Published: 28th June 2025

ANACHEM JOURNAL
ISSN: 2006-5221 (Online)

CONDUCTING POLYMERS: REVIEW ON CURRENT ADVANCES IN SYNTHESIS, CHALLENGES AND FUTURE PROSPECTS

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DOI: https://doi.org/10.5281/zenodo.15734035

ABSTRACT

When discussing electricity conduction, the medium most commonly used has always been metals. Still, these metals are not without limitations such as susceptibility to corrosion, aesthetic limitations, processability, and manipulability. Thus, the idea that polymers which are not constricted to these limitations could be viable alternatives is a giant leap in the electrical sector. These set of polymers, their advances in synthesis, applications, challenges and future prospects are reviewed.

Keywords: Bands, conducting, doping, insulators, polyacetylene, polymers, semiconductors.

INTRODUCTION

Some decades ago, the idea that plastics could conduct electricity seemed like a pipe dream, as plastics have always been synonymous with the term insulators. There have even been reported studies of plastics whose conductivity is very similar to that of copper. These plastics that conduct electricity are a type of metal containing polymers called conducting polymers (Inamuddin and Mazumder, 2024; Reynolds *et al*., 2019; Sreekala *et al*., 2023).

These conducting polymers tend to exhibit both the electrical conductivity of metals and the manipulability and processability of plastics (Inamuddin and Mazumder, 2024). The first conducting polymer was accidentally synthesized in the early 1970s when Hideki Shirakawa from the Tokyo Institute of Technology was attempting the polymerization of acetylene welding gas into polyacetylene (Inamuddin and Mazumder, 2024). The same researcher and his team then intentionally doped silver films with iodine to form an even more conductive

polyacetylene. These desirable properties of plastics, which are conferred on conducting polymers, range from corrosion resistance, aesthetics, and low specific gravity. The metallic constituent confers not only electrical conductivity, but also improved mechanical strength and thermal stability (Lu *et al*., 2020).

CONDUCTING POLYMERS

Conjugated polymers are also described as polymers whose backbone chains are composed of alternating double and single bonds. This setup thus creates overlapping orbitals having delocalized π-electrons, and these polymers are either insulators or semiconductors (Lu *et al*., 2020; Reynolds *et al*., 2019; Sreekala *et al*., 2023). These conjugated polymers are the types of polymers that can be modified into electrical conductors. Normally, the backbone of conjugated polymers is made up of adjoining sp^2 hybridized carbons; thus, one of the electrons in each of the carbons occupies its p_z orbital, these p_z orbitals collectively form the delocalized orbitals, thus the p_z electrons can be made highly mobile by the process known as doping (Reynolds *et al*., 2019; Sreekala *et al*., 2023).

The doping process systematically removes some of the delocalized electron leading to the formation of a one-dimensional electronic band by the conjugated p-orbitals. These bands can also be referred to as energy states, and this mobility of electrons leads to the transfer of current along the polymer. Electrons normally move between bands, but these electrons must contain a particular amount of energy to be able to move into a given band and these electrons require energy boosts to excite them into bands at higher energy levels (Lu *et al*., 2020). Normally, for electrons to move into a band, that band must be partially empty; that is to say, the band must not be empty or full (Kar, 2013). The process of electrical current mobility is in many ways similar to a relay race in which the baton (in this case 'electrons') is transferred from one runner to the other (in this case 'bands'), also the next runner must be ready and available to receive the baton (that is the band must not be full or empty). Unlike metals, which are excellent conductors owing to their partially filled bands, insulators and semiconductors either have full or empty energy bands (Chandrasekhar, 2018; Kar, 2013).

The highest occupied energy band is referred to as the valence band, while the subsequent energy band is referred to as the conduction band. In insulators, the gap in energy between these bands is very large, thus inhibiting the

mobility of electrons across these bands. In semiconductors, the gap is reduced but not small enough for the natural movement of electrons, thus the electron has to be boosted through light or heat sources for the electrons to be able to jump into the next energy band. Doping is used to geometrically increase the conductivity by either the addition of electrons to the valence band or the ejection of electrons from the valence band (Chandrasekhar, 2018; Lu *et al*., 2020).

THE DOPING CONCEPT

The process of removing electrons from the valence band is termed positive doping (p-doping). This is because the removal of negative electrons leads to a net positively charged molecule. In contrast, the addition of electrons into the valence band is referred to as negative doping (n-doping), as the additional electrons confer a net negative charge on the molecule (Reynolds *et al*., 2019; Sreekala *et al*., 2023).

p-Doping

As already explained, p-doping involves the removal of electrons, which is also the partial oxidation of the energy bands which make up the π-backbone of the polymer (Chandrasekhar, 2013). This is typically achieved through one of two processes: either the chemical process or the electrochemical process (Chandrasekhar, 2018).

Via the chemical process, iodine is normally used as the oxidizing agent. While the electrochemical process uses a solution made up of the monomer that makes up the conducting polymer and the dopant ion, two metal electrodes are immersed in the solution (Chandrasekhar, 2013; Kar, 2013). During the process, an electric potential is introduced into the electrochemical circuit, which knocks off electrons from the monomers that are close to the positive electrode; thus, the electron-deficient monomer polymerizes on the surface of the electrode (Kar, 2013). During the polymerization process, the electron-deficient monomer attracts the negatively-charged dopant ions, thus depositing a doped polymer film on the surface of the positive electrode, which can then be stripped off. The doping ion percentage is dependent on the magnitude of the positive charge on the electron-deficient monomer, which in turn is dependent on the electric potential introduced into the circuit (Chandrasekhar, 2013; Gupta, 2022).

n-Doping

This process involves the partial reduction of the energy bands through the addition of electrons, which can be accomplished either

through a chemical process or an electrochemical process. The chemical process utilizes sodium naphthalene as the dopant ion, while the electrochemical process is a cathodic reduction process (Chandrasekhar, 2013; Kar, 2013; Gupta, 2022).

CONDUCTING POLYMER ADVANCES

Polyacetylene: This was one of the first conducting polymers ever produced; the major constituent of its polymer backbone is polyene linear chains. There is also the possibility of substituting the hydrogen atoms attached to the carbon backbone with other pendant groups to confer other properties on the polymer (Bustamante and Scherlis, 2021; Liu *et al*., 2010). Doped polyacetylene is an excellent electrical conductor with conductivity ranging from 102 to 103 S cm^{-1}. Polyacetylene can be synthesized either through catalytic polymerization using Ziegler-Natta catalysts on acetylene monomer (Bustamante and Scherlis, 2021; Liu *et al*., 2010).

Polyaniline: This is currently the most utilized and stable conducting polymer. At a pH of less than three, polyaniline exhibits conductivity close to that of metal. The polymer backbone of polyaniline is comprised of a combination of quinoid ring and benzoid ring in different ratios, which leads to the formation of different variants of polyaniline, such as leucoemeraldine, which has a reduced state, pernigraniline, which has a fully oxidized state and emeraldine, which has a neutral state. For polyaniline to be an excellent conductor, it has to be partially oxidized (Assassi *et al*., 2023; Fisal *et al*., 2018; Yamaguchi *et al*., 2015).

Polypyrole: Due to its high stability and substantial conductivity, it is fast becoming an increasingly commercially viable conducting polymer. Polypyrole is normally prepared by the polymerization of pyrole monomer using the chemical oxidation process in the presence of hydrogen peroxide (Achour *et al*., 2018; Gahlot *et al*., 2021).

Poly (p-phenylene): these are comprised mostly of benezoid aromatic nuclei linked using carbon-to-carbon bonds. Their doped variant has been reported to exhibit high thermal stability and excellent electrical conductivity. They have also been reported to have excellent optical properties and blue light emission, which has led to their utilization in the manufacture of LEDs (Banerjee and Dutta, 2021; Baumgarten and Müllen, 2011).

Polythiophene: This is prepared mostly by electrochemical polymerization of a solution of thiophene and an electrolyte.

Polythiophene can have a conductivity of up to 100 s cm^{-1} when doped with an oxidizing agent such as iodine. Its excellent thermal stability, environmental stability, and high conductivity have led to its continuous use in the production of solar cells, due to its ability to form excellent contact with metal electrodes (Fan et al., 2022; Inamuddin and Mazumder, 2024; Lu *et al*., 2020).

Poly (p-phenylene vinylene): It is mainly synthesized through witting coupling reaction between a bisaldehyde and an aromatic bisphosphonium salt. It is the first conducting polymer whose electroluminescence property has led to its use in the fabrication of LEDs (Banerjee and Dutta, 2021; Kim and Ahn, 2020).

APPLICATIONS OF CONDUCTING POLYMERS

Polymeric Batteries: One of the earliest applications of conducting polymers has been in the manufacture of light-weight batteries. Of all the conducting polymers, polypyrole and polyaniline were reported to be the viable alternatives when used as the cathode in conjunction with lithium-aluminium alloy anode, while $LiBF_4$ or $LiClO_4$ was used as the electrolyte (Milczarek and Inganäs, 2012; Thomas *et al*., 2023). However, the major challenge with these batteries was their limited energy storage capacity and their comparatively poor charging-discharging cycles (Kumar *et al*., 2022; Milczarek and Inganäs, 2012; Thomas *et al*., 2023). In recent times, conducting polymer composites made from polyphenylene and an alkali-metal alloy have been developed and used as anodes in batteries, which have reported energy densities of approximately 65 mWh/g, compared to 39 mWh/g reported by standard nickel-cadmium batteries. This has thus refocused interests into the research of viable alternative polymeric batteries (Kumar *et al*., 2022; Milczarek and Inganäs, 2012; Thomas *et al*., 2023).

Electrochromic Displays: This is based on the principle that application of an electric potential can lead to a significant change in colour in these materials. A colour change has to do with a change in wavelength. This utilizes the principle of electrochemical doping and undoping of conducting polymers (Mu *et al*., 2022). In general, electrochemical doping of these polymers leads to adsorption of longer wavelengths; this is due to their very high adsorption coefficient in the visible range of the electromagnetic spectrum. For these conducting polymers to be viable in this application, only thin films of these materials should be needed to produce high contrast

and broad viewing angle in display devices (Mu *et al*., 2022). Conducting polymers such as polypyrole, polythiophene, and polyaniline have successfully been used to manufacture viable prototypes for display devices. One major drawback is the limited life cycle, which is currently approximately 10^6, unlike the desirable standard of > 10^7. Irrespective of this drawback, these materials have found application as electrochromic windows in automobiles and buildings and thus can be made for low light transmission and high light transmission during the day and night respectively (Mu *et al*., 2022).

Corrosion Inhibition: Traditionally metals are the go-to material for conducting electricity, but these metals are also prone to corrosion. Thus, in applications with high corrosion, such as LEDs used underwater and in saltwater mediums like swimming pools, conducting polymers are increasingly being found to be viable alternatives (Assassi *et al*., 2023; Kordas, 2020; Sambyal *et al*., 2017). Also, when the metals cannot be completely avoided, they are used as coatings for those metals, because the conducting polymers act as a corrosion-resistant barrier while still excellently transferring electrical currents through the metal conductors (Kordas, 2020; Sambyal *et al*., 2017).

Light Emitting Diodes: Another applicable property of conducting polymers is based on their electroluminescence and photoluminescence properties (Godlewski and Obarowska, 2013; Kim and Ahn, 2020). Electroluminescence is the emission of light when a voltage is applied to a material, while photoluminescence is the emission of light when the material is irradiated (Cheng *et al*., 2021; Rijith *et al*., 2021). One of the current applications of electroluminescence is in the production of LEDs, which have been manufactured using thin polyphenylene vinylene films (Godlewski and Obarowska, 2013; Kim and Ahn, 2020).

FUTURE PROSPECTS

There is currently extensive research into the formulation of conducting polymer composites that could help to reduce some of the limitations associated with its applications. Also, the incorporation of nanotechnology is currently at an advanced research stage, as this will be expected to enhance compatibility and proper interaction during doping and also during polymerization, thus creating conducting polymers having uniform conductivity across the entire material (Kausar, 2021).

There is also ongoing research into the manufacture of conducting polymers that are compatible with 3D printers, as their viability

will enable the production of more customizable and complex shapes, and reduce the overall production cost (Fan *et al*., 2022; Inamuddin and Mazumder, 2024; Lu *et al*., 2020).

CHALLENGES AND POSITED SOLUTIONS

One of the major challenges associated with conducting polymers, is its highly limited charge cycles when used in polymer batteries, but this can be controlled through exploration into the formulation and fabrication of conducting polymer composites that introduce other materials to aid the charge cycle limitation (Milczarek and Inganäs, 2012; Thomas *et al*., 2023). Due to the cytotoxicity and discrepancies in the in-vivo and in-vitro studies of conducting polymers, they have found limited application in the biomedical sector, because of the biocompatibility issues (Bhavsar and Tripathi, 2021; Khan *et al*., 2024; Yan *et al*., 2016). It is suggested that the compositing of these conducting polymers with biodegradable polymers could reduce these biomedical limitations (Bhavsar and Tripathi, 2021; Khan *et al*., 2024; Yan *et al*., 2016).

CONCLUSION

Conduction polymers are increasingly becoming a viable alternative to metal conductors, offering the added advantages of being corrosion-resistant and more aesthetically pleasing. The conducting polymers are merely doped variants of certain specialized polymers, these specialized polymers are naturally insulators or semiconductors before doping. Conducting polymers have found use in a lot of sectors.

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