Electronic Supplementary Information (ESI)

Ionic Transport Mechanism and Coupling Between the Ion Conduction and Segmental Relaxation Process of PEO_{20}-$LiCF_3SO_3$ Based Ion Conducting Polymer Clay Composites.

Tapabrata Dam, Sidhartha S. Jena, and Dillip K. Pradhan

Department of Physics and Astronomy, National Institute of Technology Rourkela, Odisha-769008, India.

S1 Preparation of ICPCC

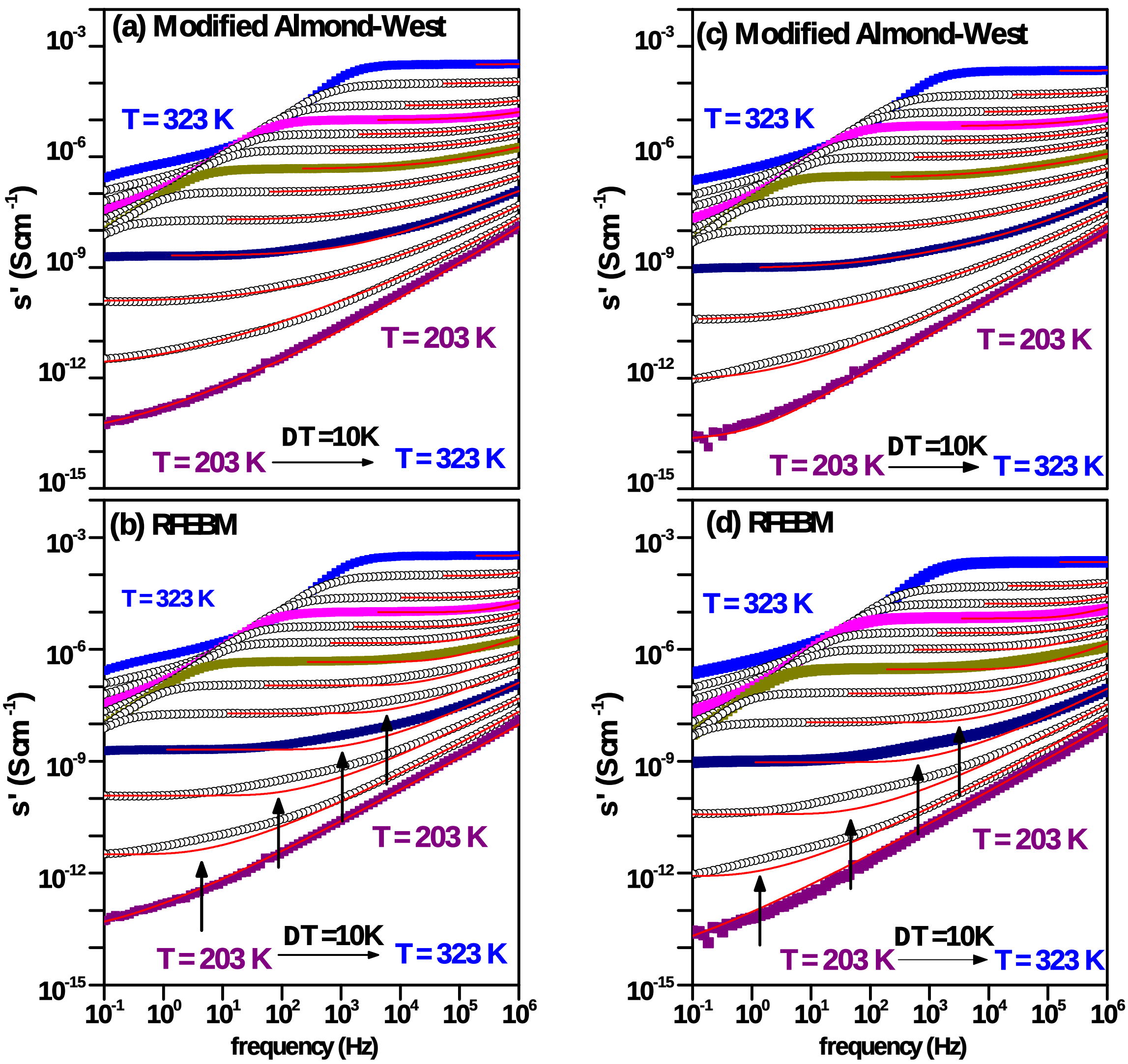
Polyethylene oxide (PEO, M.W. = 6×10^5, Sigma Aldrich), lithium trifluoromethanesulfonate ($LiCF_3SO_3$, Sigma Aldrich), modified hMMT clay (used as filler) and analytical grade acetonitrile (used as common solvent) are used to prepare ICPCC in conventional solution casting method. PEO and $LiCF_3SO_3$ are vacuum dried before use whereas acetonitrile is dehydrated using molecular sieve. Polyethylene oxide is added to acetonitrile and left to swell for 12 h, then stoichiometric amount $LiCF_3SO_3$ is added and the mixture is stirred thoroughly for 12 h resulting in a viscous slurry of polymer salt complex. For all samples the O:Li^+ is kept fixed at 20 : 1. Thereafter required amount of hMMT clay filler (wt.% with respect to polymer host) is added to the polymer-salt complex and stirred for another 12 h. The resulting slurry thus obtained is then cast on a glass petridish and solvent is allowed to evaporate slowly at room temperature to prepare a free-standing film of ICPCC. The entire operation is carried out inside PlasLabs controlled atmosphere chamber (855-AC/E) with constant flow of dry nitrogen gas. The synthesized ICPCCs are having the composition PEO_{20}-$LiFC_3SO_3$-$x$wt.% hMMT (x= 0, 2, 3, 5, 8, 10 &15).

S2 Characterization Techniques

The X-ray diffraction (XRD) patterns of the MMT, modified hMMT and ICPCC films are recorded using Rigaku Ultima IV X-Ray diffractometer operated at 40 kV and 40 mA current with Cu $K_{\alpha1}$ radiation (1.5405Å). Diffraction patterns are recorded with a scanning step of 0.002° and speed 3° per minute. Broadband dielectric measurements are carried out using a Novo-Control GMBH Alpha dielectric spectrometer for the frequency range from 10^{-1} Hz to 10^6 Hz with perturbation potential of 100 mV. Literature suggests that dielectric spectra of PSC in general are highly sensitive to moisture and to minimize the effect of moisture ICPCC films are vacuum dried at room temperature for 12 h before measurement. A parallel plate capacitor configuration is used where ICPCC films are sandwiched between a pair of stainless steel electrodes and then placed in the sample holding assembly of the cryostat. The samples are heated to 323 K and kept for 1 h before commencing the measurement to build up a good electrode-electrolyte contact and then dielectric data is collected during cooling mode from 323 K to 203 K at every 5 K interval with 10 m of equilibration time at each temperature. Temperature is controlled using Novo-Control Quattro Cryo-system using a nitrogen gas cryostat. While recording the dielectric isotherms prior attention is given to maintain good thermal stability (±0.1 K) of the samples.

S3 Temperature dependent Conductivity Spectra

Modified Almond-West and Random Free Energy Barrier Model analysis for PEO_{20}-$LiFC_3SO_3$-3wt.% hMMT and PEO_{20}-$LiFC_3SO_3$-15wt.% hMMT compositions of ICPCC series under investigation. These are the supporting plots for Fig. 3 of the manuscript. A marked difference between the experimental and RFEBM model simulated curves can be observed in all the compositions. Variations are marked with arrows in Fig. S1.



PEO$_{20}$-LiCF$_3$SO$_3$- 3 wt.% hMMT

PEO$_{20}$-LiCF$_3$SO$_3$- 15 wt.% hMMT

Figure S1: AC conductivity as a function of frequency for the ICPCC composition PEO$_{20}$-LiCF$_3$SO$_3$- 3 wt.% hMMT at temperature ranging from 203 K to 323 K. (a) Phenomenological approach (Modified Almond-West) and (b) Random Free Energy Barrier Model used for analysing conductivity spectra. AC conductivity as a function of frequency for the ICPCC composition PEO$_{20}$-LiCF$_3$SO$_3$- 15 wt.% hMMT at temperature ranging from 203 K to 323 K. (a) Phenomenological approach (Modified Almond-West) and (b) Random Free Energy Barrier Model used for analysing conductivity spectra. Represented curves are temperature dependent having interval of 10 K.