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Synthesis, Characterization and Impedance Analysis of Polypyrrole/$La_{0.7}Ca_{0.3}MnO_3$ Nanocomposites

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***Abstract*—**Perovskite manganite $La_{0.7}Ca_{0.3}MnO_3$ was synthesized by Sol-gel method. Polymerization of pyrrole was carried by in-situ polymerization method. The composite of pyrrole (Py)/$La_{0.7}Ca_{0.3}MnO_3$ composite in the presence of oxidizing agent ammonium per sulphate to synthesize polypyrrole (PPy)/$La_{0.7}Ca_{0.3}MnO_3$ (LCM) composite was carried out by the same in-situ polymerization method. The PPy/LCM composites were synthesized with varying compositions like 10, 20, 30, 40, and 50 wt.% of LCM in Py. The surface morphologies of these composites were analyzed by using scanning electron microscope (SEM). The images show that LCM particles are embedded in PPy chain. The impedance measurement of PPy/LCM at different temperature ranges from 30 to 180 °C was studied using impedance analyzer. The study shows that impedance is frequency and temperature dependent and it is found to decrease with increase in frequency and temperature.

***Keywords*—**Polypyrrole, sol gel, impedance, composites.

I. Introduction

IT is well known that transport characteristic studies help us to know many physical properties of the composite materials. Henceforth, the ceramic materials are of prime importance because of their strength, durability, and high efficiency. Thus, $LaMnO_3$ which is basically an anti-ferromagnetic material has the arrangement of spins at the transition metal sites and thus has an insulating behavior. The perovskite structure of $LaMnO_3$, exhibits strong ferromagnetism and metallic conductivity by partial substitution of La ions (3^+ valences) with A (2^+) valence ion such as Ca, Ba, Sr, Pb and they gain a variety of distinguishing physical properties like electrical transport, magnetic, and dielectric. Researches also reported that use of inherently conducting polymers with ceramics make wonders in the physical property of the composites [1]-[4]. In a way, the ionic-electronic conductors are also gaining interest among many researches because of the ionic-electronic interactions. This interaction offers unique charge storage devices. The transport properties can be enhanced by manipulating the ionic charges. Many researches have been conducted to study the transport behavior in ceramic material [5]-[8].

They observed the enhanced physical properties when tailored with the organic and inorganic composites. In our study, we have chosen PPy as the organic part and calcium-doped lanthanum manganite as the inorganic part of the composites. The choice of PPy is made in view of ease to synthesis and good physical properties.

In this paper, we present an analysis of the AC Impedance study of PPy/LCM nanocomposites using impedance analyzer in the frequency range of 100 Hz to 5 MHz with various compositions viz., 10, 20, 30, 40, and 50 wt. % of LCM in Py. The study enables us to determine the contribution of perovskite manganite to ionic transport properties of the materials, where it becomes important to know the rate capability of the energy storage devices.

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II. Experimental Details

A. Synthesis of Nanoparticle of LCM

Chemicals La_2O_3 having molecular weight 325.81, $CaCO_3$ having molecular weight 100.086 and $MnCO_3$ having molecular weight 114.946 obtained from Loba chemicals of AR grade. Nanoparticles of LCM were prepared by Sol-gel method.

Stoichiometric proportions of high purity La_2O_3, $CaCo_3$, $MnCO_3$ were properly dissolved in concentrated nitric acid, and 30 ml of distilled water was added to this mixture. Then, an equal amount of ethylene glycol was added to this mixture while constant stirring. The beaker containing this mixture was placed on a hot plate. Initially, the mixture was heated at 100 ºC, excess ethylene glycol was then removed by heating it to about 180 ºC, and at this stage, a thick sol was formed. This sol was further heated at 250 ºC in a furnace for 6h to get the precursor. This was then sintered at 700 ºC for about 6h to get nanoparticles.

B. Synthesis of PPy/Nanocomposites

The AR grade [Spectro Chem Pvt. Ltd.] Py [9] is used, and 0.3 M Py [10] solution is measured and poured into a round bottomed flask. The flask then placed in an ice tray mounted on a magnetic stirrer. 0.6 M [11] ammonium persulphate solution is continuously added dropwise with the help of a burette to the above 0.3 M Py solution. The reaction is allowed for 5 h [12] under continuous stirring by maintaining a temperature of 0 to 5 ºC [13]. The precipitated PPy is filtered and dried in hot air oven [14]. The dried precipitate is then kept in a muffle furnace at 100 °C for 2 h. The yield of the PPy is 2.18 g (100 wt.%). For 0.3 M Py solution, 0.218 g (10 wt.%) of LCM nanopowder is added and mixed thoroughly, further 0.06 M ammonium persulphate is continuously added dropwise with the help of a burette to the above solution to get a PPy/LCM 10 wt.% composite. Similarly, for 20, 30, 40, and 50 wt.%, 0.436 g, 0.654 g, 0.872 g, and 1.09 g of LCM are respectively taken, and the above procedure is followed to get

the PPy/LCM composites. The pure PPy and PPy/LCM powder is pressed in the form of pellets of 10 mm diameter and 1-3 mm thickness using hydraulic press by applying 8-10 tons pressure. The conducting silver paste is applied to the pellets of synthesized composites for impedance measurements.

III. Results and Discussion

A. SEM Analysis

The prepared nanopowder, pure PPy and PPy/ $La_{0.7}Ca_{0.3}Mn0_3$ nanocomposites were subjected to SEM to study the morphology and size distribution of the samples.

Figs. 1 (a) and (b) show the SEM images of pure LCM nano powder and PPy/10% LCM. The SEM image from Fig. 1 (a) shows that LCM nanopowder forms cluster of particles with size~90 nm. Similarly, the images Figs. 1 (b) and (c) show that the nanocluster of particles is embedded in the PPy chain.

B. FTIR Analysis

The FTIR spectra of the PPy and PPy/LCM composites are shown in Fig. 2.

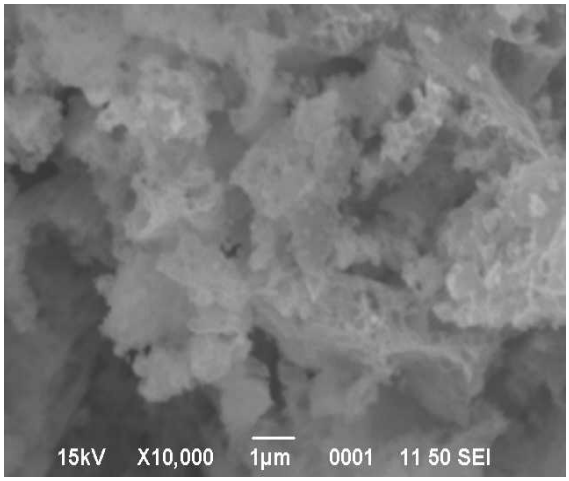

Fig. 1 (a) SEM image of pure LCM nanopowder

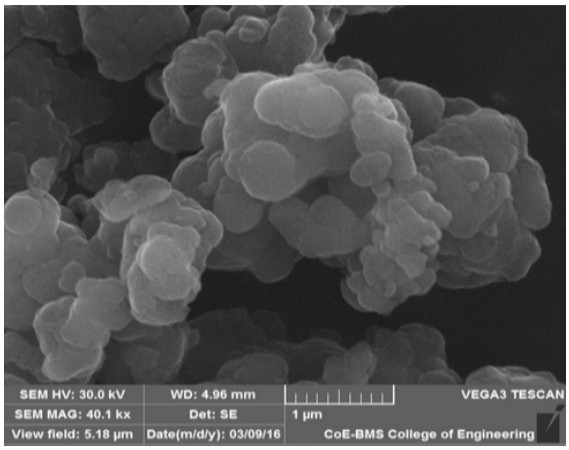

Fig. 1 (b) SEM image of PPy with 10% LCM composite

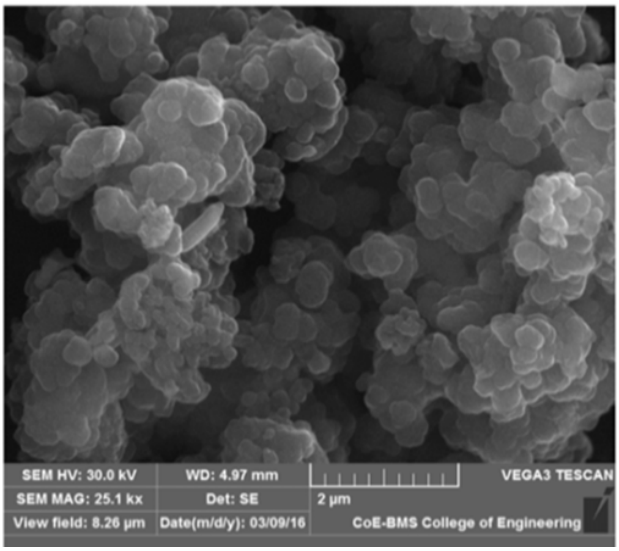

Fig. 1 (c) SEM image of PPy with 50% LCM nanopowder

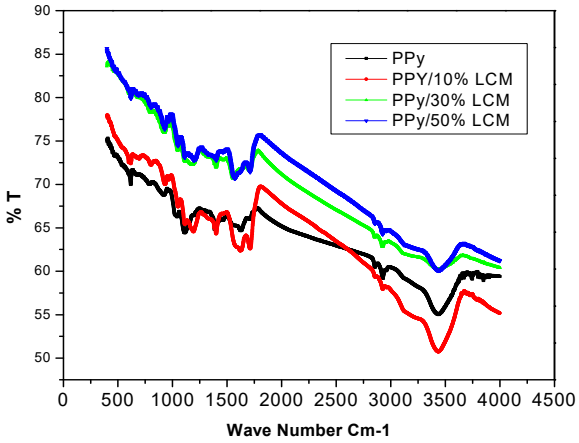

Fig. 2 FTIR spectra of PPy and PPy/LCM composites

The FTIR spectra of pure PPy, 10%, 30%, and 50% weight percentage of LCM are shown in Fig. 2. The absorption spectra reveal that the LCM nanopowders which have the most significant absorption bands are located around 600, 820, 1100, 1380, 1450, 1650, and 3400 cm^{-1}. The peak~594 cm^{-1} is due to orthorhombic structure of the rare earth manganites with central Mn atom octahedral surrounded by its nearest neighbor six oxygen ions [15]. Mn – O – Mn bending mode corresponds to ~400 cm^{-1} and La(Ca) site is located at ~200 cm^{-1}. The stretching and bending phonon mode is found to shift to the lower frequency side [16]. 1450 cm^{-1} corresponds to the fundamental vibration of the Py ring of the PPy chain [17].

C. AC Impedance Analysis

Ionic transport behaviour of PPy/LCM nanocomposites was investigated by using AC impedance analysis, the impedance studies of pure PPy and PPy/LCM nanocomposites were carried in the frequency range between 100 Hz to 5 MHz. The variation of impedance versus frequency at temperature

ranging from 90 ºC and 180 ºC for pure PPy and PPy/ LCM composites are as shown in Figs. 3 (a) and (b).

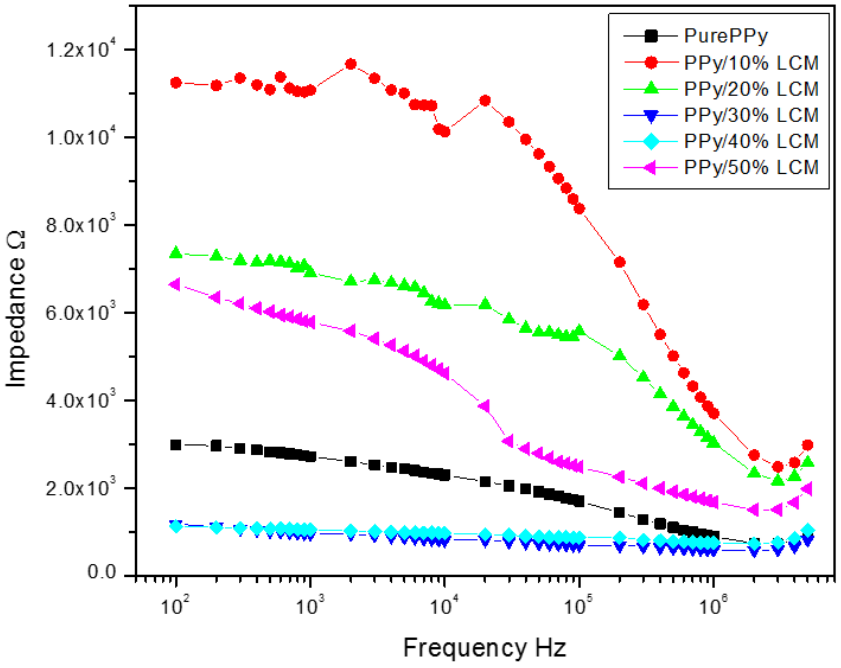

Fig. 3 (a) Impedance versus frequency plot for pure PPy and PPy / LCM Composites at 90 ºC

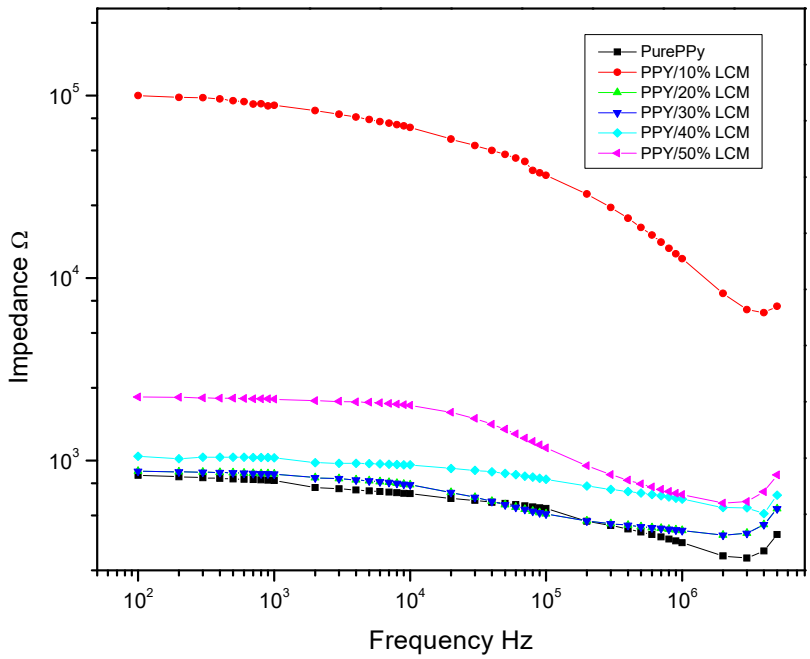

Fig. 3 (b) Impedance versus frequency plot for PPy/ LCM at 180 ºC

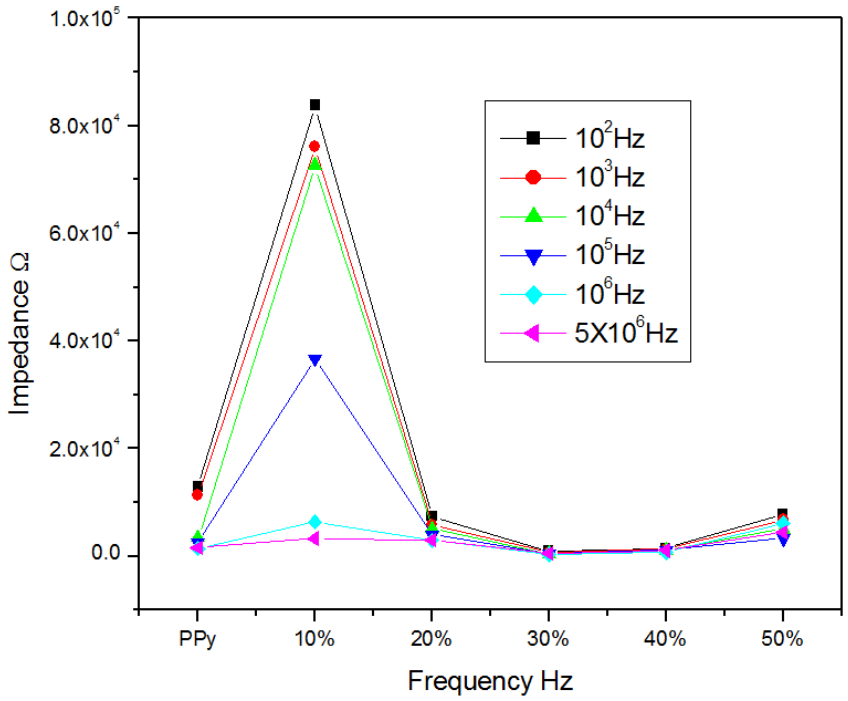

Fig. 3 (c) Impedance versus weight per cent plot of LCM at different frequencies

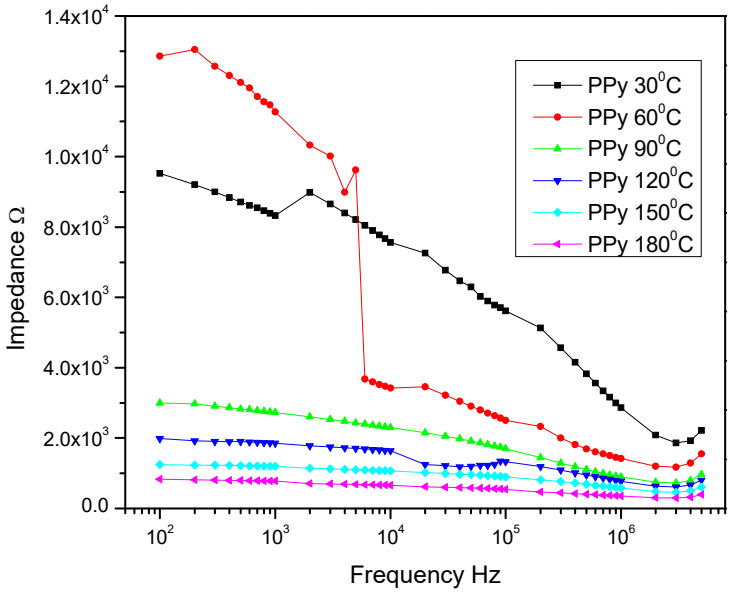

Fig. 4 Impedance versus frequency plot of Pure PPy at different temperatures

From Fig. 3 (a), it is observed that the impedance decreases with frequency from 100 Hz to 5 MHz. It is clear from the behavior that the composite behaves as a capacitive type. Therefore, the composite can be used where the device needs to be built to act as a capacitor. Impedance value is found to be more for PPy/50% LCM when compared with pure PPy. This is due to the fact that LCM nanopowder which is basically an insulator also contributes for the impedance in the circuit. Since LCM is embedded in the PPy chain, this creates obstruction for the electron hopping. Thus, the impedance increases.

From Fig. 3 (c), the impedance versus weight percent plot, the impedance increases from PPy till 10% LCM and then decreases continuously for 20%, 30%, 40% and 50% at 60 ºC. This behavior can be understood that the volume fraction is more for pure PPy and is less for 10% LCM, therefore the impedance increases. But, as the LCM composition increases in the PPy chain, the volume fraction of the PPy/LCM

composite increases. The formation of cluster of the LCM in the PPy chain [18], [19] which causes obstruction for the free movement of the electrons. As frequency increases, the phonon field due to presence of LCM in PPy increases, and hence, impedance of the composite decreases.

Fig. 4 shows the variation of impedance with frequency of pure PPy at different temperature varying 30 ºC to 180 ºC.

The PPy/10% LCM show highest impedance at various temperatures varying from 30 ºC to 180 ºC. It is observed from Fig. 3 (a) that 90 ºC temperatures would be feasible temperature for the composite. This is because as the temperature increases beyond 90 ºC upto 180 ºC and also at higher frequency side, the composite reverts to resistive phase.

IV. Conclusion

Synthesis of LCM was synthesized by Sol-gel method. The composite of PPy/LCM was synthesized by in situ method. Impedance Analysis was carried out at room temperature and at high temperature. The impedance of the composites was found to depend on the weight % of LCM and also on the temperature. The decrease in the impedance is due to the reduction in the volume fraction between PPy/LCM composite. The PPy/LCM nanocomposites can be used as capacitive circuit in the frequency range 100 Hz – 1 MHz. The PPy/LCM nano-composites might find applications in energy storage device [20]. The study enables us to determine the contribution of perovskite manganite to the impedance and transport properties of the materials.

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