Electron Transport in Polypyrrole-PF6

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> We investigate electron transport in Polypyrrole-PF6 by finding temperature dependence of resistivity and comparing the results to the Mott-Anderson theory of metal-insulator transitions. We find evidence of both metal and insulating regime transition in Polypyrrole-PF6, as well as evidence of electron hopping transport.

1. INTRODUCTION

A. Metal-Insulator Transition

The Mott-Anderson Theory for disorder-induced metal-insulator transitions states that localization and disorder in a material are related. An electron wave function becomes localized when no temperature diffusion is possible. Anderson shows that the critical value at which electronic wave functions become localized is given by

$$E_{\rm crit} = V_{\rm o}/B \tag{1}$$

Where V_o is the random potential and B is the bandwidth [1].

Localization is more likely to occur in the tail of an energy band occupied by electrons. In materials in which a Fermi gas of electrons exists, a transition into a "Fermi Glass" occurs when all wave functions become localized and no current can pass at absolute zero [2]. The mobility edge is the critical energy value which separates localized from non-localized states. As disorder in a material increases. Mott shows the Fermi energy E_f approaches the critical energy E_{crit}. As E_f crosses E_{crit}, a metalinsulator transition occurs [3]. This transition, called the Anderson transition, is characterized by vanishing conductivity at absolute zero [4].

The transport properties of a polymer are highly dependent upon the amount of disorder and doping in the polymer [5]. Polypyrrole becomes a p-type conducting polymer, or electron acceptor, when doped with PF6 [6]. PF6 accepts electrons donated from Polypyrrole, meaning that the current is carried by the hole states in Polypyrrole [7]. In our study, we used three different samples of Polypyrrole-PF6. The samples were synthesized at certain conductivity values. These values, along with the physical characteristics of these samples at room temperature (T~300K) are shown in Table 1.

B. Method

The resistance across an effective length of 1.956 mm of Polypyrrole-PF6 samples was measured using copper leads in the 4-probe technique. In order to assure proper contact between the leads and the samples, we used the pressure contact method rather than the silver pasting method. This method uses a brass clamp, followed by a layer of Teflon tape, to apply a force perpendicular to the plane of the sample, thereby keeping the sample in place on the leads. Past experiments have shown that the advantage of this method over the silver pasting method is a reduction in contact resistance between the sample and the copper leads. The maximum contact resistance was on the order of 100 .

We measured resistances for currents of values .1, 1, and 10 mA. We found evidence for heating of the sample at 1 and 10 mA. Therefore, all of the final values for conductivity were calculated from resistance readings at .1 mA.

2. RESULTS

The measured conductivities of the

Polypyrrole-PF6 samples are shown in Table 2.

Classically, a metal shows a decrease in resistance as temperature increases. As shown in Fig. 1, Polypyrrole-PF6 has an increased resistance as temperature decreases. Clearly, Polypyrrole-PF6 is not a classical metal. In order to understand any metallic like properties of Polypyrrole-PF6, it is necessary to investigate the Mott-Anderson transition.

The Mott-Anderson metal-insulator transition can be studied by finding the temperature dependence of the polymer's conductivity and comparing this to classical theories of metal and insulator transport properties.

Classically, a metal has a positive temperature coefficient for the logarithmic derivative of conductivity temperature dependence,



[7].

On the insulating side of a transition, _ approaches 0 as T approaches zero. On the metallic side, _ approaches a finite value as T approaches absolute zero [8]. In the sample with a predicted conductivity of 70 S/cm, _ approaches 0 as T approaches 0, placing the sample on the insulating side of a transition. The samples with conductivities of 155 and 241 S/cm have conductivities that decrease, but that do not approach _ = 0 as T approaches 0, thus they are on the metallic side of the transition. These results are shown in Fig. 1.

One observed characteristic of conducting polymers is that conductivity is proportional to , where n depends on the dimensionality of electron hopping [9]. In a

study by Menon et al, the polymer K-(CH)_x was found to have a linearly, negatively sloping relationship between conductivity

and [10]. We see this same relationship with Polypyrrole-PF6 with conductivities ranging from 70 to 241 S/cm. As shown in Fig. 2, the proportionality between conductivity and temperature is evidence of hopping transport in the polymer. The relationship linearity between

conductivity and breaks as the

expected conductivity of the samples increases, suggesting that the electron hopping theory does not completely explain the measured conducting polymer electron transport in these samples.

3. CONCLUSION

The proportionality between conductivity and T[^] (-1/4) indicates that electron hopping is a primary form of transport in Polypyrrole-PF6. However, the breakdown of this relationship as conductivity increases is evidence for some other mode of transport as doping level and disorder increase in the polymer. In order to fully understand the nature of conducting polymer electron transport, it will be necessary to explore the structure of a doped polymer, possibly through NMR measurements. Additional tests on Polypyrrole-PF6, as well as other conductive polymers in the conductivity range of 200-300 s/cm, will be necessary to confirm any theory of electron transport in these doped polymers.

Table 1.

Sample Dimensions

Sample	Specified _ (S/cm)	Thickness (_m)	Width (mm)
А	70	0.21	0.94
В	155	0.22	0.76
С	241	0.19	0.83

Table 2.

Conductivity Measurements

Sample	Specified (S/cm)	Measured _ at 300K (S/cm)
A	70	51
В	155	119
С	241	164





FIG. 1. Plot of resistance versus temperature for three PPy-PF6 samples.





FIG. 2. Plot of conductivity vs. temperature for three PPy-PF6 samples. No data was taken for temperatures below 15 K.

Figure 3.



FIG. 3. Plot of log(_) versus T^(1/1-4). The black lines are best-fit lines to each sample data set.

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- Mott, N. F. *Metal-Insulator Transition*. p. 30. (Taylor and Francis Ltd, New York, 1974).
- Menon, Reghu, C.O. Yoon, D. Moses, and A.J. Heeger. Metal-Insulator Transition in Doped Conducting Polymers. <u>Handbook of Conducting</u> <u>Polymers</u>. Skotheim et al. (M. Dekker, New York, 1998). p. 29.
- 3. Epstein, Arthur J. *Electron Transport in Conducting Polymers.* p. 355. (*Advances in Synthetic Metals*, Elsevier, 1999).
- Mott, N. F. *Metal-Insulator Transition*. p. 30, 33. (Taylor and Francis Ltd, New York, 1974).
- Menon, Reghu, C.O. Yoon, D. Moses, and A.J. Heeger. Metal-Insulator Transition in Doped Conducting Polymers. <u>Handbook of Conducting</u> <u>Polymers</u>. Skotheim et al. (M. Dekker, New York, 1998). p. 27.
- 6. W. G. Clark, September 2003.
- 7. W. G. Clark, September 2003.
- Heeger, Alan J. The Critical Regime of the Metal-Insulator Transition in Conducting Polymers: Experimental Studies. Presentation at the <u>Nobel Centennial Symposia</u>, 2001: Condensation and Coherence in Condensed Systems December 4-7, 2001, Chalmers University of Technology, Göteborg p. 2.
- Menon, Reghu, C.O. Yoon, D. Moses, and A.J. Heeger. Metal-Insulator Transition in Doped Conducting Polymers. <u>Handbook of Conducting</u> <u>Polymers</u>. Skotheim et al. (M.

Dekker, New York, 1998). p. 32.

- Menon, Reghu, C.O. Yoon, D. Moses, and A.J. Heeger. Metal-Insulator Transition in Doped Conducting Polymers. <u>Handbook of Conducting</u> <u>Polymers</u>. Skotheim et al. (M. Dekker, New York, 1998). p. 33.
- Menon, Reghu, C.O. Yoon, D. Moses, and A.J. Heeger. Metal-Insulator Transition in Doped Conducting Polymers. <u>Handbook of Conducting</u> <u>Polymers</u>. Skotheim et al. (M. Dekker, New York, 1998). p. 39.