REVIEW

Functionalized carbon electrodes for pH determination

Heike Kahlert

Abstract The derivatization of carbon materials has allowed electrochemists to develop electrodes for pH measurements that offer distinct advantages compared to other common methods for determining pH in solutions. In this report, an overview on recent work on the different derivatization strategies leading to potentiometric, amperometric, or voltammetric pH sensors is given. The topic is subdivided into five main categories: (1) chemical modification, (2) covalent bonding, (3) physical adsorption, (4) film formation, and (5) composite electrodes.

Introduction

There is a strong demand for more robust, reagentless pH probes that can accurately sense changes in "rough" environments such as in food industry, industrial effluents, and sewage. The most common approach to pH sensing is to use potentiometric, amperometric, or voltammetric sensors. Carbon materials have been widely used in electrochemistry and extensively studied as electrode materials because of their good electrical conductivity, low density, low thermal expansion, and low elasticity. Additionally, they are generally low cost, readily available, and suitable for modification. The most common carbon materials used in electrochemistry are carbon black, various types of graphite, glassy carbon, carbon fibers, carbon

nanotubes (CNTs) and multiwalled CNTs (MWCNTs). It has been shown [1] that various carbon materials respond to pH without preliminary activation. This response behavior was explained with the presence of chemisorbed oxygen on the graphite surface with formation of C=O groups. Various methods are known for the modification of carbon materials to improve or tune their electrocatalytic, redox, or ion-sensing properties. The present manuscript is focused on the functionalization of carbon materials for their application in pH determination. The derivatization strategies for the immobilization of pH-sensing substances can be divided into five main groups: (1) chemical modification of the carbon surface with oxygen containing functional groups, (2) covalent bonding of pH-sensing compounds initiated either by chemical or electrochemical activation, (3) physical adsorption of pH sensing compounds, (4) fabrication of film electrodes, and (5) fabrication of carbon composite electrodes. Figure 1 illustrates the main strategies for the surface functionalization of carbon materials. Recent efforts to advance derivatization strategies will be discussed first. To compare the methods, slopes, working ranges, response times, and life times are discussed if possible. Developments in the modification of carbon materials especially for biological applications were reviewed by Zen et al. in 2003 [2] and will not be considered here.
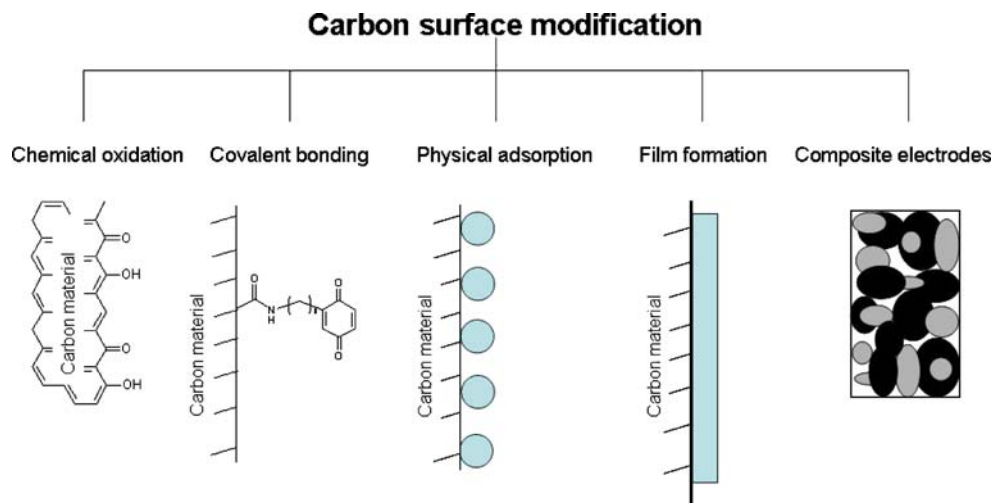
Derivatization strategies

Chemical oxidation of carbon surfaces

At room temperature and under normal atmospheric conditions, oxygen readily chemisorbs on carbon to form carbon–oxygen complexes; that is, usually, carbon surfaces
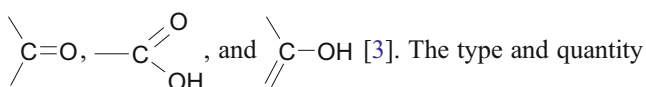
H. Kahlert (✉)
Institut für Biochemie,
Felix-Hausdorff-Str. 4,
17487 Greifswald, Germany
e-mail: hkahlert@uni-greifswald.de

Carbon surface modification

contain a variety of surface oxides. These oxide groups are similar to those found in many organic compounds, e.g.,

$\diagdown C=O, \; -C\diagup{}^{O}_{OH}$, and $\diagdown C-OH$ [3]. The type and quantity

of functional groups vary greatly with the carbon material and can be changed by special pretreatment procedures, e.g., gas-phase oxidation, chemical oxidation, radiofrequency plasma treatment, electrochemical oxidation, and even by mechanical polishing carbon electrode surfaces. The chemisorption of oxygen at higher temperatures (e.g., at 300 °C [3]) in dry air is strongly dependent on the active surface area and can be increased significantly by preoxidation procedures ("burnoff" or "activation" in dry air at, e.g., 625 °C [3]). This pretreatment causes a weight loss of the carbon material due to the formation of CO or CO_2. The influence of the pretreatment on microporosity and surface area depends on the carbon material. Porous carbon black materials show an increase in microporosity and surface area, while oxidation causes the pore diameter to increase. For rather nonporous materials or carbons with closed pores such as graphite, only a small increase in surface area was found. The reaction of carbon with chemical oxidants (e.g., inorganic acids) can lead to the complete dissolution of the carbon material under drastic oxidation conditions, to the formation of intercalation compounds (graphite oxide, graphite nitrate, graphite sulfate, etc.) or to the formation of surface oxides by mild oxidation. It is difficult to predict the conditions under which either surface or bulk oxidation or formation of intercalation compounds will result. The use of various "activated" carbon electrodes like wax-impregnated graphite electrodes, pyrolytic graphite electrodes, glassy carbon electrodes, and silicon rubber-based graphite electrodes has already been described by Szepesváry and Pungor in the early 1970s [4]. "Activated" means that these electrodes were pretreated by immersion in an aqueous solution of a suitable oxidant for several minutes, e.g., permanganate, to

form quinhydrone-like surface oxides. The average slope of pH–potential graphs was dependent on the activation solution. Without preoxidation, electrodes had a slope of −30mV per pH unit. When soaking electrodes for 1–3min in acidic 0.1N permanganate solution, the slope increases giving an average value of −60mV per pH unit. The electrodes were suitable as indicator electrodes in acid–base titrations, with potential jumps at the end point of titrations greater than those obtained with glass electrodes. However, the jumps became smaller when measurements were repeated even after 4days. Carbon black can be activated with surface oxide groups by a treatment in a mixture of nitric and sulfuric acid at temperatures of about 95 °C [5]. A linear relationship between the potentiometrically determined potentials of the carbon materials and the pH of the adjacent electrolyte solution in a range from pH2 to 7 with a slope of −59mV per pH unit was found. In our studies, we noticed that an effective surface oxidation of graphite powders can be achieved by reflux boiling of the powder with concentrated nitric acid for 60min. After the treatment, the predominant current response in voltammetric measurements coincides with the response of dissolved quinhydrone [6]. The same results can be obtained by oxidation of graphite powder with concentrated nitric acid at room temperature for 8days [7].

Plasma modification of materials has the advantage that the reaction takes place only at the material surface without changing the bulk properties. The formation of surface functional groups containing oxygen such as carboxyl or keto groups strongly depends on the plasma gas mixture and on the plasma processing time [8].

The electrochemical pretreatment of carbon electrodes can be traced back to the 1950s [9] and is now widely used to activate carbon surfaces because of the simplicity. However, the reaction conditions have to be maintained very carefully to obtain defined surfaces. A detailed study focused on the effects of potentials, pH of the electrolyte

solution, and the length of time of oxidation or reduction on the activation of glassy carbon was given by Beilby et al. [10]. As a result of this study, the authors could refine the McCreery model [11] according to which the electrochemical pretreatment of glassy carbon leads to the formation of a graphitic oxide film when the electrode is subjected to high positive potentials in acidic, neutral, and even basic solutions. However, the graphitic oxide is unstable in highly basic solutions. The anodic process at lower potentials in highly basic solutions (1M NaOH) is a different process, which apparently does not involve the formation of graphitic oxide. When MWCNTs were electrolyzed at a constant potential of 2.0V vs. saturated calomel electrode in a solution containing $2.0\,\mathrm{mol\ L^{-1}}$ of NaCl, the amount of carboxyl and hydroxyl groups was increased with increasing reaction time [12]. Scanning electron microscopy and transmission electron microscopy images before and after oxidation showed that the original MWCNTs were smooth with closed tube ends and the oxidation leads to an opening of the tube ends, a cut of some of the MWNTs, and an erosion of the surface. An electrooxidative method for the surface modification of carbon fiber electrodes has been developed by Ishifune et al. [13]. Electrogenerated $NO_3^{\bullet}$ radicals were used as mediators, formed by the anodic oxidation of NO_3^- anions. As a result, hydrophilic carbon fiber electrodes with phenolic hydroxyl surface groups were obtained.

All the surface modification methods described above lead to an increase in surface oxide structures. The main problem is that in all cases, a mixture of surface groups will be produced, and hence the formal potentials of the materials at a certain pH differ in a wide range. This prevents the application of these materials in calibration-free potentiometric pH sensors. Additionally, the response times in electrolyte solutions of different pH values and the life times of stable and defined surface groups are not satisfactory. However, the combination of activated carbons with other pH-sensing materials like quinones or anthraquinones can overcome these disadvantages.

Covalent bonding of pH-sensing materials

Covalent bonding of pH-sensing materials initiated by electrochemical activation The electrochemically assisted covalent modification of carbon surfaces, i.e., the generation of solution-based radicals and the attachment of these radicals to carbon surfaces, i.e., the formation of a covalent bond between a surface C and a modifier, is a relatively recent development in modified electrode research. The formation of radicals by the electrochemical oxidation of ω-diamines and their covalent attachment was first reported by Barbier and Pinson in 1990 [14]. The introduction of the reduction of aryl diazonium salts at carbon surfaces in 1992 [15] (illustrated in Scheme 1 for anthraquinone-1-diazonium salt) opens the possibility to use a large number of other diazonium salts to attach various functional groups to carbon surfaces.

In 1997, Allongue et al. have reported the electrochemical reduction of a wide variety of aromatic diazonium salts on various carbon materials [16], and a report by Downard in 2000 [17] was the first to review this research area. In this review, various modification methods, mechanisms, and the characterization of the monolayers are described, e.g., the oxidation of amines, reduction of aryl diazonium salts, oxidation of arylacetates, and the oxidation in the presence of alcohol. To obtain pH-sensing surfaces, Hall and co-workers have used the method developed by Pinson to

Scheme 1 The electrochemical reduction of anthraquinone-1-diazonium salt at the carbon surface
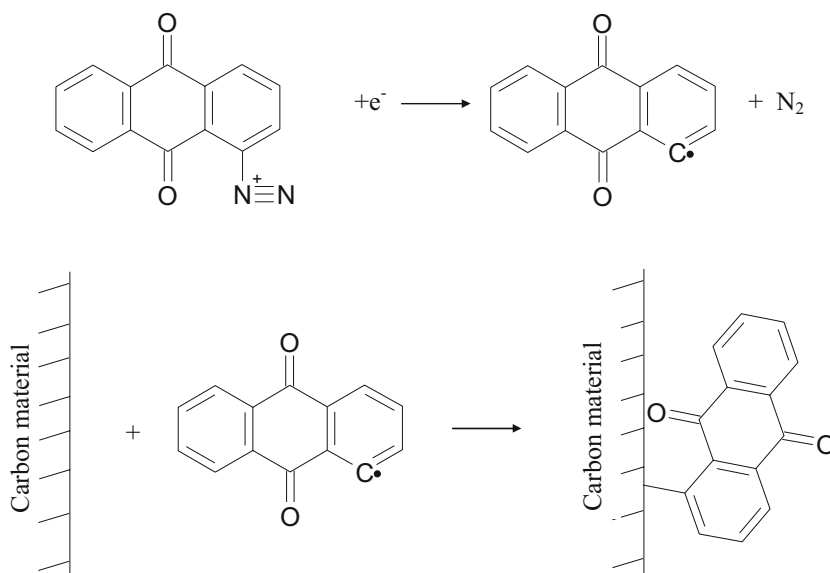
covalently attach a stilbene-tethered quinone on glassy carbon surfaces [18, 19]. *Trans*-2′,5′-dimethoxyl-stilbene-4-diazonium tetrafluoroborate was electrochemically reduced on glassy carbon to form a monolayer. Chemical demethylation forms a hydroquinone-substituted stilbene-grafted glassy carbon electrode. Whereas the potentials for the anodic and cathodic peaks in cyclic voltammetric measurements did not show good linearity when plotting peak potentials versus pH of the electrolyte solutions, the open circuit potentials exhibited a good linearity with a slope of −56mV per pH unit in the pH range from 3 to 10. Very recently, covalent attachment of anthraquinone to the surface of diamond electrodes by the electrochemical reduction of the corresponding diazonium salt was reported by Foord et al. [20]. Cyclic voltammetric measurements showed a redox couple, the potential of which is dependent on the pH of the supporting electrolyte solution with a slope of about −59mV per pH unit. The main disadvantage is that the redox couple is only clearly detectable at high pH values (>11).

All electrochemically assisted methods have the advantage that they are experimentally simple, rapid, and require only basic equipment, and covalently attached monolayers are rather stable under harsh conditions. The main disadvantage is that the carbon material has to be in the form of an electrode. This can be undesirable when further modification or the incorporation into composite electrode is aimed at. A practical difficulty for pH-sensing application is that the covalent attachments of materials like anthraquinones decrease the electron transfer rate and hence potentiometric measurements show rather long response times or are even impossible to perform.

Covalent bonding of pH-sensing materials initiated by chemical activation Compton's group has established a methodology for the homogeneous derivatization of carbon powders by chemical reduction of suitable diazonium salts with hypophosphorous acid [21]. Since then, a large number of diazonium salts containing pH-sensing groups has been used for derivatization of different carbon materials; for example, anthraquinone-1-diazonium chloride was used in the presence of carbon powder to obtain

anthraquinone covalently bonded to the carbon powder (AQcarbon; cf. Scheme 2) [21–23].

AQcarbon was immobilized onto the surface of a basal plane pyrolytic graphite electrode [24, 25], and voltammetric measurements were performed. In square wave voltammetry, well-defined peaks have been observed due to the reversibility of the anthraquinone system. From pH1 to 9, the peak potential showed a linear shift with a slope of −58mV per pH unit at 20 °C. MWCNTs were also derivatized successfully by the covalent bonding of anthraquinone and nitrobenzene via the chemical activation (reduction with hypophosphorous acid) of the anthraquinone-1-diazonium chloride and 4-nitrobenzenediazonium tetrafluoroborate [26]. Bond formation most likely takes place at an edge plane site along the nanotube. The voltammetric response of derivatized MWCNTs was found to be pH dependent over a wide pH range (1.0 to 12.0) with a slope around −60mV per pH unit. Streeter et al. [27] have immobilized AQcarbon together with solid, water-insoluble *N-N′*-diphenyl-*p*-phenylenediamine (DPPD) on the surface of a basal plane pyrolytic graphite electrode. In voltammetric measurements, both substances show two-electron, two-proton redox processes over a wide pH range with clearly resolved redox waves. Two suitable reference materials, nickel(II) and copper(II) hexacyanoferrate, were also immobilized on the graphite electrode. In square wave voltammetric measurements, the peak potentials of AQcarbon and DPPD can be determined relative to the reference materials. The suggested modification produced a combined change in peak potentials of approximately −114mV per pH unit at 20 °C. Additionally, to the modification of MWCNTs with 4-nitrobenzylamin (4-NBA) via the chemical oxidation of the benzylic amine group to the corresponding radical cation, Banks et al. have described the modification of MWCNTs by simply stirring the MWCNTs in degassed acetonitrile containing 4-NBA for 2h [28]. The 4-NBA-modified MWCNTs produced a stable voltammetric response of the potential to the pH of the solution. They explained the modification by a partial intercalation of 4-NBA between the graphite layers of the carbon surface at an edge plane-like surface defect.

Scheme 2 Anthraquinone-1-diazonium salt used in the presence of carbon powder to obtain anthraquinone covalently bonded to the carbon powder
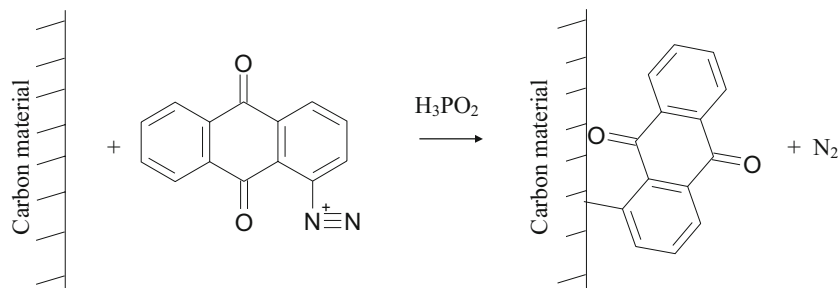
A completely different approach for the covalent attachment of pH sensing materials on glassy carbon was introduced by Holm et al. [29]. The authors have described the covalent bonding of the hydroquinone/quinone redox system on the surface of glassy carbon using first an electrochemical preoxidation treatment followed by the immobilization of the hydroquinone precursor, 2-(2,5-dimethoxyphenyl)alkaneamine, by carbodiimide chemistry (cf. Scheme 3) and a final demethylation reaction. Resulting electrodes exhibited a reversible redox system in cyclic voltammetry, the formal potential of which decrease with increasing pH with a slope of −55mV per pH unit. Unfortunately, the modified electrodes showed very high background currents leading to a limitation in sensor application.

The derivatization of carbon surfaces via chemical reactions has allowed chemists to tailor electrodes with robust surfaces resulting in reagentless pH probes that can accurately sense changes in pH even in "rough" media like effluents. However, the fabrication of the surfaces is in most cases complex, time consuming, and needs a lot of reagents. Furthermore, carbon materials have been used in voltammetric measurements. Potentiometric measurements have not yet been described in the literature. Our investigations with graphite particles modified with anthraquinone-1-diazonium chloride showed pH-sensitive voltammetric signals; however, no stable and reproducible potentials were observed in potentiometric measurements.

Physical adsorption of pH-sensing materials

Quinhydrone and several quinhydrone-like compounds can easily be adsorbed on a glassy carbon surface either by electrochemical polarization of glassy carbon in the presence of quinhydrone in an acidic solution or by simple dipping in such solutions. Gomathi and Rao stated [30] that the adsorption of quinone/hydroquinone on carbon surfaces by cycling glassy carbon electrodes in sulfuric acid containing quinhydrone leads to a stable redox system on the electrode surface, which is ascribed to the oxidation/reduction of quinone/hydroquinone, the response of which could be reproduced even after several weeks. Anthraquinone and sulfonated derivatives of anthraquinone also show strong adsorption on various electrode materials including graphite

and glassy carbon. Already, in 1976, Brown et al. [31] have described the adsorption of 9,10-phenanthrenequinone on pyrolytic graphite or vitreous carbon. They have stated that the rate of removal of 9,10-phenanthrenequinone after washing and immersing the electrode in a supporting electrolyte solution appeared to be approximately first order with a half-life of 7 to 9h. The peak potentials in differential pulse voltammetry were dependent on the pH of the solution with a slope of −60mV per pH unit. In addition, anthraquinone disulfonate can be adsorbed on graphite electrode surfaces but shows a slow loss of adsorbed layer when keeping in pure supporting electrolyte solutions for several hours [32]. Shiu et al. [33] have shown that a preanodization of the glassy carbon electrode and a potential cycling in anthraquinone sulfonate are essential to obtain stable adsorptive films. A certain decrease in surface coverage was observable after prolonged soaking, but the very last few monolayers of adsorbates were tightly bound to the surface and remained even after polishing with alumina. Voltammetric measurements showed a pH dependence of the voltammetric peak potential with a slope of −59.7mV per pH unit in a pH range from 1 to 11. Potentiometric measurements also showed a decrease in the electrode potential with increasing pH with a slope of −54.7mV per pH unit. However, the response times are rather long (authors give 10min for stable reading). The lifetime of such electrodes was estimated to be at least 2months.

The physical adsorption of nitro-containing organic compounds seems to result in layers of higher stability and without preoxidation of carbon materials. Pandurangappa et al. have investigated the physical adsorption of DPPD on the surface of graphite particles [33] as a suitable material for the detection of sulfide, but they have also found a shift of the voltammetric response with pH with a slope of −63mV per pH unit. Leventis et al. [23] have described the successful physical adsorption of anthracene, 9,10-diphenylanthracene, 9,10-phenanthraquinone, and of aromatic compounds containing nitro groups like azobenzene, 3-nitrofluoroanthene, 6-nitrochrysene, and 9-nitroanthracene on carbon powder in water/acetone solutions containing also hydrochloric acid and potassium chloride. Anthracene, 9,10 diphenylanthracene, and 9,10-phenanthraquinone were found to produce stable voltammetric peaks

Scheme 3 Covalent bonding of the hydroquinone/quinone redox system on the surface of glassy carbon
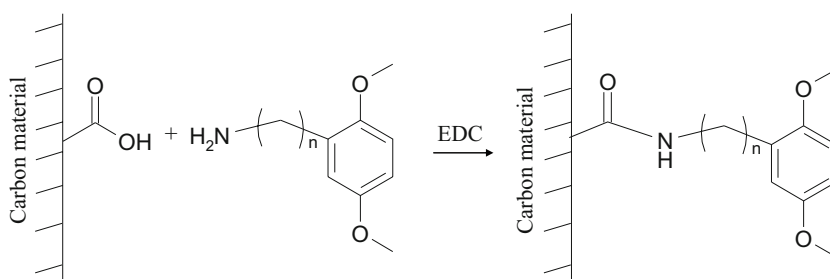
using cyclic voltammetry and square wave voltammetry. All these compounds showed Nernstian behavior, i.e., slopes of −56 to −62mV per pH unit at 22 °C in a pH range from 1 to 12.

Different substituted anthracene derivatives, among them 9,10-anthraquinone, were investigated to study the formation of monolayers physically adsorbed on hydrophobic H-terminated diamond and on oxidized (hydrophilic) interfaces prepared by electrochemical pretreatment in nitric acid [20]. Authors pointed out that the physically adsorbed material is steadily lost from the surface when immersing the electrode in an aqueous medium because of weak chemical interactions between the diamond material and the organic compound.

The physical adsorption of the pH-sensing material is a very simple procedure to functionalize carbon surfaces; however, either only voltammetric measurements can be performed, or response times are rather long. Moreover, the slow desorption of the materials is a limiting factor in the application of these materials in pH sensors.

Fabrication of film electrodes

Another approach of producing pH-sensitive electrodes involves the electrodeposition of polymer films on electrode surfaces. Mandler et al. [35] have used benzylated polyethyleneimine-quinone-modified glassy carbon electrodes for voltammetric measurements of pH. The derivatization of polyethyleneimine with benzylbromide leads to stable films on solid electrodes because the solubility in water is considerably low. Film formation was made by spin coating glassy carbon electrodes with solutions of polyethyleneimine in methanol. Anions like negatively charged quinone derivatives (anthraquinone-2-sulfonate, anthraquinone-2,6-disulfonate) were found to be strongly attached to such films and exhibit reversible redox systems in cyclic voltammetry. The peak potentials decrease with increasing pH with a slope of −55mV per pH unit. The linear working range is limited to pH values smaller than 9 as it was observed also for the conventional quinhydrone electrode. Leventis et al. [23] have shown that physisorbed diphenylamine onto the surface of carbon particles undergoes an oxidative electropolymerization reaction in contact with an aqueous electrolyte solution to form polydiphenylamine. The voltammetric behavior was studied using cyclic voltammetry and square wave voltammetry showing a typical response of polydiphenylamine. Both peaks belonging to polydiphenylamine shifted linearly in a negative direction with increasing pH with slopes of −56 to −66mV per pH unit in a pH range from 1 to 12. Basal plane pyrolytic graphite coated with poly(pyreneamine) was used by Oyama et al. to fabricate pH-sensitive ion-selective field effect transistors (ISFETs) [36]. The film preparation was achieved by electrochemical polymerization of the corresponding monomer in acetonitrile. These ISFETs showed a sub-Nernstian slope of −32.2mV per pH unit in a range from pH 3 to 10. The response could be improved remarkably when a protective neutral carrier membrane (tri-n-dodecylamine) was deposited onto the film. The slope increased to −57.5mV per pH unit. The sensors showed a slow drift of 0.1mV h^{-1} and a response time of about 4s.

Kang et al. [37] reported on potentiometric pH sensors based on film electrodes prepared by electropolymerisation of nickel(II)-4,4′,4″,4‴-tetraaminophthalocyanine or copper (II)-4,4′,4″,4‴-tetraaminophthalocyanine on glassy carbon substrates by repetitive cycling a polished glassy carbon electrode in a dimethylformamide solution containing the metal phthalocyanine. A thin layer of cellulose acetate was used as a protective layer. The film electrodes exhibited a linear dependence of potentiometrically determined electrode potentials on pH of the solution in a pH range from 1 to 13 with slopes of −55 to −56mV per pH unit. The response times are affected by the film thickness and can be less than 1min. Blair et al. [38] have described the electrodeposition of cobalt(II) porphyrin films on glassy carbon disk electrodes. Such electrodes showed linear calibration curves when potentiometric measurements were performed with a slope of −51 to −54mV per pH unit in a pH range from 2 to 12, a lifetime of about 3weeks, and a fast response less than 10s.

Film electrodes are easy to fabricate and show fast response behavior. However, film electrodes show a certain lifetime after which the surface has to be renewed. This includes an intensive polishing of the carbon electrode surface to remove old films and a new film deposition procedure.

Fabrication of composite electrodes

The mechanical immobilization of microparticles onto the surface of carbon electrodes (basal plane graphite electrodes, paraffin impregnated graphite rods) is a very simple and fast method [24, 25]. The major drawback is that the immobilized layer can become unstable when solutions flow across the electrode surface or under harsh conditions. Composite electrodes, made of graphite, a pH-sensing material, and a suitable binder, present a useful alternative to immobilized particles. Such electrodes can be produced very easily, they are very robust particle-modified electrodes, the handling is not complicated, and, depending on the binder, they can be used even at higher temperatures or under harsh chemical conditions. The preparation protocols of carbon composite electrodes entail a large number of degrees of freedom in choosing the starting carbon material, the binder, and the pH-sensing material.

The use of surface-oxidized graphite in solid composite electrodes can be traced back to the early 1970s. Szepesváry

and Pungor [4] have reported the use of silicon rubber-based graphite electrodes as indicator electrodes in acid–base titrations. At the end of the 1990s, sol–gel electrochemistry has rapidly developed as a versatile general method for the fabrication of electrochemical sensors, including a specific class of ceramic carbon electrodes (CCEs). A review of this special class of electrodes was given by Rabinovich and Lev in 2001 [39]. Tsionsky et al. have reported the immobilization of 9,10-phenanthrenequinone in a CCE [40]. Voltammetric measurements exhibit an almost Nernstian behavior of the peak potentials with a slope of −60mV per pH unit in a range from pH0 to 7. Quinhydrone-modified electrodes show an extended working range up to pH9. A naphthoquinone-modified CCE was reported by Rabinovich et al. [41] showing comparable characteristics like the modified CCE described by Tsionsky. Li and coworkers proposed a screen-printable sol–gel ceramic carbon composite pH electrode with a zeolite as the receptor of protons [42]. To fabricate pH-sensing films, the zeolite and graphite powder were mixed, and then stock sol solution was added. A surfactant agent was added to prevent silica glasses from cracking during sol–gel transition when adding graphite powder. The electrodes showed linear dependence of the potential versus pH in a range from pH1 to 12 with a slope of −60mV per pH unit. Another sol–gel carbon composite electrode was described by Nogala et al. [43]. They used water-insoluble 3,5-dimethoxy-4-hydroxybenzaldehydrazine (syringaldazine) as the pH-sensing material. In cyclic voltammograms, a reversible redox system was obtained. In differential pulse voltammetry experiments, the peak potential depends linearly on pH in a range from pH3 to 10 with a slope of −59.3mV per pH unit.

Teixeria proposed the construction of various carbon–epoxy composite electrodes modified with silica gel [44] or different metal oxides, such as PbO_2 [45], λ-MnO_2 [46], and Fe_2O_3 [47, 48, 49]. Silica gel-based carbon–epoxy electrodes were used for potentiometric determinations and showed a linear dependence of the electrode potential versus pH in a range from pH2 to 13 with a slope of −40.5mV per pH unit. PbO_2 and λ-MnO_2-based graphite–epoxy electrodes exhibited linear responses in pH ranges from 1 to 11 and 2 to 13, respectively, with slopes of −58.7 and −53.6mV per pH unit, respectively. Fe_2O_3-based carbon–epoxy electrodes showed a linear behavior over a pH range from 2 to 12 with a slope of −40mV per pH unit [47]. Fe_2O_3-modified graphite–epoxy tubular electrodes were described [48] as pH sensors in flow injection potentiometry. The potential of the tubular electrode decreases linearly with increasing pH with a slope of −26.5mV per pH unit in a working range from pH2 to 12.

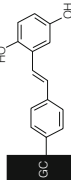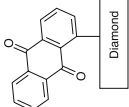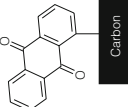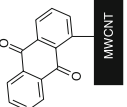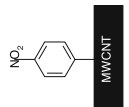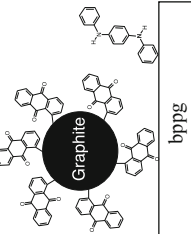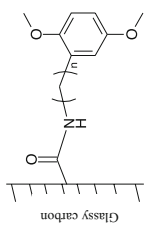Lawrence et al. [50] have describe a pH probe based on three redox-active components, anthraquinone, phenanthraquinone, and ferrocene mixed with carbon powder and an epoxy resin. In square wave voltammetry, three peaks have been observed due to three redox-active species. When the pH of the electrolyte was raised, the anthraquinone and phenanthraquinone waves shifted to more negative potentials, while the ferrocene redox wave was insensitive to pH changes and was used as the reference signal. By combining peak potentials, a shift of −114mV per pH unit at 25 °C with respect to the ferrocen reference potential was obtained.

In our group, we developed calibration-free solid composite grahite–quinhydrone electrodes with different binders like silicon, polymethylmethacrylate, and Teflon for potentiometric determinations. The graphite powder was surface oxidized before use, resulting in electrodes with an almost theoretical slope of the potential–pH dependence (−57.7mV per pH unit) [6, 7]. An effective surface oxidation was obtained in concentrated nitric acid (cf. paragraph 1). Additionally, the composite electrodes show formal potentials very close to the formal potential of the conventional quinhydrone electrode; that is, these electrodes are suitable for calibration-free potentiometric measurements by using the theoretical dependence of the electrode potential of the conventional quinhydrone electrode on the pH of the solution. The binders mentioned above allowed manufacturing either very flexible electrodes [51, 52], or stiff electrodes, which could be polished or even machined to get desired shapes of electrodes [7, 53–55]. Short response time constants and very satisfactory long-term stabilities make these sensors attractive for automatic measuring devices [53–55]. When an equimolar mixture of tetramethylquinone and tetramethylhydroquinone was used as pH-sensing material, a linear working range from pH1 to 12 was observed [7].

Concluding remarks

Derivatized carbon materials for the fabrication of pH-sensing electrodes are an interesting alternative to conventional pH electrodes like glass electrodes, other membrane electrodes, or metal–metal oxide electrodes, and increasing efforts have been made to advance derivatization strategies (a summary is given in Table 1). The inexpensiveness, high electrode-to-electrode reproducibility, the possibility to operate over a wide temperature range, and the mechanical robustness make these electrodes attractive for pH measurements under harsh conditions, where, e.g., glass electrodes fail due to the fragility. Additionally, derivatized carbon electrodes can be constructed in such a way that no toxic substances are liberated during measurements (like it is the case for metal–metal oxide electrodes). The versatility of the materials opens the possibility to construct simple

Table 1 Comparison of different pH sensors with respect to slope, working range, and response time

Derivatization strategy	Carbon material	pH-sensing group or reagent	Measuring method	Slope (mV/pH unit)	pH range	Response time	Reference
Chemical oxidation	Graphite (in silicon composite electrodes)	Surface oxides	Potentiometry	−59	n.s.	2–3s	[4]
Covalent bonding of pH sensing material	Carbon black	Surface oxides	Potentiometry	−59	2–7	n.s.	[5]
	Glassy carbon		Potentiometry	−56	3–10	n.s.	[18, 19]
Initiated by electrochemical activation	Diamond		CV	−59	11–13	n.s.	[20]
Initiated by chemical activation	Carbon powder		CV, SWV	−58 (20 °C)	1–9	n.s.	[21, 22, 23]
	MWCNTs		CV, SWV	−56 to −60 (independent on temperature)	1–12	n.s.	[24, 26]
			CV, SWV	−53 to −60 (25 °C)	1–12	n.s.	[24, 26]
	Carbon powder		SWV	−114 (20 °C)	4.6–9.2	n.s.	[25]
	Glassy carbon		CV	−55	n.s.	n.s.	[27]
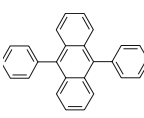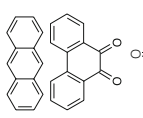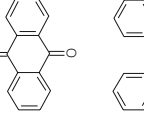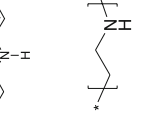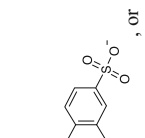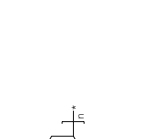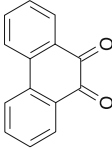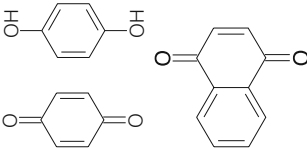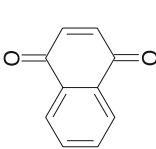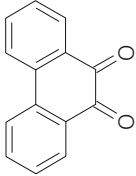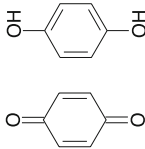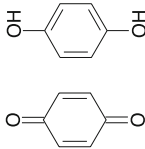
Method	Electrode material	Technique	Slope	pH range	Response time	Ref.
Physical adsorption	Carbon powder	CV, SWV	−62 (22 °C)	1–12	n.s.	[23]
		CV, SWV	−57.5 (22 °C)	1–12	n.s.	[23]
		CV, SWV	−56.3	1–12	n.s.	[23]
		DPV	−60	1–12	n.s.	[29]
	Glassy carbon (electrochemically activated)	CV	−59.7	1–11	n.s.	[31]
		Potentiometry	−54.7	1–11	10min	[31]
	Carbon powder	CV	−63	1–7	n.s.	[32]
Film electrodes	Glassy carbon	CV	−55	2–9	n.s.	[33]
		Potentiometry	−55	1–13	<1min	[35]
		Potentiometry	−51 to −54	2–12	<10s	[36]
	Carbon particles	CV, SWV	−55 to −66	1–12	n.s.	[23]

Table 1 (continued)

Derivatization strategy	Carbon material	pH-sensing group or reagent	Measuring method	Slope (mV/pH unit)	pH range	Response time	Reference
Composite electrodes	Bppg	Polypyreneamine/tri-*n*-dodecylamine	Potentiometry (ISFET)	−57.5	4–10	n.s.	[34]
	CCE	(phenanthrenequinone)	CV	−60	0–7	n.s.	[40]
		(hydroquinone / benzoquinone)	CV	−60	0–9	n.s.	[40]
		(naphthoquinone)	CV	−55 to −57	1–7.5	n.s.	[41]
	Carbon epoxy	$Ca_{1.0}(K_{0.8}Na_{3.2})[(Al_{5.6}Fe_{0.3}Ti_{0.1})Si_{30.1}O_{72}]$	Potentiometry	−60	1–12	60s	[42]
		Syringaldazine	CV, DPV	−59.3	3–10	n.s.	[43]
		Silicagel	Potentiometry	−40.5	2–13	<15s	[44]
		PbO_2	Potentiometry	−58.7	1–11	<15s	[45]
		$\lambda\text{-}MnO_2$	Potentiometry	−53.6	2–13	10s	[46]
		Fe_2O_3	Potentiometry	−40	2–12	n.s.	[47]
		Fe_2O_3 (tubular electrode)	Potentiometry (FIA)	−26.5	2–12	n.s.	[48]
	Carbon, organic binder (silicone, PMMA, Teflon)	(anthraquinone / phenanthrenequinone), ferrocene	Potentiometry	−58	0–9	<2s	[7, 51, 52]
		(hydroquinone / benzoquinone)	Potentiometry (FIA)	−54	0–9	3–5s	[53, 54, 55]
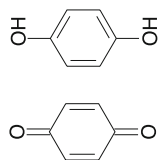
microelectrodes, which meet the increasing demands for miniaturizing measuring probes and devices. One limitation to use functionalized carbon materials for potentiometric pH measurements is that interferences from redox-active species present in the analysis media cannot be neglected in all cases. Although precise literature data are hardly available, one may assume that these interferences will depend on the specific modification method. Thus, we could show that in case of composite electrodes developed in our group for potentiometric measurements, moderate concentrations of redox-active species like, e.g., NO_3^-, S^{2-}, ascorbic acid, and Fe^{3+}, is negligible [52].

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Tetramethylhydroquinone (tubular electrode)	Potentiometry	−58	0–12	<2s	[7]

CV Cyclic voltammetry, *SWV* square wave voltammetry, *DPV* differential pulse voltammetry, *FIA* flow injection analysis, *ISFET* ion-selective field effect transistor, *GC* glassy carbon, *MWCNT* multiwalled CNT, *Bppg* basal plane pyrolytic graphite, *CCE* ceramic carbon electrodes, *PMMA* polymethylmethacrylate

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