The effects of uniaxial pressure parallel to the current and the effect of temperature on resistance of highly dedoped polypyrrole samples were investigated. Polypyrrole samples were prepared electrochemically at 0.87 V constant potential from acetonitrile solution in presence of perchlorate anion as dopant on the gold sputtered glass as working electrode. Polypyrrole samples were dedoped chemically in NH₃ for 1 h. Because of high resistance of polymer samples, the two-point probe technique could be applied for resistance measurements. Conductance of these highly dedoped polymers increases with pressure and temperature exponentially according to the Mott-variable range hopping theory (VRH). Change in the efficient number of states and also volume of the polymer due to the pressure can cause increases in the density of states near the Fermi level. Pressure should bring about an increase of orbital overlap, especially between the electron-rich of the neighbouring molecules. This increase of electron orbital overlap should be expected to increase the ease of inter-molecular electron transfer, by decreasing the distance and energy barriers to diffusion and tunnelling and by increasing the chain-chain areas of contact, thereby increasing the probability for electron transfer. So, the number of states that electron can hop from it would increase. With respect to the presence of numerous vacancies in highly dedoped polymer samples, a modified VRH model is introduced to fit the observed data based on the decreasing in polymer volume and increasing in the efficient number of states that electron can hop from it.

**INTRODUCTION**

Considerable attention has been given recently to the preparation and properties of thin films of polymeric materials bonded to or coated on metal and semiconductor electrodes [1-3]. Polymers incorporating discrete electron donor/acceptor (i.e., electron transfer) sites are an important class of conducting materials, and have been intensively investigated as electroactive films on electrodes [4-5]. In many such polymers, electron transport is thought to occur by a hopping mechanism [6-9].
In this class of materials, polypyrrole (ppy) has been investigated as a relatively stable polymer that is prepared in the form of a simply conductive polymer[10-12]. In recent years chemical and electronic structure of this polymer has been examined by several different techniques and it is indicated that several properties of this polymer can be described by a three dimensional variable-range hopping model (VRH) [13]. The average hoping distance in polypyrrole has been calculated using the VRH model to lie in the range of about 6-44 Å or more, depending upon the degree of doping, and small changes in these values are significant [14].

Effects of various parameters, such as, doping level, temperature, pressure, stretch ratio, type of dopant, preparation conditions, etc. on conductivity of doped ppy have been reported [15-17].

The electrical resistance and the apparent piezoresistance of powdered phosphoric acid-pyrrole copolymer were determined by Caplanus [18]. The electrical conductivity of ppy as a function of pressure to about 1.1 GPa was determined by Madisson et al. [19]. A second order polynomial in the form of $\sigma(p) = -ap^2 + bp + \sigma(0)$ is found to fit the observed data.

Temperature and pressure dependence of the electrical resistance of electrochemically synthesized ppy have been reported by A. Lundin et al. [20]. In that relatively highly conducting (20 S.cm$^{-1}$) polymer, it was recognized that the conducting mechanism is governed by variable range hopping. From the experimental data of resistance and compressibility, $\beta$, an expression for the pressure dependence of the conductivity was introduced:

$$\sigma(p) = \sigma(T) (1 + \beta p)\exp\left(\frac{p}{p_0}\right)^n$$

where, $n \cong 3/4$.

Tuning through the critical regime of the metal-insulator transition in phosphorous hexafluoride-doped ppy by pressure and magnetic field have been investigated by Heeger et al. [21]. The reduced activation energy function ($W = -T\Delta \ln(\rho)/\Delta T$), is temperature independent over a wide temperature range at high pressure (8-10 kbar). W, has a positive temperature coefficient, indicating a pressure-induced cross-over to the metallic regime. The enhanced interchain transport at high pressures causes the cross-over from the critical regime to metallic behaviour.

Pressure dependence of the electrical conductivity of a range of highly conductive ppy samples doped to different levels have been interpreted in terms of variable-range hopping theory by Madisson and his coworkers[14].

With attention to what cited above, the mechanism of charge transport in ppy is believed to be VRH. However, no studies have been carried out on highly dedoped ppy samples so far. In the present paper, we studied pressure and temperature dependence of conductivity of highly dedoped polypyrrole films.

A new model is presented by modification of VRH model with respect to presence of numerous vacancies in highly dedoped polymer sample, based on pressure dependence of volume of polymer and number of states near to the Fermi level.

### EXPERIMENTAL

Pyrrole used as monomer was obtained from Merck and distilled under reduced pressure before use. Tetrabutylammonium perchlorate salt (Merck) was used as electrolyte without further purification. Acetonitrile was served as solvent for preparation of electropolymerization solution. Polypyrrole was prepared from solution containing 0.1 M pyrrole, 0.1 M Bu$_4$NClO$_4$ at 0.87 V constant potential in a three-electrode one-compartment cell. The thickness of polymer film was about 5 µm. Gold-sputtered glass was used as working and auxiliary electrodes. The purpose of using Au as substrate for polymer deposition is to prevent formation of Scotty barrier at the interface of metal and polymer. Sputtering was carried out by a Leybold-Heraous instrument, model NT 450 to produce mirror-like surface. The thickness of the gold film was about 5 m and for making better electrical contact to this thin film of gold the glass substrate was first coated by a 10 µm copper film.

A saturated sodium calomel electrode was used as reference electrode. Electropolymerized ppy samples were dedoped chemically in 0.1 M NH$_3$ solution for 1 h. Resistance of these dedoped samples was measured by a two-point probe technique that was in the range of several k ohms. Because of high resistance of polymer samples, two-point probe technique could be applied for this purpose. Resistance changes in relation to uniaxial pressure was monitored by a curve tracer monitor.
and also a precise digital multimeter.

Scanning electron photograph, thickness measurements, and surface analysis was carried out by scanning electron microscope (Cambridge Instrument S360).

RESULTS AND DISCUSSION

Figure 1 shows a relative resistance change of dedoped-ppy during the cycling uniaxial pressure in ambient temperature. As it can be seen, there is a hysteresis effect during the return to the initial pressure. Change of resistance and observed hysteresis can be explained by spongy nature of dedoped polymer and gas diffusion in and out of the pores of polymer matrix.

Increasing the uniaxial pressure, parallel to the current flow, causes the prediffused air in pores of polymer to exit and polymer to be compressed to lower volume. So, the charge transfer sites in polymer chains come closer to each other and then hopping range and resistivity are reduced. This volume reduction depends mainly on the reduction of pore volume and partly on the compressibility of the polymer body itself. By reducing the pressure in the return cycle, the gas again reinfuses into the vacancy of dopant site and the resistance increases due to increasing of hopping range, but, because of gas motion in polymer matrix, the arrangement of polymer chains would be changed, so that the hysteresis is appeared. In other words, applying pressure on polymer does not cause any change in electronic structure of the polymer. Therefore, sensitivity of the highly dedoped polymer resistance to low pressure in the range of few MPa, can be related to the spongy nature of the dedoped polymer and the existence of a large number of vacancies of dopant sites in polymer matrix (in comparison with doped ppy whose conductivity only changes by pressure in GPa range).

Figure 2a shows a SEM photograph of ppy prepared in acetonitrile solution. Presence of porosity in the polymer is observable. Analysis of polymer by XRF measurement indicates no dopant ion on the surface of polymer (Figure 2b). So it demonstrates that the polymer is highly dedoped.

Figure 3 shows the dependence of relative resistance of polymer film on temperature. Resistance is reduced exponentially with increase of temperature that is an evidence for semiconducting nature of the dedoped polymer. Linearity of the plot of \( \ln(\rho/\rho_0) \) vs. \( (1/T)^{1/4} \) leads us to conclude that variable-range hopping model can be used to explain the change of resistance of ppy with pressure and temperature (Figure 4).

In Mott VRH theory the conductivity is given by:

\[
\sigma = 2e^2R^2 v_{ph}N(E_F)\exp[-2(3/2\pi)^{1/4} (\alpha^3/kN(E_F)^{1/4})^1/T^{1/4}] \\
\]

or more simply as:

\[
\sigma = \sigma_0\exp(-T_0/T)^{1/4} \\
\]

where, \( R \) is the average hopping distance, \( v_{ph} \) is a hopping frequency that may be related to the phonon frequency, \( N(E_F) \) is the density of states per unit energy interval at the Fermi energy, and \( \alpha \) is the wave function inverse localization length.

In Mott equation quantities expected to be pressure dependent are the mean hopping distance, \( R \), varying as \( 3/4[N(E_F)]^{1/4} \) that appears in the pre-exponential factor and the density of states. Density of states, expressed as \( N/V \), varies with pressure not only due to a volume change as the pressure increases, but the number of states that can take part in hopping process increases. Volume reduces by pressure and it is given by:

\[
V = V_o (1-Ap)^3 \\
\]

where, \( A \) is the coefficient of linear compressibility, \( V_o \) is volume in initial pressure and \( p \) is the pressure.

In VRH, electron transport occurs between disorder electronic states that are randomly distributed both spatially and energetically. An electron can move to a nearby
state, which is quite close in energy. Pressure should bring about an increase of orbital overlap, especially between the electron-rich of the neighbouring molecules. This increase of electron orbital overlap should be expected to increase the ease of inter-molecular electron transfer, by decreasing the distance and energy barriers to diffusion and tunnelling and by increasing the chain-chain areas of contact, thereby increasing the probability for electron transfer. So, the number of states that electron can hop from it increases. Thus, the efficient hopping states are given by:

\[ N(p) = N_0 p^n \]

where, \( N_0 \) is the states that in initial pressure ele-

![Figure 2](image1.png)

**Figure 2.** (a) SEM Photograph of dedoped polypyrrole, (b) XRF spectrum of surface of dedoped polymer coated on gold electrode.

![Figure 3](image2.png)

**Figure 3.** Relative resistance of highly dedoped polypyrrole as a function of temperature.

![Figure 4](image3.png)

**Figure 4.** Plot of \( \ln(R/R_0) \) vs. \( (1/T)^{1/4} \) for a representative of a highly dedoped sample.

![Figure 5](image4.png)

**Figure 5.** Pressure dependence of electrical conductivity for highly dedoped polypyrrole sample showing modified VRH fit.

![Figure 6](image5.png)
tron can be hopped from it.

Pressure dependency can now be incorporated into $N(E_F)$ by writing:

$$N(E_F) = N(p)/V = N_0(E_F)p^3/(1-Ap)^3$$

and,

$$\sigma = \frac{2e^2R^2}{\nu} \phi N(E_F)\exp[-2(3/2\pi)^{1/4} (\alpha^3(1-Ap)^3/kN_o)^{1/4}p^{3/4}1/T^{1/4}]$$

$$\sigma = \sigma_0 \exp[-T_{\text{exp}}(1-Ap)^3/p^3(1/T)^{1/4}]$$

Figures 5 and 6 compare the curve obtained by our model with experimental results.

A good resulting fit indicates that our model is quite suitable.

Since in high pressure, the polymer chains are completely proximate, so the behaviour of dedoped and predoped materials are similar and the presumed presence of voids in dedoped material does not significantly contribute to the high pressure behaviour of the polymer [14]. It means that the $N(E_F)$ depends only on the compressibility of the polymer body itself. But in highly dedoped ppy the voids influence mainly the transport process, whereas, the compressibility of the polymer backbone itself partly influences the transport process.

**CONCLUSION**

Effect of uniaxial pressure parallel to the current and the effect of temperature on conductivity of the highly dedoped polypyrrole samples were investigated. Presence of a lot of pores inside the polymer membrane due to dedoping of the polymer samples can cause the conductivity of the polymer to change in response to the low pressure in the range of MPa. A modified Mott’s VRH model can be used to describe the behaviour of the polymer in response of pressure and temperature. Mean hopping distance ($R$) and density of states $N(E_F)$ in Mott equation are two parameters that with pressure change. Density of states changes by increasing the pressure, because the number of states which electron can hop, as well as the volume of the polymer change by pressure. Modified model according to this view, is quite suitable to describe the behayoir of the polymer in response of the low pressures in the low temperature range.

**REFERENCES**


