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Abstract
Polymers have exceptional charge transport mechanism as a combination of delocalization and localization of charge carriers with intramolecular and intermolecular charge interaction, respectively, and most of the time, it is interpreted with Mott-Gurney space charge-limited current model. As polymers are full of traps, therefore, Mott-Gurney space charge-limited model is modified with various trap distributions as trapped space charge-limited model. The most crucial parameter affected by the nature and distribution of traps is the carrier mobility, and it is argued that space charge-limited model is an acceptable choice for the mobility measurement for polymer. Similarly, in order to account the commonly observed lowering of trap barrier height at higher electric field, the Mott-Gurney space charge-limited current is further modified with little variations, which are evaluated and discussed in detail.

Keywords: polymer electronics, organic semiconductor/polymer, space charge-limited current, charge transport, child's law

1. Introduction
From last few decades, polymer semiconductor-based electronic devices have attracted an enormous deal of interest due to their great achievements both in laboratory and as well as in commercial products [1–10]. Lightweight, flexibility, low-cost, wide-area application, deposition on various substrates, tunability, and many other advantages make these materials an excellent choice for many electronic applications such as light-emitting diode, solar cell, thin-film transistor, laser diode, etc. [11–20]. Another remarkable area of interest for conducting and semiconducting polymer is their application towards highly responsive and low-cost temperature, pressure, humidity, chemical, biochemical, and other types of sensors [21–30].
Despite all of these successes, the complete picture of charge-transport mechanism, which is highly crucial for further achievements, is still not clear [31–40]. Due to such ambiguity, different charge transport models are reported to validate the experimental results performed on various polymer devices [41–54]. Among these charge transport models, space charge-limited current model is counted as highly recited and unanimously accepted charge transport model for disorder organic/polymer semiconductor. In this chapter, we discuss the brief overview of space charge-limited current model with recent development especially for polymer semiconductors.

This chapter starts with the brief discussion of space charge-limited current model and its applications to polymer, especially for conducting and semiconducting polymer. Firstly, the concise overview of historical evaluation and charge transport mechanism of polymer will be discussed. Later on the Child’s Law, Mott-Gurney space charge-limited current model, and trapped space charge-limited current model with single-trap, exponential, and Gaussian distribution of traps and then effects of shallow and deep traps on space charge-limited current are reviewed. Mobility measurement from space charge-limited current and its comparison with other mobility measuring methods such as time-of-flight and different carrier extraction by linearly increasing voltage characteristics are evaluated in the next section. Finally, the application of Poole-Frenkel on space charge-limited equation with other modifications is reviewed before conclusion.

2. Charge transport mechanism of conducting polymer

Before 1977, it was generally considered that polymers are electrically insulator. Most of these insulating polymers such as polyethylene, polystyrene, and polypropylene have almost

![Figure 1. (a) Chemical structure of polyacetylene. (b) Comparison of improved conductivity of doped polyacetylene with other conventional materials.](image-url)
negligible free charge carriers for electrical conductivity. But at the same time, three well-known scientists Heeger, MacDiarmid, and Shirakawa reported a series of great works on the doping of polymer and demonstrated that the proper doping of conjugate polymer improves its conductivity just like as usual semiconductor or metal and they referred it as semiconducting/conducting polymer [3]. They reported first time in the history that the conductivity \(10^{-5} \text{ S/m}\) of insulating polyacetylene (molecular structure shown in Figure 1a) thin film can be increased by doping it with iodine up to a metallic polyacetylene \(10^5 \text{ S/m}\) just like as Cu metal as shown in Figure 1b. No doubt, it was a great turning point in the discipline of polymer engineering and caused to initiate a new field as “Organic Electronics” or “Polymer Electronics”. On the basis of their land-mark achievements, Heeger, MacDiarmid, and Shirakawa were awarded Nobel Prize for chemistry in 2000 [2–4].

Broadly speaking, conjugate polymers cover the extensive portion of conducting polymers. Conjugate polymers are defined as such polymer which has a combination of alternating double bonds (\(\pi\) bonds) and single bonds (\(\sigma\) bonds) as their backbone structure. As compare to the \(\sigma\) bond, the \(\pi\) bonds are usually unstable in nature and easily ionized or removed. This special combination of single and double bond for conjugate polymer offers a unique arrangement for the de-localization of charge carriers from one end to the other end of polymer chain as extended p-orbital system [19, 55]. This p-orbital overlapping supported with contiguous single bonds allows a de-localization of \(\pi\)-electrons (double-bond electrons are called \(\pi\)-electron offers \(P_x, P_y, \text{ and } P_z\) hybridization for carbon atoms) throughout the double and single-bond combination just as an ethylene as shown in Figure 2. Such de-localization of free carriers is the main reason for the charge transport within the molecular chain (intra-molecule) of a conducting polymer [56]. Just for the discussion of \(\sigma\) bond and \(\pi\) bond a simple ethylene (IUPAC name ethene \(\text{H}_2\text{C} = \text{CH}_2\)) molecular structure is shown here in Figure 2. Each carbon makes \(sp^2-sp^2\) hybridization for \(\pi\) bond and the \(\sigma\) bond is formed between carbon and hydrogen atom. The overall hybridization of \(\sigma\) and \(\pi\) bond is shown in Figure 2c for ethylene.

Figure 2. (a) Sigma (Single bond) hybridization for ethylene, (b) pi (Single bond) hybridization for ethylene and (c) both sigma and pi bond hybridization which give de-localization of pi-electron.
Conducting polymers offer a large number of topological defects as disorder. These defects, such as breaking of bonds in molecular chain, torsion, addition of both internal and external impurity, are produced during the synthesis of polymerization and cause to provide electrical traps for conductivity between molecular chains. Such disorder in conducting polymer presents localization of free carriers inside a molecular chain. Therefore, intermolecular chain transport requires hopping of free carries from one molecular chain to the other molecular chain. So overall, we can say that charge transport in polymer is the combination of both intermolecular and intramolecular charge transport process. Due to the hopping conductivity for intermolecular charge transport, the overall mobility of free carriers for most of polymer is very small as compared to the conventional inorganic semiconductors at normal operating conditions. From charge-transport point of view, there is no fundamental inconsistency between insulating, semiconducting, and conducting polymer except the difference between energy bandgaps, which is larger for insulating polymer semiconductor as compared to semiconducting polymer.

3. Metal-polymer interface

For electronic devices, metal-polymer interface plays a vital role to define the electrical response for conducting polymer. Figure 3 demonstrates the differences between typical metal-vacuum and metal-polymer interface energy band diagrams for further discussion. Apparently both energy band diagrams look same, but actually different charge injection mechanism is observed in both cases. The Fermi-energy level ($E_F$) of metal is coincide with $E_F$ of vacuum and as well as with polymer. But the barrier height between $E_F$ of metal and vacuum energy level for metal-vacuum interface is very high as compared to the barrier height between $E_F$ of metal and polymer interface. The barrier height difference between metal $E_F$ and vacuum $E_{Vac}$ is much higher than the required energy to inject electron from metal to polymer/insulator.

![Figure 3](image-url)

**Figure 3.** (a) Metal work function and (b) metal-polymer interface. Energy to inject electron from metal to vacuum is much higher than the required energy to inject electron from metal to polymer/insulator.
vacuum level is defined as metal work function [56]. On the basis of these facts, Mott and Gurneys proposed metal-insulator barrier height reduction theory and justified the low metal-insulator barrier height as compared to the metal work function, which causes space charge-limited current in insulating materials [57]. It is unanimously accepted that Mott and Gurney’s proposed space charge-limited current is also valid for most of insulating, semiconducting, and even conducting polymers [31].

4. Bulk-limited and injection-limited current flow

The limitation of current by a polymer can be classified as either (i) injection-limited or (ii) bulk-limited current flow. For injection-limited, the limitation of current through polymer is imposed by non-ohmic metal-polymer interfaces, while for bulk-limited, the limitation is imposed by the bulk properties of polymer. If conducting polymer is sandwiched between two electrodes and anyone electrode offers low barrier height (ohmic response) to the polymer-metal interface then the injected carriers from electrode forms a space charge region consisting of a large number of injected carriers and equilibrium free carriers inside polymer. As the mobility of carriers is very small, therefore, before traversing of injected carriers from one to the other electrode, more and more charges are injected. When an external electric field is applied, further charges are injected from low-barrier electrode to the polymer, and an equilibrium stage is reached when injected carriers are comparable or even higher than the free carriers concentration; at this stage, the flow of current is referred as space charge-limited current [57, 58].

5. Child-Langmuir space charge model

Space charge-limited current is a hot topic of research due to their great application for conducting/semiconducting polymers. The origin of space charge theory was founded by C.D. Child and I. Langmuir from 1911 to 1913, when they reported the derivation of space charge-limited current in a parallel-plane vacuum diode as [59, 60]

$$J = \frac{4 \varepsilon_0}{9} \frac{2e V^{\frac{3}{2}}}{m_e d^2}$$

(1)

where $J$ is space charge-limited current for vacuum diode, $\varepsilon_0$ is the dielectric constant for free space, $e$ is the coulomb charge of electron, $m_e$ is the mass of electron, $V_a$ is the applied (anode) voltage, and $d$ is vacuum spacing between two electrodes. The above equation is reported in the literature with different names such as three-halves power law, Langmuir-Child law. From the equation, it is clear that the space charge current is directly proportional to the three-halves power of the applied voltage and inversely proportional to the square of the displacement between electrodes.
6. Mott-Gurney space charge model

Apparently, Child-Langmuir space charge equation did not find any application for insulator or semiconducting materials due to the presence of vacuum and hence no scattering between electrodes. Therefore, Mott-Gurney proposed another space charge–limited current equation for polymer diode, which is similar to the Child-Langmuir equation with the following assumptions [57].

1. Active layer is trap-free for charge injection
2. Diffusion of carrier is negligible in active layer
3. Electric field at the injecting electrode is zero.

Generally, the assumptions 2 and 3 are still valid for most of organic/polymer semiconducting materials. But for assumption 1, space charge–limited current is further modified with new version as trapped space charge–limited current model and will be discussed in the later section.

When a voltage is applied to an active layer, sandwich between two electrodes as diode, then an electric field (E) is established inside the active layer. Such electric field forces the charges to move with velocity (v) toward another electrode, and therefore, the mobility (μ) of free carrier is defined as

\[ v = \mu E \] (2)

Similarly, the current density (J) passing through a semiconductor with conductivity (σ) under the influence of applied electric field E can be defined as

\[ J = \sigma E \] (3)

where σ is direct function of both mobility and carrier density of electron n(x) and hole p(x) and can be define as

\[ \sigma = e n(x) \mu_n + e p(x) \mu_p \] (4)

If we assume single-carrier devices, then Eq. (4) is simplified as

\[ \sigma = e n(x) \mu \] (5)

By incorporating Eq. (5), Eq. (3) becomes as
The injected carriers forms space charge with the distribution of electric field inside insulator and can be defined mathematically by Poisson equation as

\[ \frac{dE}{dx} = \frac{en(x)}{\varepsilon} \]  

(7)

By solving all above equation for one-dimension path with boundary conditions \( V(0) = V \) and \( V(L) = 0 \), the pure space charge–limited current without any traps will be obtained as

\[ J = \frac{9}{8} \varepsilon_e \mu \frac{V^2}{L} \]  

(8)

It is important to note that logarithmic graph (log(J) – log (V)) of above Eq. (8) yield a straight line with slope 2, which shows trap-free space charge–limited current behavior of polymer between electrodes as sown in Figure 4.

**Figure 4.** Space charge–limited current behavior for polymer semiconductor with only ohmic and trap-free space charge–limited current regions.

**Figure 4** shows the ideal current-voltage characteristics of conducting polymer diode, where there are only two regions, one is ohmic region and other is space charge region and both regions can be differentiated with the order of slope. The transition of both ohmic and space charge regions is taken place at specific voltage termed as threshold voltage \( V_T \). At low voltage,
polymer diode offers ohmic behavior \( (J \propto V) \) with slope at order 1, while at higher voltage, polymer exhibits space charge–limited current \( (J \propto V^2) \) with slope of an order 2. In other words, there is direct transition is observed from ohmic to space charge–limited region, which is not true in the presence of traps distribution inside polymer.

7. Trapped space charge–limited current model

Generally, an intermediate region is also observed between ohmic to space charge–limited region and this region is termed as trapped space charge region as shown in Figure 5. The charge transport inside polymer within this region is controlled by the trapping and detrapping of carriers at both energetic and positional distribution. Traps are nothing just as impurity and/or structural defects which provide localized states between HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energy bandgap of polymer. These localized states trap the free carriers and avoid them to take any role for charge transport process and degraded the electrical properties of polymer and hence device [61]. When applied voltage is higher than the average energy associated with traps density, then polymer behaves trap-free space charge–limited current as shown in Figure 5.

![Figure 5](image_url)

**Figure 5.** Typical space charge–limited current behavior for polymer semiconductor. Four charge-transport regions are clearly visible (i) ohmic region \( (J \propto \mu V) \), (ii) trap-SCLC region \( (J \propto \mu V^n) \) region, (iii) VTFL region \( (J \propto \mu N_t d^3) \), and (iv) SCLC region \( (J \propto \mu V^2) \) [31].

The trapped space charge–limited current depends on the distribution of traps state at the energy bandgap of the given polymer. Generally three distributions of electronic traps are reported for conducting polymers. These distributions are as follows:

1. Single energy level trap density.
2. Exponential distribution of trap density.
3. Gaussian distribution of trap density.
7.1. Single energy level trap density

For single energy level trap density ($E_T$, also called transport energy), the current for trapped space charge–limited current can be little modified as [62]

$$J = \frac{9}{8} e \varepsilon_o \mu \theta \frac{V^2}{L}$$

(9)

where $\theta$ is defined as trap factor and can be correlated with free and trapped carrier density as [63–67]

$$\theta = \frac{n_f}{n_f + n_t}$$

(10)

where $n_f$ and $n_t$ are defined as free carrier and trapped carrier density, respectively. The trapped carrier density $n_t$ can be defined with single energy level $E_T$ as

$$n_t = N_T \exp \left( -\frac{(E_f - E_T)}{kT} \right)$$

(11)

where $N_T$, $E_f$, $k$, and $T$ can be defined as trap density, Fermi energy level, Boltzmann constant, and ambient temperature, respectively.

7.2. Exponential distribution of traps

Exponential distribution of traps ($g(E)$) with characteristics width of trap energy distribution ($E_c$) between HOMO and LUMO energy bandgap of polymer can be identified as

$$g(E) = \frac{N_T}{E_c} \exp \left( -\frac{E}{E_c} \right)$$

(12)

$E_c$ is correlated with characteristic temperature ($T_c$) as $E_c = k T_c$. Now, the trapped space charge–limited current for a polymer having exponential distribution of traps can be described as [68–70]

$$J = q^{1/2} \mu_p N_T \left( \frac{2l + 1}{l + 1} \right)^{1/4} \left( \frac{l E_c}{(l+1) N_T} \right)^{1/4} \frac{V^{l+1}}{d^{2l+1}}$$

(13)

where $l = T_c / T$ and $T$ is the absolute temperature.
7.3. Gaussian distribution of traps

Bassler proposed Gaussian density of states for polymer material, which are broadened by both energetic and positional disorder [41]. Therefore, many researchers apply Gaussian density of traps ($D_T(E)$) for trapped space charge–limited current as [71].

$$D_T(E) = \frac{N_T}{\sigma \sqrt{2\pi}} \exp \left( \frac{(E - (E_c - \tau_e))^2}{2\sigma^2} \right)$$  \hspace{1cm} (14)

where $\sigma_T$ is the width of Gaussian distribution traps and $E_c - \tau_e$ is the trap energy. Similarly Steiger and his workers proved that the Gaussian trapped space charge–limited current follow the same exponential distribution of traps Eq. (13), where $l$ can be redefined as [72]

$$I = \left[ 1 + \frac{2\pi \sigma^2}{16kT^2} \right]^{\frac{1}{2}}$$  \hspace{1cm} (15)

If $2\pi \sigma^2 >> k^2 T^2$, then Eq. (15) is further simplified as

$$I = \frac{2\pi \sigma}{16kT}$$  \hspace{1cm} (16)

8. Photocurrent space charge–limited current model

When light falls on conjugate polymer, huge number of electron and holes are uniformly generated throughout the polymer as free carriers and these carriers move to their respective electrodes as photocurrent under the influence of internal electric field generated by the difference of electrode work‐function. If $G$ is the generation rate, $L$ is the length, and $q$ is the electric charge of free carriers, then the photocurrent ($J_{ph}$) can be defined as [17, 34, 73]

$$J_{ph} = qG L$$  \hspace{1cm} (17)

By incorporating the effective thickness of polymer ($L$) for photocurrent, Eq. (17) can be modified as

$$J_{ph} = qG \left( \mu_e \tau_e \right)^{\frac{1}{2}} V^{\frac{1}{2}}$$  \hspace{1cm} (18)
where $\mu_h$ and $\tau_h$ are the mobility and charge carrier life time. Blom et al. observed that the photo-generated current in this region (L) follows space charge–limited current and he derived the fundamental space charge–limited photocurrent equation as [33]

$$J_{ph} = q \left( \frac{9\epsilon_0 \epsilon_r \mu_h}{9\eta} \right) G^{\frac{3}{2}} V^{\frac{1}{2}}$$

(19)

Figure 6. Incident light power (ILP) dependence of the photocurrent ($J_{ph}$) versus the effective voltage ($V_0 - V$) measured at $T = 210$ K. The solid (thick) lines represent the $J_{ph}$ using $\mu_h = 1.2 \times 10^{-7}$ cm$^2$/V s, $\epsilon_r 2.6$, and $G \propto$ ILP, where ILP was varied from 80 to 6 mW/cm$^2$. The arrow indicates the voltage ($V_{sat}$) at which $J_{ph}$ shows the transition to the saturation regime [33].

where $\epsilon_0$, $\epsilon_r$ are the dielectric constant for free air and polymer, respectively. From above equation, Blom et al. experimentally observed that the space charge–limited photocurrent is directly proportional to the three-quarter power of photo-generation rate and half power of voltage as shown in Figure 6.

Figure 6 clearly shows that the space charge–limited photocurrent as calculated by Eq. (19) is in contrast with the square-root region for the given voltage range of the experimental results.

9. Shallow and deep traps for space charge–limited current model

Traps not only decrease the mobility for space charge–limited current but also initiate the thermal and electrical degradation for polymer electronic devices. Traps are generally classified as (i) shallow traps, and (ii) deep traps for both electron and hole. If traps are very close to the conduction band (LUMO) within energy bandgap, then traps are classified as shallow traps for electrons. Similarly if traps are in the vicinity of valence band (HOMO) within energy bandgap, then traps are identified as shallow traps for holes as shown in Figure 8. On the other hand, deep traps of electron and holes are exist far away (mid of the energy bandgap) from conduction (LUMO) and valence (HOMO) band, respectively, as shown in Figure 7.
Figure 7. Symbolic representation of shallow and deep traps for polymer semiconductor.

Figure 8. Model simulations of shallow ($E_c - E_t = 0.1$ eV) and deep ($E_c - E_t = 0.5$ eV) trap configurations represented by blue solid lines and red dashed lines. (a) Current density voltage characteristics for a shallow trap and a deep trap are plotted by blue dots and red triangles. Fittings provide the exponent of the voltage. (b) Fermi level representations at 6 V along the thickness, for a shallow trap (blue solid line) and a deep level (red dashed line) [74].
Conventional space charge and trap space charge–limited current model cannot differentiate between shallow and deep traps for both electron and hole. If space charge–limited current is modeled in frequency domain with single traps, then the dynamic picture of the traps can be obtained. By varying the single-trap energy for frequency-domain analysis of space charge–limited current model, it is possible to differentiate between shallow and deep traps for both electron and polymer with the condition that polymer is sandwiched between properly selected electrodes [74].

10. Mobility measurement and space charge–limited current

The velocity per unit electric field is defined as the mobility for polymer. Mobility is one of the most important parameter, which comprehensively defined the charge transport mechanism of polymer. The efficiency of many polymer electronic devices depends on mobility; therefore, it is very crucial to determine the exact value of mobility [43, 75]. For polymer, mobility can be measured with different methods; some of them are listed as follows:

1. Time-of-flight method [44].
2. Carrier extraction by linearly increasing voltage (CELIV) method [44] and photo-CELIV method [76, 77].

Each of this method has some advantages and disadvantages, but these methods are the most commonly used method to determine the mobility of polymer.

10.1. TOF method

The TOF is the most widely used technique for the measurement of mobility. In these techniques, short pulse of light or laser is stroke over the end surface of polymer sample, which result in the generation of photo carriers from the end surface of sample.

\[
\mu = \frac{L}{E \cdot T}
\]  

These photo carriers are immediately swept away from the end surface toward the other end surface through the influence of external DC volts applied at electrodes and give rise to the transient photocurrent as shown in Figure 9. The time (T) taken by the photo carriers from one end to the other end surface is calculated from oscilloscope. If E is the applied electric field, L is the thickness of organic layer then the mobility can be calculated as [78].
Figure 9. Schematic setup for typical TOF system for mobility measurements. Here the laser pulse can be illuminated through ITO electrode as well as a semitransparent metal electrode of polymer sample [43].

Figure 10. The schematic Photo CELIV measurement setup is shown. The measuring process consists of two steps. In first step a laser is shine at transparent electrode of sample which generates excess photo carriers. These carriers are extracted by linearly increasing voltage. The peak-extraction time helps to calculate the mobility.
10.2. CELIEV/photo CELIEV method

The charge extraction by increasing the linear voltage is another technique commonly used to measure the mobility of polymer sandwiched between electrodes. The measuring process consists of two steps. In first step, a laser is shine at transparent electrode of sample which generates excess photo carriers. These carriers are extracted by linearly increasing voltage. The peak-extraction time helps to calculate the mobility of the polymer sample as shown in Figure 10. The detail information about these methods can be found in Ref. [79–81].

10.3. Dark-injection space charge–limited mobility measurement

Dark-injection space charge–limited current (DI-SCL) is another commonly used technique for the measurement of mobility for many amorphous, disorder organic/polymer materials [82–85]. To determine the mobility of hole with DI-SCL method, the polymer sample is sandwiched between electrodes and electrodes are managed in such a way that the cathode behaves as blocking electrode and a strong voltage pulse is derived at ohmic anode. The application of voltage pulse will result a transient hole current observed at oscilloscope as shown in Figure 11. Therefore, the hole density \( \mu_h \) can be calculated as

\[
\mu_h = \frac{0.787 d^2}{V \tau}
\]

(21)

where \( \tau \) is the arrival time for early sheet of holes carriers to reach the respective cathode. The \( \tau \) is correlated with space charge free carrier transit time (\( \tau_{SCL} \)) as \( \tau = 0.787 \tau_{SCL} \) [86, 87].

Figure 11. (a) A sequence of DI signals of Au (treated with UVO)/2TNATA/Au under different applied voltages. The applied voltage varied in steps of 2 V starting from 6 V. (b) An ideal DI-SCLC transient [82].

For both CELIEV and photo-CELLIV mobility measurement method, it is not so simple to differential between electron and hole mobility, specially for bipolar charge-transport polymer. Similarly, the TOF method has two series drawbacks (1) the density of photo-generated carrier...
is not adequate (very low) to measure the mobility as compare to the usual carrier density at normal operation of many electronic devices, and another drawback is that (ii) TOF method should requires the thickness of polymer above the absorption length of polymer (>1 μm) [78]. In the same way, dark-injection space charge–limited current is required the proper selection of electrode for reliable measurements.

Recently, a comprehensive study was performed by Qiu group to compare and evaluate the performance of different mobility measurement methods reported for polymeric materials. They consider various factors such as applied electric field, injection barrier, and energetic disorder, which are crucial for the performance of polymer electronic devices and finally they concluded that the result of both space charge and TOF mobility measurement methods are very close to each other [88]. Therefore, with proper selection of electrodes, space charge–limited mobility measurement is acceptably reliable for most of the cases.

11. Modification of space charge–limited current model

As we discussed earlier, when the current density passing through the polymer with length \( L \) under the influence of applied voltage \( V \) shows directly proportional response with the square of voltage \( (J \propto V^2) \) and inversely proportional to cube of \( L \) \( (J \propto L^{-3}) \) then the polymer sample is modeled with trap-free space charge–limited current. In order to incorporate the variety of the trap distribution, the space charge–limited current model is modified as trapped space charge–limited current model. Traps are both energetically and positional distributed throughout the energy bandgap and capture the free carriers and offer some energy barrier to release them. Both space charge–limited current and trap space charge–limited currents model assume that barrier height of traps are remain constant for entire operating electric field range of the device, which is not true for some of the reported experimental results. In fact, higher electric field lowers the barrier height of traps which cause to increase the emission rate from traps and hence the current density as expected from trap space charge–limited current model as shown in Figure 12a. The lowering of trap barrier height or emission rate from traps at high electric field is identified as Poole-Frenkel effect [89], as shown in schematic energy band diagram (Figure 12b). There is some similarity between Poole-Frenkel and Schottky models [90, 91] for the lowering of traps barrier height. Schottky model represent barrier height reduction at metal-polymer interface, while Poole-Frenkel model shows the lowering of trap barrier height inside the polymer thin film. The overall current density \( J \) passing through the polymer due to Poole-Frenkel emission can be written as

\[
J = q \mu N_c \exp \left[ -q \left( \frac{\varphi_T - \frac{q E}{k T \varphi_a}}{k T} \right) \right]
\]

(22)
where $q\varphi_T$ is trap energy barrier height, and other variables have already defined earlier. Poole-Frenkel behavior can be justified for any polymer device, if a linear relation is obtained between $\ln\left(\frac{J}{J_0}\right)$ vs $\sqrt{E}$ data derived from their experimental result for such device.

Murgatroyd was the first who addressed the lowering of trap barrier height by incorporating Poole-Frenkel equation into space charge–limited current equation and drive an approximate equation as [92].

$$J = \frac{9}{8}E_0 \mu_n \exp\left(0.897\sqrt{E}\right) \frac{V_{th}^2}{L}$$  \hspace{1cm} (23)

Figure 12. (a) Lowering of energy barrier height of traps at higher electric fields, (b) Poole-Frenkel Effect

Murgatroyd equation is simple and very handy, but it is an approximate equation. Later on, Barbe determined analytically, the effect of trap barrier height reduction on space charge–limited current model and derived an equation as [93, 94]

$$\frac{J x}{\mu e \theta} = \frac{2(kT)^\frac{1}{2}}{\beta^2} \left[ \exp\left(\frac{\beta\sqrt{E}}{kT}\right) \left(\frac{\beta\sqrt{E}}{kT}\right)^3 - 3 \left(\frac{\beta\sqrt{E}}{kT}\right)^2 + 6 \frac{\beta\sqrt{E}}{kT} - 6 \right] + 6$$  \hspace{1cm} (24)
Barb's equation is used to determine the current density ($J$) as a function of electric field defined at position $x$. It is reported that both these Murgatroyd and Barbe modifications are also applicable with electrical response for many polymers devices [95–99]. As both insulating and semiconducting polymers share the same charge transport mechanism, therefore, above equations are reasonably valid for both types of polymers.

The fundamental work of Frenkel, Murgatroyd, and Barbe is to modify the space charge–limited current to accommodate the lowering of trap barrier height for only in one-dimension trap distribution. For the three-dimension trap distribution, these models not work very well. In this domain, Hartke modification is reasonably accepted for the accommodation of three-dimensional lowering of the trap barrier height for space charge–limited current model [100].

Similarly, Geurst modified the space charge–limited current model in such a way that the thickness of the semiconductor thin film is insignificant with respect to the electrode separation as 2D model [101–104]. While, Chandra derived Mott-Gurney space charge–limited current equation in two dimensions with exponentially distributed traps and other variety of polymer Schottky diodes [105–107].

12. Summary

Despite great recent achievements for conjugate polymer-based electronic devices, the clear picture of charge transport mechanism is still not available. Polymers have unique charge transport mechanism as a combination of delocalization and localization of charge carriers with intramolecular and intermolecular charge interaction, respectively. But it is unanimously believed that Mott-Gurney space charge–limited model is appreciably accepted for most of the polymers. As polymers are full of traps, therefore, Mott-Gurney space charge–limited model is also modified as trapped space charge–limited model according to the requirements of polymers. The nature of traps distribution inside polymer is varied and depends on many factors such as nature of materials itself, polymerization process, nature of dopants, and solvent. Generally, three types of traps distributions are reported in the literature for polymers named as single trap, exponential, and Gaussian distribution of traps. Therefore, trapped space charge–limited current model is further modified to accommodate all these distribution of traps. Just like as distribution of traps the nature of traps, such as shallow and deep traps, is also important to define the electrical response of polymer. The most crucial parameter affected by the distribution and as well as nature of traps is mobility, and space charge–limited current model with little variation is also used to measure the charge mobility of polymer. Different other methods such as time-of-flight method and charge extraction by linearly increasing voltage (CELIV) with or without light (photo—CELIV) sources are available to measure the charge mobility. By comparing these measuring methods for polymer, it is reported that the simple space charge–limited model is an acceptable choice for mobility measurements. Similarly, it is also observed the trap barrier height is significantly reduced at higher electric field and temperature due to Poole-Frenkel effect. Therefore, Murgatroyd and Barbe incorporated Poole-Frenkel effect and solved Mott-Gurney space charge–limited equation numerically.
and analytically, respectively. It is reported that both these modifications are experimentally verified with electrical response of many polymers devices.

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