



STUDY OF ACTIVATION ENERGY AND BULK RESISTANCE OF CONDUCTING POLYPYRROLE THIN FILM

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Abstract

Impedance analysis correlates the electrical properties to the microstructure of material. It is also useful to analyze the different contributions to the electrical properties. In the study of dielectric behavior of conducting polypyrrole, an attempt has been made to enlighten the electrical and micro-structural properties of polypyrrole of different weight percentage in relation with frequency and temperatures over the wide range. Cole-Cole plot of Z'' and Z' of complex impedance of polypyrrole for different weight percentage in the frequency range 100 Hz to 200 KHz and at temperatures 313, 333, 248, 373 and 398K is analyzed. It is found that the Cole-Cole plots are semicircles. As the semicircle does not coincide with the origin, shows that series resistance can be ascribed to the circuit. The $Z'' - Z'$ plot shows single semicircle indicating dispersion as mono-dispersive. For Debye type relaxation mechanism the centre of circle lies on Z'' axis. At the peak of Cole-Cole plot, the relaxation time τ_m is calculated. The relaxation time evaluated from Debye semicircle determines the activation energy for the dielectric. The values of bulk resistance RB and bulk capacitance CB has been calculated from $Z'' - Z'$ plot.

Keywords Impedance analysis, conducting polypyrrole, Cole-Cole plot, activation energy

Introduction

The dielectric is a material having less electrical conductivity than metals. It is characterized by dielectric constant and dielectric loss which are the function of temperature and frequency. The dielectric properties are the material properties suggesting the interaction between dielectric material and electromagnetic field. The co-relation between macroscopic quantities like ϵ' and ϵ'' observed experimentally and underlying microscopic properties have been the greatest achievement of scientific study. Among the polymers, polypyrrole is an intrinsically conducting polymer most studied because of its high conductivity, high storage ability, good thermal and environmental stability, high redox and capacitive current and bio-compatibility. Hence it is worthwhile to examine the nature of charge transport in polypyrrole. Low frequency conductivity and dielectric relaxation measurements in typical frequency range of 10 Hz to 1MHz have proven to be valuable in giving rich additional information on the conductivity mechanism that dc conductivity mechanism alone do not provides. For this reason, the technique (Gill et al, 1982, Baeriswyl et al, 1982 and Street et al, 1981) has been used extensively in many research areas in condensed matter. The dielectric properties of solid polymers have been of great interest to many workers. The close relation between the mechanical properties and electrical behavior warrants such interest, in addition to the problem of electrical

insulation. There are two types of polymers that exhibit dielectric relaxation independent of chain length. (Stockmayer et al, 1967 and North 1972) The first type is polymers dipoles attached rigidly perpendicular to the chain backbone, and the second is polymers with dipole in the flexible side chains. The polypyrrole used in this study belong to the second type of polymer. Impedance spectroscopy is well established technique for electrical and dielectric characterization of composites. The ionic component of dc conductivity is not straightforward to measure experimentally since if electrodes are used which are blocking to the ions, dc conductivity cannot be obtained by application of dc voltage because of polarization effects. To overcome this problem impedance spectroscopy is used, in which frequency dependent response is measured and dc value is taken in the limit as $\omega \rightarrow 0$. When ac field is applied to the sample and both in phase (real) and out of phase (imaginary) components are monitored, the bulk resistance and capacitance of the sample can be measured.

Material and Methods

Pyrrole monomer (E.Merg, Germany) was taken as received. Reagent grade methanol (Radial) was used as received. Polyvinyl acetate (PVAc) (Radial, medium molecular weight) was used without further purification as a counter polymer to prepare a polypyrrole (PPy) thin films. Reagent grade $FeCl_3$ (E. Merck, India) was used as oxidizing agent. General formulation of

solution was as given below. For 1-weight percent (wt %) composition of polypyrrole, the concentration of Poly (vinyl acetate) and FeCl₃ were 15-wt % and 1mole respectively. Pyrrole monomer was added 1/2.33 times the FeCl₃ in molar ratio, so as to have maximum oxidation potential and maximum yield (Rasika Dias et al 2006) By using the above procedure, the conducting polypyrrole thin films were prepared for 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12 and 40-wt% by changing the weights of pyrrole monomer in the polyvinyl acetate solution. For characterization and electrical conduction study, only 1, 5, 8, 10 and 40 wt% of polypyrrole films are taken.

Theory

Theory: The dielectric constant is the ratio of the strength of electric field in vacuum to that in dielectric for the same charge distribution. It is also defined as the ratio of capacitance C of condenser filled with dielectric to its capacitance C₀ in

Result and Discussion

Polymers are characterized by the presence of various dipolar units. This leads to a broad distribution of relaxation time. Dielectric relaxation studies provide valuable information about conduction mechanism occurring in the polymers and macromolecule metals complexes. It involves electronic, ionic, interfacial and space charge polarization. The nature and origin of dielectric loss, which may be useful to determine the structure and defects in solids, can be understood from these studies. The intermolecular and molecular motion as well as structural details (Ghanem et al, 2006) of solids can be studied from dielectric relaxation time. Its value depends upon shape of molecule and density of medium. Among the polarizations viz. electronic, dipolar, ionic and space charge polarization, the space charge polarization depends upon orderly arrangement of polymer chain. The space charge polarization occurs when the value of dielectric constant at lower frequencies is large. The origin of the space charge polarization is due to transport and accumulation of charges at the electrodes or it is due to incomplete blocking of thermally generated charge carriers.

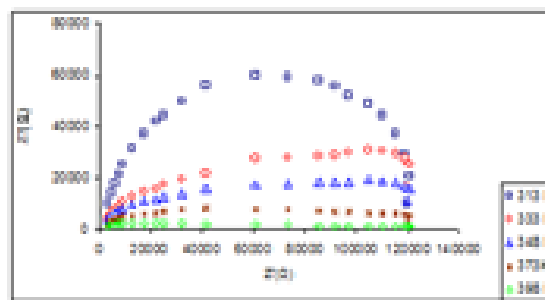


Figure 1

Pyrrole Concentration (wt %)	200 K	300 K	400 K	500 K	600 K
	$C_p \times 10^{-12}$ (F)	$C_p \times 10^{-12}$ (F)	$C_p \times 10^{-12}$ (F)	$C_p \times 10^{-12}$ (F)	$C_p \times 10^{-12}$ (F)
1	0.25	0.27	0.29	0.30	0.31
5	0.28	0.30	0.32	0.33	0.34
8	0.30	0.32	0.34	0.35	0.36
10	0.32	0.34	0.36	0.37	0.38
40	0.35	0.37	0.39	0.40	0.41

Figure 2

Conclusion

It is found that the activation energy and bulk resistance decreases with percentage of pyrrole.

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