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Effect of Salt Concentration on Resistive Switching behavior in Ion Conducting Polymer film based heterostructure

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ABSTRACT

In this report, PVDF-based polymer electrolyte with varying salt concentration (F/Li ratio) have been analysed for structural characteristics, salt concentration driven modification in properties for reliable bipolar resistive switching application. A switching device with configuration Au || *PVDF-LiClO₄* || ITO has been demonstrated that comprises Poly(vinylidene fluoride) (PVDF)-based polymer electrolyte films containing different concentrations of LiClO₄. Prior to device analysis, structural, optical, thermal and electrical properties of the PVDF-salt complex films were systematically studied to understand the influence of salt incorporation. *The* addition of LiClO₄ modified the defect-state distribution and trap characteristics of the PVDF matrix. The optimized composition exhibited an adequate trap density ($\sim 10^{13} \text{ cm}^{-3}$), providing an effective balance between charge trapping and carrier transport. Electrical transport analysis revealed a transition from ohmic conduction to trap-controlled space-charge-limited conduction with a trap-filled-limit voltage of $\sim 1.5 \text{ V}$. The device fabricated using optimal polymer salt complex film exhibited stable bipolar resistive switching with an $R_{\text{off/on}}$ ratio $\sim 10^3$ and memory retention exceeding 10^5 s . The enhanced switching performance is attributed to salt-induced trap-state engineering resulting into mixed ionic–electronic conduction. The results confirm that the device conduction mechanism is governed by trap-controlled space-charge-limited (SCLC) conduction at low voltages and ionic conduction at higher voltages.

Keywords: Memristers, Resistive switching, Ion conduction, SCLC

1. Introduction

The Memristers have emerged as a *potential* device for next-generation electronic applications over a wide range comprising data storage switching and memory etc. All this arises due to its unique ability to regulate current while retaining memory of previously transported charge. It is defined as a non-linear two-terminal component whose resistance depends on the history of charge flow, making it highly suitable for resistive switching and non-volatile

memory technologies. The concept of memristor was first proposed by Leon Chua in 1971 [1], while its experimental realization gained significant attention after 2008 [2]. Earlier reports on resistive switching in metal oxide systems such as SiO_2 , NiO , and TiO_2 thin films date back to the 1960s. However, these observations remained largely uncorrelated until the theoretical framework was established [3–5].

Resistive switching devices based on architecture and operating mechanism are generally classified *into* electrochemical metallization (ECM) and valence change mechanism (VCM) types. ECM-based memory units operate through cation migration (e.g., Ag^+ , Cu^+), wherein the application of an external bias leads to oxidation of the active electrode and subsequent metallic filament formation at the inert counter electrode. This results in a transition to a low resistance (ON) state, while reversal of polarity dissolves the filament, restoring the high resistance (OFF) state [6]. In contrast, VCM devices rely on anion migration, typically involving oxygen vacancies in metal oxide electrolytes. The switching behavior in such systems is governed by mixed (ionic-electronic-ionic) conduction and the modulation of potential barriers at electrode interfaces.

A wide variety of materials like oxides [7], nitrides [8], polymers [9], natural materials [10], and perovskites [11], have been explored for memristive applications in literature. Due to low cost, mechanical flexibility, and ease of fabrication, polymer-based resistive switching devices are considered attractive. The incorporation of ionic salts into polymer matrices provides an effective approach to control switching behavior through interaction between polymer matrices and ions in the salt. Polymer–salt complexes are especially promising since polymer matrix offers mechanical stability permitting dimensional flexibility in design while the incorporation of salt introduces dissociated ions to facilitate charge transport through migration across electron donor heteroatom sites across the host network and traps sites.

The attractive features like ionic conductivity, thermal stability, high mechanical strength and tunable physicochemical properties in ion-conducting polymer electrolytes based on poly(vinylidene fluoride) (PVDF) are main center of interest[12–15]. The resistive switching characteristics in such systems are strongly influenced by ion migration, filament formation, and trap-assisted conduction mechanisms, which also contribute to device variability, including cycle-to-cycle and cell-to-cell fluctuations. In this work, Li^+ ion-conducting solid polymer electrolytes based on PVDF as the host matrix are investigated to study the effect of salt concentration on resistive switching behavior. The fabricated Metal–Polymer–Semiconductor device exhibits bipolar switching characteristics, with significant

improvement in performance compared to pristine polymer-based Metal–Insulator–Semiconductor structures. The enhancement is attributed to the presence of traps and mobile Li^+ ions within the PVDF matrix, which facilitates space charge limited conduction and controlled ionic conduction thereby improved switching response.

2. Experimental (Materials process and device fabrication) brief:

Polyvinylidene Fluoride (IUPAC polymer name: poly(1,1-difluoroethene) (molecular wt. 534000.00, obtained from Aldrich) was solution processed with a fixed stoichiometric ratio of solvent [N-N Dimethyl formamide (DMF)] (from CDH). Initially host polymer and solvent was stirred for 24 hours at room temperature and then ultrasonicated for 1 hour. For polymer salt complex formation, in an optimal PVDF-DMF solution, LiClO_4 (from Aldrich) was

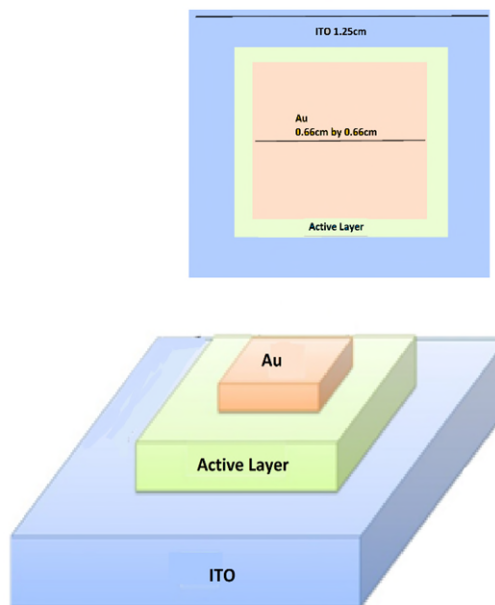


Fig 1 Device structure

added keeping at three distinct limits of F/Li^+ ratio $\approx 8, 4$ and 2 vis-à-vis PVDF. The resulting PVDF-DMF- LiClO_4 solution was used for coating film on ITO glass of dimension 0.5 sq. inch using spin coating process at 6000 rpm for 25 sec. Polymer-salt (PS) complex film was then vacuum dried at 60°C for 24 hours. Finally, ITO coated polymer salt film was gold sputtered for metallization of the active layer followed by annealing at 50°C for 5 hours. The final device architecture is shown in Fig. 1.

The pristine polymer (P_10_0) and its salt complex structural features were studied using relevant techniques such as Micro Raman spectrum (Model: Seki Techno Tron Corp, Olympus Bx5), was recorded at room temperature. XRD data were collected from thermos XRD Equinox 1000. The morphological and surface property of samples was studied using field emission scanning electron microscopy (Model Gemini, SEM 500). The DSC data were recorded from Perkin Elmer DSC 8000 and analyzed through Pyris software. Photoluminescence was carried on Lambda 35 by Perkin Elmer. TGA data were recorded using Perkin Elmer STA 6000. I-V characteristics of the device structure created by spin coating followed by metallization were recorded by a source measure unit (Keithley 2420). Impedance

spectroscopy was carried out on electrochemical analyzer from computer interfaced electrochemical work station (make CH instrument model CHI760D) for the device.

3. Results and Analysis:

3.1 Raman Spectrum

The Raman spectrum confirmed predominant β phase PVDF in the samples comprising salt concentration. The pristine sample (Fig 2a) exhibits dominant α -phase characteristics, indicating a highly ordered structure with minimal defect states. With the introduction of low salt concentration (Fig 2b), a slight enhancement of the β -phase is observed,

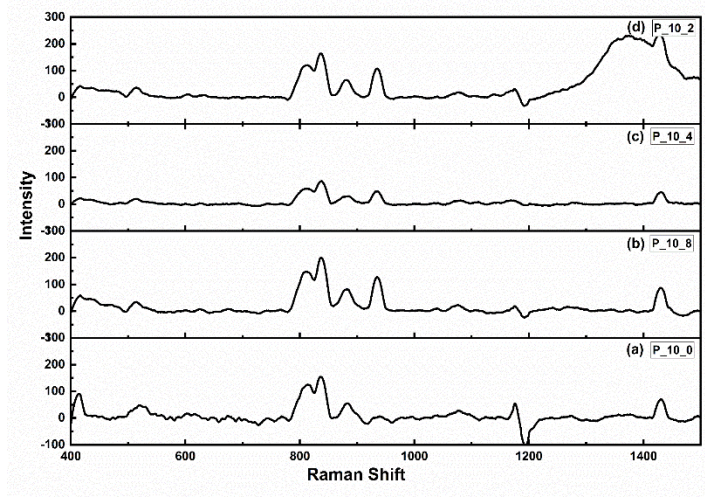


Fig 2 Raman Micrograph of (a) P_10_0 (b)P_10_8 (c) P_10_4 (d) P_10_2

suggesting initial polymer–ion interactions. The intermediate composition (Fig 2c) shows maximum β -

Table 1: Raman Spectroscopy

Modes	Phase	P_10_0	P_10_8	P_10_4	P_10_2	Ref
$\delta(\text{CH}_2) + \omega(\text{CH}_2)$	α, β, γ	Weak	Medium	Weak	Very Strong	16
$\omega(\text{CH}_2)$	$\alpha,$	Absent	Absent	Absent	Vs	17
$\nu_s(\text{CF}_2)$	β, γ	Weak	Absent	Absent	Absent	17
$\tau(\text{CH}_2) + \nu_s(\text{ClO}_4^-)$	γ	Absent	Medium	Weak	Medium	16, 17, 18
$\nu_s(\text{C-C})$	α, β, γ	Weak	Weak	Absent	Weak	16
$\nu_a(\text{CF}_2) + \rho(\text{CH}_2)$	β, γ	Strong	Very Strong	Medium	Strong	16
$\rho(\text{CH}_2)$	γ	Medium	Strong	Weak	Medium	16
$\rho(\text{CH}_2)$	α	Medium	Medium	Absent	Weak	16
$\rho(\text{CH}_2 + \text{CF}_2)$	α	Medium	Weak	Absent	Weak	16

phase composition along with significant peak broadening, indicating optimal structural modification (i.e. molecular rearrangement) and strong ion–polymer coupling. However, at the highest salt concentration (Fig 2d), excessive peak broadening and change in intensity ratio that may affect carrier mobility, indicate confirmed strong ion polymer interaction to a possible ion aggregation, leading to deep trap formation and hindered carrier mobility. The band assignment is given in Table 1.

This crystallization behavior is typical for the PVDF based co- and ter-polymers and it is confirmed in this work by the appearance of pronounced Raman peaks at $\sim 837\text{ cm}^{-1}$ (attributed to very strong Raman modes of β and γ crystal phases) and at $\sim 810\text{ cm}^{-1}$ (attributed to very strong mode of γ phase). The Quantitative analysis [19] of the fraction of β phase relative to α phase has been done with following approach and the result so obtained suggests β phase predominance.

$$\frac{\beta}{\alpha} = \frac{I(\beta)}{I(\alpha)} = \frac{I_{839}}{I_{795}} = 2.60.$$

Here, $I(\beta)$ corresponds to the intensity of the peak at 839nm and $I(\alpha)$ to that of 794nm . A β/α ratio of greater

than 1 suggested majority β phase content. This result confirmed polymer- salt (PS) complex formation and changes occurring in PVDF matrix structure of PS complex with salt concentration. The enhancement of β -phase is attributed to polymer-salt interactions, which induce dipole alignment and structural reorganization. This phase composition supports improved charge transport and facilitates trap-controlled space-charge-limited conduction (SCLC). The enhancement of the β -phase in salt-incorporated samples can be attributed to strong interactions between Li^+ ions and the $-\text{CF}_2$ dipoles of PVDF, which promote chain alignment and stabilization of the electroactive phase. This structural modification directly influences the electrical characteristics of the device which remains to be confirmed from transport measurement.

3.2 X Ray Diffraction

The XRD diffractogram of pristine polymer and the salt complexes with different salt concentration can be seen in Fig. 3. In the pristine polymer, Fig 3a, a clear hump can be seen between 17° to 36° . This shows a predominant amorphous phase. In comparison to this the PVDF-salt complex showed various peaks including salt peaks. The peak positions of the PS samples are noted in Table 2 with assignment of PVDF phase. The addition of LiClO_4 has increased the crystallinity of the polymer chain that rises with increasing salt concentration. Accordingly, salt complex with least salt concentration has the lowest crystalline as indicated by the peak at or near 20° . Literature reports peaks [19-22] near $2\theta = 18^\circ, 19.8^\circ, 26.4^\circ$ for α phase, $2\theta = 20.3^\circ$ for γ -phase and 20.6° for β phase. For LiClO_4 the expected

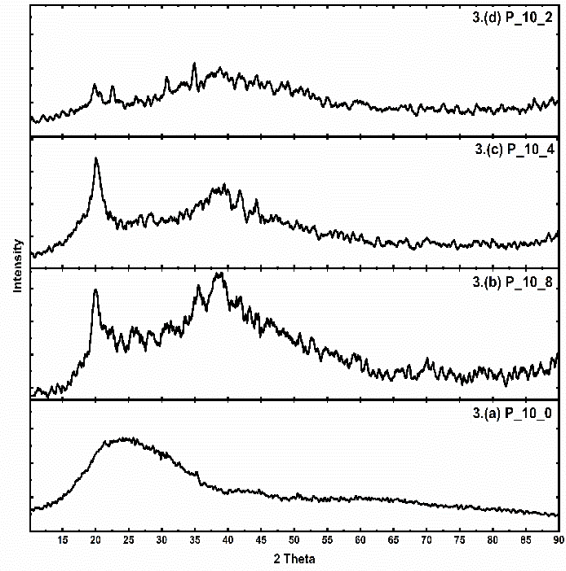


Fig 3 X-Ray Diffractogram of (a) P_10_0 (b)P_10_8 (c) P_10_4 (d) P_10_2

peaks [23,24] are likely at $2\theta = 19.85^\circ, 19.90^\circ, 21.21^\circ, 23.74^\circ, 26.56^\circ, 32.16^\circ, 36.25^\circ, 38.75^\circ, 41.03^\circ$ and 41.135° . However, in the present case the XRD pattern reveals a prominent diffraction peak around $2\theta \approx 20^\circ$, corresponding to the electroactive β -phase of PVDF.

The intensity of this peak is maximized for the sample containing 20.7% salt (Fig. 3c), indicating enhanced β -phase formation. At lower salt concentrations, mixed α and γ phases are observed, while higher salt content leads to peak broadening, suggesting increased amorphous character and suppression of crystalline phases. The enhanced β -phase content in (Fig 3c) contributes to improved polarization and charge transport, supporting the observed space-charge-limited conduction behavior. Overall, the XRD results confirm that LiClO_4 incorporation has resulted in the formation of polymer salt complex with noticeable structural disorder and possible formation of defect sites within the polymer host matrix in close agreement to the observation of Raman results.

Table 2: X Ray diffraction

Sample	Peaks	Phase Assignment
P_10_0	Hump between 17° to 36° small peaks at $17.11^\circ, 18.08^\circ, 21.41^\circ, 25.72^\circ, 26.28^\circ$	amorphous
P_10_8	$20.006^\circ, 35.575^\circ, 38.99^\circ, 41.94^\circ, 44.22^\circ$	α -phase and γ -phase
P_10_4	$20.062^\circ, 28.342^\circ, 39.392^\circ, 41.79^\circ, 44.342^\circ$	β -phase and γ -phase
P_10_2	$19.85^\circ, 22.493^\circ, 30.07^\circ, 34.92^\circ$	α -phase

3.3 Photoluminescence Spectra

The PL emission spectra with 375 nm as excitation wavelength is shown in Fig. 4. (iv). It exhibits the highest PL intensity, indicating strong radiative recombination of electron-hole pairs. This suggests a relatively higher density of recombination centres, where charge carriers recombine efficiently, resulting in intense emission. However, such strong recombination can limit charge transport, as carriers are lost through radiative pathways. Similarly, the Fig. 4 (iii) sample shows very high PL intensity, showing significant recombination. In contrast,

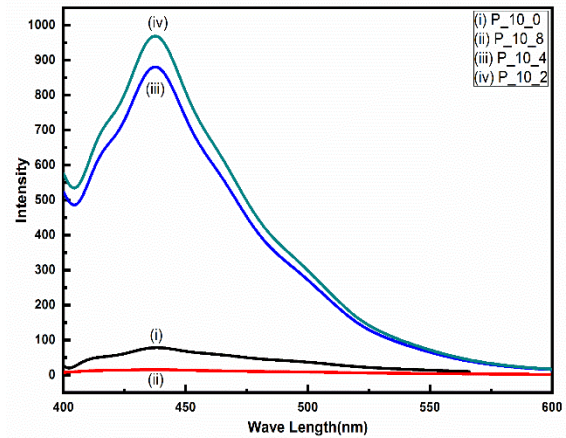


Fig 4 Photoluminescence spectrogram of (i) (P_10_0) (ii) (P_10_8) (iii) (P_10_4) & (iv) (P_10_2)

the Fig. 4 (ii) sample exhibits very weak PL intensity, indicating PL quenching. This pattern indicates enhanced charge

separation or non-radiative pathways. The presence of increased disorder and defect states facilitates carrier transport by reducing recombination probability, which is beneficial for conduction. The pristine sample Fig. 4 (i) shows almost negligible emission, confirming the absence of significant radiative recombination centres and indicating a highly amorphous structure with limited optical activity.

Detailed peak description is given in Table 3.

Three different sets of peaks were observed that can be divided into three different class. A shoulder peak observed in the range of 385–415 nm corresponds to

Table 3 Photoluminescence Spectra

Sample	Peak Intensity
P-10_2	Highest
P-10_4	Very high
P-10_8	Almost zero
P-10_0	Very weak

emission in the ultraviolet region and is attributed to defect-related transitions and shallow trap states [25,26]. These shallow traps originate from structural imperfections and localized disorder arising due to salt incorporation in the host polymer matrix. The dominant emission peak located at 435–445 nm lies in the blue region of the visible spectrum and is associated with near band edge emission, arising from excitonic recombination of charge carriers. This peak indicates the presence of relatively ordered regions within the polymer, where radiative recombination occurs efficiently. In addition, a broad emission tail extending from 450 to 600 nm is observed. It may be attributed to deep-level defect states and surface trap-assisted recombination processes [25,27]. The broad nature of this emission suggests a distribution of defect energy levels within the bandgap, that may be attributed to LiClO₄ incorporation and resulting structural disorder. The deconvoluted PL spectrum of P_10_4 reveals six emission bands centred at 390, 412, 435, 461, 478 and 513 nm, suggesting a distribution of shallow and deep trapping centres generated by polymer–salt complexation and structural modification favourable for conduction of charge. The coexistence of shallow and deep trap states plays an important role in the electrical response a material. Carrier injection and transport is supported

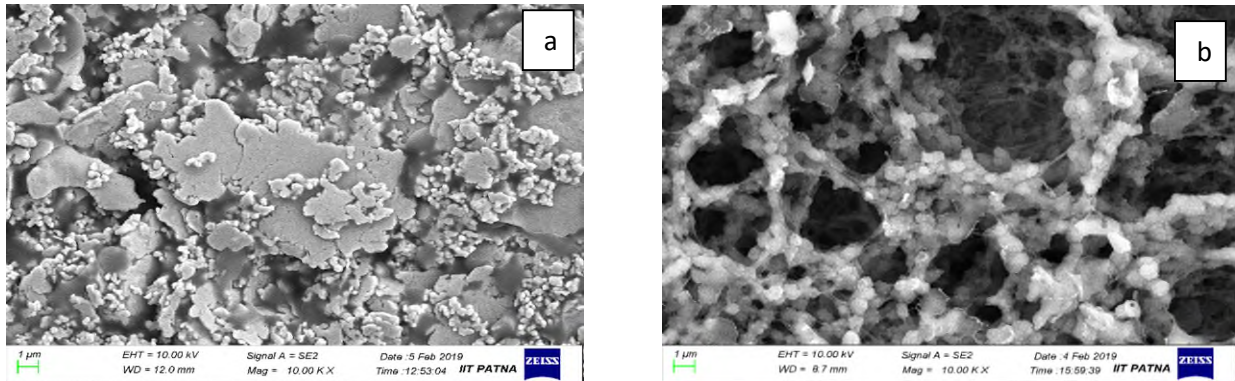


Fig 5 SEM Micrograph of (a) (P_10_0) & (b) (P_10_4)

by shallow traps, whereas deep traps act as charge-storage centres and participate in trap-filling processes associated with trap-controlled space-charge-limited conduction (SCLC) [28].

3.4 Surface Morphology Analysis (SEM)

The surface morphology of the (Fig 5a) and the polymer salt-complexed sample Fig 5 (b) was examined using scanning electron microscopy (SEM), as shown in Fig. 5(a–b). The pristine sample exhibits a typical crystalline relatively dense and compact morphology comprising spherulites and irregular agglomerated grains distributed across the surface. The surface appears dense and heterogeneous distribution of grains with limited interconnectivity. Such morphology is consistent with the polymer dominated matrix, with restricted free volume that hinders effective ion transport. Conversely, the salt-incorporated sample Fig. 5(b) displays a highly porous and interconnected network-like morphological structure. The formation of a fibrous and sponge-like morphology with prominent voids indicates significant structural reorganization due to incorporation of LiClO_4 . The increases the effective surface area due to porous and semicrystalline morphological architecture provides continuous pathway for ion migration. The observed morphological transformation can be attributed to strong interactions between Li^+ ions and the PVDF polymer chains, which disrupt chain packing and promote phase separation during the electrospinning process. This results in the formation of interconnected channels and enhanced free volume within the polymer matrix. The presence of observed microstructure acts as continuous pathways supports ion mobility [29,30], while presence of localized defects and interfaces act as charge trapping centres. Overall, the SEM results confirm that LiClO_4 incorporation significantly alters the surface morphology of PVDF, leading to the formation of a porous network with electroactive sites that may act as sites for that facilitating charge transport if the sample with optimal properties is used in device design.

3.5 Differential Scanning Calorimetry

The DSC thermograph shows change in crystalline melting temperature (T_m) and crystallization temperature (T_c) of the host polymer. The DSC results show that Fig 6(iii) has the highest value of Specific heat capacity at constant pressure C_p , crystallinity and change in Gibbs free energy ΔG in Table 4. The T_c of material shows double crystallinity peak in Fig 6(iii). and it is consistent with the literature report [31]. The software was set for endo up. It is also observed that the degree of crystallinity (X_c) increases with salt addition and reaches a maximum at Fig 6(iii), followed by a decline at higher concentrations. In addition, the change in Gibbs free energy (ΔG) is most negative for Fig 6(iii),

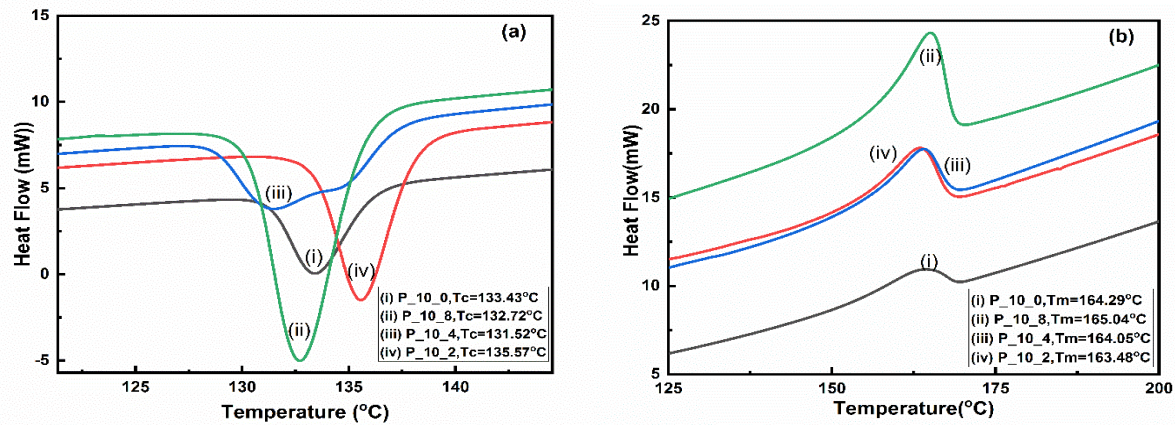


Fig 6(a) DSC Thermograph of (i) (P_10_0), (ii) (P_10_8), (iii) (P_10_4) & (iv) (P_10_2) showing T_c , (b) DSC Thermograph of (i) (P_10_0), (ii) (P_10_8), (iii) (P_10_4) & (iv) (P_10_2) showing T_m

highlights better thermodynamic stability. These results confirm that an optimal salt concentration promotes structural ordering, whereas excess salt disrupts the polymer host matrix creating stability issue. Thermodynamic analysis confirms a strong dependence of structural stability and disorder states on salt concentration of the samples. The intermediate composition (P_10_4) exhibits the highest change in enthalpy ΔH and entropy ΔS in combination with the most negative ΔG , suggesting a thermodynamically stable and dynamic polymer salt system. This is also coupled with maximum crystallinity, corroborating the formation of well-organized conductive pathways as observed in SEM observation. In contrast, the highest salt concentration sample (P_10_2) shows significantly reduced ΔH , ΔS , and crystallinity, indicating structural instability and ion aggregation with trap centers.

Table 4: DSC results

Sample	ΔH	$T_m(\text{K})$	$\Delta S = C_p[\ln T_2/T_1]$	$\Delta G = \Delta H - T_m * \Delta S$	X_c
P_10_0	53.7968	435.99	5049.01	-22,01,267.05	51.382
P_10_8	58.0947	439.02	1367.78	-6,00,426.03	55.487
P_10_4	76.4542	436.82	8647.37	-37,77,269.12	73.022
P_10_2	22.6859	436.28	605.39	-2,64,097.37	21.668

3.6 Thermogravimetric Analysis

The thermogravimetric analysis curve is given in Fig.7. It indicates relative change in mass of the samples attributed to degradation occurs in multiple stages, corresponding to moisture loss [Stage I ($<150^\circ\text{C}$)], initial polymer decomposition [Stage II ($150\text{--}350^\circ\text{C}$)], and backbone degradation at higher temperatures [Stage III ($350\text{--}500^\circ\text{C}$)].

Table 5: TGA results

Sample	P_10_0	P_10_8	P_10_4	P_10_2
Temperature	Decomposition %age	Decomposition %age	Decomposition %age	Decomposition %age
100	6.8	24.45	16.51	26.47
200	9.93	38.28	32.03	45.35
300	12.46	42.30	39.52	54.17
400	14.54	62.22	57.6	71.32

The reduced thermal stability in salt-containing samples is

attributed to the plasticizing effect and structural modification induced by Li^+ ions. The pristine polymer is stable till 400°C [31] and only 14 percent is decomposed. On the other hand, the salt complexes of different stoichiometric ratios started decomposing at much lower temperature, near 300°C. The decomposition between 300°C to 400°C is due to salt. The decomposition is very fast till 100°C. Above 400°C the decomposition is due to degradation of polymer. Near 475°C the salt complexes disintegrated fully. Clearly thermogravimetric analysis

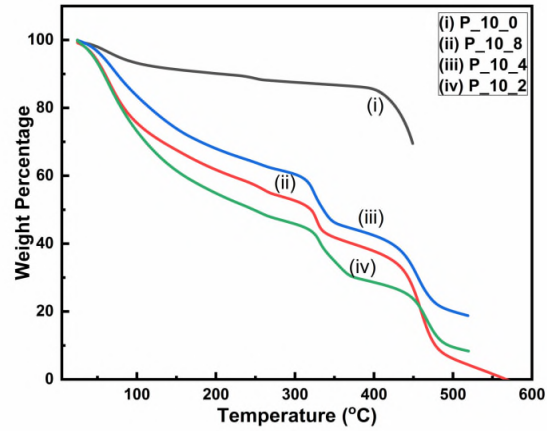


Fig 7(a) Thermogravimetric analysis curve, of (i) (P_10_0), (ii)(P_10_8), (iii) (P_10_4) & (iv) (P_10_2) showing weight loss with T

(TGA) reveals a significant influence of salt concentration on the thermal stability of the PVDF-based polymer salt complex system. The pristine sample (P_10_0) exhibits the highest thermal stability, whereas the salt-incorporated samples show earlier degradation. Among them, (P_10_2) demonstrates the lowest thermal stability, indicating that higher salt concentration disrupts the polymer matrix and weakens intermolecular interactions. The thermal stability details are given in Table 5.

4. Device Architecture and Performance

4.1 Resistive Switching Behaviour

The schematic architecture of the resistive switching device is shown in Fig 1. Fig. 8 Presents bipolar resistive switching response for the device structure $\text{Au}||\text{PVDF-DMF-LiClO}_4||\text{ITO}$ cell where resistive response of PVDF-DMF has been shown with that of PVDF-DMF- LiClO_4 over a range of ± 5 V as the representative result [32]. During testing

Table 6: Resistive switching results

Parameters	P_10_2	P_10_4	P_10_8	P_10_0
V_{set} (V)	1.95	3.17	3.06	3.35
V_{reset} (V)	-1.81	-3.07	-4.1	-4.63
$R_{\text{off/on}}$	10	10^3	10^2	10
Power (μW)	19406	104.21	5812.6	17.28

ITO was grounded. For switching cycle consisting low resistance state (LRS-ON) to high resistance state (HRS-OFF) over a potential window ± 5 V passing through 0V, the set voltage has been obtained between 2-4 volts and reset voltage was obtained between 3 to 4.8 volts. Four different device structures were fabricated and tested for switching response and results were reproducible up to 27 cycles. The device with (P-10-0), Fig 8(a) active material (pristine polymer), poor switching action was noted in comparison to salt complexes as active layer. A comparison of switching action (I-V plot) has been presented in Table 6 with comparative record of measured parameters for all the three structures under taken. Although the set and reset voltage are not consistent for all cycles and exact but the switching

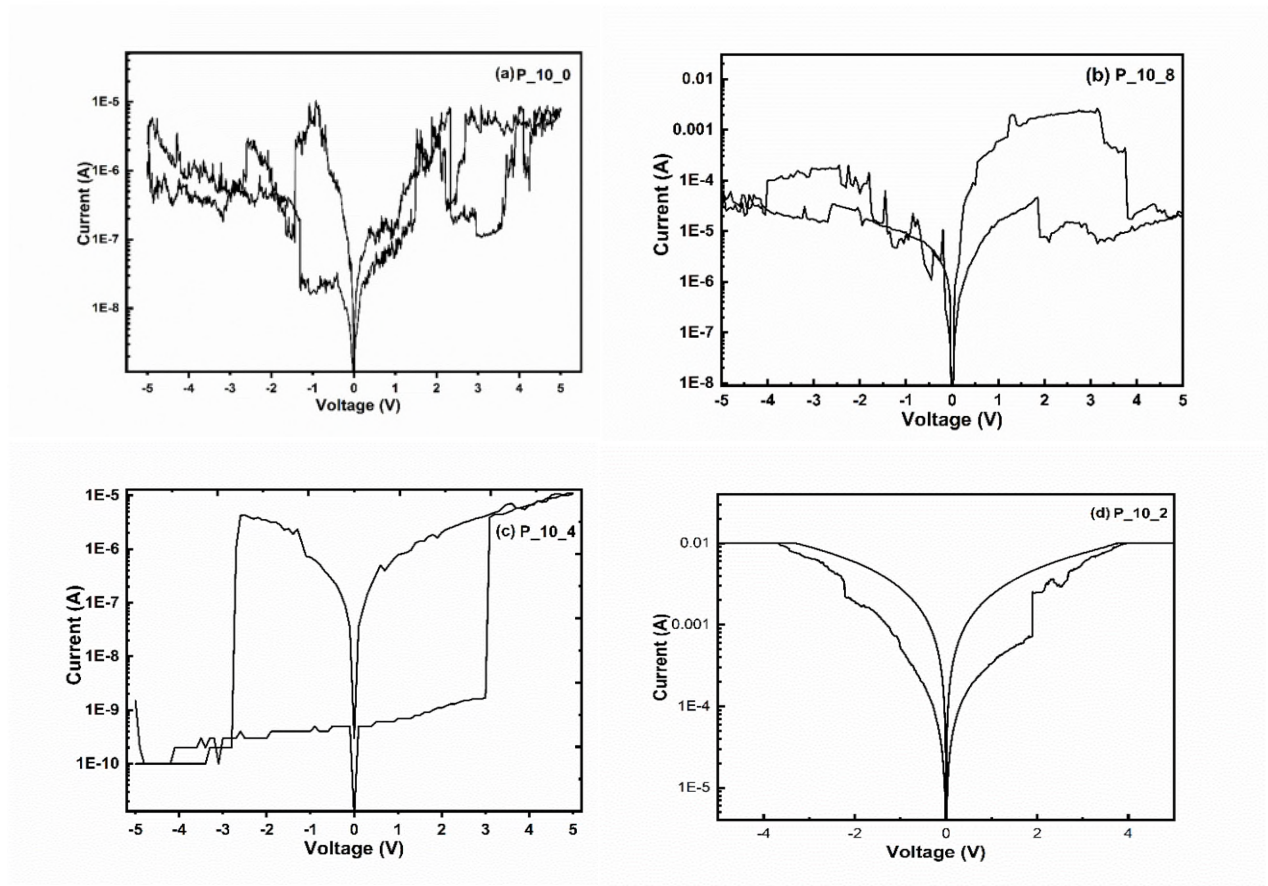


Fig 8 Resistive switching I-V curve of Au||PVDF-DMF-LiClO₄||ITO with active material(a) (P_10_0), (b)(P_10_8), (c) (P_10_4) & (d) (P_10_2)

response is good. From the I-V plot it can be seen that salt complex with intermediate salt ratio shows the best result

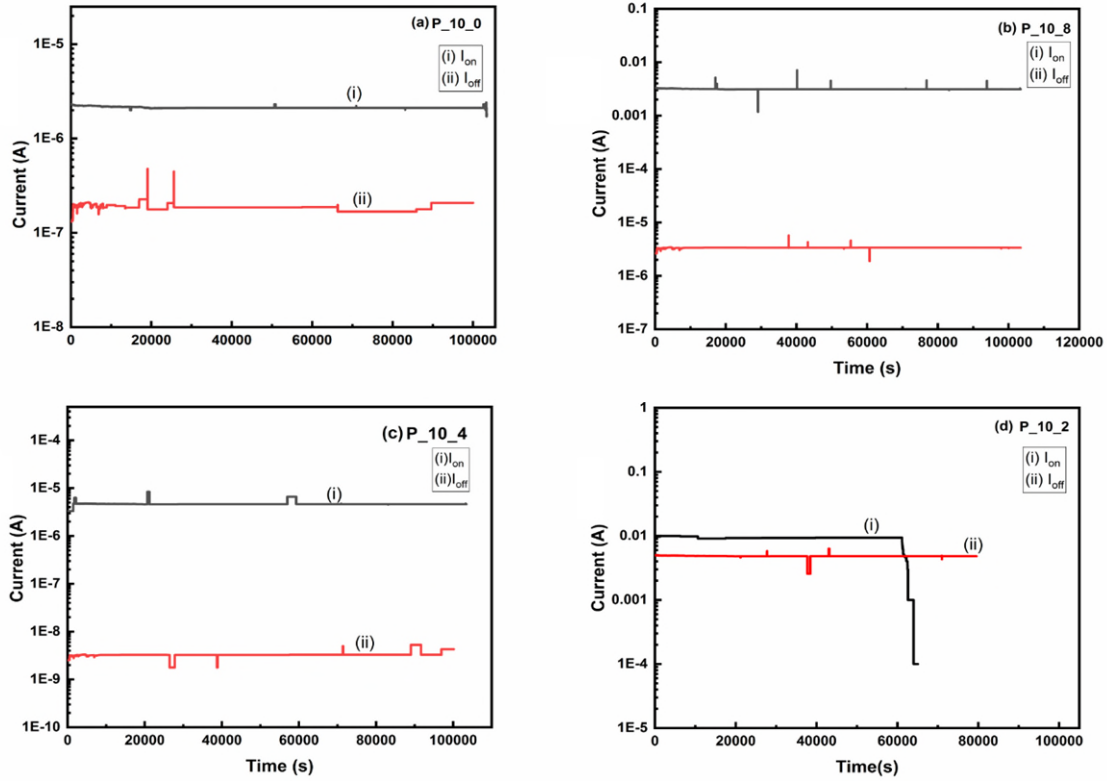


Fig 9 Retention curve of Au||PVDF-DMF-LiClO₄||ITO with active material (a) (P_10_0), (b) (P_10_8), (c) (P_10_4) & (d) (P_10_2)

among all four devices in terms of switching ratio and switching response stability in the present studies. Endurance level is low for device based on pristine polymer P_10_0 and polymer salt complex F/Li = 8, 2, (P_10_8) & (P_10_2).

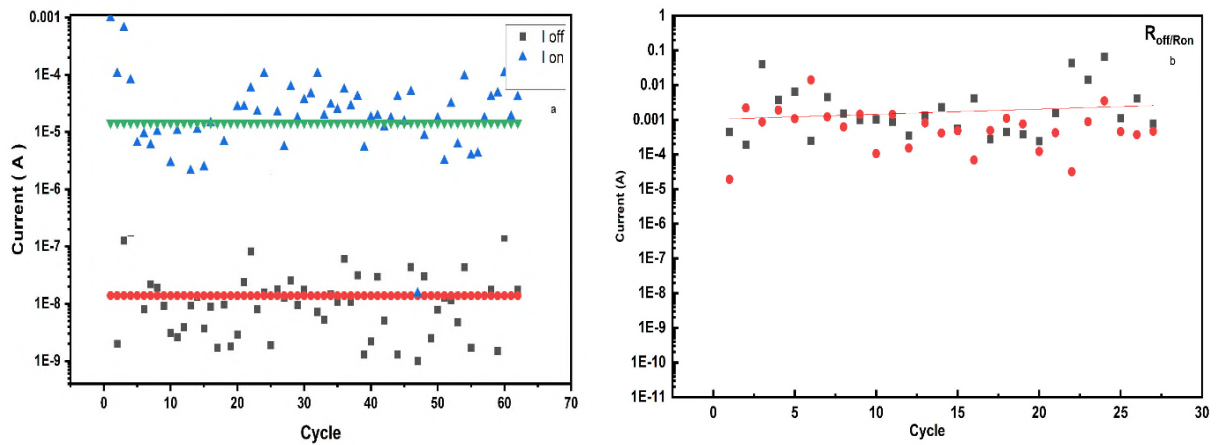


Fig 10 (a) I_{on} and I_{off} vs cycle plot showing difference & (b) $R_{on/off}$ vs cycle graph of order of Au|| (P_10_4) ||ITO

This result establishes that concentration of the salt controls the V_{set} and V_{res} and there by $R_{\text{off/on}}$ ratio. The V_{set} and V_{res} value in device with Polymer salt complex has been in between 2.5 to 4.5 volts. Fig 9 shows the retention of all the devices. Except the highest concentration of salt device all are stable for 10^5 s. This is due to high concentration of salt disturbing the system. However, the Plots in Fig 10 showed results reliable more than 25 cycles for (P_10_4). In continuation to the plot Fig. 10(a) for (P_10_4) sample, the ON state current and OFF state current exhibited ratio of more than 10^3 . The plot of ON current (I_{on}) and OFF current (I_{off}) vs cycle shows steady leap of 10^3 order of current value for sample (P_10_4). In Fig (b) the plot of $R_{\text{off/on}}$ against cycle shows almost constant order as current. Enhancement of several orders of magnitude that F/Li = 4 composition is remarkably better result than the pristine polymer device and also compared to PS with other salt concentration. A complete comparison is given in Table 6. Though current value is more in the highest salt concentration device, which also increases the overall power requirement but the $R_{\text{off/on}}$ ratio is poor. The resistive switching device in (P_10_4) composition the present study, with optimal salt concentration has demonstrated an ultra-low power, $104.21\mu\text{W}$ for operation.

4.2 Electrical Transport Analysis

In order to understand the mechanism of switching response of the device, it was felt necessary to study electrical transport behavior using AC impedance analysis. An alternating voltage of 5mV with different DC bias was applied and corresponding real and imaginary impedance were recorded with frequency. The obtained nyquist plot and bode plot are shown in the Fig 11 and 12 respectively. It is comprised of semi-circles with their centers lying below the real axis (Z_r) at all the applied voltages. It indicates marked deviation from the ideal Debye behaviour of the interface [33]. From the above impedance spectroscopy plot; nyquist and bode plot (Fig 12) it is visible that bulk resistance (R_b) and the relaxation time(τ) increases linearly with DC bias voltage. Such a result suggests formation of space charge / ionic polarization layers in the device charge transport is pure electronic charge. The tail at high Z_r (low frequency) shows electrode polarization and diffusive ionic motion (Warburg-like behavior) [34] [35]. It is also seen that peak is shifted to lower frequencies as the DC bias is increased Fig 12. This refers to situation where increase in bias causes the dipoles take more and more time to follow the alteration of the applied field. At low frequencies, like 100 Hz to 1kHz, the space charge polarization is dominant. Interfacial or space charge mechanism is the dominant phenomenon in polymer matrix due to semicrystalline texture. The imaginary impedance (Z_i) spectra exhibit broad relaxation peaks, indicating non-Debye type relaxation. With increasing DC bias, the peak shifts toward lower frequency, corresponding to an increase in relaxation time. At higher bias, peak broadening suggests the involvement of multiple relaxation

processes, including ionic motion due to deep trap states. The distortion observed in Nyquist plots at higher bias also shows this.

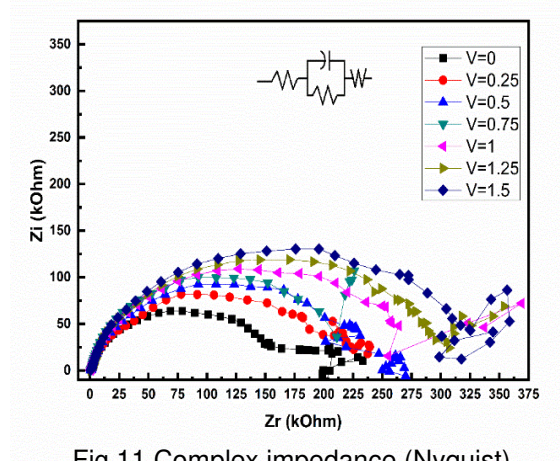


Fig 11 Complex impedance (Nyquist) plots of the Au|| (P_10_4) ||ITO device resistive switching device recorded under DC bias voltages

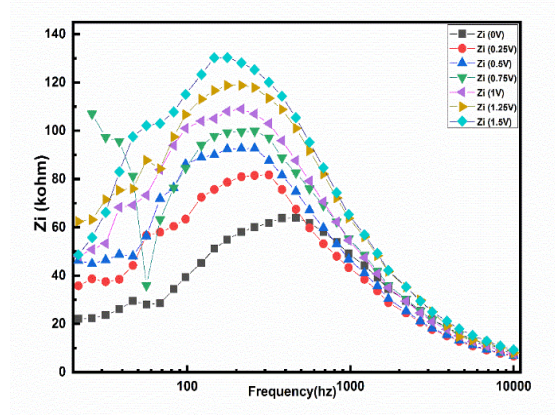


Fig 12 Frequency dependence of the real part of impedance (Z') measured under different DC bias voltages (0–1.5 V) of Au|| (P_10_4) ||ITO device

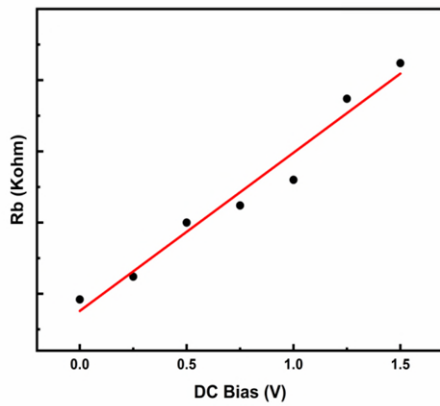


Fig 13 Variation of the bulk resistance (R_b) with applied DC bias voltage for the Au|| (P_10_4) ||ITO resistive memory device

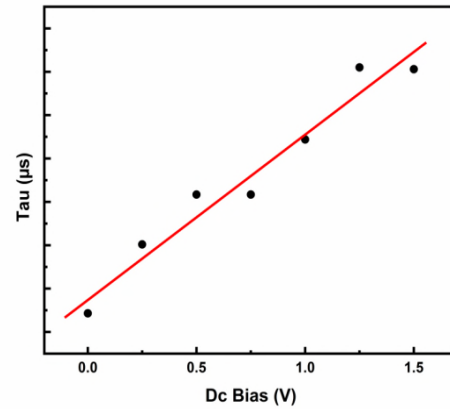


Fig 14 Variation of the relaxation time (τ) as a function of DC bias voltage for the Au|| (P_10_4) ||ITO resistive switching device

Impedance analysis demonstrates a transition from trap-controlled conduction at low applied bias to a non-linear region at higher applied bias, evident by distortion in Nyquist plots and a shift in relaxation peaks. This transition corresponds to the trap-filled limit and onset of ionic motion, which is responsible for the SET process observed in SCLC-based I–V switching response. The RESET process is attributed to the relaxation of ionic species and

redistribution of space charge under reduced bias. There is a systematic linear increase of relaxation time (τ) with applied DC bias (Fig 14) which indicates a field-dependent charge transport *system*. The increase in τ with voltage indicates the involvement of slow-moving ionic charges, particularly Li^+ ions, which accumulate at the electrode interfaces and contribute to space charge formation. This behavior deviates from purely electronic conduction and confirms the presence of ionic dynamics within the system. These results strongly support that mixed ionic–electronic conduction mechanism controls the resistive switching behavior.

4.3 Discussion

Understanding charge transport mechanism leading to switching response in the device $\text{Au}||\text{P}_{10_4}||\text{ITO}$ is important. It appears from the results in the present study and previous reports that in general two types conduction mechanism. For analyzing the mechanism of the process of resistive switching current density(J) and electric field applied(E) was calculated from the I-V results. Analysis of Space charge limited conduction mechanism [36, 37] indicated a combined effect of ohm's law, trap filled limit current and Child's law.

The trap filled region is a transition region from ohm's law to Child's law. It can be expressed as

$$J_{ohm} = qn_0\mu E$$

$$J_{TFL} = \frac{9}{8} \mu \epsilon \theta \frac{E^2}{d}$$

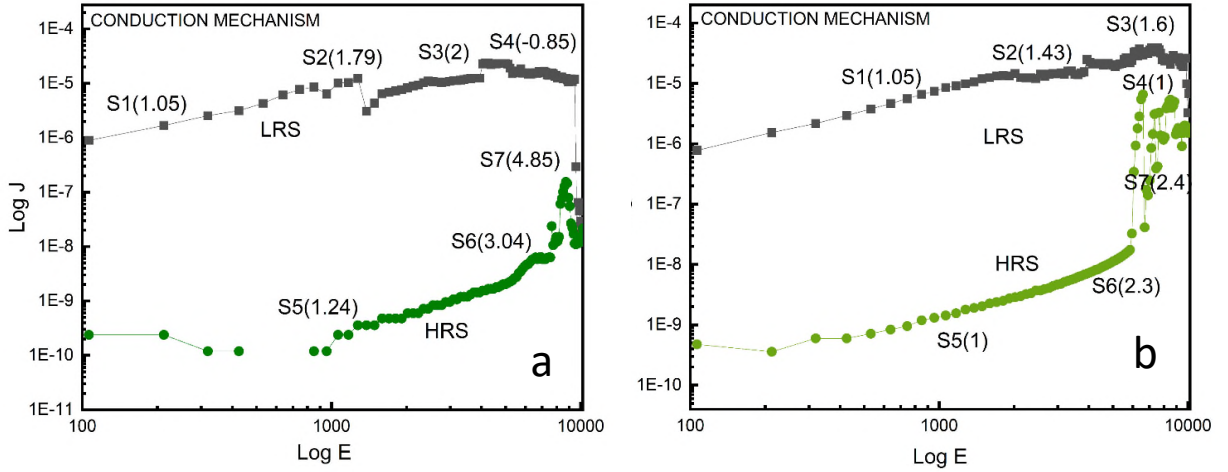


Fig 15 Double logarithmic plots of current density (J) as a function of electric field (E) for the $\text{Au}||(\text{P}_{10_4})||\text{ITO}$ device during (a) positive voltage sweep ($0 \rightarrow +5 \text{ V}$ and $+5 \rightarrow 0 \text{ V}$) and (b) negative voltage sweep ($0 \rightarrow -5 \text{ V}$ and $-5 \rightarrow 0 \text{ V}$). The fitted slopes (S1–S7) reveal successive transitions from Ohmic conduction to trap-controlled space-charge-limited conduction (SCLC), followed by trap-filled-limit behavior and high-field ionic effects associated with Li^+ ion migration.

$$J_{child} = \frac{9}{8} \mu \epsilon \frac{E^2}{d}$$

Subsequently the log graph of current density (Log J) and electric field (Log E) were plotted for analyzing Space charge limited conduction mechanism. The area in the curves where slope is 1 shows ohmic behaviour. Regions where slope value is 2 or near 2 are trap assisted controlled space charge limited mechanism. There were areas where the slope is more than 2. These are regions where the deep level traps and voids were also filled by the mobile charge carriers or deep level trap assisted SCLC mechanism. The trap density was found to be $\sim 10^{13} \text{ cm}^{-3}$, suggesting a moderate density of localized states.

Table 7(A): Slope Analysis					
Graph 1:	Region	Slope (m)	Voltage Range (approx.)	Conduction Type	Inference
HRS: 0 → 5 V)	S1	1.05	~0–0.5 V	Ohmic	Free charge carriers dominate (no traps active)
	S2	1.79	~0.65–1.5 V	Trap-controlled SCLC	Trap filling begins; deviation from ideal V ²
	S3	2.0	~1.5–2.5 V	Ideal SCLC	All traps filled → trap-free SCLC
	S4	-0.73	2.5V-5V	Li ⁺ ions drift and accumulate	internal electric field opposite to applied field and current drops down
LRS: 5 → 0 V)	S5	1.24	~0.1–1.5 V	Trap-influenced conduction	Traps start emptying; not ideal SCLC
	S6	3.04	~2.25–3.5 V	Trap-filled limit / steep conduction	Sudden current drop due to de-trapping + ionic effect
	S7	4.85	~3.5–4 V	Ionic-dominated / instability	Strong deviation → ionic migration + filament rupture
Table 7(B): Slope Analysis					
Graph 2:	Region	Slope (m)	Voltage Range (approx.)	Conduction Type	Inference
LRS: -5 → 0 V)	S1	1.05	~-0.1 to -1 V	Ohmic	Symmetric behavior, electron conduction
	S2	1.43	~-1 to -2 V	Trap-controlled SCLC	Fewer traps compared to SET
	S3	1.6	~-2.5 to -3.5 V	Weak SCLC	Not reaching ideal V ² → ionic interference
HRS: 0 → -5 V)	S4	1.0	~0 to -2.3 V	Ohmic	Initial conduction dominated by free carriers
	S5	2.3	~-2 to -3 V	SCLC (trap-filled)	Trap-filled conduction but influenced by ions
	S6, S7		-3V TO -5 V	Disturbed	

These results confirm that the device conduction mechanism is governed by trap-controlled space-charge-

limited conduction. There are regions where slope is far more than 2. These regions are affected by ionic species.

The lithium ion plays a very crucial role. So, it can be concluded that slope value 3 and 4.85 are due to ionic contribution. The details of the voltage and slope analysis with comparative and detailed variation is given in Table 7. At higher electric fields (>2.5 V), the transport behaviour deviates from ideal SCLC due to migration of Li⁺ ions present in the PVDF:LiClO₄ matrix.

$$J_{ion} = J_o e^{(\beta E)}$$

A linear dependent ln(J) on E is indicative of ionic conduction. This reduction in effective electric field leads to current saturation, negative differential resistance (NDR), and eventual RESET switching.

5. Summary

PVDF-based polymer electrolyte films containing varying concentrations of LiClO₄ were systematically evaluated for resistive memory applications. Among the compositions studied, the optimized sample, P_10_4 (≈20.7 wt.% LiClO₄, F/Li ≈ 4), exhibited stable bipolar resistive switching behavior, achieving an R_{off/on} ratio of approximately 10³ and demonstrating consistent performance over more than 25 switching cycles.

Comprehensive structural, spectroscopic, and thermal characterizations revealed that P_10_4 possesses the most advantageous combination of properties, including enhanced structural ordering, improved thermal stability, and a predominant electroactive β-phase. Photoluminescence analysis identified defect-related trap states, while the incorporation of LiClO₄ effectively optimized the trap distribution, thereby facilitating charge transport and storage. In addition, the intrinsic dipolar characteristics of PVDF contribute to the stability of the non-volatile switching behavior. Electrical characterization indicated a conduction mechanism that evolves from Ohmic behavior to trap-controlled and subsequently trap-free space-charge-limited conduction (SCLC), underscoring the importance of trap-assisted transport during the SET process. At elevated voltages, departures from ideal SCLC behavior, together with the observation of negative differential resistance (NDR) and impedance variations, suggest the involvement of Li⁺ ion migration and associated ionic effects. Accordingly, the resistive switching mechanism can be attributed to a coupled ionic–electronic transport process. While SCLC governs charge transport at low and intermediate electric fields, ionic migration and polarization effects become increasingly significant at higher fields, resulting in current saturation, NDR behavior, and RESET switching.

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Author Contributions

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