stretching vibration. Absorption peak at 2950 (cm⁻¹) is due to C-H stretching vibrations. The absorption peak at 3424 (cm⁻¹) is due to O-H stretching vibrations. From all the stretching and bending vibrations and shifting of peaks resulting from interactivity among polymer and salt complexes and IL [17].

3.3 AC impedance studies:

AC impedance analysis studied for PMMA (60 wt %): CH₃COOLi (40 wt %) : EMIMTFSI (0, 0.5, 1 wt %) polymer electrolyte films. The prepared polymer electrolyte films are sandwiched between two SS (Stainless steel) electrodes and impedance analysis is studied. From Fig. 3 represents cole-cole plots, where Z' as real and Z'' as imaginary axes [18].

Fig. 3 Impedance analysis for PMMA (60 wt %) : CH₃COOLi (40 wt %) : EMIMTFSI (0, 0.5, 1 wt %) polymer electrolyte films.



Conductivity values derived using equation

$$\sigma_{ac} = \frac{t}{R_b * A} S/cm \rightarrow (1)$$

Where,

't' represents thickness of the polymer electrolyte film, ' R_b ' represents bulk resistance and 'A' is the area of the polymer electrolyte[19].

From the above equation (1) calculated conductivity value for PMMA(60 wt %): CH_3COOLi (40 wt%) : EMIMTFSI (0, 0.5, 1 wt %) polymer electrolyte films. Basically in impedance analysis at lower frequency range spike is observed and at higher frequency range a semi-circular arc is noticed. This is due to capacitance effect in between electrode and electrolyte interfaces. From Fig. 3 impedance graphs represents vertical spikes are observed and are aligned along imaginary axis at lower frequency range which indicates characteristics of ideal capacitance and this is due to influence of non-blocking electrodes[20]. The intercept value on Z' axis to be considered as ' R_b ', using this bulk resistance impedance value is calculate by equation (1). The conductivity

value for PMMA:CH₃COOLi (60:40 wt%) is $6.16 \times 10^{-5} \text{ S/cm}$ and as increasing the ionic liquid ratio EMIMTFSI (0.5, 1 wt %) there is enhancement of conductivity values and are obtained as $1.19 \times 10^{-4} \text{ S/cm}$ and $3.4 \times 10^{-4} \text{ S/cm}$.

Table 1: Conductivity values for PMMA (60 wt %): CH₃COOLi (40 wt%) : EMIMTFSI (0, 0.5, 1 wt %) polymer electrolyte films.

Serial number	Combination of PE		References
	PMMA (60 wt %): CH ₃ COOLi (40 wt%) : EMIMTFSI (0, 0.5, 1 wt %)	(σ) S/cm	
1	(60:40:00)	6.16×10^{-5}	[11]
2	(60:40:0.5)	1.19×10^{-4}	Present work
3	(60:40:1)	3.4×10^{-4}	Present work

On intensifying IL ratio results in increasing amorphous state which helps for mobility of cations in polymer chains which is due to compatibility between polymer salt complexes and to the ionic liquid[21].

Table 2: Comparison of conductivity values for PMMA (60 wt %): CH₃COOLi (40 wt%) : EMIMTFSI (0, 0.5, 1 wt %) polymer electrolytes with literature.

Sl.no	PE Combination	Conductivity value (σ) S/cm	References
1	PVA : PMMA : LiBF ₄	2.801×10^{-5}	[22]
	PMMA: LiBOB : EC: PC	5.54×10^{-5}	

2			[23]
3	PMMA: (Mg(CF ₃ SO ₃) ₂ :EC:DEC	5.58×10 ⁻⁵	[24]
4	PMMA (60 wt %): CH ₃ COOLi (40 wt %): EMIMTFSI (0, 0.5, 1 wt %)	3.4×10 ⁻⁴	Present Work

As comparing with literature, present work with PMMA(60 wt %): CH₃COOLi (40 wt%):EMIMTFSI (0, 0.5, 1 wt %) combination has obtained good conductivity value and also it could be good agreement for EDLC application.

3.4 Dielectric analysis:

Dielectric studies details the electrical behaviour of the material. The dielectric permittivity of the material calculated from

$$\varepsilon^*(\omega) = \varepsilon' - j\varepsilon'' \rightarrow (2)$$

Where, ε' as dielectric constant and ε'' as dielectric loss of the material[25].

Fig. 4 (a) Dielectric constant (ε') spectra for PMMA(60 wt %): CH₃COOLi (40 wt%) : EMIMTFSI (0, 0.5, 1 wt %) polymer electrolyte films.

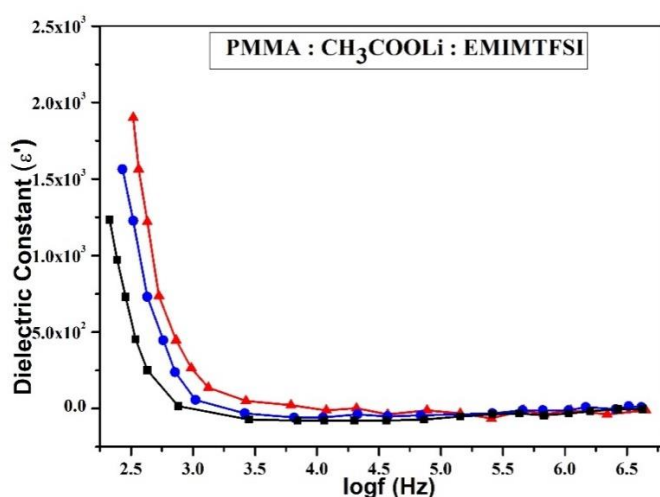


Fig. 4 (b) Dielectric Loss (ε'') spectra for PMMA(60 wt %): CH₃COOLi (40 wt%) : EMIMTFSI (0, 0.5, 1 wt %) polymer electrolyte films

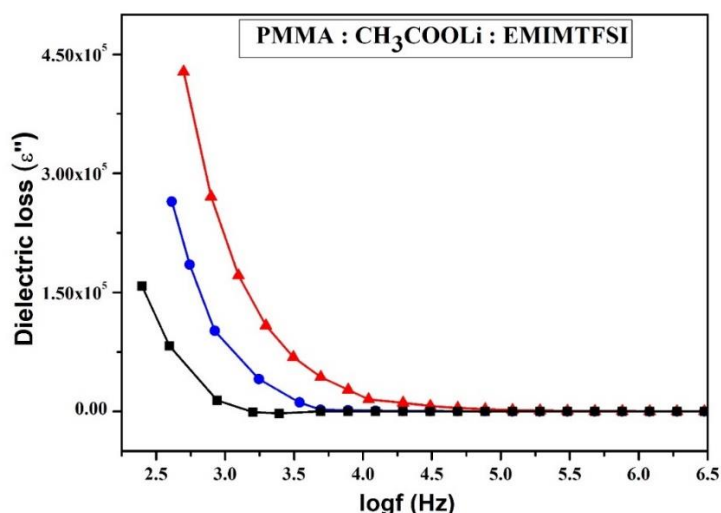


Fig. 4 (a) and 4(b) shows highest dielectric permittivity of PMMA (60 wt %): CH₃COOLi (40 wt%) : EMIMTFSI (1 wt %). Fig 4 (a) gives the information about charge storage through dielectric constant and Fig 4(b) gives the information about dissipation of energy takes place through charge carriers results in transport of charge carriers and polarization effect[26].

At high frequency range due to the high electric field dipoles cannot orient themselves and difficult to line up towards the applied electric field by reason of less relaxation time. So, there is lack of bulk ion distribution in both dielectric constant and dielectric loss[27]. At minimum frequency region because of more relaxation time the ions orient themselves and line up towards electric field applied, this is also because of the polarization effect[28]. EMIMTFSI ratio incorporated in polymer and salt complexes which perfectly blends into them, besides good structural properties of ionic liquid helps for cation mobility through chains of the polymer and also helps for ion transportation using hopping mechanism. Due to this effect the ionic conductivity is increased[29].

4. EDLC preparation:

4.1 Preparation of the active electrodes:

The two identical electrodes are arranged by picking the active area of 1cm² from aluminium foil. Carbon black (Super P), Activated carbon (Hi media), PVDF as binder (10:80:10) are added into 15ml quantity of NMP solution, mixed together to get homogeneous paste. The prepared blend is smeared on the both active electrodes and warmed around 80° C for 2 hours to get dehydrated active carbon electrodes.

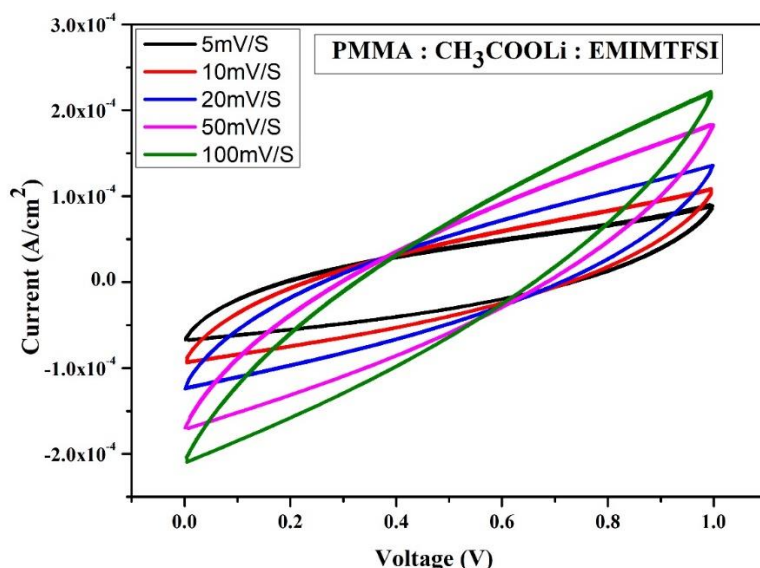
4.2 Fabrication of EDLC cell:

To assemble EDLC cell we club identical two active electrodes with PE of PMMA (60 wt %) :CH₃COOLi (40 wt%) : EMIMTFSI (1 wt %). Thus working and capability of EDLC cell is examined through CV studies and Charge-discharge studies by metrohm autolabpotentiostat.

4.3 CV studies for the EDLC cell:

CV studies are conducted by fabricated EDLC cell for the highest conductivity of the polymer electrolyte film PMMA(60 wt %): CH₃COOLi (40 wt%) : EMIMTFSI (1 wt %) in between potential from 0V to 1V.

Fig. 5 Cyclic Voltammograms for PMMA (60 wt %) : CH₃COOLi (40 wt %) : EMIMTFSI (1 wt %) polymer electrolyte films.



From Fig.5 for the 5mV/S represents perfect capacitor with rectangular shape. On account of non-appearance of redox reactions, there are no peaks and it is owing to non-faradaic reactions. The leaf-like shape observed is due to some internal resistance [30]. The scan rate is always inversely related to the capacitance values. At low scan rate the rapid movement of ions attributed to less relaxation time and they migrate into active electrode pores and also congregates near the electrolyte and electrode interface. All this triggers for the development of double layer which intensifies the storage capability [23].

The specific capacitance formula is

$$C_{\text{spec}} = \frac{\int_{V_1}^{V_2} I(V) dV}{2m(V_2 - V_1) \frac{dV}{dt}} \rightarrow (3)$$

Area of the CV plot represented by $I(V) dV$ calculated from Origin 8.5 software, m is the active electrode mass, $(V_2 - V_1)$ is the potential range, dV/dt is the scan rate[31].

For the PE of PMMA(60 wt %): CH_3COOLi (40 wt%) : EMIMTFSI (1 wt %) are tested for CV analysis from 0V to 1V potential range with different scan rate values (5 mV/S, 10 mV/S, 20 mV/S, 50 mV/S) the capacitance values are obtained as (7 F/g, 5.1 F/g, 3.9 F/g, 2.7 F/g, 0.9 F/g).

Table 3: Comparison of capacitance values for PMMA (60 wt %): CH_3COOLi (40 wt%) : EMIMTFSI (0, 0.5, 1 wt %) polymer electrolytes with literature.

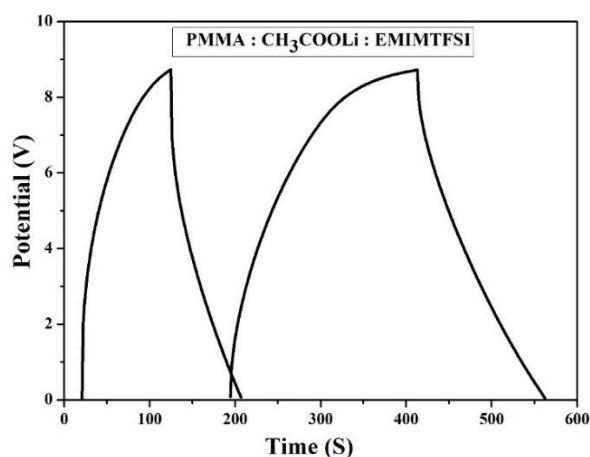
Sl. No.	Polymer Electrolytes Combination	Type of Electrode	Specific capacitance value - C_{spec} (F/g)	References
1	PAM:PVA: NH_4SCN	Activated Carbon	1230 (mF/g)	[32]
2	HEMA:DVIMBr	Activated Carbon	25 (mF/g)	[33]
3	PVA+ Phosphoric Acid	Graphene Electrodes	12.4($\mu\text{F}/\text{cm}^2$))	[34]
4	PMMA (60 wt %): CH_3COOLi (40 wt%) : EMIMTFSI (0, 0.5, 1 wt %)	Activated Carbon	7 (F/g)	Present Work

From the results we may conclude that it could be a favourable candidate for EDLC application from obtained results and also by comparing from the above Table 3. The table below gives the information few literatures work.

4.4 Charge-discharge studies:

The electrochemical storage behaviour of EDLC can be measured using charge-discharge studies. Fig. 6 shows the charge-discharge curves for selected cycles. From figure we can notice discharge region is almost linear which resembles double layer capacitance[35].

Fig. 6 Galvanic charge-discharge curves EDLC cell.



The specific capacitance (C_{spe}) value from the charge-discharge plot is derived using the

$$\text{equation } C_{spec} = \frac{i}{s \left(\frac{dv}{dt} \right)} \rightarrow (4)$$

Where, i indicates applied current, mass of the electrode active material represents s , (dv/dt) indicates slope of the discharge curve[36].

The energy density can be calculated from

$$E = \frac{C_{spec} (dv)^2}{2} \times \frac{1000}{3600} \rightarrow (5)$$

The power density can be calculated from

$$P = \frac{I \times (dv)}{2 \times m} \times 1000 \rightarrow (6)$$

The capacitance value C_{spec} calculated as 7.4 F/g, Power density value is 750 W kg⁻¹, Energy density value is 0.8 Wh kg⁻¹. These are the obtained values for EDLC application using prepared polymer electrolytes.

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Conclusions:

Solution casting technique used to make Polymer electrolytes PMMA(60 wt %): CH₃COOLi(40 wt%) : EMIMTFSI (0, 0.5, 1 wt %).PE film of PMMA(60 wt %): CH₃COOLi(40 wt%) : EMIMTFSI (1 wt %) attained highest conductivity as 3.4×10^{-4} S/cm.From CV studies the highest C_{spe} 7 F/g.From charge-discharge studies C_{spe} value is 7.4 F/g and the power density (P) value is obtained as 750 Wkg⁻¹, Energy density (E) value is 0.8 W h kg⁻¹. Therefore, the prepared polymer electrolyte film could be a promising candidate for EDLC application.

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