Advances In Synthesis and Energy Applications of Conductive Polymers

Meryem Sena AKKUŞ [1*], Bülent Yeşilata[2]

[1] Energy Systems Engineering, Ankara Yıldırım Beyazıt University, Ankara
ORCID No: https://orcid.org/0000-0003-2550-550X
[2] Energy Systems Engineering, Ankara Yıldırım Beyazıt University, Ankara
ORCID No: https://orcid.org/0000-0002-1552-5403

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Abstract

This study provides a thorough summary of the latest advancements in conductive polymer manufacturing techniques and their diverse range of energy applications. Because of their distinctive electrical, optical, and electrochemical characteristics, conductive polymers have attracted a lot of attention and are now considered cutting-edge materials for energy-related technologies. The paper investigates a variety of synthesis medhods, including chemical, electrochemical polymerization, plasma polymerization, nano sized production etc. The focus is on adjusting synthesis parameters, such as dopants, functional groups, and nanostructured structures, to modify the characteristics of conductive polymers for certain energy uses. Furthermore, the important functions that these polymers play in a variety of energy conversion and storage technologies are thoroughly examined in this article. Elucidating their roles in improving energy density, cyclic stability, and power output, it highlights their importance in supercapacitors, batteries, and energy harvesting systems. In summary, this article presents a detailed on the synthesis techniques and diverse energy applications of conductive polymers, purposing to guide researchers, engineers, and practitioners toward harnessing for the development of energy technologies.

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1. INTRODUCTION

Today, the amount of energy used and produced by a society can be counted as an indicator of the level of welfare reached by developed countries. Consumption of natural resources continues at a faster rate to provide the energy needed for the sustainability of the economy and the development of other countries (Özkan et al., 2019). Fossil fuels are the most widely used energy source. There are studies on the possibilities of renewable, sustainable, and environmentally friendly energy sources due to the limited availability of fossil fuels and the damage they cause to the environment (Barreto et al., 2003). Ongoing scientific research is being driven by the growing demand for energy, particularly from renewable sources like sunlight, wind, nuclear, wave, and geothermal heat, etc.

*Resp author; e-mail: msakkus@aybu.edu.tr

These renewable energy sources do, however, vary with time and place. To deal with this variability, using energy harvesters in conjunction with converters has shown to be a workable solution.

Conductive polymers (CPs) are defined as a class of organic materials with electrical and optical properties similar to inorganic semiconductors. Materials science has been progressed in many technological applications, especially in electronic technology, with conductive polymer materials. The Nobel Prize in Chemistry was awarded to the discoverers of conductive polyacetylene in 2000 (Shirakawa et al., 2003). Although conductive polymers are at the forefront of their conductivity properties, they also have unique electronic, magnetic, wetting, optical properties, mechanical, and microwave absorption properties of these materials. Because of these features, it has many usage areas such as electronic devices, sensors, a catalyst, energy, and biomedicine etc. (Das & Prusty, 2012). These superior properties are the result of their chemical structure. They are conjugated and have a backbone of neighbouring sp2 hybridized orbitals. Therefore, delocalized π electrons are located throughout their backbone structure. Nevertheless, conjugation alone is not enough for conductivity. A dopant is required to alter the band structure of the semiconducting molecular structure backbone. The added dopant allows electrical transport by causing hole or electron mobility in the polymeric structure (Vandesteeg, 2007). In the CPs studies, primarily polyaniline (PANi) as well as poly(3,4-ethylenedioxythiophene) (PEDOT), polypyrrole (PPy), Polythiophenes (PTs) and polyphenylene vinylene (PPV) are investigated.

2. SYNTHESIS METHODS OF CPS

The main aim in the synthesis of CPs is to preserve the conjugated structure of the monomer during the synthesis process. This makes both monomer selection and polymerization process selection important. Most of the CPs monomers are chosen electron-rich molecules such as pyrroles, thiophenes. Such monomers are widely used as they undergo linear polymerization. CPs are synthesized by using many methods such as chemical, electrochemical polymerization, photochemical, concentrated emulsion, and plasma polymerization. The most widely used of these synthesis methods are chemical and electrochemical methods. However, recently, research on the synthesis and application of nanostructured CPs has also increased. Chemical method in the synthesis of CPs occurs through reduction or oxidation of the monomers followed by polymerization of the respective monomers. To obtain the desired quality and weight polymer, the oligomers and/or low molecular weight polymers must be sufficiently reactive and soluble in the medium to polymerize. In addition, it allows the specific oxidant selection to selectively generate cation radicals at the appropriate position on the selected monomer. The advantage of this method, the mass production cost is acceptable. There are also disadvantages of this synthesis method such as not being able to control the oxidation step and the obtained product containing impurities (Kumar et al., 2015).

Electrochemical reaction carries out oxidation of the monomer in the supporting electrolyte solution. By applying an external potential, a reactive radical cation is produced. After the first oxidation step, two methods are possible for the formation of the polymer. In the first method, the radical cation of the monomer can combine with the monomer to form a dimer. In the second method, two radical cations can combine to form a dimer, also. Next, the synthesized dimer is oxidized again and then initiates electroactive polymer formation (Naveen et al., 2017; Zhang et al., 2018). The advantages of this polymerization are that the reaction rate and doping method can be controlled. Besides, it is a simple, selective, reproducible method and easy to control the film thickness and molar mass. The disadvantage of this method is that the products obtained by this method are insoluble polymers, also (Kumar et al., 2015; Zhang et al., 2018).

In concentrated emulsion method polymerization method, there are two phrases that do not mix with each other. The monomer phase is dispersed as an emulsion in the dispersion phase. By using various emulsifiers, the monomer phase is stably emulsified in the dispersion phase. In emulsion polymerization, water is generally used as the emulsion medium. The monomer is dispersed in this medium with the help of an emulsifying agent. The polymerization initiator is a water-soluble substance and produces free radicals. The emulsifier is an active substance and contains hydrophilic and hydrophobic groups (Awuzie, 2017). The desired product is precipitated and then purified. The emulsifier has two important advantages in emulsion polymerization. The first is to influence the polymerization locus and thereby increase the molecular weight of the product. The second is to improve the solubility, conductivity and processability of the synthesized polymers (Palaniappan & John, 2008).

Plasma polymerization is one of the new processes to produce thin films from a group of organic and organometallic materials. These films are rather high cross-linked. Therefore, they are insoluble in water, thermally and chemically stable, and have high mechanical strength. In addition, these films can easily adhere to surfaces such as polymers, glass, or metal (Biederman, 2004). As a result of these extraordinary properties, CPs synthesized by this method have been widely used in some applications such as in membrane systems, biomedical materials, electronics, optical devices, etc. (Kumar et al., 2015).

When CPs are designed and synthesized in nanoscale, many characteristic properties are improved. Therefore, they have better device performance in energy applications compared to their bulk solid CPs. Until now, some synthesis strategies have been improved to produce many CPs materials. Two main synthesis strategies, template-based and template-free, are applied, taking into account “morphology control” and “size control” of nano sized CPs (Yin & Zheng, 2012). In template-based synthesis is a significant and effective method for the synthesis of nano CPs with the wanted shape and controlled dimensions. This synthesis strategy means a process using nanostructured materials as templates, providing the spatial confinement function to encourage 1D or 0D growth of CPs on their inner pores and/or outer surfaces supported by some physical and chemical measures (Zhang et al., 2018). In the template-free synthesis strategy, nanostructured CPs are produced without any templates. Therefore, it is thought a simple and economic method compared with the template-based strategy. In this process, the nanostructured CPs can be synthesized by controlling the reaction conditions, such as temperature, a molar ratio of dopant to monomer, pressure, etc. (Zhang et al., 2018).

3. ENERGY APPLICATION OF CPS

Due to the attractive properties of CPs, these materials make them promising candidates for applications in high-performance energy devices. Therefore, this advanced material plays an important role as electrodes, catalysts, electrode/catalyst support, and so on in energy conversion and storage applications such as solar cells, fuel cells, lithium-ion batteries, supercapacitors. Remarkable advances in these applications of CPs are reviewed in this section, where information on the relations between the material structures and some device performances are given below.

3.1 Solar Cell

Solar cells, one of the effective and promising devices, convert sunlight energy into electrical energy. In recent years, organic or hybrid photovoltaic devices, including polymer solar cells (PSCs), hybrid solar cells (HSCs), and organic tandem solar cells (OTSCs), have been attractive because of their advantages such as light weight, flexibility, thin, cost-effective production, etc. It is interesting compared to the silicon solar cells sold, and research are increasing day by day. Nowadays, the progress on the synthesis of CPs as well as the fabrication of especially 0D or 1D CPs materials and improved performance, has paved a way for next generation solar cells types (Roncali, 2011). PSCs consist of an anode, a cathode, an n-type layer, and a p-type layer. In addition, to produce PSCs, it is obligatory to use transparent anode with organic-based materials. CPs can be used in these layers. For example; PTh derivatives (P3HT, P3OT, etc.), are the commonly used p-type materials, whereas fullerene and its derivatives are the most significant n-type materials (Murad et al., 2020). In addition, CPs materials play an important role in the construction of HSC, also. In this solar cell, p-type electron donor is generally used CPs, whereas n-type electron acceptor are used inorganic semiconductors such as ZnO, TiO_2, CdS, Si, etc., (Yin & Zheng, 2012). The efficiency of this solar cell was higher than the organic solar cell. Such a combined design has been a more effective design than the case in solar cells containing only organic or only inorganic. The OTSC structure is more complex than other organic solar cells. Its architecture includes the stacking of two subcell units. The first subcell is designed to capture short-wavelength energetic photons, whereas the second subcell is also designed to receive long-wavelength energetic photons (Zheng et al., 2015). Therefore, the OTSCs demonstrate the potential to come through a wide solar spectrum and solve associated problems concerning the thickness of the active organic absorbing layers in single junctions because of low carrier mobility (M. Li et al., 2017). For OTSC, examples of the large band gap polymers are given poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylene vinylene], P3HT, and poly((2,7-(9,9-dioctyl)-fluorene)-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothia-diazole) whereas examples of the small band gap polymer material poly(5,7-di-2-thienyl-2,3-bis(3,5-di(2-ethylhexyloxy)phenyl)-thieno[3,4-b]pyrazine) (PTBEHT) is given. All large band gap polymers can be used complementary with PTBEHT (Hadipour et al., 2008; Li et al., 2013). In another study carried out TiOx was coated as a dense and homogeneous film on the BHJ solar cell. Smooth and sharp interfaces in the TiO_x/PEDOT: PSS interconnect layer have been found to produce a unified direction of the electric field located throughout the tandem cells. They found that an organic tandem cell with $TiO_{1.76}$/PEDOT: PSS interconnect layer provides a power conversion efficiency of 20.27%. This efficiency is a remarkable result among organic solar cells so far (Zheng et al., 2022).

3.2 Fuel Cells

Fuel cells convert the chemical energy of a fuel directly into electricity by electrochemical reactions. Fuel cells that use polymeric material in their structure are fuel cells with polymer electrolyte membranes such as proton exchange membrane fuel cells (PEMFC) and direct methanol fuel cells (DMFC). In fuel cells with a polymer electrolyte membrane, the proton exchange membrane is the most important part. This membrane both prevents the separation of anode and cathode and prevents the mixing of reactant gases. In addition, this membrane is selectively permeable. As they carry protons from the anode to the cathode, they prevent electron passage. This polymeric membrane should be good chemical, mechanical and thermal stability, high proton conductivity, low cost, and meet the needs of the fuel cells (Gubler & Scherer, 2010). Commercially, perfluorosulfonic acid polymers materials such as Nafion (Du Pont, USA), Flemion (Asahi Glass, Japan), and Aciplex (Asahi Kasei, Japan) are used as membranes in polymeric fuel cell systems (Saito et al., 2004). Various organic membranes have been researched and improved with high performance compared with the commercial product. One of them is the development of a CP based PEM (Kausar, 2017). CPs based fuel cell operating at high temperatures has been identified as an up-and-coming resolution to meet technical problems. Some examples of literature, Polybenzimidazole (PBI), acid-doped PBI (Jensen et al., 2005), poli(2,5-benzimidazol) (Asensio et al., 2003), poly(etheretherketone) (PEEK) /

poly (benzimidazole) (PBI) (Kerres et al., 1999), SPEEK/PANI (X. Li et al., 2006; Nagarale et al., 2006) have been successfully used as membranes for fuel cell systems. These membranes have high conductivity, thermal stability, and mechanical properties. They can be operated at higher temperatures than Nafion's operating temperature.

3.3 Lithium Ion Batteries

CPs are very up-and-coming materials for organic-inorganic composites in lithium-ion batteries because of their lightweight, multi-cycle working, high electrical conductivity, and high coulombic efficiency. These problems are overcome by the use of conductive polymers in the case of poor conductivity and insufficient cycling life problems, which are encountered only in batteries made of inorganic materials. CPs materials with inorganic matters could be proper as an electrode (Sengodu & Deshmukh, 2015). In addition, nanostructured PCs have a high specific capacity and have good cycling performance, so they are very attractive to use as electrodes in Li-ion battery applications (Malta et al., 2003). To get better the entrapment of polysulfide, Cui et al. used encapsulated carbon/sulphur particles with PEDOT: PSS. This work provided an efficient alternative to trap polysulfides and minimize the resolution of polysulfides from cathodes. In addition, as a result of this study, it was determined that the discharge capacity in the 150th cycle was above 600 mA h g^{-1} (Yang et al., 2011). In another study, the performance of Li-ion battery was investigated when silicon-PANI composite is used as anode. The result is a high-performance Li-ion battery with a current density of 6.0 A g^{-1}, a capacity protection of over 90%, and a cycle life of 5,000 cycles (Wu et al., 2013).

3.4 Supercapacitors

Supercapacitors are the most interesting energy storage devices that can be used in application areas such as electric transportation vehicles and uninterruptible power supplies. Compared to lithium-ion batteries, these energy storage devices have higher specific power. CPs are used as electrodes in composite structure in supercapacitors (Das & Prusty, 2012). Multiple or binary composites based on nano sized PPy, PANI and PEDOT have very good performance in supercapacitors at electrodes (Gao, 2017). Wang et al. investigated the nanostructured PEDOT/ nano cellulose fiber composite in supercapacitors. The PEDOT was covered as a thin layer on nano cellulose fibers. The composite shows high specific capacitance (90 F g^{-1}) with 1.7 Ω equivalent series resistance and capacitance retention of 93% after 15,000 cycles with high cycling stability. In addition, it has 1.5 mW h cm^{-3} and 1470 mW cm^{-3}, volumetric energy, and power density, respectively (Wang et al., 2016). In another study was studied the supercapacitor performance of the carbon-PANI composite using a core-shell model of nanoporous carbon derived from a metal-organic framework and a CP. These nanocomposites showed a specific capacitance value in the range of 300–1100 F g^{-1}, high specific energy of 21 W h kg^{-1}, high specific power of 12 kW kg^{-1}, and excellent capacitance retention of 86% after 20,000 cycles (Salunkhe et al., 2016).

4 CONCLUSION

In conclusion, this comprehensive investigation of the synthesis processes of conductive polymers and their use in energy storage and energy harvesting applications highlights their critical role in expanding the field of contemporary energy technologies. This discussion of synthesis processes has demonstrated the adaptability and tunability of these materials, providing a range of ways to customize their characteristics, like conductivity, stability, and morphology, to meet particular application needs. The enormous potential of conductive polymers is highlighted by the insights gained from their use in energy devices, such as solar cell, fuel cell, batteries, supercapacitors, etc.

They have the potential to improve energy practice performance, cyclic stability, and power delivery by acting as active materials, electrodes, or conductive additives.
The future of conductive polymers essentially consists of ongoing improvement, a wider range of applications, sustainable production techniques, functional integration into different technologies, the creation of sophisticated composites, and getting past commercialization and regulatory obstacles. Together, these paths open the door for conductive polymers to be widely used in various sectors and technologies.

Conflicts of Interest

The authors declared that there is no conflict of interest

Contribution of Authors

Designed the study, and wrote the manuscript: M. S. Akkuş, Research mentor, supervision: B. Yeşilata

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