

# Hole Injection Initiated by Ionic Conduction in Electrically Stressed Insulating Polymers

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**ABSTRACT:** A new mechanism leading to hole injection into insulating polymers under normal operating fields is presented. In general, it is unlikely that holes can be injected into large band-gap insulating materials under normal operating fields less than  $1 \text{ MV cm}^{-1}$ , particularly for materials that are not in the form of thin films. However, insulating polymers consist of a large amount of various unavoidable ionic impurities, so ionic conduction plays an important role in their electrical properties. The presence of such ions modifies the field distribution in the material with the tendency

of enhancing the field toward the anode, thus increasing the probability for hole tunneling from the anode to the material. The appearance of positive space charge near the anode after a prolonged period of electrical stressing, as observed by many investigators, may be considered as the experimental evidence of the mechanism. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1864–1867, 2003

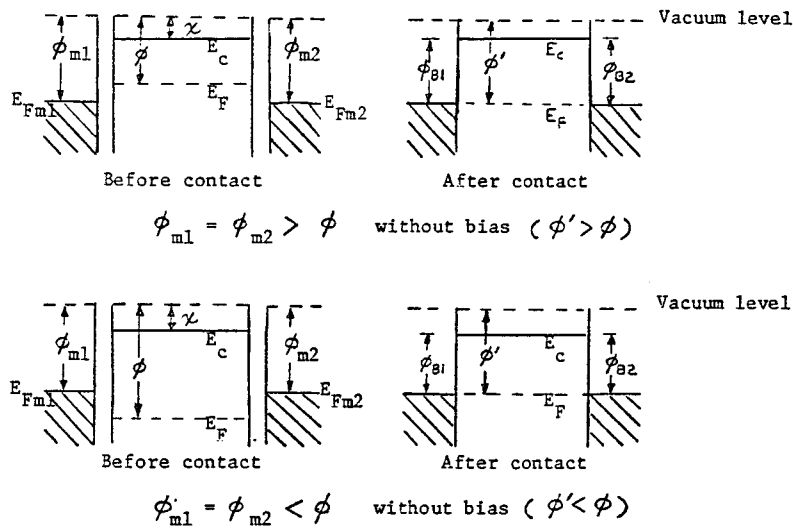
**Key words:** hole injection; insulating polymers; ionic conduction; space charge; interfaces

Most electrical contacts between a metal and an insulator are neutral contacts. The so-called neutral contact means that the regions adjacent to the contact on both sides are electrically neutral. This implies that there is no space charge and no band bending present within the insulator in the absence of electric fields, so that both the conduction band and the valence band edges are flat up to the interface. A condition like this is sometimes referred to as the flat-band condition. To satisfy this condition, the work function of the metal  $\phi_m$  must be equal to the work function of the insulator  $\phi$ . In wide band-gap insulators, there is always the transfer of a small amount of charge carriers between the metal and the insulator to bring the Fermi level of the metal to align with that of the insulator. However, if the trapped space charge in the insulator attributed to such a transfer of charge carriers is too small to cause significant band bending, then we can consider such a contact as neutral.<sup>1</sup> Figure 1 shows the neutral contacts formed between a metal and an insulator with different work functions. In this figure,  $\phi_{m1}$  and  $\phi_{m2}$  are the work functions of the metallic electrodes and  $\phi$  is the work function of the insulator,  $\chi$  is the electron affinity, and  $E_F$  is the Fermi level.

When a steady dc voltage is applied across a metal–insulator–metal (MIM) system, electrons will be injected from the cathode to the insulator by three possible processes: (1) Schottky emission, (2) thermally assisted tunneling, and (3) tunneling by traps, as shown in Figure 2. If the applied voltage is sufficiently high, direct tunneling from the Fermi level of the metal to the conduction band based on the Fowler–Nordheim type tunneling injection is possible. The probability of tunneling depends on both the population of the electrons available for tunneling and the barrier height. The population of the available electrons is the highest at the Fermi level of the metal and decreases exponentially at levels higher than the Fermi level, but the barrier height for tunneling decreases at levels higher than the Fermi level; thus there is a trade-off between these two factors in governing the tunneling processes. Because insulating polymers contain a large quantity of various traps and ionic impurities, carriers injected from the electrical contacts will quickly be trapped to form trapped space charges.

For most insulating polymers, the energy band-gap is wide and is of the order of 9 eV, and most metals have work functions less than 4 eV. Thus, the neutral contact imposes that the potential barrier height  $\phi_n$  for electron injection from the cathode is lower than that of  $\phi_p$  for hole injection from the anode, as shown in Figure 2. At normal fields less than  $1 \text{ MV/cm}$ , it is very unlikely that there would be any significant hole injection. However, Liu and Kao<sup>2</sup> were the first to observe hole injection to polyethylene thin films at fields of about  $2 \text{ MV/cm}$  and higher. For applied fields less than  $1 \text{ MV/cm}$ , an-

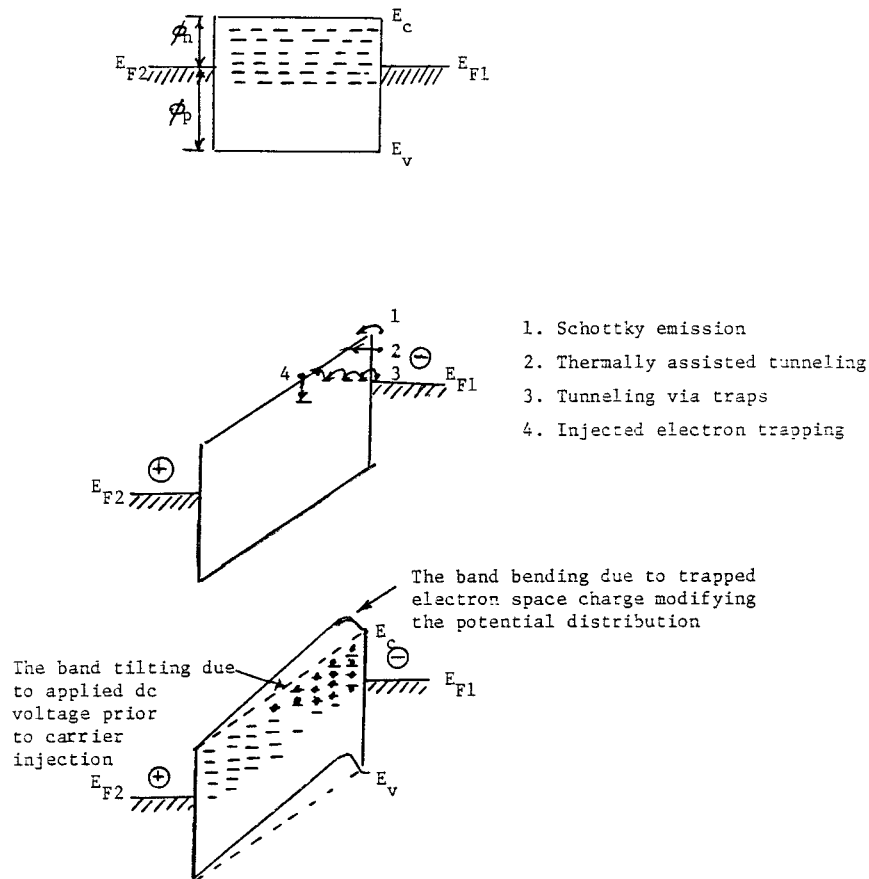
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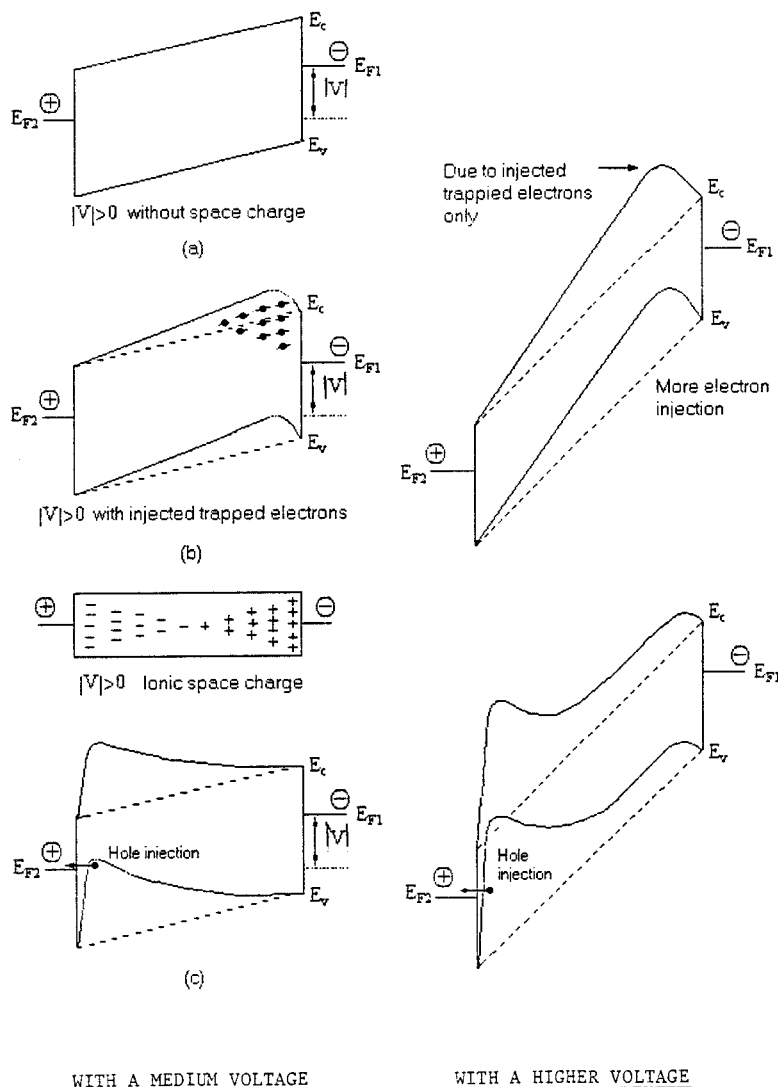
**Figure 1** Energy level diagrams illustrating the neutral contacts formed between a metal and an insulator with different work functions.

other mechanism is required to enable hole injection. It is worth noting that at fields lower than 60 kV/cm, Tahira and Kao<sup>3</sup> observed significant electron injection from the cathode to polyethylene films. The well-known charging current decay phe-

nomenon is attributed to the trap-filling process. As soon as the trapped electron space charge is formed, the band starts to bend, thus reducing the field toward the cathode and enhancing the field toward the anode, as shown in Figure 2.



**Figure 2** Schematic diagrams illustrating the electron injection processes and the effect of trapped electron space charge on the band bending and thus the potential distribution.



**Figure 3** Schematic diagrams illustrating the effects of the combined space charges formed by injected trapped electrons and ions on the band bending and thus the potential distribution resulting in hole tunneling from the anode to the polymer.

In nonionic solids, the ionic conduction is extrinsic, depending almost entirely on the nature and the concentration of ionic impurities. Insulating polymers generally contain ions (e.g., ionomers, polyelectrolytes) or groups capable of ionizing, or in which ionic materials have been introduced. In most insulating materials, water is always a source of ions. It is generally not easy to identify the ions experimentally. For insulating polymers, it is reasonable to assume that they are mainly derived from fragments of polymerization catalyst, degradation and dissociation of the polymer itself, absorbed water, and other impurities introduced into the polymer during the fabrication processes. For example, insulating polymers such as poly(vinyl chloride) may contain  $H_3O^+$ ,  $Na^+$ ,  $K^+$ ,  $OH^-$ ,  $Br^-$ , for instance.

A molecule AB can be dissociated into  $A^+$  and  $B^-$ :



In thermal equilibrium, the concentration of ions  $n_k$  can be expressed as

$$n_k = [A^+] = [B^-] \quad (2)$$

An equilibrium dissociation constant  $K_d$ , according to the mass action law, is defined as

$$K_d = \frac{[A^+][B^-]}{[AB]} = \frac{n_k^2}{(1-b)[AB]_0} \quad (3)$$

where  $[AB]_0$  and  $[AB]$  are the concentrations of the total original molecules and the nondissociated molecules, respectively; and  $b$  is the fraction of molecules that are dissociated. Dissociation is a thermally activated process, and thus  $K_d$  can be written as

$$K_d = K_{d0} \exp(-E_d/\epsilon_r kT) \quad (4)$$

where  $K_{do}$  is a constant,  $E_d$  is the activation energy for dissociation, and  $\epsilon_r$  is the dielectric constant. From eqs. (3) and (4) it may be seen that  $K_d$  increases very rapidly with increasing dielectric constant.

If AB molecules are the only dissociable species present in the materials, then their concentration can be expressed as

$$N_o = [AB]_o \quad (5)$$

and the extrinsic ionic conductivity can be written as

$$\sigma_{ion} = qbN_o(u_+ + u_-) \quad (6)$$

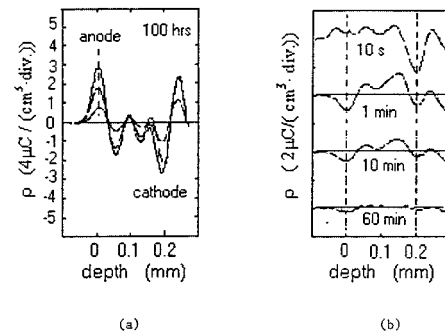
where  $u_+$  and  $u_-$  are the mobilities of the positive and the negative ions, respectively. If the material consists of more than one kind of species as well as free ions, then the total ionic conductivity should be expressed as

$$\sigma_{T(ion)} = \sum_i \sigma_{i(ion)} \quad (7)$$

Given that  $b$  increases with increasing  $K_d$ , the dielectric constant plays a very important role in ionic conductivity. This is why water absorbed by the material would cause a great increase in ionic conduction.

The positively charged cations moving toward the cathode and the negatively charged anions moving toward the anode under an applied electric field will create hetero-space charges near the electrodes. If the charges of the ions are not neutralized at the electrodes, they will accumulate near the electrodes, producing an internal potential and hence an internal field opposite to the applied voltage, as shown in Figure 3(c). The positive ions tend to neutralize the injected trapped electrons near the cathode, whereas the negative ions tend to enhance the field toward the anode, thus modifying the potential barrier near the interface and creating the chance for the tunneling of holes to tunnel from the metal to the valence band of the polymer, as shown in Figure 3(c). Obviously, the higher the applied field, the greater the extent of hole tunneling, as expected.

The ionic conduction process is very slow because the movement of an ion involves the transport of a mass and the activation energy for the ion to surmount a potential barrier as well as that for the creation of a neighboring vacancy for the ion to move in.<sup>4</sup> It can be imagined that to create the condition for hole tunneling, the applied field must be sufficiently high and also the stressing time must be sufficiently long for the formation of a high concentration of hetero-space charges. Several investigators<sup>5</sup> have observed hole injection from a metallic electrode to the polyeth-



**Figure 4** Typical space charge distributions in polyethylene after being electrically stressed at 100, 300, and 500 kV/cm for 100 h: (a) under dc stresses after 100 h, and (b) under short-circuiting conditions after 100 h stressed at 500 kV/cm.

ylene after being subjected to electrical stressing for a prolonged period of time. Typical results on space-charge distributions in polyethylene after being subjected to electrical stressing for 100 h, measured by the pulsed electro-acoustic method are shown in Figure 4. It can be seen that under a dc stress, part of the trapped hole space charge can still be seen, although the major part has been overshadowed by the negative ionic space charge as shown in Figure 4(a). After short-circuiting the specimen, both the anode and the cathode are brought to the same potential and the injected trapped hole space charge clearly appears at 1 min after short-circuiting, as shown in Figure 4(b). Upon short-circuiting, all charges inside the specimen will gradually be neutralized from each other. A similar phenomenon has also been observed by other investigators.<sup>6</sup>

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