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Reza Ghanbari

*Ferdowsi University of Mashhad*

Shaban Reza Ghorbani

*Ferdowsi University of Mashhad, ghorbani@uow.edu.au*

Hadi Arabi

*Ferdowsi University of Mashhad*

Javad Foroughi

*University of Wollongong, foroughi@uow.edu.au*

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# The charge transport mechanisms in conducting polymer polypyrrole films and fibers

## **Abstract**

Smart materials based on inherently conducting polymers are of practical interest and extend the advantages of electromaterials from the nanoscale to macroscale applications. However understanding mechanisms of their electrical properties are still remained challenging. Herein, we report the transport properties of chemically and electrochemically prepared conducting polymer polypyrrole films and fibers. Conduction mechanisms of the as-prepared polypyrrole (PPy) were investigated using their electrical properties as a function of temperature (7-300 K). The results of the PPy resistivity were evaluated using a linear combination of Mott's and Efros-Shklovskii's Variable- Range Hopping (Mott-VRH and ES-VRH) models. It was found that the localization length was about 10 and 15 monomer units for the PPy-fiber and PPy-film, respectively. The contributions of Mott-and ES-VRH conductivities versus temperature exhibited that electrical conductivity of the PPy-film is two-dimensional Mott-VRH at temperatures of lower than ~100 K. It was indicated that the contribution of ES-VRH are larger than the contribution of Mott-VRH at temperatures of higher than ~185 K. It was also found that ES-VRH law predominates at room temperature showed that average size of crystallites in the PPy-film was about three times larger than PPy-fiber.

## **Disciplines**

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# The charge transport mechanisms in conducting polymer polypyrrole films and fibers

Ghanbari, Reza<sup>1,2</sup>; Ghorbani, Shaban Reza<sup>1,2,\*</sup>; Arabi, Hadi<sup>1,2</sup>; Foroughi, Javad<sup>\*3</sup>

<sup>1</sup>*Renewable Energies, Magnetism and Nanotechnology Lab., Department of Physics, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran*

<sup>2</sup>*Research Center for Hydrogen Storage and Lithium – Ion Batteries, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran*

<sup>3</sup>*ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, University of Wollongong, Wollongong, NSW 2519, Australia*

smart materials based on inherently conducting polymers are of practical interest and extend the advantages of electromaterials from the nanoscale to macroscale applications. However understanding mechanisms of their electrical properties are still remained challenging. Herein, we report the transport properties of chemically and electrochemically prepared conducting polymer polypyrrole films and fibers. Conduction mechanisms of the as-prepared polypyrrole (PPy) were investigated using their electrical properties as a function of temperature (7 – 300 K). The results of the PPy resistivity was evaluated using a linear combination of Mott's and Efros-Shklovskii's Variable-Range Hopping (Mott-VRH and ES-VRH) models. It was found that the localization length was about 10 and 15 monomer units for the PPy fiber and film, respectively. The contributions of Mott and ES-VRH conductivities versus temperature exhibited that electrical conductivity of the PPy-film is two-dimensional Mott-VRH at temperatures of lower than ~100 K. It was indicated that the contribution of ES-VRH are larger than the contribution of Mott-VRH at temperatures of higher than ~185 K. It was also found that ES-VRH law predominates at room temperature showed that average size of crystallites in the PPy film was about three times larger than PPy fiber.

**Keyword:** Polypyrrole; conducting polymers, Conduction;; Nanocrystallite. Transport properties, electrical properties

Smart materials are one of frontier technologies in engineering and manufacturing. A smart material is capable of recognising appropriate environmental stimuli, processing the information arising from the stimuli, and responding to it in an appropriate manner and time frame. It is well known that inherently conducting polymers (ICPs) provide some interesting possibilities in this regard. ICPs are polymers capable of conducting electricity and have the ability to sense and actuate, leading many researchers to envisage “*intelligent polymer systems*” based on ICPs. Fabrication of conducting polymers in different forms is necessary to achieve such smart materials system. Fibre spinning for example, can bring new opportunities to develop ICPs. Conducting polymer fibres are likely to be important for electronic textiles, actuators and biomedical applications, as they allow the possibility to incorporate desirable features such as chemical sensing or actuation that are not feasible other synthetic fibres.

Polypyrrole (PPy) as a conducting polymer has potential applications in electrical and electronic devices because of its high electrical conductivity, environmental stability and redox activity.

PPy can be synthesized using either chemical or electrochemical polymerization of pyrrole. PPy films are normally synthesized by electrodeposition of pyrrole on the surface electrodes. PPy powders<sup>10</sup> and fibers<sup>11</sup> can be chemically prepared using different dopants such as di(2-ethylhexyl) sulfosuccinate (DEHS),<sup>12</sup> PF<sub>6</sub><sup>13</sup> and ferric toluenesulfonate (Fe.pTS).<sup>14</sup>

In these systems, polymer chains can be aligned in a region and they make up a nanocrystalline region (crystallite size of polyacetylene, polyaniline and polypyrrole of order 10, 5 and 2 nm, respectively<sup>15</sup>). These nanocrystalline regions are distinguished by disordered regions. These amorphous regions increase scattering of charge carriers. Therefore, size of the crystalline regions and crystallinity percent is very important in charge transport.<sup>15</sup> In addition, the electrical conductivity behaviors is influenced by doping level, degree of disorder, intracrystallite interaction and synthesis methods and conditions. PPy has more disorder than polyaniline and polyacetylene, and the crystalline regions of PPy are smaller than them.<sup>15</sup> A further important point in conducting polymers is the understanding of charge transport mechanisms. The conduction mechanisms have not yet completed in this heterogeneous materials.<sup>16</sup> The electrical transport in such heterogeneous systems is described by phenomena such as quasi-one dimensional transport, localization effects, hopping and tunneling transport<sup>15, 17</sup> and percolation<sup>18</sup>. Since charge carriers are most strangely localized, hopping mechanism is become important.<sup>13</sup>

In this paper, the conduction mechanisms have been studied by investigation of temperature dependence of the electrical conductivity for two types of samples: chemically prepared PPy-fiber and electrochemically prepared PPy-film. For description of resistivity a linear combination of Mott's and Efros-Shklovskii's variable-range hopping models has been used. In this model, resistivity well explains with two and three-dimensional Mott-VRH for PPy-film and PPy-fiber, respectively. Also, the contribution of each of the Mott and the ES-VRH conductivities has been investigated at temperatures of 7 – 300 K.

Chemically and electrochemically PPy were synthesized using pyrrole as a monomer and di-(2-ethylhexyl)sulfosuccinate (DEHS) as a dopant. PPy films were prepared using electrodeposition and PPy fibers were chemically prepared using a wet-spinning process as described previously.<sup>12, 19</sup> SEM micrographs of as-prepared PPy fiber and PPy film were shown in Fig. 1.<sup>19</sup> The electrical resistivity was measured using a standard four-probe method over a wide range of temperatures from 7 to 300 K using a physical properties measurement system (PPMS, Quantum Design). The distance of contacts was 0.97 mm. Both measured PPy-film and PPy-fiber were placed on the Cu block substrate, which was isolated from samples using insulating varnish, and four Au wires were attached to sample using silver paste.

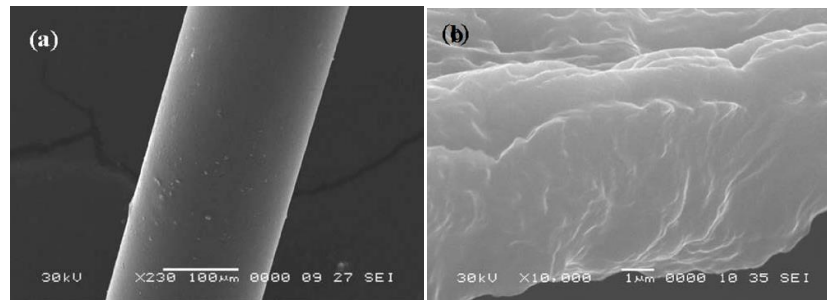


FIG. 1. SEM micrographs of (a) chemically prepared PPy-fiber and (b) electrochemically prepared PPy-film.<sup>19</sup>

The temperature dependence of the resistivity,  $\rho(T)$ , has been shown in Fig. 2 for both the chemically prepared PPy-fiber and the electrochemically prepared PPy-film at temperature ranges of 7 - 300 K. Also, their conductivities have been shown in the inset of Fig. 2. It can be seen that conductivities are 0.1 and 0.01 S/cm at temperature of 8 K for the PPy fiber and film, respectively, and they increase to 14 and 50 S/cm at room temperature ( $T = 300$  K). In the inset of Fig. 2, it can be seen that conductivity of the PPy-fiber is higher than conductivity of the PPy-film at temperatures lower than 100 K. While, the PPy-film has higher conductivity at the temperatures higher than 100 K, and it grows much faster than the PPy-fiber up to room temperature, which is clearly showed that this nanoscale layer has improved charge transport properties at high temperatures.

Charge transport in disordered systems can most be explained by Mott's variable-range hopping (Mott-VRH) model. In these systems, charge carriers are polarons after doping and they are localized in gap region.<sup>20</sup> Their conductivity caused by hopping (*i.e.* phonon-assisted

tunneling between electronic localized states centered at different positions<sup>15</sup>) localized electron between two atomic sites. It was found that the number of available energy states for hopping decreases with decreasing thermal energy  $k_B T$  and therefore hopping average length increases.<sup>15</sup> With estimated the density of states at the Fermi level  $N(E_F)$ , the following expression was found for the conductivity<sup>21</sup>

$$\sigma_{Mott}(T) = \sigma_0 \exp\left[-\left(\frac{T_{Mott}}{T}\right)^\gamma\right] \quad (1)$$

where  $\gamma = 1/(1+d)$  with  $d = 1, 2, 3$ , which is called hopping dimensional. The pre-exponential  $\sigma_0$  represents the conductivity at the high temperature limit and it is also temperature dependent. But it is often neglected compared to the stronger temperature dependent of the exponential term.<sup>15, 21</sup>  $T$  is temperature and  $T_{Mott}$  is called the Mott characteristic temperature, which is related to the effective energy separations between localized states and it can be expressed by following equation<sup>21, 22</sup>

$$T_{Mott} = \frac{21.2}{k_B N(E_F) \xi^3} \quad (2)$$

where  $N(E_F)$  is the density of states at the Fermi level,  $\xi$  is the localization length of the wave function for the localized charge carrier, and  $k_B$  is Boltzmann constant.

The Coulomb interaction between localized states has been neglected in Mott's conductivity. Theory of the Coulomb interaction between the localized electrons, which creates a "soft gap" in the density of states at the Fermi level was first described by Efros and Shklovskii.<sup>23</sup> <sup>24</sup> According to this theory, the density of states at the Fermi level vanishes by coulombian correlations. For this case, conductivity, called Efros-Shklovskii's variable-range hopping (ES-VRH) conductivity, is expressed by:<sup>23, 25</sup>

$$\sigma_{ES}(T) = \sigma'_0 \exp\left[-\left(\frac{T_{ES}}{T}\right)^{\frac{1}{2}}\right] \quad (3)$$

where  $T_{ES}$ , the characteristic temperature for the ES-VRH conductivity, is given by:

$$T_{ES} = \frac{2.8e^2}{\kappa\xi} \quad (4)$$

where  $\kappa$  is the dielectric constant.

In the most of the heterogeneous systems, which are composed of partially crystalline and disordered regions, the conductivity occurs through both the tunneling and the hopping. It was found that the conduction shows metallic behavior in the crystalline regions (intracrystallite conduction) and it occurs in between two crystalline domains through hopping (intercrystallite conduction).<sup>20</sup> In this case, intracrystallite conduction electrons are considered as localized in crystalline domains. Therefore, conductivity can be estimated from the intercrystallite hopping conduction. It was found that increasing crystallite sizes and decreasing thickness of poly(3,4-ethylenedioxythiophene) (PEDOT) film caused to increase the electrical conductivity, in contrast to inorganic materials.<sup>26</sup> Generally for these systems, the resistivity can be explained by a linear combination of Mott-VRH and ES-VRH models, which is provided an explanation for the intercrystallite hopping and the dimensionality of the films, as:

$$\rho(T) = \left[ \sigma_0 \exp\left[-\left(\frac{T_{Mott}}{T}\right)^{\frac{1}{1+d}}\right] + \sigma'_0 \exp\left[-\left(\frac{T_{ES}}{T}\right)^{\frac{1}{2}}\right] \right]^{-1} \quad (5)$$

where  $\sigma_0$  and  $\sigma'_0$  are Mott's and ES's conductivity coefficients, respectively, and their ratio is an important parameter because it determines that whether Coulomb interaction is significant or not.

In Fig. 2, the solid curves show the best fitting of Eq. (5) to the resistivity data for both the PPy-film and the PPy-fiber. As can be seen in Fig. 2, the  $\rho(T)$  data was well described by Eq. (5) at the whole temperature range of 7 – 300 K, as shown by the solid curves in Fig. 2. Therefore, the linear combination of the Mott-VRH and the ES-VRH expression well describes the experimental data. For the chemical PPy-fiber, the best fitted value of  $d$  is 3, three-dimensional (3D) VRH conductivity. While for the electrochemical PPy-film, with the best fitted value of  $d$  is 2, two-dimensional (2D) VRH conductivity.

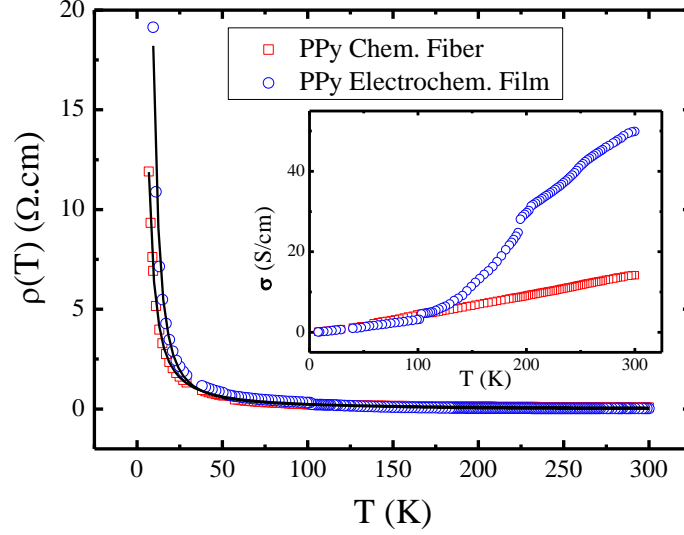


FIG. 2. The temperature dependence of the resistivity,  $\rho(T)$  for the chemically prepared PPy-fiber and the electrochemically prepared PPy-film. The solid curves are the theoretical curves obtained basing on the model of the Eq. (5) that show the best fitted of Eq. (5) to the experimental data. Inset: the experimental data of conductivity for both the PPy-film and the PPy-fiber.

Since the 3D conduction pathways can arise from increasing disorder, thus the chemically prepared PPy-fiber is more disordered sample and therefore, it shows small charge transport. But in the electrochemically prepared PPy-film, disorders are less than the chemically prepared PPy-fiber that is due to prepare improved layered sample by the electrochemical process. Therefore, conduction pathways are better aligned in the film than them in the fiber sample and thus film has higher conductivity.<sup>26</sup> The best fitted parameters of the Mott and ES characteristic temperatures have been shown in Table (1) for both the PPy-fiber and the PPy-film. It can be seen in Table 1, that  $T_{\text{Mott}}$ , which is directly proportional to the degree of disorder, in the film is lower than it in the fiber.

TABLE 1. Physical parameters obtained for both the PPy-fiber and PPy-film.

Sample	$T_{\text{Mott}}$ (K)	Conductivity dimension of VRH	$T_{\text{ES}}$ (K)	$\xi$ (nm)
PPy Chem. fiber	20446	3	2362	2.88
PPy Electrochem. film	5111	2	33950	4.58



To extract the localization length  $\xi$  from Eq. (2), the density of states is assumed to be  $5 \times 10^{20} \text{ (eV.cm}^3\text{)}^{-1}$ .<sup>13</sup> Therefore, the values of 2.88 and 4.58 nm were obtained for the localization length,  $\xi$  for the PPy-fiber and PPy-film, respectively. It was found the value of  $\sim 3 \text{ \AA}$  for the length of the pyrrole monomer unit,<sup>13, 19</sup> thus the localization lengths correspond to about 10 and 15 monomer units for the PPy-fiber and PPy-film, respectively. In VRH model, the average hopping length between two sites (and two crystallites here), is given by  $R_{\text{hop}} = (3/8)(T_{\text{Mott}}/T)^{\gamma} \xi$ .<sup>27</sup> The values of 3.43 and 5.05 nm are obtained for  $R_{\text{hop}}$  at temperature of 200 K, and they increase to 7.67 and 14.79 nm at temperature of 8 K for the PPy-fiber and PPy-film, respectively.

Similar to Eq. (5), the conductivity is as  $\sigma(T) = \sigma_{\text{Mott}}(T) + \sigma_{\text{ES}}(T)$ . In order to compare the contribution of the Mott and ES-VRH conductivities, the  $P$  parameter is defined as  $P_{\text{Mott}} = \sigma_{\text{Mott}}(T) / \sigma(T)$  and  $P_{\text{ES}} = \sigma_{\text{ES}}(T) / \sigma(T)$ , which represent the Mott and ES-VRH conductivity contributions, respectively, with  $P_{\text{Mott}} + P_{\text{ES}} = 1$ . The results of both conductivity contributions versus temperature are plotted in Figs. 3(a) and 3(b) for the PPy-fiber and the PPy-film, respectively. They depend on temperature strongly and determine where Coulomb interaction is significant or not. As can be seen in Fig. 3(a), for the PPy-fiber, the contribution of ES-VRH conductivity is about zero at very low temperatures ( $T < 25 \text{ K}$ ), thus conductivity is completely the 3D Mott-VRH conductivity. The ES-VRH conductivity starts to arise with increased temperature, until their contribution is equal at room temperature, where both conductivity of the Mott-VRH and the ES-VRH have equal effect. For the PPy-film (Fig. 3(b)), the conductivity is completely 2D Mott-VRH at temperatures of lower than  $\sim 100 \text{ K}$ . Then, with increasing of temperature the ES-VRH contribution quickly starts to arise until the Mott and the ES-VRH conductivity have same contribution at temperature of  $\sim 185 \text{ K}$ . At temperatures higher than it ( $T > 185 \text{ K}$ ), the contribution of the ES-VRH conductivity is more than the Mott-VRH conductivity. Therefore, the ES-VRH conductivity predominates at temperatures higher than temperature of 185 K up to room temperature and the Mott-VRH conductivity is suppressed completely.

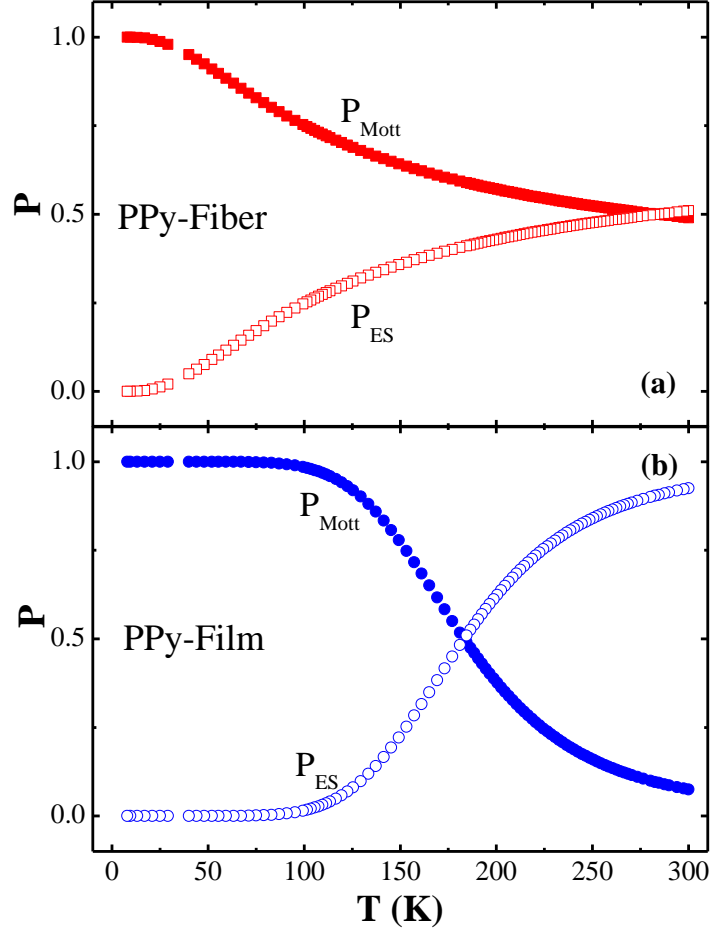


FIG. 3. The contribution of Mott and ES-VRH conductivities versus temperature for (a) the PPy-fiber and (b) the PPy-film.

At temperature of lower than  $\sim 100$  K for the PPy-film, Coulomb screening effects is suppressed completely and the conductivity is completely explained by 2D Mott-VRH conductivity. In addition, at temperatures of higher than  $\sim 100$  K, Coulomb screening effect is weakened with increasing of temperature, thus Coulomb interaction becomes more important. As seen, at this temperature, the conductivity of PPy-film strongly increases. Also at temperature of  $\sim 185$  K, the contribution of the ES-VRH conductivity gets more than the Mott-VRH conductivity. But in the PPy-fiber, Coulomb screening effects slowly diminish with increasing of temperature.

Since the average crystallite size correspond to the ES characteristic temperature as  $T_{ES} \propto (1/S)^3$  where  $S$  is average crystallite size,<sup>26</sup> It was obtained that the average crystallite size ratio in fiber to film ( $S_{\text{fiber}}/S_{\text{film}}$ ) was 0.35. This result shows that the average crystallite size in PPy-film is about three times larger than the PPy-fiber.

In summary, the electrical characterization of the chemically and electrochemically prepared conducting PPy films and fibers were carried out to evaluate their charge transport properties

The electrical conductivity of the PPy-fiber and the PPy-film were 14 and 50 *S/cm* at room temperature, respectively. It was found that the conductivity of the PPy-fiber was higher than conductivity of the PPy-film at temperatures of lower than ~100 K. While at temperatures of larger than ~100 K, the PPy-film conductivity increases strongly than the conductivity of PPy-fiber up to room temperature, where the PPy-film conductivity was higher by a factor 3. The resistivity data were successfully explained by a linear combination of Mott-VRH and ES-VRH models, which describes the intercrystallite electron hopping, as a function of temperature. The results show that dimensionality of the PPy-fiber conductivity is 3D VRH while it is 2D VRH for the PPy-film. It was found that the localization length for the PPy-fiber and PPy-film was about 10 and 15 monomer units, respectively. At  $T < 25$  K, the conductivity of the PPy-fiber was completely explained by the 3D Mott-VRH conductivity. While the ES-VRH conductivity contribution started to arise with increasing of temperature, until their contribution was equal at room temperature. The electrical conductivity of the PPy-film was completely 2D Mott-VRH at  $T < 100$  K, however, with increasing of temperature, the ES-VRH contribution quickly increased until it predominated at room temperature. The results showed that average size of crystallites in the PPy-film was about three times larger than it in the PPy-fiber.

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