

MXene Nanofiller Doped Ion Conducting Polyethylene Oxide for Electrochemical Devices

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Abstract

Nanofiller-doped polymer electrolyte-based electrochemical devices are now emerged as a novel material for electrochemical devices. This paper reports a solid polymer electrolyte film doped with a new nanofiller synthesized by the solution casting technique. Electrical, Optical, and photoelectrochemical characterization are presented in detail. Electrochemical impedance spectroscopy (EIS) shows with the dispersion of nanofillers conductivity increases attains maxima and decreases. The maximum conductivity was at 0.05 wt% nanofiller concentration of 3.25×10^{-5} S/cm. The calculated ionic transference value was 0.92 which shows the domency of the system as ionic. The linear sweep voltammetry confirms a high electrochemical stability window (ESW) of 4.01V. Sandwiched electrical double-layer capacitors (EDLC) has been developed using carbon-based electrodes and sandwiched nanofiller dispersed polymer electrolyte, showing a high specific capacitance value of ~ 200 F/g.

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Abstract

Nanofiller-doped polymer electrolyte-based electrochemical devices are now emerged as a novel material for electrochemical devices. This paper reports a solid polymer electrolyte film doped with a new nanofiller

synthesized by the solution casting technique. Electrical, Optical, and photoelectrochemical characterization are presented in detail. Electrochemical impedance spectroscopy (EIS) shows with the dispersion of nanofillers conductivity increases attains maxima and decreases. The maximum conductivity was at 0.05 wt% nanofiller concentration of 3.25×10^{-5} S/cm. The calculated ionic transference value was 0.92 which shows the domency of the system as ionic. The linear sweep voltammetry confirms a high electrochemical stability window (ESW) of 4.01V. Sandwiched electrical double-layer capacitors (EDLC) has been developed using carbon-based electrodes and sandwiched nanofiller dispersed polymer electrolyte, showing a high specific capacitance value of ~ 200 F/g.

Keywords— Polymer electrolyte, Conductivity, Nanocomposite polymer electrolyte, Supercapacitors

Introduction:

Nanofiller as dispersoid in polymer electrolytes is a known established system playing a dominant role in day-to-day devices[1–3]. Nanofiller with polymer electrolyte matrix plays a dual role in the sense one side enhances electrical conductivity (σ) by establishing a quantum size effect, other side enhances mechanical stability of an atom[4–7]. The ionic conducting polymers, known as Solid polymer electrolytes [SPE] , that has been extensively researched and produced since the 1970s. Wright first described ionic conductivity in polyethylene oxide (PEO)/salt compounds in 1973[8]. In 1979, Armand claimed that at temperatures between 303K and 353K, the electrical conductivity of PEO/salt complexes might reach 10^{-5} S cm⁻¹. [9]. Polymer electrolytes have been developed primarily for Li⁺ and Na⁺ ions, two of the most common and abundant alkali metal ions.

In this study, we focus on the polymer-salt electrolyte combination PEO: NaI in which the conductivity results from the conduction of Na⁺ ions. PEO compounds with NaPF₆ [10], NaSCN, NaI, and NaCF₃SO₃ were the subject of earlier work on Na⁺ ion conducting polymeric electrolytes [11]. Additionally, the sodium batteries that use these electrolytes are rechargeable solid-state devices [12], [13]. A polymer electrolyte of poly (ethylene oxide) and sodium iodide (PEO-NaI) has been demonstrated to conduct Na⁺ ions and to some extent anionic conduction. To enhanced the conductivity of PEO-based electrolytes at lower operating temperatures, researchers proposed multiple techniques to incorporate nano-scale an inorganic fillers, that includes SiO₂ [14], Al₂O₃[15], TiO₂ [16], ZnO [17], ZrO [18], CeO₂ [19], and CuO [20], without involving the other physical properties, such as electrolyte reactivity towards electrode, mechanical stability, etc [21,22].

In MXene multilayer nanoflake doped polymer electrolyte, we have tried to develop a new nanofiller i.e. Ti₃C₂T_x MXene doped polymer electrolyte system. Polymer electrolyte chosen as host PEO:NaI in which maxima in ionic conductivity was reported at 12 wt % sodium iodide (NaI) concentration 1.05×10^{-7} S/cm. We have dispersed MXene at various wt%. (i.e., 0.01% to 0.07%). These multilayer nanoflake polymer electrolytes were systematically characterized by various characterization tools and their results are summarized in present paper.

Experimental Details:

Material and Method :

The polymer PEO with an average molecular weight of 100,000 was purchased from ADRICH Chemistry Pvt. Ltd. in USA, while NaI (extra pure) with a molecular weight of 166.01 g/mol was purchased from FINAR Reagents Pvt., India. Ti₃C₂T_x MXene multilayer nanoflake having molecular weight of 167.62g/mol was purchased from Nanoshel UK Limited with purity of 99.9%. Before use, the multilayer nanoflake and other solvents utilized in this investigation were thoroughly dried.

Synthesis of solid polymer electrolyte

Solution casting was used to prepare polymer-salt electrolyte thin films containing nanofillers in polyethylene oxide matrix. In maximum conducting PEO:NaI polymer electrolyte homogenous solution, we have added different wt% ratios of nanoflake to develop nanofiller doped polymer electrolyte film. To remove solvent

traces (if any) we have vacuum dried all films. Finally, we have fabricated a sandwiched structure maximum conducting nanofiller doped polymer electrolyte and r-Go as the active material.

Supercapacitor Fabrication

The MXene doped ion-conducting polymer electrolyte layer (having maximum conductivity) placed between two designed r-GO symmetric electrodes, and the device's performance was determined using an electrochemical workstation analyzer (CH640D). Active electrodes based on non-porous carbon (area 1x1cm²) graphite sheets is used as a current collector. These carbon electrodes were then finally dried in the vacuum oven overnight at 80°C. As an active electrode material for 1 cm² area of current collector, we used generally 1 mg of paste of nonporous carbon.

Result and Discussion

Conductivity Measurement

To determine the bulk electrical conductivity of the polymer electrolyte sheets, complex impedance spectroscopy was performed. To perform experiment, we have sandwiched polymer electrolyte films in between two stainless steel electrodes and then sample holder was connected to EIS measurement (CH640D) in between frequencies 100Hz to 1mHz.

To evaluate ionic conductivity values, we have used equation (1):

$$\sigma = G \frac{l}{A} \quad (1)$$

where σ is the specific conductivity, G is conductance i.e., $G=1/R_b$ where R_b is the bulk resistance, l is the thickness of the film and A is the area of the polymer film covered by electrodes.

Concentration Dispersoid (wt%)	Conductivity (σ) (Scm ⁻¹)
Pure PEO	1.30 x 10 ⁻⁸
PEO + 12% NaI (A)	1.05 x 10 ⁻⁷
A + 0.01 MXene	1.30 x 10 ⁻⁶
A + 0.02 MXene	1.43 x 10 ⁻⁶
A + 0.03 MXene	2.91 x 10 ⁻⁵
A + 0.04 MXene	2.05 x 10 ⁻⁴
A + 0.05 MXene	3.25 x 10 ⁻⁵
A + 0.06 MXene	1.08 x 10 ⁻⁶
A + 0.07 MXene	2.016 x 10 ⁻⁶

Table 1: Ionic conductivity values of MXene doped polymer electrolyte systems calculated at ambient temperature

Electrochemical impedance spectroscopy (EIS) was used to characterize the electrical behavior of various electrolyte layers. In contrast to pure polymer polyethylene oxide (PEO) and polymer salt complex PEO: NaI and films with varying quantities of nanofiller. To insight role of nanofiller in the polymer we have chosen PEO: NaI as host. It has to be acclaimed that PEO has a conductivity of around 1.30 x 10⁻⁸ S/cm in the absence of salt. The maximal electronic conductivity was 1.05 x 10⁻⁷ S/cm after adding 12 wt% of NaI. Further, addition of nanofiller (MXene) conductivity increases and conductivity maxima obtained at 0.04 wt% of dispersoid with σ value of 2.05 x 10⁻⁴ S/cm. Nyquist value of one typical sample is shown in fig. (1) and using equation 1 we have evaluated the σ values and listed in Table 1

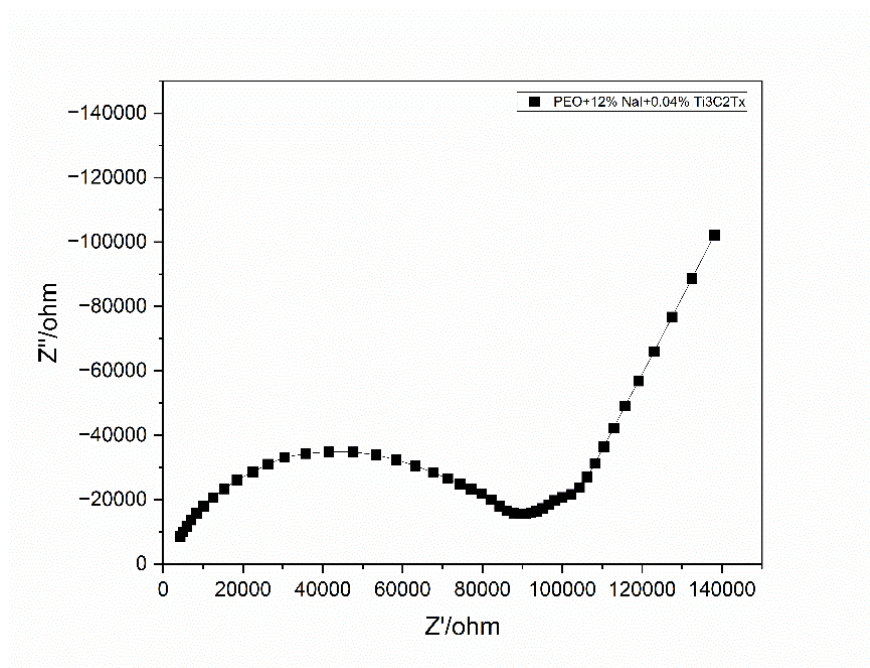
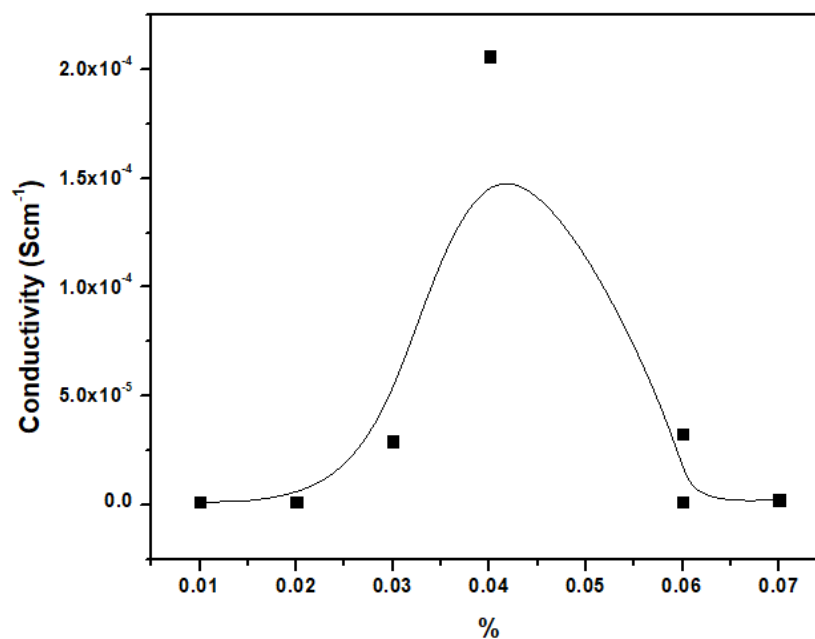


Figure 1: Nyquist Plot of complex impedance PEO + 12% NaI + 0.04% $\text{Ti}_3\text{C}_2\text{T}_x$ MXene



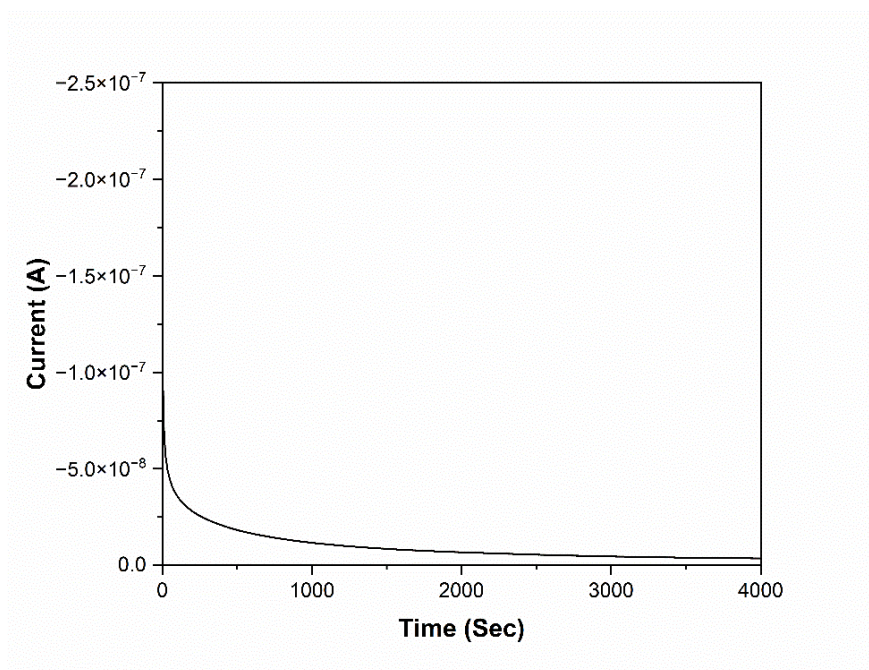
From fig. (2) it was clear that conductivity increases attain maxima and then decreases which is common phenomenon in nanofiller doped polymer electrolyte

Figure 2 : Ionic conductivity vs Concentration of MXene in nanofiller doped polymer electrolyte

3.1.2 Transference Number Measurement

Using Wagner’s direct-current polarisation approach, illustrated in fig. 3, the total ionic transference number of the produced electrolyte comprised of solid, flexible polymers was computed. This approach is based on adopting suitable electrodes for a mixed conductor, it is possible to suppress either ionic or electronic transport while still determining the contribution of unsuppressed species. This approach involves sandwiching the sample between two electrodes, one of which is reversible (non-blocking) and can interchange both ions and electrons with the electrolyte, and the other of which is blocking (non-reversible) and can only do so. In order to polarise the sample, an insignificant potential is provided throughout the cell, causing the mobile ionic species to migrate in the direction of the blocking electrode. A layer depleted of mobile ions is formed close to the blocking electrode, which causes the current to decline over time gradually. This example shows how the current is calculated as a function of time till saturation level. This cell is polarised using d.c. voltage; in this case, we polarised the cell up to 0.92 before allowing it to self-discharge. The initial total draft (I_t) in the current vs. time figure is the sum of the improvement from ions and electrons. In contrast, the constant residual current (I_e) is exclusively attributable to the ionic current. The ionic transference number is thus provided by equation (2) and (3):

$$t_{ion} = 1 - \frac{I}{I_t} \quad (2)$$



$$t_{ion} = 1 - t \quad (3)$$

Figure 3: Polarization current vs. time for the highly conducting MXene doped polymer electrolyte

t_{ion} value greater than 0.9 itself suggested that system is predominantly ionic in nature.

3.1.3 Linear Sweep Voltammeter (LSV)

The linear sweep voltametric (LSV) response was measured to assess the electrochemical stability window with nanofiller doped polymer electrolyte films. Figure 4 implies the linear sweep voltammogram for a highest electric conductivity nanofiller enhanced polymer electrolyte layer from -2.5 V to 2.5 V. The polymer electrolyte film was placed among two SS electrodes for LSV analysis carried out by CH instrument workstation. It is evident that there is no faradic peak in the voltage range roughly between -1.8 V and 1.8 V. The

outcome is a novel nanofiller doped solid electrolyte for EDLC application, with a nano filler doped polymer electrolyte layer exhibiting an ESW of about 4.01 V.

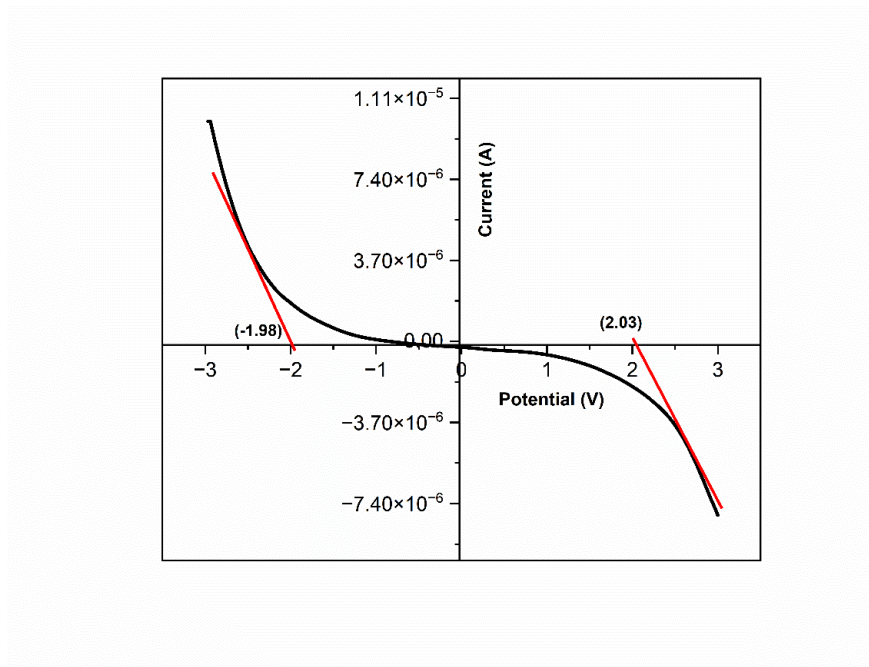
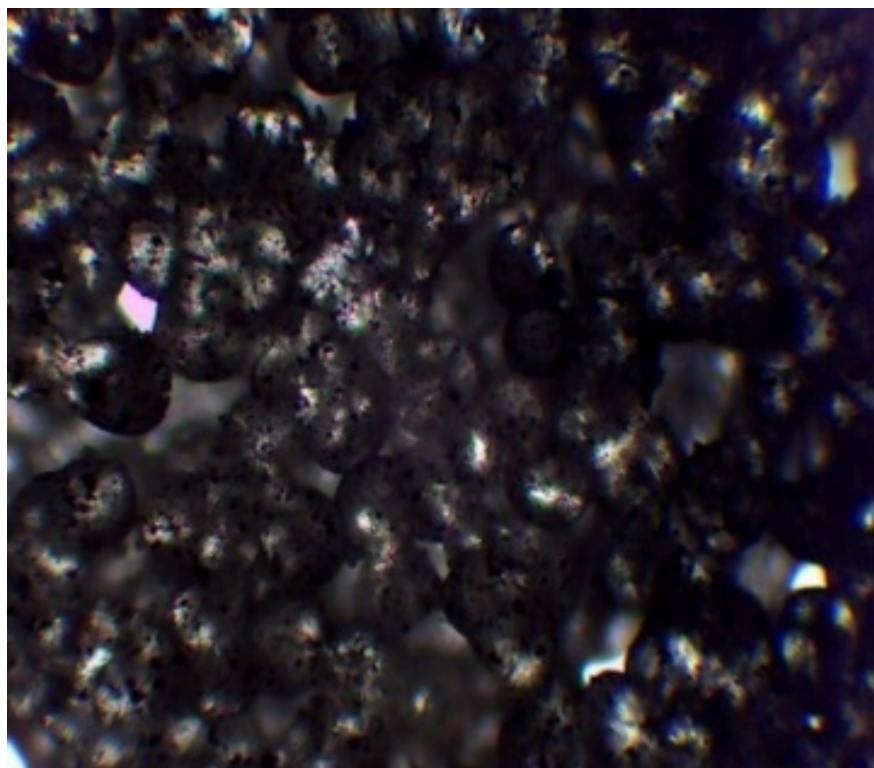
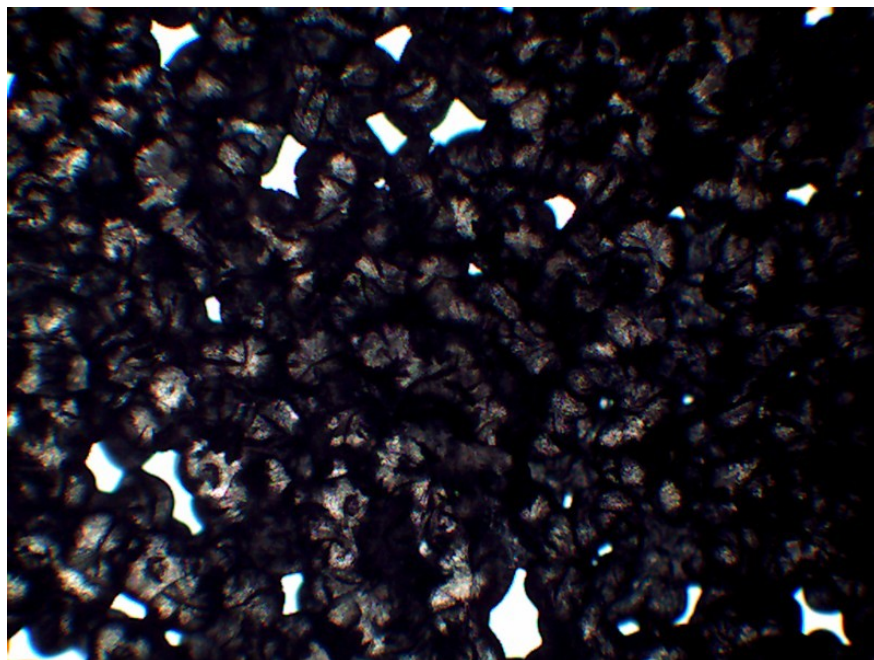
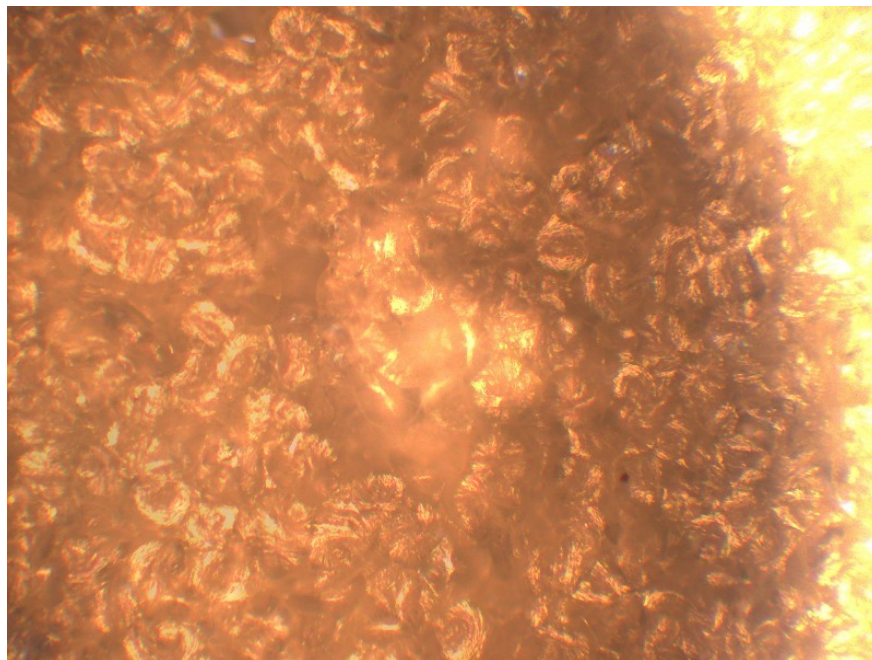


Figure 4: LSV of maximum conducting nanofiller doped polymer electrolyte film

Optical Microscopy Analysis

Optical micrographs of optimized polymer-salt complex (PEO: NaI), rise nanofiller doped polymer electrolytes, and pure polymer (PEO) electrolytes are displayed in Figure 5. Figure 5(a) depicts the optical micrograph of the pure polymer PEO. It has been found that pure PEO has greater white patches (spherulite's) than polymer salt complex films and nanofiller-doped polymer electrolyte films. This illustrates the material's immense degree of crystallinity, which is suggestive of the host polymer PEO's semi-crystalline structure. Also, the PEO polymer exhibits surface morphological roughness. The surface morphology has changed as a result of the 12 wt % NaI addition to the PEO polymer matrix. Due to the salt doping, spherulites crystalline size has randomly decreased. The dark area seen in Figure 5(b) denotes an increase in the matrix's amorphous nature for the polymer salt complex. The surface morphology of the PEO + 12 wt% NaI polymer matrixes significantly change when 0.04 wt% MXene is added, as can be seen in Fig. 5(c).





Pure PEO (b) PEO + 12 wt% NaI

Figure 3 : Optical micrographs of (a) pure polymer, (b) polymer salt-complex and (c) MXene doped polymer electrolyte at 10x magnifications

3.3 Characterization of EDLC

The electrolyte layer of the supercapacitor cell, constructed of an optimised ion-conducting polymer, contained the non-porous carbon active material positioned between two symmetric electrodes. Low-frequency impedance spectroscopy (IS) and cyclic voltammetry (CV), which were used to determine the specific capacitance of the EDLC device, were used to assess its performance.

3.3.1 Cyclic voltammograms (CV)

Cyclic voltammograms were used to observe the electrochemical interaction between the acetone nitrile, PEO, and iodide/iodine polymer electrolyte sheets. It is apparent that NaI+TiC films exhibit good redox behavior with two redox peaks at slow scan rates, in Nano filler-containing PEO: NaI film. Figure 5 shows the hysteresis curve which exhibit the supercapacitor behavior. The graph's specific capacitance C_{sp} value for the EDLC device has been determined using eqn (4)

$$C = \frac{I}{s} \quad (4)$$

Where C_{sp} is the one electrode's capacitance, m is the active electrode material's mass at one electrode, I is the average current, and s is the scan rate ($s = 5 \text{ mV/s}$). Thus, the specific capacitance of EDLC is determined to be 190 F/g . Additionally, the EDLC's C_{sp} value was calculated using the low-frequency impedance spectroscopy data mentioned in the following section.

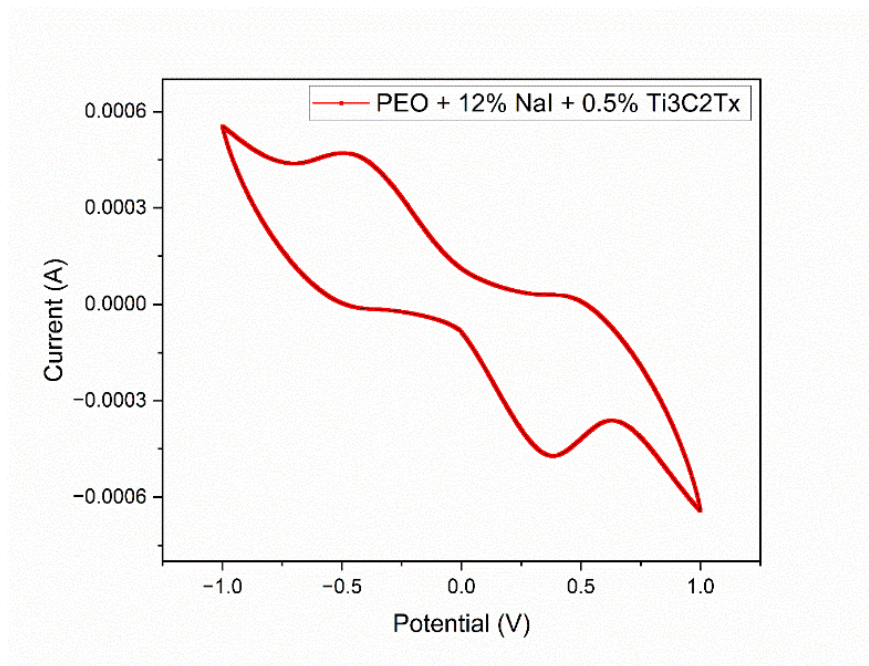


Figure 5: EDLC cyclic voltammogram with the maximal conducting MXene doped polymer electrolyte film acquired at a scan rate of 5 mV/s in the potential range -1 to 1 V.

3.3.2 Low frequency – impedance spectroscopy (IS)

The low-frequency impedance spectroscopy was conducted as shown in Figure 6. A high-frequency zone and a low-frequency region are represented. A semicircle is typically used to represent the high frequency area, reflecting both the charge-transfer processes at the electrode-electrolyte interfaces and the bulk properties of the electrolytes. A capacitive spike can be seen in the low frequency area, which is a result of charges building up and double layers forming at the electrolyte-electrode contact.

The specific capacitance that is measured at low-frequency through impedance spectroscopy is obtained, as illustrated below

$$C = \frac{-1}{2\pi f Z'' m} \quad (5)$$

Where m is the mass of the active electrode material (carbon) at one electrode (considered to be $m = 1$ mg), f is the frequency, and Z'' is the imaginary portion of the impedance at low frequencies. The specific capacitance was subsequently determined to be 186 F/g, which is nearly the same value as the value derived from CV data, using low frequency calculations.

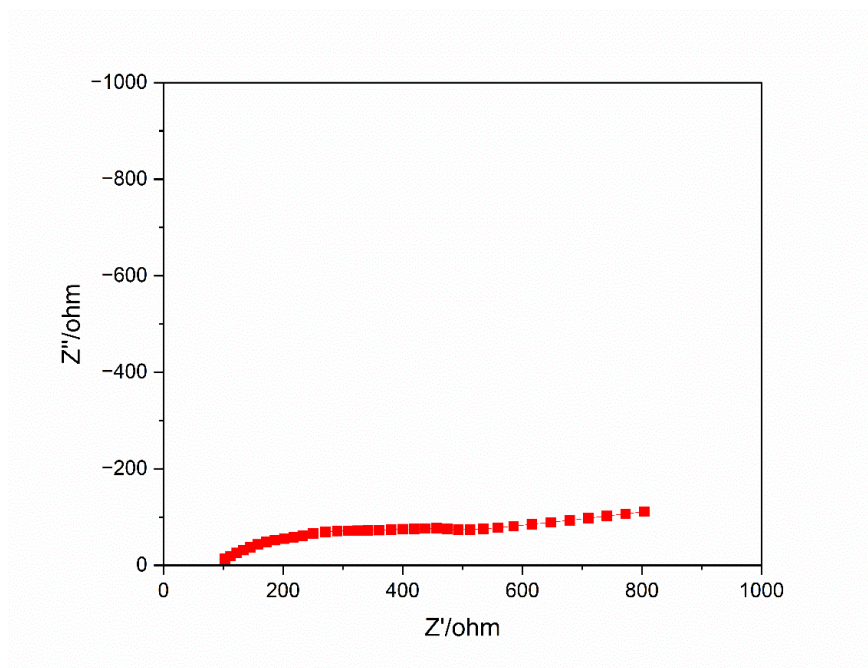


Figure 6: Low frequency impedance measurement to evaluate specific capacitance

Conclusion

MXene, a novel conducting nanofiller, has been effectively employed as a plasticizer with additive material for conductivity enhancement in ion-conducting electrolyte polymer films composed of polyethylene oxide and sodium iodide using the conventional solution casting procedure. The amendment the surface morphology of polymeric electrolyte sheets has changed after being doped with various weight percentages of this novel nanofiller, as demonstrated by POM. This shows that the amorphous phase in the polymer electrolyte system has increased as well as the overall amorphousness of the polymer electrolyte material. But a 0.04 weight percent nanofiller doped polymer electrolyte film has been proven to be stable at 400 C. After nanofiller was added to the polymer matrix, there was an increase in ionic conductivity, and the composition with 0.04 wt% nanofiller had the highest value of ionic conductivity (2.05×10^{-4} S/cm). The EDLC cell was constructed using an optimized polymer MXene doped electrolyte film. The specific capacitance C_{sp} signifies calculated from the cyclic voltammetry curve along with impedance data were 186 F/g and 190 F/g, respectively. Considering the optimised ion-conducting polymer electrolyte, the ionic transference number of mobile species for the improved ion-conducting polymer electrolyte was determined to be 0.92, confirming that the system is primarily ionic in nature.

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