

# Structural and Dielectric Properties of Ionic Liquid Doped Metal Organic Framework based Polymer Electrolyte Nanocomposites

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**Abstract.** Metal Organic Frameworks (MOFs) are mesoporous materials that can be treated as potential hosts for trapping guest molecules in their pores. Ion conduction and phase behavior dynamics of Ionic Liquids (ILs) can be controlled by tunable interactions of MOFs with the ILs. MOFs incorporated with ionic liquid can be dispersed in the polymers to synthesize polymer electrolyte nanocomposites with high ionic conductivity, electrochemical and thermal stability for applications in energy storage and conversion devices such as rechargeable Li-ion batteries. In the present work we have synthesized Cu-based MOF [Cu<sub>3</sub>(1,3,5-benzene tricarboxylate)<sub>2</sub>(H<sub>2</sub>O)] incorporated with the ionic liquid 1-Butyl-3-methylimidazolium bromide at different weight ratios of MOF and IL. The synthesized MOF-IL composites are dispersed in Poly (ethylene oxide) (PEO). Frequency dependent behavior of permittivity and dielectric loss of the nanocomposites depict the non-Debye dielectric relaxation mechanism. The room temperature Nyquist plots reveal decreasing bulk resistance upto 189  $\Omega$  with optimum ionic conductivity of  $1.3 \times 10^{-3}$  S cm<sup>-1</sup> at maximum doping concentration of IL in the nanocomposite system.

## 1. Introduction

Metal Organic Frameworks (MOFs) are uniformly sized microporous group of hybrid materials containing an infinite network of inorganic metal clusters coordinated with organic linkers through metal ligand coordination bonds [1]. Owing to their high surface area and large pore volume, MOFs can be used in different applications such as gas adsorption, purification, separation, catalysis and ion exchange [2]. MOFs are highly designable and can be treated as host materials for small guest molecules to enhance their electrochemical properties. Ionic Liquids (ILs) are molten salts consisting of asymmetric organic cations and symmetric inorganic anions that can undergo unlimited structural variations and have a melting point below 100°C [3]. In recent years, researchers are paying much attention towards ionic liquids because of their significant properties such as low vapour pressure, high viscosity, good solvability for both organic and inorganic compounds, high thermal and electrochemical stability and high ionic conductivity. Due to their unique properties ionic liquids have potential applications in electrochemical devices, enzymatic catalysis, sensing and solar energy conversion [4]. MOFs can be used as potential host materials for controlling the phase behavior dynamics of ILs via the nanosizing of ILs and tunable interactions of MOFs with the ILs [5].



Kazuyuki Fujie et al. [6] investigated the phase behavior and ionic conductivity of lithium ion-doped ionic liquid (IL) EMI-TFSA incorporated into ZIF-8 MOF. The bulk (EMI0.8Li0.2) TFSA showed two orders of magnitude higher ionic conductivity than that of (EMI0.8Li0.2) TFSA in the micropores. The composite polymer electrolytes based on MOF can also be a good approach to enhance the performance parameters in energy storage and conversion devices. N. Angulakshmi et al. [7] prepared Magnesium-benzene tricarboxylate metal organic framework (Mg-BTC MOF)-incorporated composite polymer electrolytes (CPE) composed of poly(ethylene oxide) (PEO) and lithium bistrifluoromethane sulfonylimide (LiTFSI). The ionic conductivity of CPE incorporated with Mg-BTC MOF was enhanced up to two orders of magnitude even at 0°C with improved thermal stability and compatibility. The discharge capacity of the lithium polymer cell composed of Li/CPE/LiFePO<sub>4</sub> was found to be 110 mAh g<sup>-1</sup> with a current rate of 1-C at 70°C. Claudio Gerbaldi et al. [8] reported that the incorporation of aluminium-based MOF as the filler to poly(ethylene oxide)-based nanocomposite polymer electrolyte (NCPE) membranes can enhance the ionic conductivity of the system up to two orders of magnitude with high stability and excellent cycling profile at moderate temperature.

In the present work a Cu based MOF [Cu<sub>3</sub>(1,3,5-benzene tricarboxylate)<sub>2</sub>(H<sub>2</sub>O)], (popularly known as MOF-199) has been incorporated with ionic liquid (1-butyl-3 methylimidazolium bromide) with different concentrations and dispersed in polymer Poly(ethylene oxide) matrix with a view to enhance the structural and electrochemical properties of the nanocomposite system.

## 2. Experimental

### 2.1. Materials

Copper (II) acetate monohydrate was purchased from SD Fine-Chem Limited, India. Benzene tricarboxylic acid, N-N-Dimethyl Formamide, Triethylamine, Ethanol and Acetonitrile were purchased from Merck Specialities Pvt. Ltd., India. 1-butyl-3-methylimidazolium bromide and Poly(ethylene oxide) were purchased from Sigma Aldrich.

### 2.2. Preparation of Cu based Metal Organic Framework

Cu based Metal Organic Framework has been prepared by solvothermal technique. Two separate solutions in 1:1:1 ratio of DMF, ethanol and distilled water (4 ml each), have been prepared. 0.86 g of copper acetate monohydrate and 0.5 g of benzenetricarboxylic acid were dissolved separately into the prepared solutions. The two samples were mixed and stirred for 30 minutes to mix them homogeneously. 0.5 ml of triethylamine was added drop wise to the magnetically stirred solution [9]. The solution was kept stirring for 24 h, followed by filtering and washing with 20 ml of DMF. The sample was kept under vacuum drying for 3 – 4 h at 373K and 1.5 g bluish green colored product yield was obtained.

### 2.3. Preparation of IL doped MOF based polymer electrolyte nanocomposite

MOF-IL composites were prepared by direct mixing using mortar and pestle at 30%, 40% and 50% of doping concentrations of IL. MOF-IL Polymer electrolyte nanocomposites were prepared by solution casting method. 1g of poly(ethylene oxide) (PEO) was dissolved in 20 ml of acetonitrile and stirred for 4 h at 50° C. Then 0.5 g of each MOF-IL composite of different doping concentration was dispersed separately into the polymer solution and allowed mixing by ultrasonication for 2 h. Then each of the solutions were cast on petri-dishes and dried at room temperature for 1-2 days to get flexible bluish white colored films having thickness 30-40 µm.

### 2.4. Analysis and Characterization Techniques

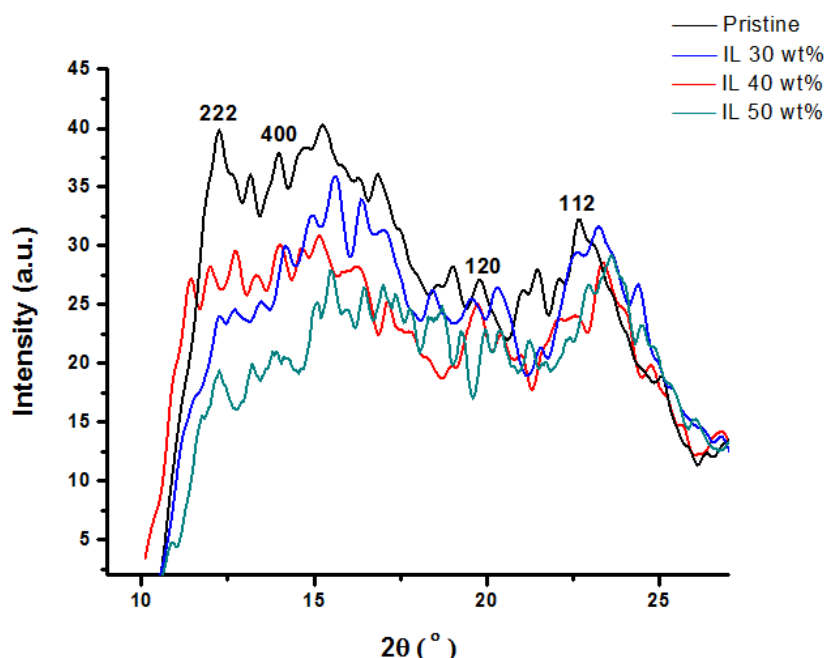
The XRD patterns of pristine MOF-polymer films and doped ones were obtained by Advanced D8 X-ray diffractometer (Bruker AXS, Germany). Thermogravimetric analyzer (Perkin Elmer STA 6000) was used for analyzing the thermal stability of the pristine and IL doped MOF-polymer films. The surface morphology of MOF-IL composite was observed by a scanning electron microscope (SEM, Jeol 6390 LV). The ac impedance studies of MOF-IL polymer nanocomposite films were investigated by Hioki 3532-50 LCR HiTester in the frequency range from 42 Hz to 5 MHz.

### 3. Results and Discussion

Figure 1 shows the XRD patterns of pristine and IL doped MOF-PEO nanocomposites. The peaks at (120) and (112) planes correspond to the diffraction pattern of PEO. The peaks at (222) and (400) reflect the formation of MOF-199. Due to the incorporation of ionic liquid into the MOF-polymer system, the intensities of the XRD peaks decrease substantially. Due to the interaction of BMIM<sup>+</sup> and oxygen atom of PEO chain, the degree of crystallinity is decreased with increasing concentration of ionic liquid [10]. The crystallite size (*L*) has been calculated using Scherrer equation:

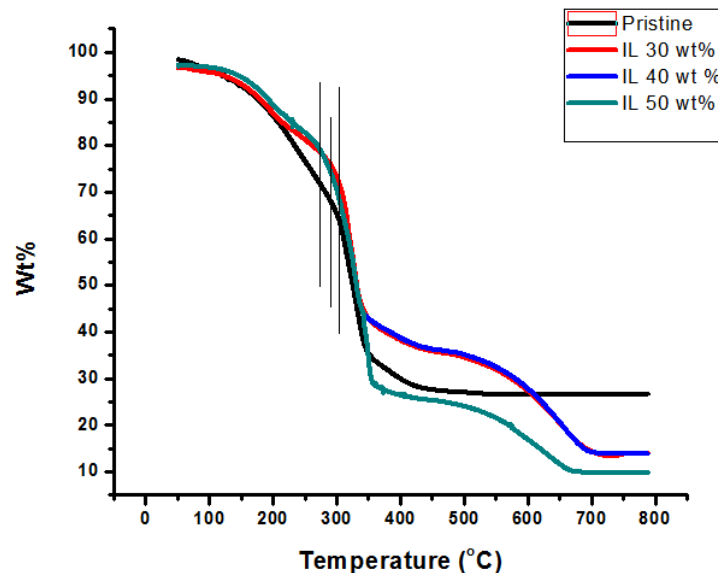
$$L = K\lambda / \beta \cos\theta \quad (1)$$

where *K* is the crystallite shape constant taken to be 0.89,  $\lambda$  is the X-ray wavelength (1.5406 Å),  $\beta$  is the value of full width at half maximum of diffraction peaks at angle  $2\theta$ . The crystallite size of the nanocomposite system is found to decrease from 4.46 Å to 3.63 Å with increasing concentration of IL from 30% to 50%.



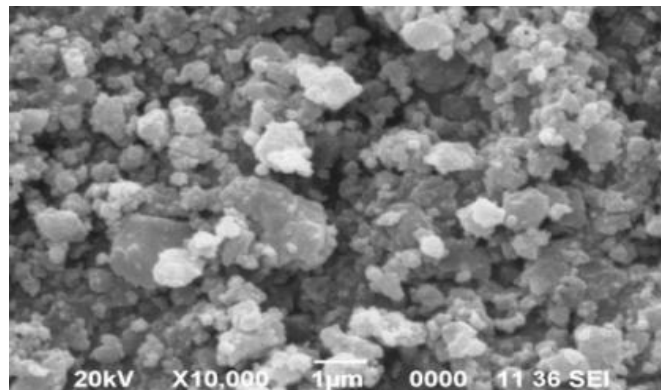
**Figure 1.** X-Ray Diffraction pattern of pristine and ionic liquid doped MOF-PEO nanocomposites.

Thermal stability of pristine and IL doped MOF-PEO nanocomposites is shown by thermogravimetric plots in Figure 2. Reduction in thermal stability is observed due to the enhancement in amorphicity with increasing doping concentration of ionic liquid in the MOF-PEO nanocomposites. The pristine sample shows thermal stability upto 310°C while in case of IL doped ones thermal stability is decreased upto 214°C.



**Figure 2.** Thermogravimetric analysis of pristine and IL doped MOF-PEO nanocomposites.

The Scanning Electron Microscopy image of IL doped MOF is represented in Figure 3 shows crystalline morphology of the nanocomposite system.

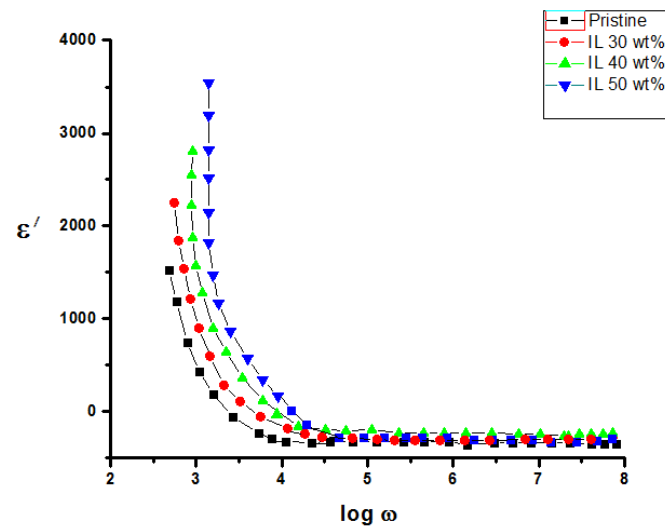


**Figure 3.** SEM micrograph of IL doped MOF nanocomposite.

Figure 4 represents the frequency dependence of the real ( $\epsilon'$ ) part of the dielectric function for the pristine and IL doped MOF polymer nanocomposite at room temperature. This can be attributed to the non Debye type behavior of accumulation of space charge region at the interface of the electrolyte. The real part of the dielectric function can be calculated using the formula:

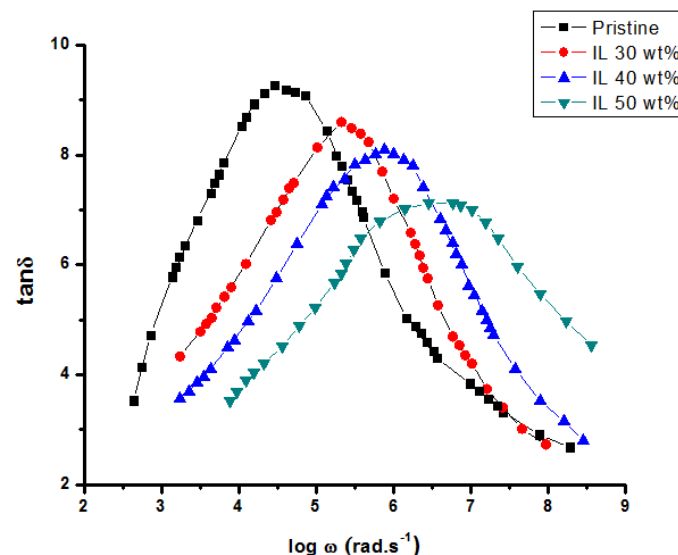
$$\epsilon' = \frac{Cd}{\epsilon_0 A} \quad (2)$$

where,  $d$  is the thickness of the polymer film,  $C$  is the measured capacitance value,  $A$  is the area of the film and  $\epsilon_0$  is the permittivity of free space [11]. As crystallinity of the samples decreases upon increasing doping concentration of the ionic liquid, segmental motion of the polymer chain increases and that can enhance the asymmetry in relaxation process.



**Figure 4.** Variation of real part of permittivity ( $\epsilon'$ ) with angular frequency.

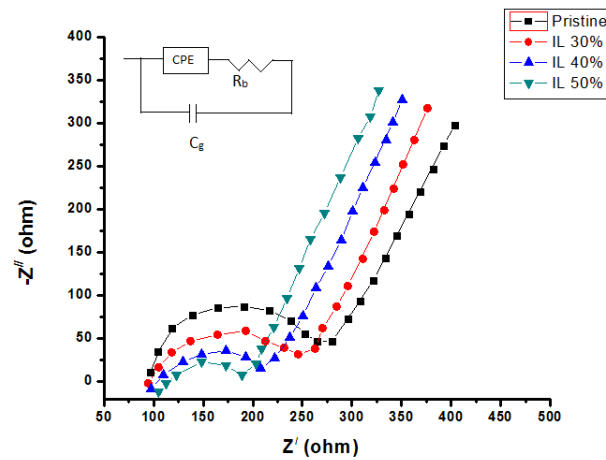
The dielectric loss with the room temperature variation of frequency for pristine and IL doped MOF-PEO nanocomposites is depicted in Figure 5. Shifting of  $\tan \delta$  peaks towards high frequency side with increasing IL doping is observed. This is due to the enhancement of hopping frequency of the charge carriers with the increase in uptake of ionic liquid in the porous nanocomposite system.



**Figure 5.**  $\tan \delta$  vs. angular frequency plots for pristine and IL doped MOF-PEO nanocomposites.

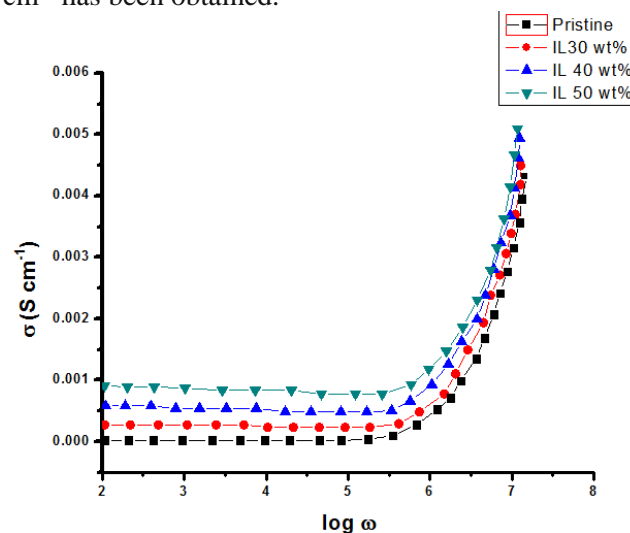
The room temperature Nyquist impedance plots of the pristine and IL doped MOF-PEO nanocomposites are shown in Figure 6. The plots contain semicircular arcs at the high-frequency that are due to the parallel combination of capacitances ( $C_g$ ) and bulk resistances ( $R_b$ ). The bulk resistance

represents the movement of ions and the capacitance represents the dielectric polarization of polymer nanocomposites [12].



**Figure 6.** Room temperature Nyquist plots for pristine and IL doped MOF-PEO nanocomposites.

At the low-frequency region spikes are observed due to the formation of electric double layer. In inset of Figure 6 the equivalent circuit is shown having  $R_b$  in parallel with  $C_g$  in series with the constant phase element (CPE) [13]. Enhancement in ionic conductivity is observed as the bulk resistances of the nanocomposites are found to be decreased from  $274 \Omega$  to  $189 \Omega$  with increasing doping concentrations of ionic liquid. At maximum doping concentration of 50% of IL, ionic conductivity of  $1.3 \times 10^{-3} \text{ S cm}^{-1}$  has been obtained.



**Figure 7.** Room temperature variation of ac conductivity with frequency of pristine and IL doped MOF-PEO nanocomposites.

The room temperature variation of ac conductivity with frequency of pristine and IL doped MOF polymer electrolyte nanocomposites is shown in Figure 7. The dispersive behavior of ac conductivity at higher frequency regions is due to the non random forward-backward hopping of charge carriers

from one coordination site to the others [14]. With increasing doping concentration of ionic liquid the segmental motion of the polymer chain enhances leading to long range hopping of ions [15].

#### 4. Conclusion

Structural and dielectric properties of Cu based MOF polymer electrolyte nanocomposites have been investigated for different doping concentrations of ionic liquid. XRD patterns reveal the reduction in crystallinity as well as crystallite size from 4.46 Å to 3.63 Å upon IL doping. Permittivity spectra depict the dielectric relaxation mechanism in the IL doped nanocomposite systems which is dominated by hopping of ions. Optimum ionic conductivity of  $1.3 \times 10^{-3} \text{ S cm}^{-1}$  has been obtained at maximum doping concentration of IL. Thermogravimetric analysis shows the reduction in thermal stability due to enhancement in amorphicity with increasing doping concentration of ionic liquid into the pores of MOF. The ac conductivity studies confirm the hopping of ions to new coordination sites to intensify ionic conductivity.

#### Acknowledgement

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