

A Critical Study of Electrical and Electrochemical Properties of Conducting Polymers



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Introduction

Over the past several decades, conducting polymers (CPs) have gained increasing attention owing to their strong potential as alternatives to their inorganic counterparts, leading to significant fundamental and practical research efforts. In the late 1970s, many scientists considered CPs (or 'synthetic metals') to be intractable and insoluble. Since the discovery of polyacetylene in 1977 by Hideki Shirakawa, Alan MacDiarmid, and Alan Heeger, various important CPs have been investigated continuously, including polypyrrole (PPy), polyaniline (PANI), polythiophene (PT), poly(3,4-ethylenedioxythiophene) (PEDOT), trans-polyacetylene, and poly(p-phenylene vinylene) (PPV) [1]. In general, CPs possess alternating single (σ) and double (π) bonds, and these π -conjugated systems lend the CPs their inherent optical, electrochemical, and electrical/electronic properties. It is known that the parameters that most affect the physical properties of CPs are their conjugation length, degree of crystallinity, and intra- and inter-chain interactions.

CPs provide the advantages of chemical diversity, low density, flexibility, corrosion resistance, easy-to-control shape and morphology, and tunable conductivity over their existing inorganic counterparts [2,3]. However, the development of the properties of CPs has not been completely commensurate with those of their metallic and inorganic semiconductor counterparts. Consequently, CPs have been modified or hybridized with other heterogeneous material components to overcome their inherent limitations in terms of solubility, conductivity, and long-term stability. Judicious coupling of CPs with other materials can result in materials with attractive properties and new application

Conductive Mechanism

Inherent Molecular Structure

The electrical conductivity of a material is mainly determined by its electronic structure. The energy band theory is a useful way to visualize the differences among conductors, insulators, and semiconductors. The band gap is the energy difference between the valence and conduction bands of a material. When the valence band overlaps the conduction band, the valence electrons are free to move and propagate in the conduction band. This is an intrinsic characteristic of conductors. Semiconductors possess small energy gaps that electrons can cross upon excitation to reach the conduction band, leaving behind a hole. This allows both hole and electron charge transport, which allows the conduction of current. In the case of insulators, the band gap is too large to be crossed by electrons, and therefore they do not conduct electricity.

However, the energy band theory does not clearly explain why CPs, being organic materials, conduct electricity. Many studies have addressed the transport properties of CPs at the molecular level [23,24]. Here, polyacetylene is used as an example to illustrate the principles of conduction in CPs (Figure 1) because of its simple chemical structure and remarkably high electrical conductivity. From the perspective of chemists, the common electronic feature of pristine CPs is the presence of conjugated single and double bonds along the polymer skeleton. Both single and double bonds include a localized σ -bond, which forms a strong chemical bond. Additionally, each double bond also contains a localized π -bond, which is weaker.

Doping

CPs have been doped using different methods in order to achieve high conductivities [29]. Un-doped polymers have been reported as insulators but, upon doping, their conductivity can change from insulating to metallic. Owing to their unique chemical structures, however, the doping mechanism for CPs is completely different to that for their inorganic counterparts. Dopants in the polymer undergo redox processes in which charges are transferred with subsequent formation of charge carriers [30]. The role of the dopant is not only to withdraw electrons from the CP but also to add electrons to the CP backbone. A simple explanation of the effect of doping is that electrons are extracted from the highest occupied molecular orbital (HOMO) of the valence band (oxidation) or transferred to the lowest unoccupied molecular orbital (LUMO) of the conduction band (reduction). This oxidation/reduction process creates charge carriers in the form of polarons (radical ions), bipolarons (dications or dianions), or solitons in the polymer. CPs can be categorized into degenerate and non-degenerate systems based on their bond structures in the ground state. Degenerate polymers possess two identical geometric structures in the ground state while non-degenerate polymers exhibit two

different structures with different energies in the ground state (e.g., benzenoid and quinoid structures, where the energy of the benzenoid is lower than that of the quinoid). Solitons are known to be the charge carriers in degenerate systems such as polyacetylene. Conversely, polarons and bipolarons serve as the charge carriers in both degenerate and non-degenerate systems such as PPy and PT [31,32]. The movement of these charge carriers along polymer chains produces conductivity. In solid-state physics terminology, the oxidation and reduction processes correspond to p-type and n-type doping, respectively [10]. In p-type doping, the electron moves directly from the HOMO of the polymer to the dopant species and creates a hole in the polymer backbone. Conversely, in n-type doping, electrons from the dopant species move to the LUMO of the polymer, resulting in increased electron density. Hence, the density and mobility of charge carriers can be tuned by doping [33–36]. CPs can undergo both p-type doping and n-type doping, as shown in Figure 2. The doping process generates positive or negative polarons/bipolarons. These charge carriers are delocalized over the polymer chains, which facilitates the electronic conductivity. Generally, the negatively charged carriers in n-doping are not as stable as positively charged forms, which makes p-doping more popular in academic research as well as for practical applications. Representatively, the conductivity in PPy is an outcome of p-type doping. The PPy chain exhibits four distinct electronic band structures with different doping levels. In the undoped state, PPy is an insulator with a large band gap of approximately 3.16 eV (Figure 3a). Upon oxidation, a π -electron is removed from the neutral PPy chain, and a local deformation from the benzenoid structure to a quinoid one occurs to form a polaron [24,37]. This gives rise to two localized electronic levels within the band gap while the unpaired electron occupies the bonding state (Figure 3b). Upon further oxidation, a second electron is removed from the PPy chain, resulting in the formation of a doubly charged bipolaron (Figure 3c). The benzenoid-to-quinoid deformation is stronger in the bipolaron than in the polaron. As the polymer is further oxidized, an overlap between bipolarons occurs, leading to the formation of two narrow bipolaronic bands

CONCLUSION

We have described the electrical and electrochemical studies of CPs that have become important over the last few decades. Understanding these properties is of key importance in the development of CPs for application in various fields. The theoretical modeling of the transport properties of CPs is still challenging due to the extreme complexity of the polymeric conjugated systems. However, continuous study of the origins of conductivity and knowledge of doping reactions have made it possible to control the kinetics of the charge-transfer reactions. Electrons are either added to or extracted from the delocalized π -bonded polymer backbone, leading to the formation of charge carriers such as polarons, bipolarons, and solitons. The mobility of these carriers is affected by a variety of factors,

such as the dopant, temperature, and inherent structure. The conductivity can be improved successfully by electrochemical doping, both n-type and p-type, to induce an insulator-to-metal transition in the CPs. CPs offer many advantages in applications as in electrochemical capacitors, actuators, and sensors. However, the major disadvantages of CPs when used in these applications include their inferior long-term stability. Furthermore, the conductivity of CPs still has much room for improvement. The conductivity of CPs is lower than that of metals, and this has limited their use in specific applications such as transistors and memory devices. It is believed that overcoming these existing problems will make CPs strong candidates for a diverse range of future applications.

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CPs Conducting polymers

PPy Polypyrrole

PANI Polyaniline

PT Polythiophene

PEDOT Poly(3,4-ethylenedioxythiophene)

PPV Poly(p-phenylene vinylene)

HOMO Highest occupied molecular orbital

LUMO Lowest unoccupied molecular orbital

CSA Camphor sulfonic acid

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