Frequency and Temperature dependence studies in PTh-V$_2$O$_5$ composites

Jyoti Kattimani, T. Sankarappa* , R. Ramanna and J. S. Ashwajeet
Department of Physics, Gulbarga University, Gulbarga-585106, Karnataka, INDIA

Available online at: www.isca.in, www.isca.me
Received 5th June 2015, revised 10th June 2015, accepted 17th June 2015

Abstract
By oxidation method, Polythiophene (PTh) has been prepared. Composites were prepared by mixing Polythiophene and V$_2$O$_5$ in different weight percentages. Their phases were confirmed by XRD and SEM studies. Dielectric properties and AC conductivity were measured over broad range of frequency and temperature. Conductivity varied with temperature is the semiconductor fashion. Dielectric constant and loss both were found to decrease with increase in frequency and increased with increase in temperature. Conductivity variation with temperature has been analysed in terms of small polaron hopping theory of Mott.

Keywords: Polythiophene, nanocomposites, conductivity, polaron hopping, activation energy.

Introduction
The conducting polymers have been of great importance as this exhibit unique optical, electrical, chemical and thermal properties. Among these polymers, polythiophene (PTh) received, attention due to its high conductivity and thermal stability. The conductivity of these materials can be tuned by doping. Dopant anion plays an important role in polymerization. Polymer nanocomposites are considered to be hybrid. Nano composites of polymers are used in drug delivery, conductive paints, batteries etc. Vanadium oxides are polyfunctional materials and shows metal semiconductor transition. V$_2$O$_5$ is used as an active electrode in a rechargeable lithium battery, electro chromic devices, catalysts etc. The conductivity of PTh-ZnO composites were measured and found it to be order of $10^4$ $\Omega\text{m}^{-1}$. The room temperature conductivity of polypyrrole-TeO$_2$ and PTh-TeO$_2$ composites have been reported to be 1 x $10^3$ $\Omega\text{cm}^{-1}$ and 2 x $10^2$ $\Omega\text{cm}^{-1}$ respectively. In these composites, conductivity have been observed to have increased by 10 orders of magnitude compared to their pure PPy and PTh. PPy-V$_2$O$_5$ composites of different wt% in the range from 10 to 50 wt% were prepared by chemical oxidative method. The room temperature conductivity of these composites at 100 KHz revealed that the addition of vanadium oxide nanoparticle results in the decrease in conductivity up to 10% V$_2$O$_5$ and remain constant for higher amount of V$_2$O$_5$. The ac conductivity of pure PPy increased with frequency and PPy-V2O5 composite showed constant up to the frequency of 10$^5$ Hz and then increased steeply. Polyaniline-V$_2$O$_5$ composites showed constant conductivity up to 10$^7$ Hz. DC conductivity of polyaniline-V$_2$O$_5$ composites of different wt% of V$_2$O$_5$ was found to change from 10$^{-7}$ to 10$^{-9}$ $\Omega\text{cm}^{-1}$, attaining a maximum value for 30 of V$_2$O$_5$. Here, we present the result of dielectric results for PTh-V$_2$O$_5$ nanocomposites. AC conductivity has been determined using dielectric data. Frequency and temperature dependence of both dielectric data and conductivity data has been thoroughly analyzed.

Material and Methods
PTh was prepared at 323K using AR grade Thiophene, Ferric chloride, Methanol and Chloroform. Homogenous aqueous solution of thiophene was prepared. Chloroform and ferric chloride solutions were mixed drop by drop to the PTh solution. The mixture magnetically stirred for 24 hours and filtered. The precipitate so formed was washed with chloroform and then with methanol. In this process, the precipitate changed its colour to brown indicating the formation of Polythiophene. The powder was dried up and subsequently ground. The PTh-V$_2$O$_5$ composites were prepared by mixing Polythiophene and analytical grade V$_2$O$_5$ in different wt% defined as (PTh) 100-x (V$_2$O$_5$)x, where x= 5%, 10% and 15% labelled as PTh-VO1, PTh-VO2 and PTh-VO3 respectively. Powders were subjected to XRD and SEM studies. From these studies, it is confirmed that the grains in these composites are of nano size. Powders of the composites were pressed into pellets. Capacitance, C, and dissipation factor, tanδ, were measured as function of frequency and temperature in the range from 50Hz to 3MHz and 300K to 423K respectively. These measurements were carried out in a precession impedance analyser (Wayne Kerr make Model No. 6500B). Temperature was sensed using Chromel-Alumel thermo- couple with the accuracy of ± 1K.

Results and Discussion
Dielectric properties: Using the measured capacitance and dissipation factor the dielectric parameters were determined for all the composites, using the expressions given in reference. Figure-1 shows the variation of dielectric constant, $\varepsilon'$ with frequency for all the three composites. From this figure, we note that, $\varepsilon'$ decreases gradually with frequency up to 70 KHz and become constant for higher frequencies. Dielectric loss factor, $\varepsilon''$ variation with frequency for all the three composites is...
plotted in figure-2. ε'' varied with frequency in the same fashion as that of ε'. Temperature variation of ε' for PTh-VO1 is shown in figure-3. In this figure, we see that ε' increases with temperature. Similar nature of variation of ε' with temperature has been observed for the remaining composites. The change in ε'' with temperature for PTh-VO1 is shown in figure-4. Similar behaviour of ε'' with temperature has been observed for the remaining composites.

\[ \text{Conductivity, } \sigma = \varepsilon'' \times \varepsilon_0 \]  

(1)

Where: ε_0 is free space permittivity which is equal to 8.85 x 10^{-12} Fm^{-1}. Conductivity variation with temperature for different frequencies for the composite PTh-VO2 is shown in figure-5.

It can be seen in figure-5 that conductivity increases with increasing temperature indicating semiconducting type of behaviour. It also increased with increasing frequency. Similar results have been reported for polyaniline doped with silver nanoparticles, polyaniline doped with cobalt and polyaniline doped with nickel oxide\(^{25-27}\). All the present composites behaved in the same way. Variation of conductivity of all the present composites was found to be within the same order of magnitude i.e, 10^{-4} (\Omega^{-1}m^{-1}).

Conductivity variation with V_2O_5 content for two different frequencies at temperature of 403K is shown in figure-6. From figure-6 it is clear that conductivity decreased with increasing V_2O_5 content.

The conductivity data as a function of temperature has been fit
to the Mott Small Polaron Hopping (SPH) theory. This theory gave the conductivity expression as:

$$\sigma = \sigma_0 \exp \left\{ - \frac{E_a}{K_B T} \right\}$$  \hspace{1cm} (2)

Where $E_a$ the activation energy for small polaron hopping.

The plots of $\ln(\sigma T)$ versus $1/T$ were made as per equation-2 for the composite PTh-VO2 and shown in figure-7. The linear lines were fit to the data in the high temperature region where the data appeared linear. Activation energy, $E_a$ for ac conductivity was calculated using the slopes of the fit linear lines.

Activation energy, $E_a$ versus V$_2$O$_5$ content determined for the present composites for different frequencies are plotted in figure-8.

From the figure-8 one can note that $E_a$ increases with increase of V$_2$O$_5$ content and decreased with increase of frequency. Increase in $E_a$ with increase in V$_2$O$_5$ concentration may be that addition of V$_2$O$_5$ content to the PTh network contributes more to the scattering of polarons. Similar results have been reported for polyaniline doped with V$_2$O$_5$, polyanilinedoped with CeO$_2$ and polypyrrole doped with Ag$^{17,29,30}$.

**Conclusion**

Polythophene has been synthesised at 323K by chemical method. PTh-V$_2$O$_5$ composites were prepared by mixing Polythiophene and V$_2$O$_5$ in different weight percentages. The changes in dielectric properties with temperature and frequency were measured over broad ranges. Dielectric constant decreased with increase in frequency and increased with temperature. Dielectric loss decreased with increase in frequency and
increase in frequency and increased with V
obtained. Activation energy was found to be decreas ed with 
crease of both temperature and frequency. By empl oying 
expression, activation energy for ac conductivity has been 

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