



Investigations on the Addition of Different Plasticizers in poly(ethylmethacrylate)/poly(vinylidene fluoride-co-hexa fluoro propylene) Based Polymer Blend Electrolyte System

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Abstract: Plasticized polymer blend electrolytes were prepared on the addition of different plasticizers with the constant ratio of poly(ethylmethacrylate) (PEMA), poly(vinylidene fluoride-co-hexa fluoro propylene) PVdF-HFP and lithium bis(trifluoro methanesulfonimide) $\text{LiN}(\text{CF}_3\text{SO}_2)_2$. The complexation of the salt with the polymer blend was confirmed by X-ray diffraction (XRD). Fourier transform infrared studies show the evidence of the complexation between PEMA, PVdF-HFP and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$. The ionic conductivity is enhanced in accompany with improved micro structural homogeneity, at low PEMA contents. The highest ionic conductivity $6.39 \times 10^{-3} \text{ Scm}^{-1}$ has been observed for ethylene carbonate (EC) based complex because of the higher dielectric constant (89.6) at 40°C among the other plasticizers. **Keywords:** Polymer blend electrolyte, different plasticizers, ionic conductivity, lithium ion battery.

Introduction

One of the main objectives in polymer research is to develop polymeric system with high ionic conductivity [1]. The polymer electrolytes are the new trend in advancement of the solid state ionics. Polymer electrolytes are safe, flexible, mechanically stable and can offer higher energy density as compared to commercial liquid electrolytes [2]. Polymer electrolytes are potential candidates as a medium for charge transport in electrical double layer capacitors, rechargeable batteries, chemical sensors and smart electronics [3]. Polymer electrolytes have application in electrochemical devices such as super capacitors [4], high energy density batteries [5], fuel cells [6] and electrochromic devices [7]. The solid polymer electrolytes have been of growing importance in applications which range from primary batteries to rechargeable batteries with high specific energy. Solid polymer electrolytes have many advantages, namely, high ionic conductivity, high specific energy, a solvent free condition, wide electrochemical stability windows, light and easy process ability.

Very recently PEMA as host polymer has drawn the attention of researchers due to its high ambient temperature ionic conductivity, which resembled that of liquid electrolytes. PEMA exhibit very good mechanical and electro-chemical properties compared with PMMA. PEMA is reported [8] to exhibit higher mechanical strength than PMMA. PEMA has excellent chemical resistance, high surface tension and offers high optical transparency. High transparency, sufficient mechanical strength, elasticity and good adhesion onto substrates [9] make PEMA suitable for use as a host for ionic conduction in electrochromic devices. On the other hand, PVdF-HFP consisting of crystalline VdF and amorphous HFP units allows ionic conductivity to occur with ease [10]. PVdF-HFP has high dielectric constant about 8.4, and thus can accommodate high concentration of charge carriers. Addition of plasticizers causes decoupling of ionic motion from that of polymer chain and increases ionic mobility by lowering the viscosity of ionic environment. $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ is an appealing salt since it decreases the polymer host's crystallinity and is more thermally and chemically stable than other traditional lithium salts. In this study, PEMA and PVdF-HFP were chosen so as to develop a polymer

blend electrolyte system with $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ as salt. Distilled acetone was used as solvent. The objective of this study is to find the suitable plasticizer (DEC, EC, DMC, PC & GBL), which could be used with $\text{P}(\text{VdF-HFP}) - \text{PEMA} - \text{LiN}(\text{CF}_3\text{SO}_2)_2$ for effective use in lithium battery applications.

Experimental section

Materials used

Poly(ethylmethacrylate) (PEMA) (average molecular weight 51.4×10^4) and poly(vinylidene fluoride-co-hexa fluoro propylene) (PVdF-HFP) (average molecular weight 4×10^5), lithium bis(trifluoro methane sulfonimide) ($\text{LiN}(\text{CF}_3\text{SO}_2)_2$), Ethylene carbonate (EC), Propylene Carbonate (PC), Dimethyl carbonate (DMC) and Diethyl Carbonate (DEC), Gamma-butyrolactone (GBL) bought from Aldrich, USA were used for the polymer electrolyte preparation.

Purification

Every chemical substance may be having a small amount of moisture, dust and other foreign elements. Hence the chemical substance should be purified before use. The polymer host and inorganic salt were purified by heating process using vacuum heating arrangement.

Preparation

The specific amount of PVdF-HFP, PEMA with inorganic salt $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ and plasticizer of each composition were weighted and PEMA were taken in a relative density bottle and kept inside the vacuum heating arrangement and heated up to 100°C for nearly 10 hours respectively. Then the inorganic salt was heated by the same procedure upto 100°C for nearly 10 hours. In this work, distilled acetone was used as a solvent. PVdF-HFP, PEMA, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ with different plasticizers were dissolved in acetone separately. After their dissolution, they were mixed together in a conical flask.

The conical flask which contains polymer-salt complex was placed on the top of the magnetic stirrer arrangement. The mixture was stirred for about 24 hours at room temperature. Then it was heated to 60°C and stirred for one hour at the same temperature. At the end of the stirring process, the mixture coagulated into a gel like formation. The slurry thus obtained was poured into a round Teflon die of 2 cm which has a piston like arrangement at the centre. The movable centre piston can be pushed from the bottom by applying a little finger pressure so that the piston arrangement can move up. The polymer films were dried under argon atmosphere at room temperature for 24 hours in order to evaporate the presence of residual solvents in the polymer films. This procedure provided mechanically stable, free standing and flexible films. The prepared polymer films of thickness 0.1 to 1 mm were obtained.

Characterization techniques

The XRD equipment used in this study was X'pert PRO PANalytical diffractometer. The Fourier transform infrared spectra (FTIR) were recorded in the range of $4000-400 \text{ cm}^{-1}$ using Perkin-Elmer Spectrophotometer. Conductivity measurements were carried out using Keithly LCZ meter (Model 3330) with signal amplitude of 10 mV in the frequency range of 40 Hz – 100 KHz at various temperatures ranging from 303 to 373 K, using stainless steel as the blocking electrode. The surface morphology of the prepared electrolytes was examined by JEOL JSM – 5310 Scanning electron microscope (SEM).

Results and discussion

X-ray diffraction analysis

The X-ray diffractograms shown in Fig.1 suggest that the sample of this study exhibit the co-existence of a multiphase system, which means that the polymer matrix possesses crystalline PVdF and amorphous HFP regions simultaneously. This can be due to a confirmation of partial crystallization of PVdF units in the copolymer which gives a semi-crystalline structure of $\text{P}(\text{VdF-HFP})$. In order to investigate the effect of various plasticizers (EC, PC, DEC, DMC, GBL) - $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ system XRD analysis has been performed. The characteristic diffraction peaks of the $\text{P}(\text{VdF-HFP})$ at angles 18.09 and 20.47° is reduced upon the addition of the plasticizers and lithium salt. The diffractograms in Fig.1 (d-h) reveals that the amorphous nature is predominant in the complex which is due to the addition of plasticizers. The maximum conductivity value $6.39 \times 10^{-3} \text{ Scm}^{-1}$ is

obtained for EC Fig.1 (e) based complex which is in accordance with the lower degree of crystallinity as compared to the four systems developed.

The peaks observed for 2θ values around 16.5° for pure PEMA disappear in complexed polymer films. The presence of broad humps in the pattern for PEMA confirms the amorphous nature of the polymer. The diffraction pattern of $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ shows intense peak at angles at $2\theta=13.6, 15.9, 18.9$ and 21.4° which reveals the crystalline nature of the ionic salt [11]. Most of the peaks pertaining to $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ disappeared in the complexes, which indicates the complete dissolution of the salt in the polymer matrix.

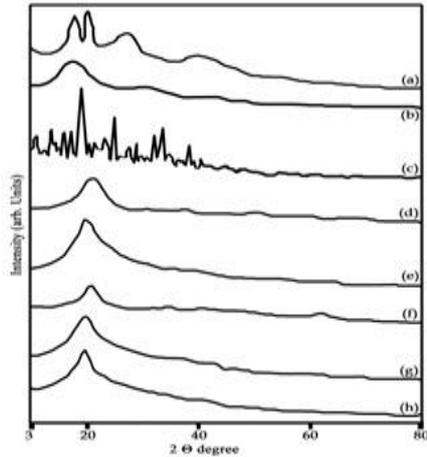


Fig. 1. XRD Patterns of pure (a) PVdF-HFP (b) PEMA (c) $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (d) PVdF-HFP - PEMA - $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ - DEC (e) PVdF-HFP - PEMA - $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ - EC (f) PVdF-HFP - PEMA - $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ - DMC (g) PVdF-HFP - PEMA - $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ - PC (h) PVdF-HFP - PEMA - $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ - GBL

FTIR analysis

FTIR is an important tool for investigating polymeric structure that provides information about the interaction/ complexation between the various constituents in the polymeric film. In order to understand the interactions between Li^+ ions and the polymer hosts in the polymeric electrolytes, the IR spectra of pure materials, polymer-salt and polymer-salt-plasticizer samples are presented. The FTIR spectra of pure PEMA, PVdF-HFP, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ and EC, PC, DMC, DEC and GBL based complexes are shown in Fig.2 (a-h) respectively.

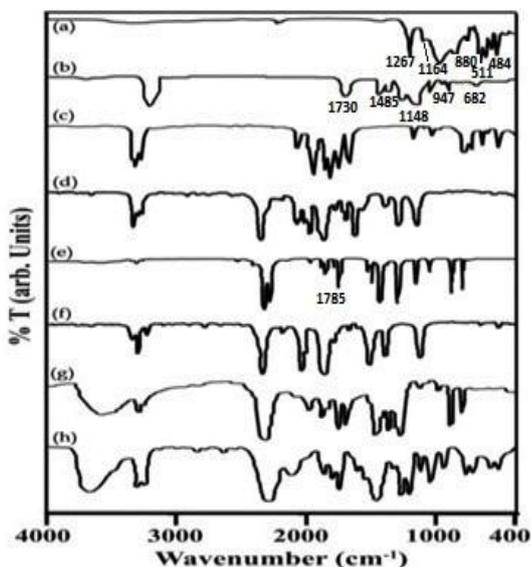


Fig. 2. FTIR Spectra of pure (a) PVdF-HFP (b) PEMA (c) $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (d) DEC (e) EC (f) DMC (g) PC (h) GBL.

FTIR spectra were recorded in the transmittance mode. The crystalline phase of the PVdF-co-HFP polymer is identified by the Vibrational bands at 511 and 484 cm^{-1} are assigned to the bending and wagging vibrations of $-\text{CF}_2$ respectively. The crystalline phase of the PVdF-co-HFP polymer is identified by the Vibrational bands at 1164 and 1267 cm^{-1} are assigned to the symmetrical stretching of $-\text{CF}_2$ and $-\text{CF}$ groups respectively. The peak at 880 cm^{-1} is assigned to the vinylidene group of the polymer [12, 13]. Spectrum of PEMA shows Vibrational peaks at 2983 and 2940 cm^{-1} which are ascribed to the asymmetric and symmetric C-H stretching of the methylene group of PEMA respectively [14]. The absorption peak of PEMA at 1730 cm^{-1} is assigned to the C=O carbonyl group. The Vibrational peaks corresponding to the $-\text{CH}_2$ scissoring, $-\text{CH}_2$ wagging and $-\text{CH}_2$ rocking are observed at 1485, 947 and 756 cm^{-1} respectively. The C-H bonding due to $\text{C}=\text{CH}_2$ group is observed at 939 cm^{-1} . Some other carboxylic acid ester groups were observed as broad features at 1148 cm^{-1} .

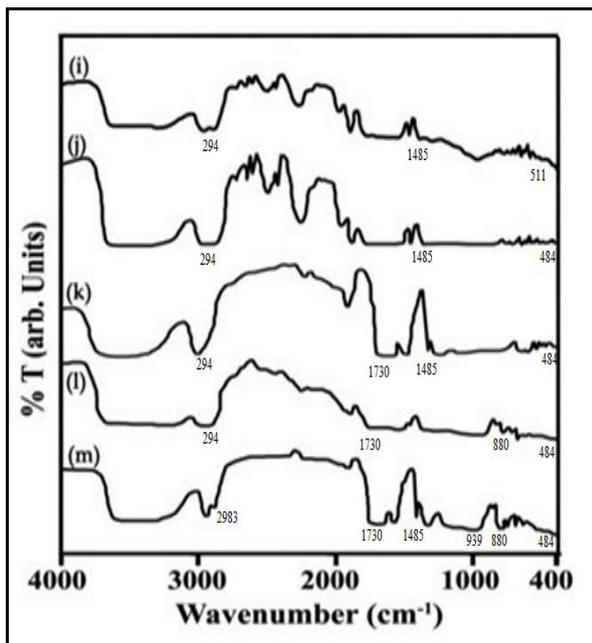


Fig. 3. FTIR Spectra of complexes

- (i) PVdF-HFP - PEMA - $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ - DEC
- (j) PVdF-HFP - PEMA - $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ - EC
- (k) PVdF-HFP - PEMA - $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ - DMC
- (l) PVdF-HFP - PEMA - $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ - PC
- (m) PVdF-HFP - PEMA - $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ - GBL.

The spectra of the samples containing plasticizers in the polymer salt complexes are shown in Fig.3. However the C=O bonds in EC (1785 cm^{-1}) seems to have overlapped and broadened Fig.3(j). This may be due to the association through the redistribution of charge accompanying the formation of ionic pair increases aggregation. This is attributed to the carbonyl group (C=O) and oxygen atoms in the EC ring [15]. The broadening of the C=O band in the plasticized polymer salt complexes indicates that the plasticizer just interacts physically with the polymer and the salt. No chemical reaction occurred between the plasticizer and polymer or between the polymer and to the salt [16].

With the addition of lithium salts to PEMA, the C=O stretching band broadened and shifted to lower wave numbers. This indicates that there is an interaction between the carbonyl group of ester and lithium salts via a coordinate bond and hence complexation has occurred. To justify the co-ordination of the lithium salt, the FTIR spectra of pure $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ was observed. The $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ion has a vibrational spectrum, which is very sensitive to its state of coordination, producing a series of different IR bands as its environment changes. The peak appearing at wave numbers 1333 and 1142 cm^{-1} are due to the S=O asymmetric stretch and C-F stretch. This seems to have disappeared in the complexes which confirmed that interaction has occurred. The O- CH_3 asymmetric stretch bands of PEMA at 1433 cm^{-1} are found to exist at the same wave numbers in the complexes and in pure PEMA. This indicates the co-ordination to the salt did not occur at these groups [17]. By comparing the band spectra of pure polymers and complexes, it is apparent that the band assignments are shifted in the FTIR spectra. In addition, some new peaks are present and some disappear in the complexes. Thus

the spectral analysis confirms the complexation of PVdF-co-HFP and PEMA polymer, plasticizers and lithium salts.

Conductivity measurements

The ionic conductivity of the polymer electrolytes mainly depends on the actual concentration of conducting species and their mobility. According to theoretical analysis of watanabe and ogata [18], two semicircles should appear in the impedance spectrum for a symmetric cell *i.e.* one at high frequencies corresponding to the bulk electrolyte impedance and the other at low frequencies related to the interfacial impedance. It has also been reported [19-21] that the high-frequency semicircle does not appear in practical impedance plots for plasticized polymer electrolyte membranes. This feature indicates that the conductivity is mainly due to ions.

The room temperature conductivity of the polymer electrolytes are measured by knowing the values of the bulk resistance R_b , area A and thickness l of the film by applying the equation $\sigma = l/R_b A$. The impedance curves of EC based PEMA,PVdF-HFP,LiN(CF₃SO₂)₂ system are shown in the Fig. 4 for the temperature range of 303-343K.

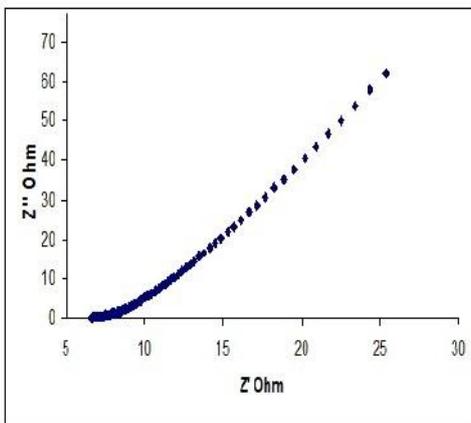


Fig. 4. Z real Vs Z imaginary plot for PVdF-HFP - PEMA- LiN(CF₃SO₂)₂- EC at room temperature.

The high frequency response yields information about the properties of electrolyte. The low frequency response carries information about the electrode/ electrolyte interface. It is observed that as the temperature increases, the conductivity also increases for all complexes.

The effect of the plasticizer on the polymer mobility and conductivity depends on the specific nature of the plasticizer including viscosity, dielectric constant, polymer-plasticizer interaction, ion plasticizer coordination, structure and molecular weight. The plasticizer with low viscosity provides ionic pathways for the migration of free Li ions. The high dielectric constant of the plasticizer helps in an increase in the salt dissociation.

Table 1. Conductivity values of PVdF-HFP (20) - PEMA (5) - LiN(CF₃SO₂)₂ (8) - X (67) [where X =DEC, EC, DMC, PC & GBL] at different temperatures.

Film s	X	Conductivity values of PVdF-HFP - PEMA - LiN(CF ₃ SO ₂) ₂ - X in Scm ⁻¹				
		303 K	318 K	333 K	353 K	373 K
A ₁	DEC	1.22×10^{-5}	3.81×10^{-5}	7.51×10^{-5}	9.66×10^{-5}	2.23×10^{-4}
A ₂	EC	6.39×10^{-3}	1.12×10^{-2}	2.49×10^{-2}	5.94×10^{-2}	9.69×10^{-2}
A ₃	DMC	7.52×10^{-5}	1.18×10^{-4}	1.96×10^{-4}	3.64×10^{-4}	4.23×10^{-4}
A ₄	PC	3.17×10^{-3}	4.90×10^{-3}	9.55×10^{-3}	2.69×10^{-2}	3.54×10^{-2}
A ₅	GBL	1.48×10^{-4}	2.70×10^{-4}	6.00×10^{-4}	1.26×10^{-3}	3.02×10^{-3}

From Table 1. it is observed that the complex PEMA, PVdF-HFP-LiN(CF₃SO₂)₂-EC shows a maximum conductivity value of $6.39 \times 10^{-3} \text{ Scm}^{-1}$ at 303K as compared to other prepared gel electrolytes which is mainly due to the higher dielectric constant (89.6 at 40°C) of Ethylene carbonate. The conductivity is obtained in the decreasing order of EC, PC, GBL, DMC and DEC based electrolytes which are in accordance with their dielectric constants 89.6, 64.4, 39.1, 3.12 and 2.82 at 40°C. These results are in accordance with those reported earlier using different plasticizers like EC, PC, GBL, DMC and DEC [22].

The variation of log conductivity versus inverse absolute temperature of the developed complexes is given in Fig.5. From the plot it is observed that as temperature increases the conductivity also increases for all compositions. The non-linearity in the plot indicates that the ionic transport in polymer electrolytes is dependent on polymer segmental motion. This can be explained on the basis of VTF relation [23-25]. It supports the idea that, ionic transport may be expected to take place along the plasticizer- rich phase which act as a tunnel for ionic transport.

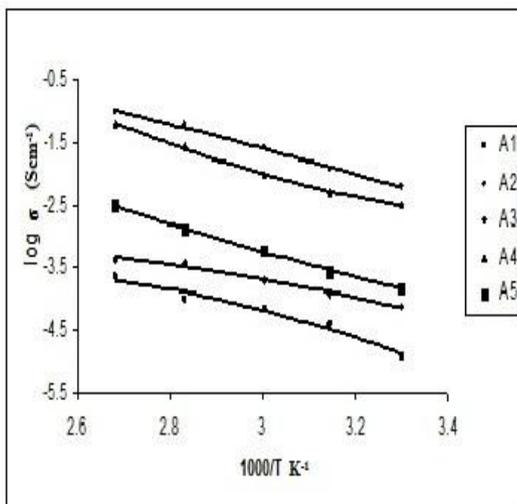


Fig. 5. Arrhenius plot of $\log \sigma$ versus $1000/T$ for PVdF-HFP - PEMA - LiN(CF₃SO₂)₂ - X [where X = DEC, EC, DMC, PC & GBL]

SEM Analysis

The analysis of microstructure of the polymer electrolyte plays an important role in determining the structure, spatial arrangement of atoms or molecules in the electrolytes [26]. In polymer blends, the domain size depends on a number of factors including the type of solvent and its evaporation rate and polymer, plasticizer, salt interactions [27]. However, the size of the dispersed domain is largely governed by the level of polymer compatibility.

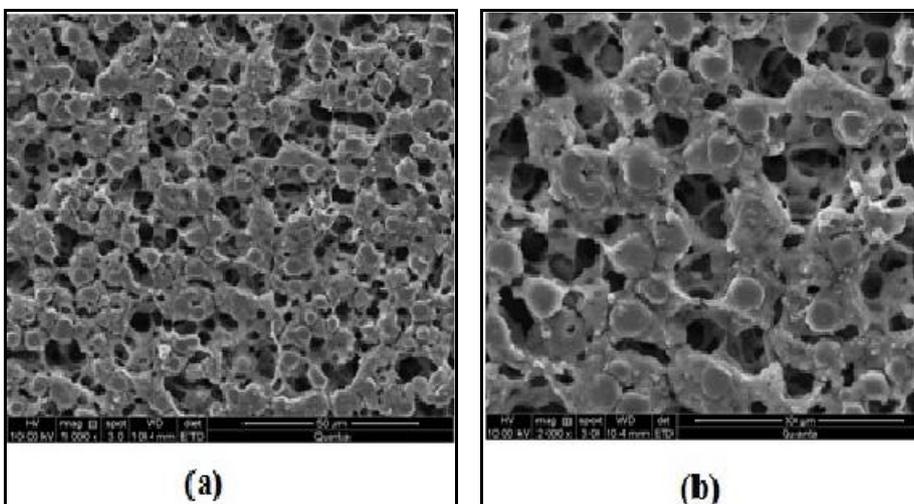


Fig. 6. SEM micrographs of PVdF-HFP - PEMA - LiN(CF₃SO₂)₂ - EC at 1000 & 2000 magnifications.

Scanning electron micrographs (SEM) of the polymer electrolyte film with maximum conductivity are shown in Fig. 6 (a & b) at 1000 and 2000 magnifications. It is evident from the figure that the surface of the film shows highly porous structure. These pores are responsible for the entrapment of plasticizer which could be responsible for the higher conductivity of the polymer electrolyte (film A₂). Further, it is confirmed that the amorphous nature of the electrolyte is increased due to the addition of salt and plasticizer.

Conclusion

Plasticized polymer electrolytes comprising PC, EC, DMC, DEC and GBL complexes with PVdF-HFP (20) – PEMA (5) – LiN(CF₃SO₂)₂ (8) system are prepared using solvent casting technique. The structure and complexation of the developed polymer electrolytes have been confirmed using XRD and FTIR studies. The addition of plasticizer into the complexes reduced the peak intensity of the blended polymer electrolytes. The maximum conductivity value has been obtained for EC based complex because of their higher dielectric constant as compared to the other plasticizers studied. The maximum conductivity obtained at 303 K is $6.39 \times 10^{-3} \text{ Scm}^{-1}$. The surface morphology of the developed films is analyzed by scanning electron microscope.

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