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Recent Advances in Conducting Polymers: Applications in Electrochemistry

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Abstract

Scientists define conductive polymers as materials with highly reversible redox behaviour and unusual plastic-metal combination properties. Researchers have largely considered them for diverse applications due to their multifunctional characteristics, such as simple synthesis, acceptable environmental stability, and beneficial optical, electronic, and mechanical features. As a result, one of their distinguishing features is their ability to catalyze multiple electrode reactions. A thin layer of conducting polymer deposited on the substrate electrode surface can boost the kinetics of several solution species during the electrode process. Such electrocatalytic procedures using modified conducting polymer electrodes have the potential to be useful in a wide range of applied electrochemistry fields. This article looks at some of the most recent applications of conductive polymers as active electrode materials in energy storage, electrochemical sensing, and conversion fields like electrochemical supercapacitors, lithium-ion batteries, fuel cells, and solar cells.

***Keywords:** Environmental stability; Supercapacitors; Electrode materials; Solar cells*

Introduction

It is well understood that electrochemistry refers to phenomena in which a chemical modification is caused by electric forces and, conversely, chemical processes cause electric forces. This field is concerned with the properties and behaviours of solid and liquid electrolytic conductors. Many of these phenomena occur at the electrolytic and electronic conductor interfaces, where the electric charge passage is linked to a redox chemical reaction. This rate of reaction can be tracked using an electric current with increased sensitivity. The contacts comprise the electrodes of galvanic cells, whic h can be used to convert chemicals to electrical energy as batteries or to generate chemical products through electrolysis.

The development of novel techniques for performing fast in situ analyses has been regarded as a major challenge because they offer high sensitivity and accuracy for the detection of diverse materials with varying properties in real samples. Experts in the field have demonstrated that electroanalytical procedures would be one of the more promising alternatives for quantitative and qualitative analyses in place of traditional techniques. Benefits of electrochemical sensing mechanisms include simplified instruments, miniaturization, increased selectivity and sensitivity, simplified utilization, minor sample pretreatment, portability, and shorter analysis time. To put it another way, electrodes can detect substances found in the host while causing no harm to the host system. Nonetheless, electrochemical sensors are limited by electrochemically active interference in the sample, poor stability, a difficult electron transfer pathway, and Lower Limits of Detection (LOD) and sensitivity. As a result, various electrochemical procedures are combined with various sensing electrodes to improve their LOD and sensitivity via electrode material modification.

Because of the abundance of energy resources in nature, energy storage and conversion play an important role in energy conservation and utilization. Notably, a few hours of storage time is critical in the majority of applications; however, a few months

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of storage time is sometimes required. Because of its flexibility, higher energy conversion efficiency, and ease of maintenance, Electrochemical Energy Storage (EES) technology has been introduced as an encouraging tool for the storage of electricity in small- and large-scale applications.

It is worth noting that the use of electrochemical energy storage and conversion instruments allows for the storage of surplus energy when there is more supply than demand, and its release when there is more demand than supply. This results in increased grid efficiency, reliability, and lower costs. On the one hand, grid-scale energy storage necessitates electrochemical machines with appropriate power and energy output characteristics, as well as a longer cycle life, higher efficiency, and lower costs. As a result, rapid advancements in the development of electroactive substances for EES tools provided numerous appealing organic mechanisms suitable for higher power and energy uses.

For the first time, Lethebyin demonstrated the electrochemical procurement and description of polyaniline (PANI) created by oxidising aniline on a platinum electrode in dilute sulfuric acid. As a result, the conductivity of polyacetylene was investigated and increased tenfold by using iodine vapours. Polyacetylene instability in air has resulted in the discovery of numerous, novel Conducting Polymers (CPs) for use in basic research and industrial applications. As a result, since Heeger, MacDiarmid, and Shirakawa were awarded the Nobel Prize in Chemistry in 2000 for their pioneering work on CPs, academic and industrial researchers have paid close attention to these materials. Earlier research on these materials focused on the true mechanism of PolyPyrrole (PPy) formation. Park's group studied CPs electrochemistry extensively and demonstrated the autocatalytic growth system of PANI with its growth kinetics on the electrode surface.

CPs have generally been introduced as one of the classes of organic polymers with metallic or semiconductor features, such as magnetic, electrical, optical, and electronic properties, in order to retain the characteristics of conventional organic polymers, such as simpler synthesis, corrosion resistance, and lower costs. These materials can be insulators or semiconductors in neutral or undoped form, which can be converted to doped form via redox reaction to form delocalized charge carriers. However, one advantage of CPs over many organic polymers is their adjustable chemical structures, which can be changed to change the conductivity of the polymer. CPs have charge mobility, as well as p-electron backbones, which handle their unusual electronic properties such as lower energy optical transition, better electrical conductivity, higher surface area, high electron affinity, and mechanical flexibility. Conjugation length, degree of crystallinity, and intra and inter-chain interactions are the most effective parameters in constructing the physical properties of CPs.

Anodic oxidation of appropriate monomers, such as thiophene, aniline, and others, is one of the applicable methods for preparing CPs. The formation of oligomers, nucleation and growth steps, and the formation of polymeric materials are the most important aspects for clarifying the mechanism of electropolymerization from the standpoint of molecular electrochemistry. Mechanistic details are important for optimizing electropolymerization conditions. They are crucial in determining the quality of the CPs produced. The analysis of the "doping" process is a focal point of electrochemical research. Even in the early stages of CP research, it was clear that these processes could not be compared to traditional inorganic semiconductor doping. This means that the doping process corresponds to redox reactions in the polymer matrix in electrochemical terms. It is critical to understand the phenomenology of such redox reactions, which occur at the maximum level of oxidation before material degradation.

Experts in the field, on the other hand, have been significantly drawn to CPs due to their respective potent applications in energy storage and conversion, electrochemical sensors, and so on. As a result, this review focuses on new studies of CPs as I electrodes for electrochemical sensors and (ii) electrochemical energy storage and conversion tools such as supercapacitors, fuel cells, Lithium-Ion Batteries (LIBs), and solar cells.

Conducting polymers' electrochemical properties

Polyacetylene, an organic polymer discovered in 1977, exhibited a unique, high electronic conductivity for organic material when doped with iodine. Researchers have since studied conducting polymers due to their unique electrical properties. These materials, unlike traditional organic polymers, have properties such as electrical conductivity, higher electron affinity, and redox activities.

These materials contain a electron backbone that controls unusual electronic properties such as electrical conductivity, lower energy optical transitions, higher electron affinity, and lower ionization potential. Furthermore, the conducting polymer's extended -conjugated system has alternating single- and double-bonds along the polymer chain.

It is worth noting that the conduction mechanism in these polymers is extremely complicated because they exhibit conductivity over a range of approximately 15 orders of magnitude, and several of them contain diverse mechanisms in distinct regimes. Electrical conductivity in conducting polymers has increased by orders of magnitude. Furthermore, CPs can be electrochemically

doped, implying that CPs oxidation results in a p-doped state and CPs reduction results in an n-doped state. The conductivity of CPs may be controlled by redox reactions. Electrochemical preparation techniques can address the polymer's properties, morphology, thickness, and conductivity. For explaining the electronic phenomena in such systems, researchers have generally used the terms soliton, polaron, and bipolar. Conjugation length, polaron length, overall chain length, and charge transfer to nearby molecules all influence conductivity in conducting polymers. Several models based on inter-soliton hopping, hopping between localized states aided by lattice vibrations, intra-chain hopping of bipolarons, varied range hopping in three sizes, and the charging energy restricting tunnelling between conducting domains could justify such conditions.

It is possible to functionalize CPs and monomers with unique materials to tailor their properties. As a result, adding substituents improves the performance and physicochemical properties of the main polymer chain, such as improved mechanical and electrical properties. It is possible to prepare CPs composites from strongly conductive nanomaterials as well as catalysts to improve CPs properties.

Conducting polymer applications

Electrochemical detection

According to the research, electrochemical sensors and biosensors are electrochemical cells with three or two electrodes. A typical three-electrode system consists of a reference, counter, and working electrode; the working electrode is made of a chemically stable solid conductive substance such as gold, carbon, or platinum; the reference electrode is usually made of silver metal coated with a layer of silver chloride (Ag/AgCl), and a platinum wire is used as an auxiliary electrode. A two-electrode system, on the other hand, consists of only the reference and working electrodes. As a result, electrochemical procedures can be divided into three types of measurements: (i) current (voltammetric & amperometric), (ii) potential difference (potentiometry), and (iii) impedance (electrochemical impedance spectroscopy), with bio-sensors based on current measurements being the most widely used. Electrochemical sensors and biosensors have been credited with making significant contributions to fields as diverse as medical diagnosis, medicine, the environment, and food analysis. Because of their distinct advantages over other substances, conducting polymers have been shown to make an encouraging contribution to the development of the most recent electrochemical biosensors and sensors. Notably, the recovery time, responsivity, higher selectivity and sensitivity, and reasonable stability all help to produce an acceptable sensor and its function. In general, the presence of a p-conjugated mechanism in the charge transfer of conducting polymers resulted in the provision of an appropriate carrier for transferring electrons from the redox-active centre to the electrode surface.

As previously stated, experts in the field of energy storage are increasingly considering electric vehicles, grid-scale storage, and portable electronics for the optimal utilization of renewable energy resources such as solar and wind energies. As a result, research into novel technologies for the generation and storage of electrical energy should be prioritized. As the novel substances are synthesized and prepared, a number of environmentally friendly energy conversion and storage mechanisms, such as super capacitors, solar cells, LIB, and fuel cells, will be strongly designed. Conducting polymers have been regarded as encouraging substances for converting and storing energy due to their metal-like conductivity and reversible electrochemical doping/de-doping capability. Molecular backbones are often made up of conjugated double bonds; moreover, heavily conjugated polymer chains can be reversibly assigned electrochemical properties via a doping/de-doping technique. As a result, by modulating and controlling the doping levels, their conductivity may be altered in various ranges between 1010 and 104 S cm1, spanning the whole spectrum from insulators to semiconductors to conductors. These conducting polymers retain the advantages of traditional polymers, such as cheaper cost, easier procurement, a sufficient affinity for a variety of other chemicals, and improved durability and flexibility. Finally, the CPs, notably PPy PANI and PEDOT, offer sufficient potential for utilization as active electrode materials in electrochemical applications.

It is worth noting that, while developing electroanalytical sensing mechanisms to determine various analytes, sensing electrodes were frequently modified with appropriate substances to achieve the desired increase in selectivity and sensitivity. The majority of electrocatalytic materials are composed of noble or transition metal elements, either as pure electronic conducting metals or alloys or as electronic semiconductors. As a result, many active research efforts have focused on the substitution of precious metals with low-cost organic compounds. Well-defined 2D covalent organic polymers and carbon organic frameworks, for example, behave similarly to CPs in that they contain -conjugated polymeric layers containing heterocycles and aromatic moieties with precisely controlled molecular structures. Certain redox reactions can be catalysed by CPs due to their intrinsic electrocatalytic properties. It is also possible to incorporate metals into the inter-chain cavities of these materials in order to generate electrocatalysts. CPs have also been used to immobilize redox mediators, resulting in increased homogeneous electron transfer in the catalytic cycle. This

method is based on the efficient immobilization of biomolecules such as proteins and enzymes via very strong interactions with avidin via biotin affinity coupling. As a result of their high conductivity and other properties discussed previously, they are suitable as catalysts for a variety of redox reactions. According to the findings, designing and building CPs-modified electrodes is a highly efficient process in electrochemical sensor technology.

Drug testing

In 2017, one of the voltammetric sensors for streptomycin (STR) trace analyses was described. This sensor was created by electrochemically reducing graphene oxide with a glassy carbon electrode (GCE) modified with a STR-imprinted poly(pyrrole-3-carboxy acid) (PPy3C) film (ERGO). The ERGO was first deposited on the GCE surface via electroreduction and the deposition of a STR-imprinted PPy3C film. The sensor's features and morphology were then characterized using Differential Pulse Voltammetry (DPV), Scanning Electron Microscopy (SEM), and Cyclic Voltammetry (CV). The sensor for STR displayed two linear concentration ranges based on optimal conditions: 2 to 80 and 80 to 1000 nM. It also had a LOD of 0.5 nM, was practicable, and had good molecular recognition.

Environmental pollution examination

Braik created a new highly sensitive electrochemical biosensor by combining superoxide dismutase and MWCNTs with the conducting polymer poly(3,4-ethylene-dioxythiophene) (PEDOT) in various configurations. After characterising the materials, researchers optimised the experimental conditions and specified the analytical variables of superoxide dismutase biosensors based on the PEDOT/CNT or CNT/PEDOT-modified GCE, as well as those with only one component (MWCNT, PEDOT). The biosensor containing CNTs on top of PEDOT demonstrated the most acceptable analytical function, which was caused by the synergistic effects with the rapid and selective responses to O^{2-} , the higher sensitivity of ~1115 µA $cm^{-2}M^{-1}$ and lower LOD of 1 µM, which have been used to determine the antioxidant capacity of beverages. Within two months, this biosensor demonstrated significant stability and slightly increased its initial sensitivity.

Food examination

The hydrothermal method was used by the scientists to prepare the MoS_2/graphene-carbon nanotubes (MoS_2/GN-CNTs) nanocomposite. This nanocomposite exhibited higher electrochemical sensitivity toward luteolin by combining the higher catalysis of MoS_2 with the better electronic conductivity of GN-CNTs. To improve selectivity, a MIP film based on carbazole monomer and luteolin template was electropolymerized and deposited. The analysis revealed that the resultant electrochemical sensor MIP/MoS_2/GN-CNTs/GCE performed better. Furthermore, the LOD and linear detection range were 9.0 nM and 0.040–2.0 mM (S/N = 3), respectively, while the sensitivity was 381.3 mA mM^{-1} cm^{-2}. The results showed that there was no interference from 1000-fold concentrations of K^+, Na^+, Cl, Ca^{2+}, NO^3, Mg^{2+}, SO_4^{2-}, CO_3^{2-}, 500-fold concentrations of glucose and mannitol, 250-fold concentrations of cysteine, lysine, glycine, oxalic acid, and citric acid, and 100-fold concentrations of urea, DA, and ascorbic acid with luteolin detection. Furthermore, 5-fold concentrations of the analogues rutin, naringenin, and catechin, as well as 2-fold concentrations of quercetin, morin, and kaempferide, had no effect on the detection. As a result, the researchers used their sensor to determine luteolin in carrot and chrysanthemum tea samples, with results that were consistent with those obtained using high-performance liquid chromatography.

Storage and conversion of energy

Because of the depletion of fossil fuels, experts in the field consider energy to be the most pressing global issue. To deliver maximum power, energy storage devices require electrode materials with high electronic conductivity. Because of their wide range of conductivities, from semiconductor (10^{-11} to 10^{-3} S cm^{-1}) to metal (10^{-1} to 10^{-6} S cm^{-1}) behaviour, CPs are very appealing materials. Controlling the synthetic parameters (e.g., doping agent, temperature, pH, etc.) or designing different morphologies, surface area, redox activity, and so on can improve their charge storage. When compared to carbonaceous electrode materials, CPs have a very high current density and are inexpensive. Taking PANI as an example, a PANI-based supercapacitor device can achieve a specific energy of 10 W h kg^{-1} with a slightly lower specific power of 2 kW kg^{-1}, whereas a carbon-based supercapacitor device can only achieve a specific power of 3 to 4 kW kg^{-1} and a specific energy of 3 to 5 W h kg^{-1}. Because of their high charge/discharge cycling rate, high conductivity, large surface area, high specific capacitance, and good redox reversibility, CPs are used in energy storage devices in particular. Conducting polymers have high specific capacitance values in general and may be useful materials for developing the next generation of energy storage and conversion.

Conclusion

Electrochemical sensors and biosensors have been credited with making significant contributions to fields as diverse as medical diagnosis, medicine, the environment, and food analysis. Because of their distinct advantages over other substances, conducting polymers have been shown to make an encouraging contribution to the development of the most recent electrochemical biosensors and sensors. Notably, the recovery time, responsivity, higher selectivity and sensitivity, and reasonable stability all help to produce an acceptable sensor and its function. In general, the presence of a p-conjugated mechanism in the charge transfer of conducting polymers resulted in the provision of an appropriate carrier for transferring electrons from the redox-active centre to the electrode surface.

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