Supporting Information

Decoupling of ion transport from polymer segmental relaxation and higher ionic-conductivity in poly (ethylene oxide)/succinonitrile composite based electrolytes having low lithium salt doping

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1. Experimental

1.1 Positron annihilation lifetime spectroscopy (PALS)

A fast-fast coincidence PALS spectrometer (time resolution: Gaussian having FWHM of 0.240 ns) consists of two barium fluoride (BaF_2) scintillation detectors was used to record the PALS spectra of pure PEO, PEO/xSN (x = 0, 10, 30 and 45 wt.%) composites, and PEO/45SN-Li and PEO-Li electrolytes. PALS spectra (total counts > 1×10^6) of polymeric samples were acquired by sandwiching the positron source, which is an envelope of 8 μm thick kapton films having carrier free radioisotope ^{22}Na (~ 10 mCi), between sufficient thickness of the samples. The fraction of positrons annihilating within the source (0.373±0.015 and 1.76±0.17 ns with corresponding intensities of 12.41±0.82 and 0.39±0.05) was estimated from PALS spectrum of silicon single crystal, and used as source correction for analysis of PALS spectra of the polymeric samples. Laplace inversion based computer program CONTIN [S1] has been used to analyze the PALS spectra in terms of lifetime distributions. According to this algorithm, a PALS spectrum is expressed as:

$$N(t) = I_1\lambda_1 \exp(-\lambda_1 t) + \sum_{i=2,3} I_i \int_0^\infty \alpha_i(\lambda)\lambda \exp(-\lambda t) d\lambda \qquad \text{(S1)}$$

where N(t) represents time distributed counts, λ and I represent the annihilation rates and the corresponding intensity, respectively, with $\Sigma I = 1$. The index i = 1, 2, and 3 correspond to *para*-positronium, free positron, and *ortho*-positronium annihilation. The function α (λ) is expressed as

$$\alpha_i(\lambda)\lambda d\lambda = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(\ln\lambda/\lambda_{i0})^2}{2\sigma^2}\right] d\lambda \qquad \text{(S2)}$$

where σ is the standard deviation of the function.

1.2 Temperature Dependent Broadband dielectric spectroscopy (BDS)

Temperature dependent (203–313 K; with interval of 5 K) BDS measurements in broad frequency range of $0.1–1 \times 10^7$ Hz were carried out for PEO/45SN-Li and PEO-Li electrolytes using Impedance analyzer (Novocontrol, Germany, Alpha analyzer) coupled with a Quatro Cryo system. The temperature stability during the measurement was maintained at ± 0.1 K. The BDS measurements were carried out on circular polymeric samples of diameter 20 mm placed between the standard parallel plates (20 mm diameter circular gold plated) of the sample cell and applying ac voltage of 0.2 V. The measurements for the electrolyte samples were carried out during heating and cooling cycles. During test runs, no hysteresis was observed between measurements performed during cooling and heating cycles. The data reported was finally recorded during the cooling cycle from 313–203 K at temperature interval of 5 K. The BDS data can be represented using different experimental and interrelated parameters like dielectric permittivity, conductivity and electric modulus.

2. PALS Methodology:

PALS is an established experimental technique for investigation of static and dynamic free volumes associated with polymeric chains in polymeric materials. PALS methodology is based on the fact that positrons implanted in polymeric materials are thermalized quickly interacting with the constituent atoms of polymers. Thermalized positrons in polymeric materials have two distinct fates e.g. (i) these can annihilate with the opposite spin electrons emitting two 511 keV gamma photos in opposite direction, and (ii) the positrons can form a bound state with electrons called positronium (Ps) having binding energy of -6.8 eV. Ps can exist in two energy states because of two possibilities (parallel and anti-parallel) of spin orientation of electron-positron pair in Ps. The singlet (*para*-positronium, *p*-Ps) and triplet (*ortho*-positronium, *o*-Ps) are formed in 1:3 ratios, and undergoes annihilation with intrinsic lifetime of 0.125 and 142 ns, respectively. The *p*-Ps intrinsic annihilation lifetime remains undisturbed due to short time of interaction with the material, however *o*-Ps having longer intrinsic lifetime is localized in the low density regions due to exchange-correlation potential. In case of polymeric materials, free volumes act as preferential trap for *o*-Ps because of low atomic density at free volume as compared to bulk of

the polymers. The localized *o*-Ps undergoes annihilation through an additional mode emitting two gamma 511 keV photons. This mode of annihilation is called *pick-off* annihilation. The rate of *pick-off* annihilation depends on the interaction of *o*-Ps with free volume wall or in other words, *o*-Ps *pick-off* lifetime is related to the free volume size present in the studied polymeric material. Among different models correlating the *o*-Ps *pick-off* lifetime with the average free volume size, [S2, S3], the Tao-Eldrup model is highly successful, and widely applied for polymeric materials. This model is based on the fact that *o*-Ps, a quantum mechanical particle, is localized in a spherical infinite potential (free volume hole), and the annihilation probability depends on the overlap integral of localized *o*-Ps wave-function with the wave-function of the electron from the electronic layer at the surface wall. According to the Tao-Eldrup model, *o*-Ps *pick-off* lifetime (τ_{po}, ns) is correlated to the average pore radius R (nm) through the following equation.

$$\frac{1}{\tau_{po}} = 2\left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R}\right) \right] \tag{S3}$$

In reality, a free volume size distribution exists in polymeric materials due to heterogeneity of polymer chain packing and as a result, an *o*-Ps lifetime distribution is expected. The lifetime distribution is evaluated analyzing PALS spectra using CONTIN algorithm [S1].

The evaluated *o*-Ps annihilation lifetime distribution can be transformed to free volume radius distribution (S4) through equation 1 [S4].

$$n(R) = \frac{2\Delta R}{(R+\Delta R)^2}\left[\cos\left(\frac{2\pi R}{R+\Delta R}\right) - 1 \right]\alpha_3(\lambda) \tag{S4}$$

The relative free volume (Fv) of polymeric materials is calculated as

$$Fv = \frac{4}{3}\pi R^3 I_{o-Ps} \tag{S5}$$

where, R and $I_{o\text{-}Ps}$ are the average radius (nm) and *o*-Ps intensity (%).

References:

(S1) Provencher, S. W. A constrained regularization method for inverting data represented by linear algebraic or integral equations. *Comput. Phys. Commun.* **1982**, *27*, 213–227.

(S2) Tao, S. J. Positronium Annihilation In Molecular Substances. *J. Chem. Phys.* **1972**, *56*, 5499–5510.

(S3) Eldrup, M.; Lightbody, D.; Sherwood, J. N. The Temperature Dependence of Positron Lifetimes in Solid Pivalic Acid. *Chem. Phys.* **1981**, *63*, 51–58.

(S4) Sharma, S. K.; Sudarshan, K.; Pujari, P. K. Unravelling the sub-nanoscopic structure at interphase in Poly (vinyl alcohol)-MOF nanocomposite and its role on thermo-mechanical properties. *Phys. Chem. Chem. Phys.* **2016**, *18*, 25434–25442.

Table S1. Ion-concentration factor, K, of PEO/45SN-Li and PEO-Li electrolytes at different temperatures.

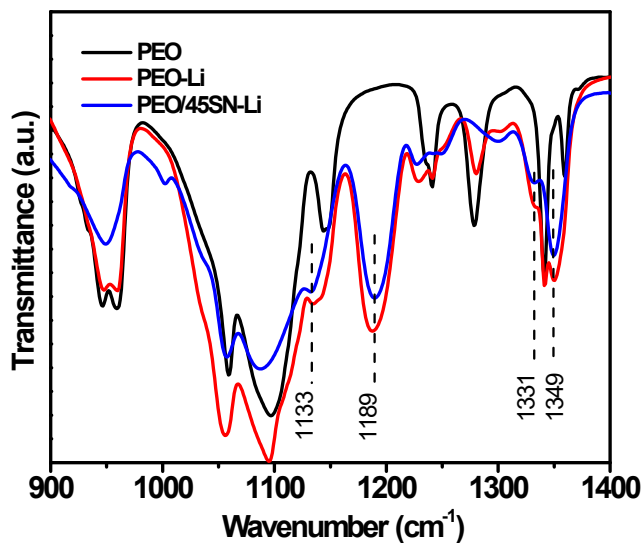| Temperature (K)	K	
	PEO/45SN-Li	**PEO-Li**
273	1.0822×10^{-9}	6.8715×10^{-13}
253	2.2067×10^{-10}	1.0547×10^{-13}
233	8.0854×10^{-12}	4.7907×10^{-14}

Figure S1. FTIR spectra of pristine PEO, PEO/45SN-Li and PEO-Li electrolytes. The dashed vertical lines show the characteristic peaks of $-SO_2-$ from TFSI$^-$ ion.
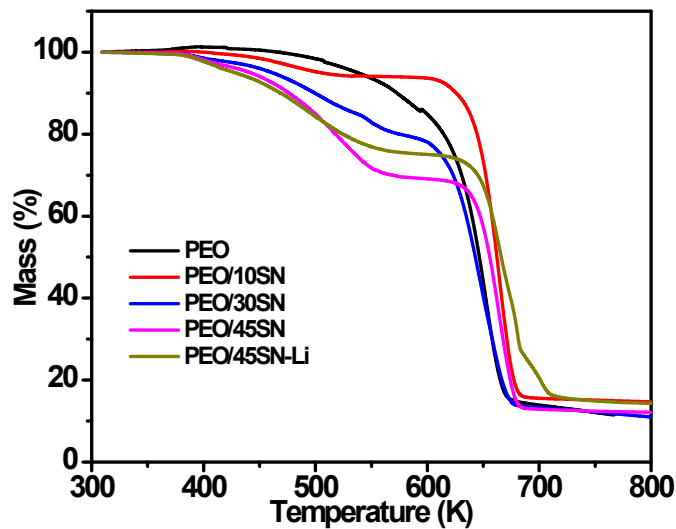

Figure S2. TGA thermograms of pristine PEO, PEO/xSN composites, and PEO/45SN-Li electrolytes.
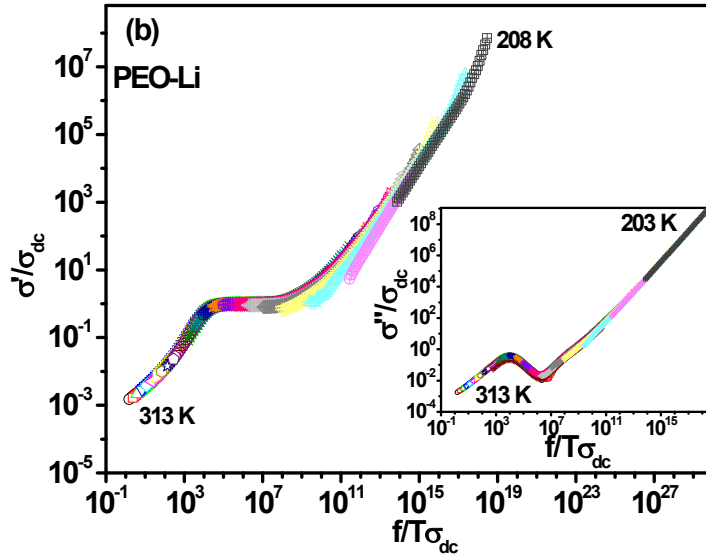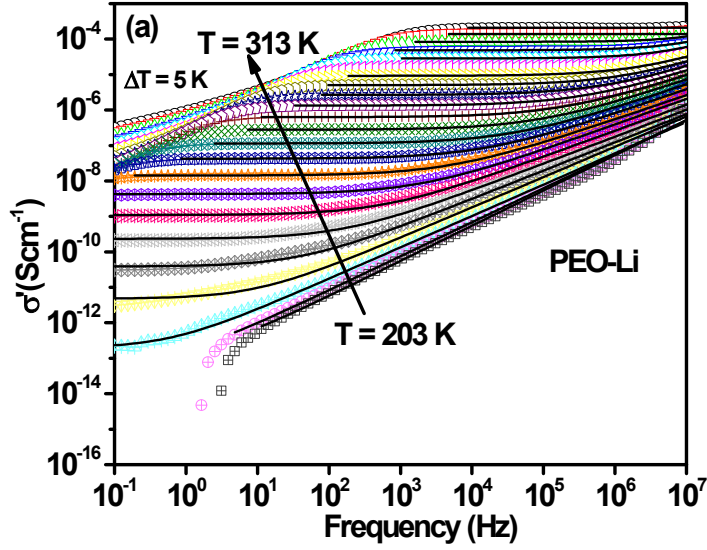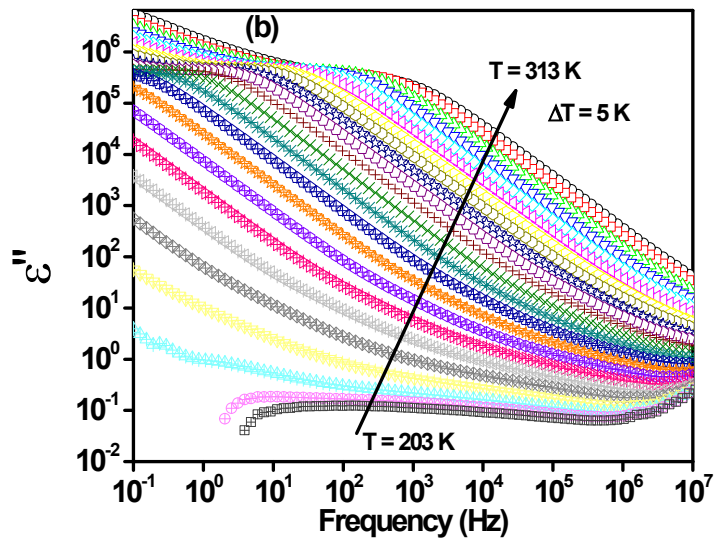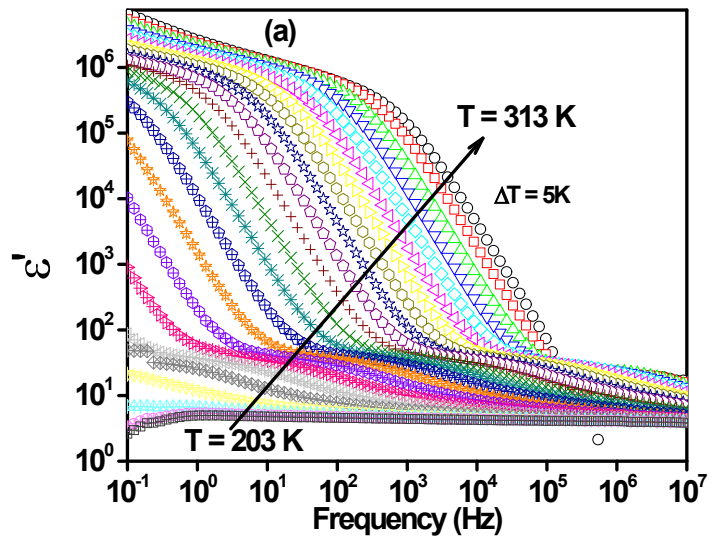
Figure S3. (a) Frequency dependent real component of ac conductivity in temperature range (203–313 K) of PEO-Li electrolyte; the solid lines through data points show the fitting using A-W model, eq. 1 **(b)** Scaling of real and imaginary component (inset) of ac conductivity of PEO-Li electrolyte according to Summerfield scaling approach.
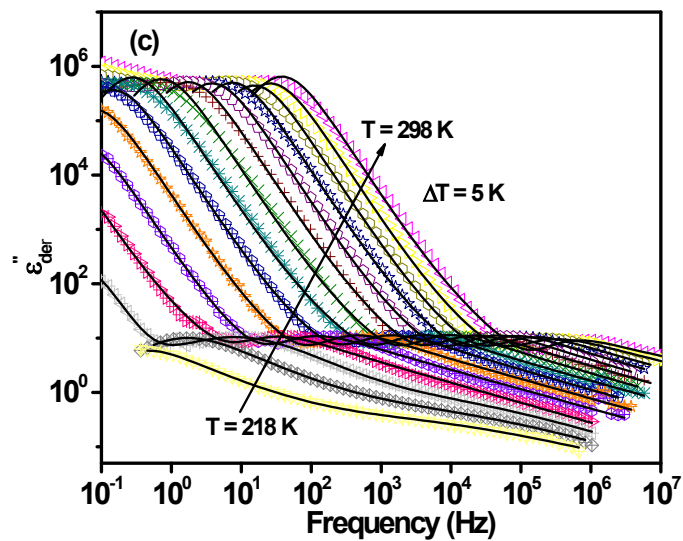
Figure S4. **(a)** Frequency dependent real component (ε'); **(b)** imaginary component (ε'') of complex permittivity (ε^*) in temperature range 203–313 K with temperature interval of 5 K; **(c)** ε''_{der} of PEO-Li electrolyte in temperature range 218–298 K with temperature interval of 5 K, solid lines are fitting to sum of two HN functions, eq. 6.