



Polyvinylpyridine-based electrodes: sensors and electrochemical applications

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Abstract

Polyvinylpyridine (PVPy) is a linearly structured polymer-containing aromatic heterocyclic compound. PVPy is easily prepared via radical polymerization of vinylpyridine using an initiator of azobisisobutyronitrile in which different haloalkanes can be used for the quaternization of pyridine units. The pyridine moieties of the polymer backbone can lead to an enhanced electrical conductivity in this polymeric material. For this reason, this vinyl polymer has been extensively applied in electrode organization for electrochemical applications. Thus, we aimed to review the uses of PVPy in the electrode structure and/or its application for the modification of electrochemical electrodes in systems such as sensors for monitoring and determining humidity and various chemicals.

Keywords Polymer · Electrodes · PVPy · Sensor · Electrochemical

Introduction

PVPy synthesis methods

Polyvinylpyridine (PVPy) is the most notable polymer that has the potential for use in electrical applications and drug delivery; it can also be used as a chemical reagent. The vinyl group of the monomer can be attached to the pyridine unit in a para position to prepare (poly(4-vinylpyridine) (P4VP)). Due to this characteristic, PVPy has been synthesized by anionic graft polymerization of 4-vinyl pyridine in starch and dextrin [1]; block anionic copolymerization of poly(para-xylylene), polystyrene, and polyvinylpyridine [2]; and polymerization of 4VP in the presence of a quaternization agent, ammonium persulfate, and cross-linkers [3]. PVPy synthesis can also be

achieved by ionic mechanisms using stereospecific polymerization [4], by electrochemical polymerization of 4VP on the surface of graphite [5], and via electrochemical copolymerization of aniline monomers and 4VP [6].

PVPy properties

PVPy can connect to various reagents such as oxidizing agents (i.e., periodate, iodate, and bromates) for the oxidation of chemicals. The benefits of these polymer-supporting reagents can be ascribed to their ease of work-up, recovery, and separation from reaction media via simple and facile filtration procedures [7]. PVPy, due to its pyridine ring, can be quaternized for the removal of anionic compounds such as chromate or arsenates from the aqueous medium in order to promote ion exchange and ion pairing reactions in aqueous environments. Quaternization leads to a deficiency in the electron density in the pyridine ring; thus, N atoms are more attracted toward nucleophile compounds [8]. PVPy has attracted the attention of many researchers from the electric and electrochemical fields due to its conductivity and capability for doping. PVPy has frequently been employed in various forms (e.g., blends, block copolymers, and composites) to synthesize conductive materials for electrical usage [9–19]. For example, CO was electrocatalytically reduced by modification of the graphite electrode which contained a cobalt phthalocyanine P4VP membrane. PVPy can also be used to

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adsorb chemicals and metal ions from various solutions. This capability can be ascribed to the N atoms and aromatic ring in the PVPy structure. Thus, PVPy application to remove phenols from solutions can be a reasonable aim. For example, the copolymer vinyl pyridine-divinylbenzene was used for this purpose, and it showed an excellent capacity for removing phenols (3000–3500 mg L⁻¹) from wastewater [20]. From PVPy applications as an adsorbent, quaternized P4VP can be used for the selective extraction of mercury [21], and quaternized P4VP/Hg film electrodes can be used for selective determination of Pb²⁺ using voltammetry [22].

PVPy applications

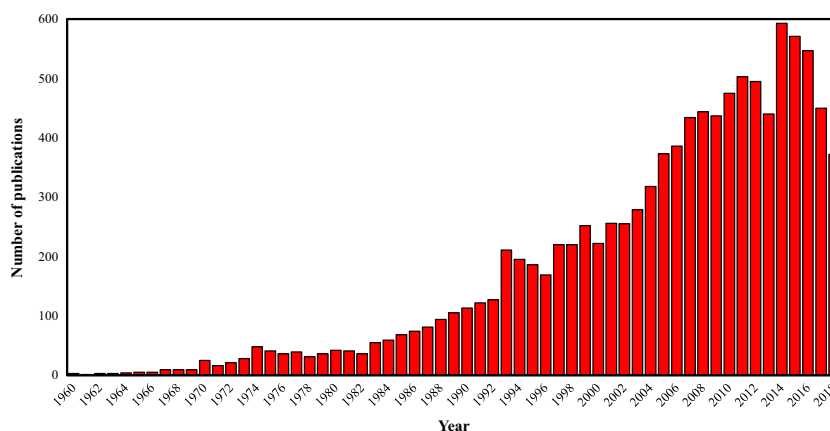
Figure 1 shows the increase in the number of publications on PVPy/P4VP since 1960 according to scinapse, an academic search engine. The high electrical conductivity and good redox mediation potential are advantages of P4VP in polymer nanocomposite-based electrodes [10, 15, 17]. Thus, it is a good candidate to improve the electrocatalytic activity, stability, and electron transfer kinetics of various electrodes [10–14]. It is worth mentioning that P4VP is a hydrophobic polymer in polar solvents, while in aqueous media at low pH, it is quaternized and is as the cationic polyelectrolytes [14]. Because of the health and environmental problems resulting from various contaminants such as heavy metal ions and organic materials, different researchers tend to invent new adsorbents to remove pollutants from aqueous solutions. PVPy, also owning a unique chemical structure, has been used for this purpose. For example, cross-linked P4VP was applied as a sorbent for the removal of phenolic compounds [23], macroporous poly P4VP was used for the adsorption of sulfur dioxide in aqueous solutions [24], and quaternized and cross-linked P4VP resin was employed as an efficient sorbent for selective mercury extraction from aqueous solutions [25]. PVPy, due to its structural and chemical characteristics, has attracted the attention of organic chemists and has been intensively applied to oxidize various organic chemicals. For

example, PVPy-based oxidation reagents have been applied for the oxidation of alcohols [26]; efficient and selective oxidation of different organic compounds [27]; good-yielding oxidation of methyl substituted cycloalkanes [28]; oxidative deprotection of trimethylsilyl ethers and selective oxidization of alcohols [29]; oxidation of primary and secondary alcohols, allylic alcohols, thiols, acyloins, and hydroquinones [30]; versatile, effective, and mild oxidation of alcohols, thiols, oximes, and amines [31]; oxidation of benzylic and allylic alcohols, aliphatic primary and secondary alcohols, olefinic and acetylenic double bonds, aromatic hydrocarbons, ketals, thiols, and oximes [32]; and oxidation of allylic and benzylic alcohols [33]. PVPy and/or its derivatives have also been employed as other chemical reagents to participate in organic reactions, for example, as a bromination reagent to brominate ketones and 1,3-diketones; for selective bromination of activated aromatic compounds in nonaqueous solutions [34]; for selective and convenient para-bromination of aromatic compounds [35]; and for bromination of a number of ketones and alkenes [36], aromatic compounds (e.g., methoxybenzene, 1,1-diphenylethylene, and toluene) [37], and norbornene, cis- and trans-1-phenylpropene, and 1-phenylcyclohexene [38]. Also, PVPy-based reagents were applied to reduce aldehydes [39] and, in another study, aldehydes and ketones [40]. Moreover, they were used for hydrofluorination and hydrobromination of alkynes and alkenes and also for fluorination of alcohols [41]; for direct and efficient iodination of anilines, methoxyarenes, and phenols; and for regioselective iodination of aromatic and heteroaromatic compounds and halogenation of the acetylenic and olefinic compounds.

PVPy-based sensors

Redox polymer-coated electrodes have been the subject of many electrochemical studies during the last decades. One of the most important applications of these systems is their use as a suitable catalyst in electrochemical reactions because

Fig. 1 Growth in publications about PVPy/P4VP since 1960 according to an enquiry in scinapse, an academic search engine for papers



of the high local concentration of catalytic sites that can be created at the surface of the electrode, even when a low content of the catalyst is used. One of the important fields for using PVPy is redox polymer-based sensors to determine humidity, various chemicals, and metal ions.

Humidity sensors

Sakai et al. [42] prepared an alumina substrate containing a pair of gold electrodes and cross-linked and quaternized P4VP on the substrate surface. They reported that the impedance of the sensor changed from 10^7 to $10^3 \Omega$ for the entire humidity range. Also, the effect of sensor preparation conditions (e.g., quaternizing reagents and reaction time) on the electrical features of the device was verified. The schematic of the resistive-type humidity sensor based on a polymer-sensitive film is shown in Fig. 2.

In another study, Sakai et al. [42] also studied the performance of humidity sensors. They graft-polymerized PVPy on polytetrafluoroethylene films and then prepared sandwich- and surface-type sensors via vacuum deposition of gold electrodes. The sandwich-type sensor revealed a longer life compared with the surface-type sensor because the conductive path was not directly exposed to the atmosphere. Additionally, the sensor was entirely insoluble in water and exhibited superior durability at high humidity. Li et al. [43] cross-linked P4VP and then quaternized it with 1,4-bromobutane on an interdigitated gold electrode to make a polyelectrolyte film as a humidity sensor, which was further coated with a polypyrrole layer via vapor-phase polymerization. The measurements and investigations revealed that the impedance of the composites is as low as 105 even at 0 relative humidity and the composite impedance was changed linearly with relative humidity in the range of 0–60% with good sensitivity. They showed that the composite is a promising sensor material for the detection of low humidity. Also, the sensitive mechanism of the device can be explained on the

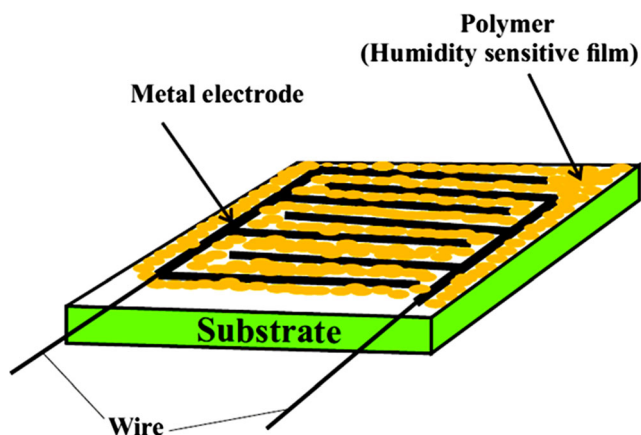


Fig. 2 A resistive-type humidity sensor based on a polymer-sensitive film

basis of the intrinsic electronic conduction and ionic conduction. In ref. [44], copolymerized butyl methacrylate with 4-vinylpyridine (4VP) has been investigated in order to enhance its stability. Queerization of the resulting copolymer was done with halocarbon to prepare the humidity-sensitive material, and its sensing properties were investigated. The humidity sensors were prepared by dip coating the quaternized copolymer solution in methanol on the surface of interdigital gold electrodes and then drying. The copolymer showed a high sensitivity to humidity variation over a wide range of relative humidity (33–97%). Additionally, it exhibits good stability at high humidity and is a promising material for impedance-type humidity sensors. In another study, Li et al. [45] prepared a blend of polypyrrole (PPy) and poly(ionic liquid) (PIL) and composited it with quaternized and cross-linked P4VP (QC-P4VP) by simple mixing of the solution and then thermal treatment. The structure and morphology of the composite (QC-P4VP/PIL-PPy) were characterized by FT-IR and scanning electron microscopy analysis. Afterward, the thin-film humidity sensors were prepared from the composite by the facile dip-coating procedure. Then, investigation of humidity sensing features of the sensors revealed higher sensitivity (impedance change from 10^7 to 10^3 over the range of 11–95% relative humidity), much smaller hysteresis ($\sim 1\%$ relative humidity), better sensing linearity as compared with sensors based on QC-P4VP alone, good reproducibility, and fast response. The fabrication of the resistive-based humidity sensors using the cross-linked and quaternized copolymer of 4VP with butyl methacrylate has been mentioned in ref. [46]. Formation of the cross-linked network in the sensing film and introduction of the butyl methacrylate monomer in the polymer chain were found. The impedance changes of the sensor revealed a high sensitivity and good linearity in a semi-logarithmic scale. The prepared sensor exhibited the advantages of very small hysteresis ($< 1\%$ relative humidity), quick response, and resistance to humid and chemical vapor. In another work, Li et al. [47] grafted P4VP onto a carbon black (CB) surface, which was further quaternized and cross-linked with bromobutane and 1,4-dibromobutane compounds. The final product was used as a resistive-based humidity sensor which the investigations revealed to have a high conductivity even at very low humidity; also, its conductivity was based on both ionic and electronic conduction. The content of CB, the cross-linking, and quaternization reaction affected the relative contributions of the two types of conduction, thus modulating the humidity sensing properties of the composite. In optimized conditions, the CB/P4VP composite revealed a very extensive sensing in the range of 0–97% relative humidity that this phenomenon leads to solving the issue of low humidity detection for resistive-type polymer-based humidity sensors. The cross-linking reaction of carbon black with 1,4-dibromobutane led to the creation of a network structure and

good dispersal of the CB particles with a small size (150–200 nm) in the polymeric network.

Sensors for detecting various chemicals

Kulys and Samalius [48] used different polymers for modification of paraffin-impregnated graphite and organic metal electrodes. It was found that N-methyl(polyvinyl)pyridine modified on the biocatalytic current is increased in L-lactate oxidation by cytochrome b_2 , while it is decreased by cardiolipin. Changes in the rate of bioelectrocatalytic processes at the altered electrodes were determined by the change in the electron transfer distance resulting from the modified protein globule orientation at the interface. Silva et al. [49] constructed a MWCNT/P4VP nanocomposite to complex copper ions on a glassy carbon electrode. Then, the modified electrode was used in the amperometric detection of L-cysteine in food supplements. The analytical curve revealed a linear response range for the detection of L-cysteine in the concentrations of 5–60 mol L⁻¹. The obtained detection and quantification limits were 1.50 and 5.00 mol L⁻¹, respectively. In another investigation, Csoregi et al. [50] synthesized a copolymer of polyaziridine and PVPy (quaternized via methylene carboxylate) and used it as a restricting layer for glucose mass transport in the desirable electrode organization for the subcutaneous monitoring of glucose. When the electrode was subcutaneously implanted in a rat body, it retained its in vitro calibration and tracked/detected the concentration of blood glucose before, during, and after intraperitoneal infusion of glucose. A typical sensor for the detection of blood glucose is shown in Fig. 3.

Ekomoa et al. [51] introduced electrochemical molecularly imprinted polymers (e-MIPs) in screen-printed carbon electrodes (SPCE) as the sensing unit to detect an organic pollutant. In this structure, the copolymer of 4VP and ferrocenylmethyl methacrylate (and ethylene glycol

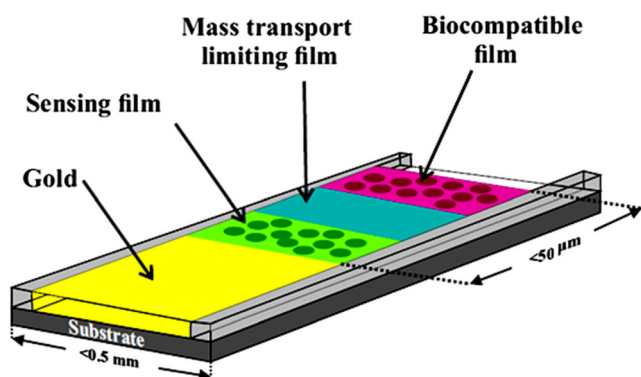


Fig. 3 The sensor for detecting the concentration of blood glucose before, during, and after intraperitoneal infusion of glucose. The sensing and biocompatible films are fabricated from glucose oxidase and poly(ethylene oxide) respectively. The copolymer of polyaziridine/PVPy is employed as a restricting layer for the mass transport

dimethacrylate as a cross-linker) was used as a redox polymer for the recognition of bisphenol A (an endocrine disruptor) as a target. Electrochemical investigations of e-MIP-SPCE revealed a high sensitivity in the presence of bisphenol A in aqueous medium as compared with e-NIP-SPCE (nonimprinted sample) with a detection limit of 0.06 nM. e-MIP-SPCE also showed selectivity toward ketoprofen and carbamazepine. Another study was done by Thangamuthu et al. [52] in which a glassy carbon electrode was modified with Mo(CN)₈⁴⁻-incorporated P4VP (PVP/Mo(CN)₈⁴⁻) and used for direct detection of L-ascorbic acid in Celin tablet and orange fruit juice without any special treatment. The electrode showed the most repeatable responses and demonstrated an accurate detection of vitamin C content as compared with the titration procedure with 2,6-dichlorophenol indophenol, which allowed the direct estimation of L-ascorbic acid without the need for heavy buffering. Moreover, the rate constant (k'_{ME}) of the modified electrode was reasonably high ($\sim 1 \times 10^{-2}$ cm s⁻¹), exhibiting higher sensitivity of the PVP/Mo(CN)₈⁴⁻ electrode and faster ascorbic acid oxidation; also, the price of the chemicals used in this electrode was not high. In another study, Sun et al. [53] used the ionic self-assembly technique for coating the multilayers of P4VP and a glucose oxidase complex of osmium on a quartz sheet surface or a gold electrode. Cyclic voltammogram investigations revealed that osmium electrons were successfully transferred between the immobilized glucose oxidase and the electrode surface. Moreover, device usage for glucose sensing can be expected. In ref. [54], a 4VP monomer was anodically polymerized on the surface of a pencil 2B graphite paste electrode. That paper indicated that the type of solvent and supporting electrolyte influenced polymerization. The surface morphology of the grown film was compared with that of films on other electrode types (i.e., pyrolytic graphite paste and pencil rod). It was found that glucose can be determined up to at least 14 mM. Other advantages were the electrode's simplicity and fastness and its easy preparation method. In another attempt to develop PVPy-based electrodes, Liu and Anzai [55] prepared a new electrochemical indicator (P4VP derivative bearing Os (5,6-dimethyl-1,10-phenanthroline)₂Cl) for detecting DNA hybridization. The PVPy-supported complex selectively bonded to the double-helical DNA chains, thus enabling the electrochemical detection of DNA at the picomolar level. Poyard et al. [56] also prepared bioelectrodes of Pt/poly-(4VP-co-Styrene)/laponite-glucose oxidase-polyphenol oxidase by using glutaraldehyde as a cross-linker. Then, the prepared product was used for biosensing glucose. The biosensors were effectively used for the accurate determination of glucose without any interference. Even in a complicated medium such as serum, the high sensitivities of the electrodes remained constant in solutions containing up to 10% of serum. The electrodes revealed a short response time, good accuracy, and reproducibility, and were fitted with most of the analytical

requirements for medical analysis. It was also shown that these biosensors completely reject the usual compounds; i.e., the effect of species (which are electroactive such as *p*-acetaminophen, urate, and ascorbate) can be fully eliminated. Narváez et al. [57] produced alcohol and fructose biosensors with an enzyme immobilization procedure which mimics flexibility and natural interactions of living systems. First, an MPS (3-mercapto-1-propane sulfonic acid) monolayer was used to cover a gold electrode surface (Au:MPS); secondly, the cationic poly[(vinylpyridine)Os-(bpy)₂Cl] redox polymer (quaternized with bromoethylamine) and then poly(styrene sulfonic acid) were deposited on the electrode. The horseradish peroxidase (HRP)-alcohol oxidase couple and fructose dehydrogenase were electrochemically connected to the redox polymer interface in a layer-by-layer architecture. The sensitivity values obtained for the biosensors were 19.3, 58.1, and 10.6 mA M⁻¹ cm⁻¹ for sensing fructose, H₂O₂, and methanol, respectively, that the values can be controlled by rational manipulation and deposition of the charge in the catalytic layers. The method was modular because it allowed the selection of enzyme combinations and also the rational modulation of their analytical properties was possible. Kenausis et al. [58] cross-linked glucose oxidase and a redox polymer (via complexing PVPy with [Os(4,4'-dimethoxy-2,2'-bipyridine)₂Cl]⁺²⁺) on a carbon electrode surface and used the prepared sensor system for sensing glucose and lactate. They showed that at a glucose concentration of 1 mM, the addition of 0.1 mM ascorbate leads to a 17% increase in the current. Moreover, at 5 mM glucose, switching the atmosphere from argon to oxygen caused 11% reduction in the current's value. In another investigation of PVPy-modified electrodes, Ghadimi et al. [59] prepared a novel glassy carbon electrode modified with a composite film of P4VP/multiwall carbon nanotubes and used it for the voltammetric detection of paracetamol. The produced electrode revealed the effects of the combination of P4VP and nanotubes on the electrooxidation of paracetamol in a phosphate buffer solution; i.e., the P4VP conductivity and high physical properties of nanotubes were combined together for enhancing paracetamol oxidation kinetics. The P4VP/multiwall carbon nanotube-coated electrode also exhibited excellent electrochemical activity to paracetamol oxidation as compared with bare and multiwall carbon nanotube-coated electrodes. Based on the benefits of the electrode, the following can be mentioned: a paracetamol concentration in the range of 0.02–450 μM with a detection limit of 1.69 nM was achieved, electrode stability was retained for more than 2 months, the reproducible responses were obtained at 99% of the initial current of paracetamol, and any physiologically common interferences such as uric acid and ascorbic acid were not exhibited. Inoue et al. [60] used an electrode coated with a horseradish peroxidase-redox polymer for the electrochemical monitoring of hydrogen peroxide generated from leucocytes. This electrochemical sensor continuously

monitored extracellular hydrogen peroxide. The device included an indium-tin-oxide electrode coated with an osmium-PVPy gel polymer (containing horseradish peroxidase (Os-HRP)) and a poly-dimethylsiloxane well to house the cells on the chip. The enzymatic reduction of extracellular H₂O₂ occurred at the modified electrode surface (Os(II) acted as an electron donor), leading to responses (reduction current) in the sensor. It was found that the device is able to successfully detect extracellular H₂O₂ production. However, solution stirring led to scattering of data, and an obvious increase in the reduction current was revealed after H₂O₂ injection even at 50 nM of hydrogen peroxide. Mao and Yamamoto [61] modified a glassy carbon electrode with a bilayer film of glutathione sulfhydryl oxidase (GSH-SOx) and an osmium-PVPy gel polymer (Os-gel-HRP). Then, they used it as a new amperometric biosensor for monitoring glutathione and glutathione disulfide. Sensitivity of the bienzyme-based sensing material to glutathione and glutathione disulfide was investigated by cyclic voltammetry, flow cell amperometry, and flow injection analysis. Linear responses of the sensor to glutathione and glutathione disulfide in the ranges 1–200 μM and 2–120 μM were achieved with a sensitivity of 1.195 nA/mM and 0.60 nA/mM for glutathione and glutathione disulfide, respectively. Mugweru et al. [62] fabricated a glucose-sensing device on a gold electrode coated with flexible polyimide sheets by photopolymerization of biocompatible poly(ethylene glycol) diacrylate (PEG-DA) to create hydrogels and encapsulate the sensing units. They coated the electrode (Cr and Au layer-deposited polyimide sheets) with a P(Os)-EA (poly[(vinylpyridine-osmium(bipyridine)₂ chloride]-coethylamine) redox polymer. After deposition, the redox polymer, a mixture of PEG-DA, GOx (glucose oxidase), and DAROCUR (the photoinitiator), was put on the electrode surface. The fabricated microarray sensors did not show crosstalk between adjacent elements and also were addressable as evaluated via cyclic voltammetry. Moreover, the glucose sensors showed the desired linear response in the biological range. Cyclic voltammetry investigations showed that the entrapped glucose oxidase revealed a linear response to glucose concentration increments (0–360 mg/dL). Moreover, a Nafion/GOx/P4VP microelectrode was used for sensing glucose [63]. In that study, a wireless amperometric measurement was developed for glucose detection in hyperglycemia and diabetic rats (during pre- and post-insulin administration). The results revealed that the wireless sensing kit was able to monitor glucose in both brain and subcutaneous tissues. The physiological data also opened a new insight into the production of implantable glucose sensors. Li et al. [64] prepared amperometric biosensors on the basis of the MWCNT/PVP/Prussian blue composite. The composite films were synthesized by casting films of MWCNTs wrapped with PVP on the surface of gold electrodes and then by electrochemical deposition of Prussian blue on the MWCNT/PVP matrix. The

modified electrode exhibited a prominent electrocatalytic activity in hydrogen peroxide reduction. The fast amperometric response of this sensor to hydrogen peroxide demonstrated that its detection sensitivity was $1.3 \mu\text{A } \mu\text{M}^{-1}$ of H_2O_2 per square centimeter while its detection limit was 25 nM. The results were much better than those reported for Prussian blue–based amperometric sensors. Moreover, the glucose biosensor (produced by casting a glucose oxidase–containing Nafion film above the MWCNT/PVP/Prussian blue film) was promising for detecting glucose. The observed high reproducibility, high stability, and high sensitivity of the MWCNT/PVP/Prussian blue composite made it promising for durable and reliable detection of glucose and H_2O_2 .

The ability of PVPy-based materials to detect metal ions and their extensive applications in this field have been reported. For example, the fabrication of a poly(Hg(II)-4VP) membrane electrode has been reported in ref. [65]. The electrode, with the plasticizer tris (2-ethyl hexyl) phosphate, revealed a Nernstian response with a slope of $30 \pm 1 \text{ mV decade}^{-1}$ in the range of 10^{-7} – $10^{-2} \text{ M Hg}^{2+}$ and at pH 3–4. The advantages of the electrode were as follows: its response and lifetime were less than 25 s and more than 120 days, respectively; the device's detection limit was $0.5 \times 10^{-7} \text{ M Hg}^{2+}$; the interferences from other cations were not serious (except for Ag^{1+} at a Hg^{2+} concentration less than 10^{-4} M); the electrode's performance agreed well with the standard method with a correlation coefficient (R^2) of 0.9998 for water analysis; and it also was a convenient indicator in the potentiometric titration of Hg^{2+} with iodide. Lorenzo and Abruia [66] modified glassy carbon electrodes with quaternized PVPy into which $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Mo}(\text{CN})_8]^{4-}$, or $[\text{Ir}(\text{Cl})_6]^{3-}$ was incorporated by an ion exchange mechanism. The modified electrode was employed to determine silver ions from aqueous solutions. The determination was based on the silver ions' preconcentration by the formation of a silver complex with the polyanionic metal species. In ref. [67], a P4VP/mercury film electrode to determine trace Bi^{3+} in real samples by square-wave anodic stripping voltammetry (SWASV) has been introduced. In comparison with conventional film electrodes (for sensing mercury), this modified electrode showed improved resistance to interfering surface-active compounds and common ions, increased sensitivity when used in combination with SWASV, and better mechanical stability of the mercury film; in addition, detection can be achieved without deoxygenation and the electrode can be easily renewed.

PVPy-based electrodes for redox reactions

Redox reactions are an electrochemically important reaction that plays a remarkable role in living systems. The reported studies about PVPy usage in the electrode instruction to monitoring the redox reactions are tabulated in Table 1 [68–74].

In ref. [68], polymer-modified carbon paste electrodes were synthesized by mixing P4VP into a graphite powder/Nujol oil matrix. Then, the electrodes were able to electrostatically bind to $\text{Fe}(\text{CN})_6^{4-}$ since the solution pH was held at an acidic range to retain the polymer in a protonated state. $\text{Fe}(\text{CN})_6^{4-}$ absorbed by the electrode was changed in the range of 5×10^{-10} – $5 \times 10^{-8} \text{ mol/cm}^2$ depending on the PVP content of the paste and the $\text{Fe}(\text{CN})_6^{4-}$ concentration in the solution. The resulting surfaces could be rapidly regenerated with a 5–10% reproducibility. Also, the $\text{Fe}(\text{CN})_6^{4-}$ /PVP electrodes were able to catalyze the ascorbic acid oxidation. In another study, electrocatalytic CO_2 reduction using a graphite electrode coated with a P4VP membrane containing cobalt phthalocyanine (CoPc) has been explained by Abe et al. [69]. The CoPc-incorporated polymer worked as an excellent and selective catalyst for CO production, and this is attributed to the coordinative and weakly basic property of CoPc and PVP. It was considered that the coordination between PVP and CoPc leads to an increase in the electron density on the central metal ion which must facilitate the formation of the intermediate. The weak basic characteristic of PVP allows CO production which requires a protonation-deprotonation process. The CO_2 reduction was influenced by pH condition. Moreover, the microenvironment around cobalt phthalocyanine (provided by protonated pyridine) was also an important factor in the reduction process. Moreover, the monomers of 4VP, pyrrole, methylene green, aniline, and ortho-phenylenediamine were electropolymerized on carbon cloth electrodes [70]. Afterward, the catalytic effect of the polymer-coated electrode on NADH (b-nicotinamide adenine dinucleotide) oxidation was investigated via cyclic voltammetry. It was found that electrode processes during polymerization are diffusion controlled and high current densities were achieved at different monomer concentrations. All of the polymers were electrocatalytically active to oxidize NADH. The cyclic voltammogram of PANI shows that the anodic peak potential (E_{pa}) has shifted to more positive values, indicating that the monomer was rapidly depleted in the electrode's vicinity by changing to a radical cation, while the voltammogram of 4VP exhibits a redox process of quasi-reversible type as its peak separation (ΔE_p) is 200 mV. Zhao et al. [71] incorporated cobalt phthalocyanine derivatives such as nonsubstituted cobalt(II) phthalocyanine (CoPc), cobalt(II) octacyanophthalocyanine (CoPc CN_8), and cobalt tetrasulfonatophthalocyanine (CoPc(SO_3H) $_4$) in a poly(4VP-co-styrene) film coated on a graphite electrode. Then, the modified electrode was used for electrocatalytic proton reduction. The catalytic efficiency of the prepared complexes was in the order of $\text{CoPc} > \text{CoPc } \text{CN}_8 > \text{CoPc}(\text{SO}_3\text{H})_4$. Also, the catalytic proton reduction was strong to be dominated by the electron transfer within the matrix. Vreeke et al. [72] modified an electrode with a horseradish peroxidase (HRP) film covalently bound to an epoxy network containing PVPy-

Table 1 The reported PVPy-based electrodes for oxidation-reduction processes

Prepared PVPy-based material	Studied subject	Ref.
Carbon paste electrodes of P4VP/graphite powder/Nujol oil	Electrostatic adsorption of $\text{Fe}(\text{CN})_6^{4-}$ and ascorbic acid oxidation	[68]
Graphite electrode coated with a P4VP membrane containing cobalt phthalocyanines	Electrocatalytic CO_2 reduction	[69]
Polymer (e.g., P4VP)-coated electrodes	The catalytic effect in NADH oxidation	[70]
Graphite electrode coated with Co^{2+} phthalocyanine-incorporated poly (4-VP-St)	Electrocatalytic proton reduction	[71]
Electrode modified with horseradish peroxidase covalently bound to an epoxy network having a PVP-complexed $[\text{Os}(\text{bpy})_2\text{Cl}]\text{S}^{3+/2+}$ redox center	Electroreduction of H_2O_2	[72]
$[\text{Ru}(\text{bpy})_2\text{Cl-P4VP}]$ redox polymer	Catalyzes $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couples	[73]
Pt/Nafion/GC and Pt/PVP/GC electrodes	The electrocatalytic behavior in methanol and formic acid oxidation	[74]

complexed $[\text{Os}(\text{bpy})_2\text{Cl}]\text{S}^{3+/2+}$ redox center. Afterward, the prepared modified electrode was used for the electroreduction of hydrogen peroxide. It was found that at low H_2O_2 concentrations ($< 1 \times 10^{-4}$ M), the current density is nearly independent of the HRP to polymer ratio. At higher concentrations ($> 1 \times 10^{-4}$ M), when the film becomes rich in HRP up to a ratio of 1:5, the current density is increased. Andrieux et al. [73] used a $[\text{Ru}(\text{bpy})_2\text{Cl-P4VP}]$ redox compound to catalyze Fe^{2+} oxidation to Fe^{3+} in 1 M HCl in terms of current and potential. The polymer also enabled the catalysis (although to a lesser extent) of Fe^{3+} reduction to Fe^{2+} in the same medium, despite the standard potential of the $\text{Ru}^3/\text{Ru}^{2+}$ couple being positive compared with that of $\text{Fe}^{3+}/\text{Fe}^{2+}$. The experimental data were verified and the catalytic efficiency was optimized using well-known kinetic models, and the validity of these models was confirmed. Maksimov et al. [74] deposited platinum on Nafion (NF) and PVPy-coated carbon electrodes. The rate of hydrogen evolution on Pt (deposited on NF and PVP films in the small range of overvoltage ($\eta < 30$ mV)) was limited by the removal of hydrogen from the external surface of the electrode. For the Pt/NF-coated electrode, this process occurs at a smaller overvoltage compared with that of a smooth Pt surface. The higher hydrophobicity of the Pt/NF surface facilitates the formation of bubbles and decreases hydrogen supersaturation in the near-electrode layer. The electrocatalytic behavior of platinum deposits on NF and PVP were studied in the oxidation of methanol and formic acid. It was found that the interaction of metal particles with the polymer matrix and the dimensional effect influence electrocatalytic processes. In the Pt/PVP-modified electrode, the dimensional effect was more pronounced, while in the Pt/NF-coated system, the effect of metal particles was more important. In another work, high catalytic effects were observed for the reduction of Ce^{4+} and the oxidation of Fe^{2+} when electrodes were modified with $[\text{Ru}(\text{bipy})_2\text{Cl-P4VP}]\text{Cl}$ or $[\text{Ru}(\text{bipy})_2\text{pyridine-P4VP}]\text{Cl}_2$. The high concentration of electroactive compounds in the

coating and the fast electron exchange of the Ru complexes were the valuable reasons behind these enhanced reactions. The attached P4VP/Ru complexes acted as the intermediate, and the rate constant was related to the second-order reaction between the polymer and the redox couple in solution. Catalytic or inhibition effects were observed, depending on the rate constant magnitude of this second-order reaction [75].

PVPy-based electrodes for electrochemical studies

In addition to the aforementioned applications, chemical investigations of PVPy-coated electrodes are also important and many studies have been done in this view. Lindholm [76] investigated the charge transport rate and redox capacity with different electrochemical procedures on glassy carbon electrodes. The electrodes were coated with cross-linked PVPy thin films containing either hexachloroiridate or hexacyanoferrate anions. The results showed that there is a good agreement for the apparent diffusion coefficient evaluated with chronocoulometric and impedance spectroscopy methods. Moreover, it was concluded that at higher hexachloroiridate concentrations in the film, a smaller number of redox sites are electroactive in impedance spectroscopy in comparison with cyclic voltammetry. In another work, the redox couple of $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ was trapped in a P4VP film on a carbon electrode [77]. Then, the electrode impedance was investigated. The impedance plane display revealed a charge transfer resistance coupled with an interfacial double-layer capacity. At lower frequencies, evidence of a Warburg impedance was not shown, while a transition to a low-frequency capacity led to this phenomenon. The analysis of the obtained data led to measurement of the heterogeneous rate constant for electron transfer from the electrode surface to the redox couple. Lindholm [78] spin-coated the cross-linked P4VP onto a glassy carbon electrode (embedded in insulating Teflon sleeves) surface and then IrCl_6^{2-}

ions were incorporated into PVP films by immersing the electrodes in a buffer solution of hexachloroiridate(IV). Then, the charge propagation current from chronocoulometric procedures was compared with charge transport through a P4VP/IrCl₆²⁻ film during the mediated oxidation of Fe²⁺. The electron exchange current and substrate diffusion current were both linearly changed with the substrate concentration. This phenomenon supports treatment validity. The polymer electrode based on a mixture of cellulose acetate and PVPy has been reported in ref. [79]. It was found that the incorporation of the ion exchanging polymer into the cellulose acetate allows the attaching of counterion reactants in acidic media while retaining the size exclusion discriminative characteristics of the cellulose acetate matrix. The transport and loading features were investigated via rotating disk and cyclic voltammetry measurements. The obtained coating exhibited properties better than those of the two components alone. Counterion reactants were retained for extended periods in comparison with pure PVPy coatings. Shaidarova et al. [80] studied the electrochemical characteristics of a glassy carbon electrode modified with a PVPy film (containing electrodeposited palladium). It was found that palladium particles deposited on the PVPy film revealed an electrocatalytic activity in H₂C₂O₄ oxidation. The decrement was exhibited in the oxidation potential of oxalic acid while the current of its oxidation was increased as compared with that of an unmodified electrode. The catalytic current of oxalic acid oxidation linearly changed with its concentration in the range of 1×10^{-2} – 1×10^{-6} M. The synthesis of glassy carbon electrodes and their modified version with a Rh-electrodeposited PVPy film has been investigated by Shaidarova et al. [81]. It was found that the electrodeposited rhodium particles are electrocatalytically active in the oxidation of pyrocatechol and hydroquinone. The modified electrode was used to determine adrenalin, noradrenaline, and dopamine (which have a pyrocatechol fragment in their structure) in pharmaceuticals. Torrence et al. [82] carried out an electrochemical flux study of hydroquinone and ferricyanide using PVPy modified electrodes, and they found that incorporation of organosilane-modified glass microspheres into the polymer matrix was altered by the electrochemical flux. It was also shown that the polymer itself has a remarkable role in the formation and the characteristics of the interfacial region. The image of the interfacial region was taken via fluorescence microscopy, and the image revealed a highly concentrating interfacial region created for all of the polymer-modified glass microsphere composites. In ref. [83], the surface modification effect of an n-type semiconductor on the electrochemical features of a soluble ferrocene derivative was investigated. The incorporation of a croconate violet (anionic dye) into PVPy-coated polycrystalline SnO₂ electrodes led to remarkably altered kinetics of electrooxidation of redox couples (in the solution phase). The suggested mechanism was diffusion of the electroactive substrate and/or an electron through the dye-contained polymer film. Lindall et al. [84] bonded [Ru³⁺(EDTA)(OH₂)]⁻ to pyridine rings in poly(VP-co-styrene)

(PVPS) by treating a PVPS-coated glassy carbon electrode with dilute [Ru³⁺(EDTA)(OH₂)]⁻ solutions. This polymer enabled the incorporation of [MO⁴⁺(CN)₈]⁴⁻, and the amount of incorporated anions is increased by holding the electrode in the Ru²⁺ state in line with expectations due to the balancing of charge. Similarly, [Ru²⁺(NH₃)₅(OH₂)]²⁺ was covalently bound to PVPS to create a polymer which can bind [MO⁴⁺(CN)₈]⁴⁻ by ion exchange in which the bound amount depends on the Ru oxidation state. The ([Ru³⁺(EDTA)(OH₂)(py)]₂[Ru²⁺(NH₃)₅(py)]) system can incorporate redox-active ions from either [MO⁴⁺(CN)₈]⁴⁻ or Mo²⁺ solutions, but at lower amounts than those for the pure [Ru²⁺(NH₃)₅(py)]²⁺ and [Ru³⁺(EDTA)(OH₂)(py)]⁻ polymeric systems. The diffusion coefficient of the charge transfer was higher for the polymer mixture, indicating a higher concentration of redox sites. The mixture of polymers enabled the binding of both Mo²⁺ and [MO⁴⁺(CN)₈]⁴⁻, yielding a redox polymer which can be changed to six different redox states. The fabrication of an organic light-emitting diode (OLED) device based on self-assembled P4VP with poly(N-vinyl-carbazole) (PVK) and 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole as transport layers has been reported in ref. [85]. The OLED device was prepared on indium-tin-oxide (ITO)-coated glass, and then an aluminum sample was deposited on its surface as a counter electrode. The self-assembly was on the basis of electrostatic attraction of oppositely charged polymers. It was found that this self-assembly can be employed to create alternating multilayers, not only by the poly(phenyl-vinylene) and derivatives but also by partial protonation of P4VP by which the charge on P4VP is generated by the protonation phenomenon. This result has also opened the path to polymer-analogous reactions, which can introduce other electrooptically active species to be assembled via electrostatic self-assembly (ESA) in nanodevices. In another study, the redox characteristics of an organodisulfide cathode (2,5-dimercapto-1,3,4-thiadiazole, DMcT) was improved by incorporating it into a basic polymer such as PVPy [86]. The cyclic voltammetry indicated that the redox process of DMcT on the PVPy film was enhanced, the redox current was increased in both the oxidation and reduction processes, and the enhanced redox property of DMcT may be attributed to the basic environment of the PVPy matrix in which DMcT acted as a thiolate anion that can be oxidized at lower overpotentials. Due to these advantages of the electrochemical binding of the thiolate anions to the PVPy matrix, it is suggested that the DMcT/PVPy electrode can behave as an improved cathode in lithium batteries. Cheng et al. [87] used the hydrogen-bonded self-assembly of P4VP and ferrocenyl-modified percec-type dendrons to prepare two redox-responsive complexes with different dendritic tail chain numbers (P4VP-*n*Fc, *n* = 1, 2). At room temperature, P4VP-1Fc was crystalline while P4VP-2Fc was liquid crystalline. Cyclic voltammetry investigations revealed that the electrode process of P4VP-*n*Fc (*n* = 1, 2) films was diffusion controlled, and the reversibility of the electrode process for the P4VP-2Fc films was better than that of P4VP-1Fc. The results

showed that the electrochemical activity of the redox-responsive P4VP-ferrocenyl dendron complex can be facilely tuned by changing the dendritic tail chain numbers. Ultrathin multilayer films of a polybasic lanthanide heteropoly tungstate-molybdate complex ($\text{Pr}(\text{SiMo}_7\text{W}_4)_2$) and a cationic P4VP (partially complexed with osmium bis(2,2'-bipyridine) (QPVP-Os)) were coated on a gold electrode (pre-coated with a cysteamine monolayer) by Cheng et al. The electrochemical features of the multilayer films were studied via cyclic voltammetry and electrochemical impedance. Electrochemical impedance spectroscopy was especially used to verify the layer deposition processes and it provided important information, e.g., charge transfer resistance and double-layer capacitance. All results showed regular film growth with each layer adsorption. Moreover, it was found that the multilayer films were uniformly fabricated in a layer-by-layer fashion and it was expected that the electrochemical impedance spectroscopy will be used in other multilayer systems as well [88]. Cheng et al. [89] also studied the electrochemical features of multilayered films. The preparation steps of layers were as follows: grafting of a 4-aminobenzoic acid (4-ABA) monolayer film on a glassy carbon electrode to prepare a layer of 4-ABA/GCE; modification of the 4-ABA/GCE surface by QPVP-Os (quaternized P4VP complexed with $[\text{Os}(\text{bpy})_2\text{Cl}]^{2+/+}$) yielding QPVP-Os/4-ABA/GCE; and deposition of silicotungstic heteropolyanions ($\text{SiW}_{12}\text{O}_{40}^{4-}$, denoted as SiW_{12}) to the surface of QPVP-Os/4-ABA/GCE. It is proved that the multilayer system is uniform and stable and the average thickness for a bilayer of QPVP-Os/ SiW_{12} in the multilayer structure is 30.2 Å and the electrocatalytic effects were improved with increasing layer numbers but reached the maximum at a certain layer number. The highest electrocatalytic effect can be attained by optimizing the appropriate layer number. Thus, this advantage of the multilayer films is very valuable especially in sensor systems because it allows easy optimization of the analytical conditions to attain the best function and properties. The voltammetric behavior of Cr^{6+} in PVPy-modified Pt electrodes has been investigated in ref. [90]. Cr^{6+} was incorporated into a PVP film in acidic solution. In the presence of ions, the reduction of Cr^{6+} in the Pt/PVP electrode occurred without the passivation observed with this reduction in classical electrodes. Due to the irreversibility of the reduction and the demonstrated ability of the $\text{PVP}^+-\text{Cr}(\text{VI})$ complexes, the behavior was different from that of other metal complexes studied in such electrodes. The partitioning of Cr^{6+} into Pt/PVP from dilute solutions suggests that the system may be suitable for the electroanalytical detection of ions by an analogous stripping voltammetry. Such films of P4VP can be synthesized by adsorption onto a Pt substrate. After protonation of the film, Cr^{6+} was introduced to the film by an ion exchange mechanism. Sakaguchi et al. [91] produced dye-sensitized solar cells (DSSCs) which were solidified with chemically cross-linked gelators without losing the performance of DSSCs before gelation. The electrolytes contained in ionic liquids (1-methyl-3-propylimidazolium iodide) were solidified with PVPy and

1,2,4,5-tetra(bromomethyl)benzene. A small amount of water was added to reduce the initial viscosities of ionic liquid-type gel precursors, which made it possible for the gel precursors to impregnate into the nanopores of TiO_2 layers and also for reducing charge transfer resistances between the counter Pt and electrolytes. It was found that the short-circuit current (J_{sc}) and open-circuit voltage (V_{oc}) are enhanced after dipping TiO_2 layers in N3 dye in dilute carboxylic acid solutions and then drying. Moreover, the carboxylic acid treatments led to decreasing resistance of TiO_2 layers. This pathway was suitable for increasing the performance of the DSSC-contained ionic liquid-type electrolytes. The electrochemistry of cytochrome *C* in PVP-modified gold electrodes has been studied by Qu and coworkers [92]. PVPy-modified electrodes were fabricated by dropping a P4VP iso-butyl alcohol solution on the gold electrode surfaces and then drying. Electrochemical investigations of cytochrome *C* found that the promoter effect is related to the PVPy content in the gold electrodes. From the results, it can be seen that nitrogen in the polymer structure has an important role in enhancing the electron transfer of cytochrome *C*. Poly(4-diazosulfonate styrene-co-4-vinylpyridine) (P(DSS-co-VP)) was self-assembled with polyaniline via H bond interactions [93]. The self-assembled film was then photo-cross-linked under UV condition to create a covalently cross-linked network. For photocurrent measurements, an ITO glass modified with a P(DSS-co-VP)/PAN multilayer film was used as the electrode. The obtained data exhibited that the polyaniline-self-assembled films have good photoelectron conversion characteristics. Scott et al. [94] investigated the spectroelectrochemical observations for transparent graphite electrodes coated with P4VP and $\text{Ru}^{3+}(\text{EDTA})$. Comparison between simultaneously measured electrochemical and spectral responses from the bound complexes revealed that all of the Ru^{3+} within the PVP was not reduced to Ru^{2+} during reduction voltammetric scans, but it was totally reduced when the potential of the electrode was retained at potentials negative of the peak potential for a period of several minutes. With sufficiently heavy coatings of the PVP- $\text{Ru}^{3+}(\text{EDTA})$ complex on the transparent electrode, $\text{Ru}^{3+}/\text{Ru}^{2+}$ electroreduction led to a change in its color to golden, while reoxidation caused the discharge of color. In another work, $[(\text{PVP})_x\text{M}(\text{bpy})_2\text{Cl}]\text{Cl}$ polymers ($x = 3, 10, 20,$ and 100 for $\text{M} = \text{Ru}$; $x = 10$ for $\text{M} = \text{Os}$) were prepared and coated on silver electrodes by Taylor et al [95]. Then, they performed surface-enhanced resonance Raman spectroscopy (SERRS) of the modified electrodes and the major bands in the spectra were addressed. PVP spectra showed a remarkable potential dependency, and significant bands appeared as a result of this due to the production of peroxide species from the dissolved oxygen. The SERRS intensity appeared to fit a Langmuir isotherm at low loadings, while at higher loadings, the intensity loading curves revealed a decay which could be partially modeled on the basis of Beer's law treatment. But the discrepancy in the observed data exhibited that (i) the lower-loading polymers have preferentially adsorbed pyridine groups; (ii) the

attenuation by the polymer is greater than the assumed; and (iii) the SERRS intensity decayed much faster than the predicted values. The intensity loading curves for polymer-modified silver electrodes were promising for understanding self-absorption and damping because these polymers carried higher than possible apparent chromophore concentrations in the solution [95]. Alternatively, Lu and Whang [96] modified indium tin oxide electrodes with P4VP-bound $\text{Ru}(\text{bpy}=2,2'\text{-bipyridine})_2\text{Cl}^+$ and then investigated their electrogenerated chemiluminescence (ECL) and electrochemical features. The product was used for oxalate oxidation via direct and Ru^{3+} -mediated oxidation of oxalate compounds, and the effect of the surface concentrations of immobilized $\text{Ru}(\text{bpy})_2(\text{PVP})\text{Cl}^+$ and also the pH effect were investigated. Two irreversible oxidation waves and two ECL emission waves were shown in a sodium oxalate solution during the potential scan. It is believed that direct oxidation of oxalate is inhibited in oxidized Pt electrodes or carbon electrodes; thus, the two ECL waves observed in this study can be revealed only at the ITO electrodes. Belanger [97] modified platinum electrodes with a P4VP layer into which ferricyanide redox compounds were added in acidic solution. Then, the electrodes were further coated with a Nafion overlayer. The electrochemical responses of ferricyanide redox compounds (bound to the coatings) were determined as a function of supporting electrolyte concentration, time, and pH of the solution. Moreover, the observable shifts in the formal potential and transformation of the cyclic voltammograms were revealed from these experiments. In these conditions, application of a Nafion layer on top of the first P4VP film prevented the leaching out of $\text{Fe}(\text{CN})_6^{3-}$ (attached to P4VP) and the iodide counterion (from the CH_3I quaternizing agent) from the polymer film. In another work, Shaidarova et al. [98] produced a glassy-carbon electrode coated with a cobalt phthalocyanine-doped PVPy film. Afterward, they investigated the electrochemical features of the prepared electrode in a reaction of benzoquinone-hydroquinone redox couples. The electrode revealed an electrocatalytic activity in the hydroquinone oxidation. The current of the hydroquinone oxidation peak and the current of the reverse benzoquinone reduction peak at the electrode changed with their concentrations in the range of 10^{-6} to 10^{-3} M. In ref. [99], carbon black electrodes that contained the cross-linked poly(styrene)-co-poly(vinylpyridine) were created and their electrochemical characteristics were also reported. Vinylpyridine and styrene were copolymerized in the presence of divinylbenzene and conductive carbon black to prepare the bulk-modified electrodes. The electrodes' behavior was similar to that of coated electrodes with pyridine-containing polymers, but they could be polished to renew and regenerate their surface. $\text{Ru}^{3+}\text{EDTA}$ was incorporated into the electrodes via coordination to the pyridine sites, while the incorporation of ferricyanide occurred by ion exchange at protonated pyridyl sites. The ferricyanide-added composite layer served as an electrocatalyst for ascorbic acid oxidation. At low values of pH, sensitivity and swelling degree of the surface depended on (i) the

vinylpyridine fraction in the composite, (ii) the cross-linking degree by divinylbenzene, and (iii) the identity of the used buffer solution. Moreover, a polymer complex between the sulfonated water-soluble polyaniline and PVPy was synthesized by Tallman and Wallace [100]. When the prepared complex was immobilized on carbon or platinum electrodes, mild conductivity was revealed and the electrodes were electroactive. Hayashi et al. [101] developed a real-time electrochemical imaging protocol that applied a multiple enzyme-modified microelectrode. The synthesized multiple electrode was modified with an Os-PVPy-based polymer containing horseradish peroxidase (HRP) for sensing hydrogen peroxide (which is a very usual product resulting from the enzyme oxidase). To measure glutamate, the electrode was modified with a bilayer of Os-PVPy-HRP and glutamate oxidase. In that methodology, the limit of detection was 1 mM. Katakis and Heller [102] co-immobilized FAD oxidases on electrode surfaces with PVPy (N derivatized by bromoethylamine and $\text{Os}(\text{bpy})_2\text{Cl}_2$). Poly(ethylene glycol) diglycidyl ether was used to cross-link the redox polymer-enzyme hydrogels on the surface of the electrode. The function of the modified electrode as a sensor was verified, and the sensitivity and linear ranges were respectively $0.3 \text{ A M}^{-1} \text{ cm}^{-2}$ and 0.2 mM for L-lactate and $0.02 \text{ A M}^{-1} \text{ cm}^{-2}$ and 2.7 mM for L- α -glycerophosphate, which were comparable with $0.02 \text{ A M}^{-1} \text{ cm}^{-2}$ and 10 mM for glucose. The time of 0–90% response for all electrodes was 1 s or less. Formate, with a faradaic efficiency of 40% (at an overpotential of -0.67 V), was synthesized using a Cu electrode coated with a P4VP film, and its catalytic activity was retained after 30 h of operation [103]. The remarkable catalytic characteristics of novel hybrid materials were attributed to the formation of Cu-polymer complexes and also to new inherent mechanisms of the electrode stabilization by the N-heteroaromatic polymer. This was the first reported electroreduction of CO_2 with complexes of the copper-N-heteroaromatic ligand. This study also offers a novel, simple method to design and produce robust electrocatalysts for CO_2 reduction on the basis of earth-abundant metals. Li et al. [104] coated a glassy carbon electrode with PVA-g-PVP copolymer and horseradish peroxidase to prepare suitable biosensors for H_2O_2 detection. To achieve a wider detection range and higher sensitivity, the optimum composition of the copolymer can be required. This peroxidase electrode is suitable for actual usage because of its good sensitivity, reproducibility, and stability. In another attempt, modified ordinary pyrolytic graphite (OPG) electrodes were modified via P4VP which contained cobalt tetrasulfonated phthalocyanine (CoTsPc) in acid solutions [11]. The electrocatalytic activity of the modified electrodes for oxygen reduction and stability of H_2SO_4 solutions were investigated. The OPG/ CoTsPc /PVP electrodes were more active for oxygen reduction solutions in comparison with the electrode of CoTsPc -adsorbed OPG without PVP. The increase in activity can be attributed to the creation of an adduct between PVP and CoTsPc . The activity of the OPG/ CoTsPc /PVP system was

constant over a 10-h period while that of OPG/CoTsPc decreased by about 37%. The PVP layer revealed that the CoTsPc and/or Co diffused out of the complex into the solution phase. OPG/CoTsPc/PVP stability may also be attributed to the low solubility of the adduct between PVP and CoTsPc. Thicker PVP films led to a reduction in the diffusion-limiting current of oxygen reduction. A cellulose acetate and P4VP-coated glassy carbon electrode was used for amperometric monitoring of flowing streams. In these investigations, specially, enhanced selectivity was achieved in flow injection and liquid chromatography systems resulting from excluding cationic species from the surface. Dual-electrode detection schemes, using bare and PVP-coated electrodes, can be used for obtaining additional information of peak identity/integrity. Despite the increased diffusional resistance, low detection limits of ca. 0.04 (for ascorbic acid) and 0.10 ng (for uric acid) were obtained [12]. Osmium/polyvinylpyridine gel/horseradish peroxidase and xanthine oxidase (XOD) bienzyme were coated on glassy carbon electrodes. Then, the modified electrodes were used as an amperometric biosensor for online hypoxanthine measurement to sense produced hydrogen peroxide from XOD catalytic enzyme reactions. The low operational potential, low detection limit, high sensitivity, good reproducibility, and significant specificity of the sensor (used in a continuous-flow system) suggested its potential as an online sensing device for durable, reliable, and continuous measurement of hypoxanthine in combination with a convenient *in vivo* sampling method [105].

In another work, Carrara et al. [106] used an iridium-based redox copolymer of polyvinylpyridine/polystyrene in the structure of an electrode system to investigate electrochemiluminescence energy transfer. The results showed the possibility of synthesizing novel materials with improved emission wavelengths by precise selection of the emitting centers for any sensing and optoelectronic applications.

An innovative photoelectrochemical (PEC) process based on a graphite electrode modified with an electroactive polyvinylpyridine-osmium (Os-PVP) complex was reported by Barroso et al. [107]. It was demonstrated that the Os-PVP complex, previously applied to “wiring” of redox enzymes, can be employed for “wiring” of CdS QDs too. This strategy facilitates convenient and reproducible fabrication of modified graphite electrodes capable of sensing enzymatically generated CdS QDs using a very simple and available experimental setup. In addition to its low price, the PEC system is able to detect ALP and ALP-labeled analytes with better sensitivity than conventional chromogenic and fluorogenic assays. Kramer and McCrory investigated the carbon dioxide reduction reaction (CO₂RR) by cobalt phthalocyanine (CoPc) adsorbed onto edge-plane graphite (EPG) electrodes. It was found that the electrodes modified with CoPc immobilized in a poly-4-vinylpyridine (P4VP) film showed dramatically enhanced activity and selectivity compared with those modified with CoPc alone [108].

Zappia et al. used rod-coil BCP, namely polycyclopentadithiophene-benzothiadiazoleblock-poly(4-vinylpyridine) (PCPDTBT-*b*-P4VP), in an electrode structure for use in solar cells. The employment of the rod-coil BCP as an additive (in the solar cell) was demonstrated to be an effective alternative to the standard post-deposition thermal treatment. The device with 1% of the additive (the BCP copolymer) performs better than the thermally annealed one and shows an improvement of 60% in power conversion efficiency (PCE) if compared with the pristine CdSe NCs/PCPDTBT cell [109]. Interdigitated gold electrodes with deposited polystyrene-*b*-poly(4-vinylpyridine) were used as humidity sensors. Both concentration of polymer solution for film preparation and the sulfonation duration seriously affected the sensing properties of the BCP-based sensor. Under optimal conditions, the BCP-based sensor demonstrated a high response to relative humidity. Moreover, quick response, good sensing repeatability, and relatively small hysteresis were shown [110].

A novel enzymatic biofuel cell was designed with a polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) as “ON” and “OFF” switch. The bioanode and biocathode were created by sequential assembly of PS-*b*-P4VP and laponite-supported glucose oxidase or laccase on a glassy carbon electrode, respectively. The prepared biofuel revealed an obvious “ON-OFF” switching property at pH values above and below the pK_a . At the “ON” state, the open-circuit potential ($E_{\text{cell}}^{\text{ocp}}$) and maximal power output density ($P_{\text{max-ON}}$) reached 0.42 V and 3.49 $\mu\text{W cm}^{-2}$, while at the “OFF” state, the $E_{\text{cell}}^{\text{ocp}}$ and $P_{\text{max-OFF}}$ were only 0.22 V and 0.39 $\mu\text{W cm}^{-2}$ [111]. P4VP-grafted poly(vinylidene difluoride) (P4VP-*g*-PVDF) nanoporous polymeric electrodes were found to be sensitive for Hg²⁺ determination. The resulting sensor was intended to be integrated into existing systems or used as a stand-alone portable device. A first-generation prototype exhibiting its own integrated potentiostat, its software, and set of membrane-electrode pads is presented [112].

A new poly(4-vinyl pyridine) (P4VP)-based cadmium (Cd) ion-selective electrode (ISE) was developed. At an optimal pH of 6.4, a slope of 27.7 ± 0.8 mV decade⁻¹, a linear concentration range of 1×10^{-7} to 1.0×10^{-1} M Cd²⁺, and a limit of detection ($S/N = 3$) of 2.51×10^{-8} M were obtained. The ISE was very selective toward Cd²⁺. Moreover, the response time and shelf life values of less than 1 min and 90 days, respectively, were observed [5]. A modified glassy carbon electrode (GCE) with a composite film of graphene nanosheet and poly(4-vinylpyridine) (GR-P4VP/GCE) was used to develop a voltammetric sensor for hydroquinone (HQ) and catechol (CC). The electrode process was very reversible and the electrode was revealed to have a synergistic effect of P4VP and GR on the electrocatalytic oxidation of CC and HQ. This electrode showed excellent sensitivity values in the measurement of HQ (detection limits of 8.1 nM) and CC (detection

limits of 26 nM); was not affected by traditional interferences (e.g., phenol, nitrophenol, aminophenols, bisphenol A, and chlorophenols); and also was successfully employed for simultaneous detection of spikes in HQ and CC in tap and lake waters [113].

Poly(4-vinylpyridine) (P4VB) was grafted to MWCNTs and then Prussian blue (PB) nanoparticles were deposited on the polymer-modified MWCNTs. The as-prepared electrodes modified with PB/P4VP-g-MWCNT composites were used in the electrochemical detection of L-cysteine and exhibited two reversible redox waves attributed to fast surface-controlled processes. In an optimum condition for these as-prepared electrodes, a detection limit of L-cysteine as low as 0.01 μM was obtained with a sensitivity of 778.34 $\text{nA } \mu\text{M}^{-1} \text{ cm}^{-2}$ [114].

Cross-linked and quaternized P4VP nanofiber composites with Ag nanoparticles were prepared and deposited on glass or interdigitated gold electrodes, and the electrodes were used as humidity-sensing material. Under optimal conditions, the composites showed a fast response, high response to humidity, sensing repeatability, small hysteresis, and good capability of detecting very low humidity. The highly desirable humidity sensing properties of the prepared composites can be attributed to their balanced hydrophilicity and distinct nanostructure [115].

Films combining a P4VP layer and poly(N,N'-diethylacrylamide) (PDEA) hydrogel containing glucose oxidase (GOD) were successfully synthesized on an electrode surface (designated as P4VP/PDEA-GOD). The cyclic voltammetric response of ferrocenedicarboxylic acid in P4VP/PDEA-GOD film electrodes revealed reversible on-off behaviors to temperature, environmental pH, and SO_4^{2-} and ClO_4^- concentrations. The films could also be used to explain the switchable electrochemical oxidization of glucose. These films can open a novel path to the development of a new type of multi-controllable biosensors based on bioelectrocatalysis via immobilized enzymes [116].

Conclusion

PVPy, due to its electrical conductivity and good electrochemical characteristics, has been used in various electrode constructions for sensing humidity, metal ions, and other chemicals. Also, PVPy-modified electrodes have been employed in electrochemical investigations and also in the verification of redox reactions. On the basis of this history, to modify the surface of the electrodes, PVPy can be used in combination with other electroactive materials such as conductive polymers and inorganic materials to prepare suitable sensors to determine and monitor solution and stream compositions. It is worth mentioning that this review opens insights into novel and convenient ways of preparing PVPy-based electrodes in the future in order to give better and superior

electrochemical features in comparison with reported PVPy-based electrodes.

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