

Sol-Gel-Derived Ceramic-Carbon Composite Electrodes: Introduction and Scope of Applications

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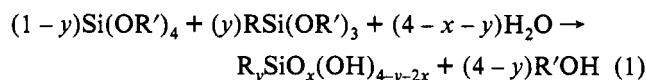
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A new class of composite electrodes made of sol-gel derived carbon-silica materials is introduced. Modified porous composite carbon-silica electrodes can exhibit hydrophobic or hydrophilic surface characteristics and can serve as an indicator (inert) electrode, as a potentiometric (selective or reference) electrode, and in amperometric sensing and biosensing. The composite (carbon) ceramic electrodes (CCEs) are rigid, porous, easily modified chemically and have a renewable external surface. The electrodes offer higher stability than carbon paste electrodes, and they are more amenable to chemical modification than monolithic and (organic) composite carbon electrodes. Experimental examples demonstrating the scope of electroanalytical applications of the composite carbon-silica electrode and its modifications are presented.

Composite electrodes made of carbon powder (or inert metals) dispersed in insulating organic polymer (e.g., epoxy¹ or poly(chlorotrifluoroethylene)²) or viscous liquid (e.g., paraffin oil or Nujol³) were found useful in the various fields of electroanalysis.^{4,5} This paper demonstrates an alternative, equally versatile, class of ceramic composite electrodes (CCEs). The electrodes are made of graphite powder dispersed homogeneously in sol-gel derived ceramic material such as porous silica or Ormosil (organically modified silica⁶). Methods for the preparation of CCEs and examples demonstrating the power and versatility of modified CCEs are presented.

The evolution of sol-gel technology,⁷⁻⁹ a meltless method for the formation of silica and metal oxides, and the subsequent invention of the sol-gel doping technique,¹⁰ provided analytical chemists with the possibility to tailor supporting inorganic matrices with the versatility that was traditionally attributed only to organic polymers.^{11,12} Indeed, sol-gel derived ceramics

found a plethora of analytical applications in biosensing,¹³⁻¹⁵ chromatography,^{16,17} photometric sensing,¹⁸⁻²² and other applications.⁷⁻⁹ A most useful route for the formation of porous silica is by using alkoxysilane precursors (e.g., tetramethoxysilane or tetraethoxysilane) that hydrolyze (in the presence of water) and condense to form a colloidal suspension (sol) that after gelation and drying forms the xerogel (i.e., dry gel). A base or acid is used for catalyses and for control of the specific surface area and pore size distribution of the xerogels. Most of the applications of sol-gel derived ceramics require poreless materials which are produced by a final high-temperature sintering step. The sol-gel derived composite-carbon electrodes that are described here are not sintered. Sintering lowers material porosity, which is in itself advantageous, as is the ability to introduce and immobilize heat-sensitive compounds during the molding step. The surface properties of the xerogel (such as polarity, ion exchange capacity, and concentration of silanol groups) can be modified by using as precursors compounds containing the silicon-carbon bond. The Si-C bond remains unchanged during the hydrolyses and polycondensation, and the functional group (R) remains exposed at the surface of the porous structure that is denoted by the general formula $R_ySiO_x(OH)_{4-y-2x}$, where R and OH are the surface groups:



where $0 < y < 1$ and $0 < x < 2$. For example, when methyltrimethoxysilane or phenyltrimethoxysilane is used, the methyl or phenyl groups remain exposed at the surface of the porous network and alter its cage polarity and hydrophobicity.

Sintered sol-gel electrodes were extensively studied for electrochemical²³ and electrochromic²⁴ applications. Recently,

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modified porous silica²⁵ and vanadium oxide sol-gel electrodes were reported,²⁶ and electrochemical techniques were found useful in studies of structural transitions during the sol-gel process.²⁷⁻²⁹ This article demonstrates a new class of electrodes made of carbon powder dispersed in sol-gel derived silica or modified silica for the production of indicator, reference, selective, and biocatalytic ceramic electrodes. Attention is given, even in this first report, to providing a variety of applications that will also highlight the versatility in tailoring virtually any required electrode configuration including thin layers, monolithic structures, and even miniature electrodes.

EXPERIMENTAL DETAILS

Materials. All the organosilane compounds were purchased from ABCR Inc. (Karlsruhe, Germany). High-purity carbon powder ($\sim 10\text{--}20\ \mu\text{m}$) was purchased from Ultra Carbon Corp. (Bay City, MI); 3 mm diameter glassy carbon (Atomergic Chemicals, Farmingdale, NY) was used. Platinum foil (99.99% purity) was purchased from Alfa. Analytical grade reagents and triply distilled water (resistivity $>20\ \text{M}\Omega/\text{cm}$) was used unless otherwise specified.

Apparatus. An EG&G PARC Model 273 potentiostat-galvanostat, in conjunction with a Watanabe WX 4421 $x\text{--}y$ recorder was used for voltammetric and steady-state studies. A three-electrode cell equipped with a Pt-flag counter and a saturated calomel electrode (SCE) was used. Fast scan rate voltammetric experiments were conducted on a BAS-100B electrochemical analyzer. All experiments were conducted at ambient conditions at $\sim 25\ ^\circ\text{C}$. Water contact angle was measured using Rame-Hart Inc., NRL C.A., Gohiometer Model No. 100-00230.

Electrode Preparation. Each application of the composite silica-carbon electrodes requires a somewhat different preparation protocol. No attempt is made here to present the optimal preparation procedure for each application. On the contrary, a constant ratio of the carbon and sol-gel precursors was preferred (whenever possible) in order to decrease response deviations due to changes of the physical characteristics of the ceramic material. In this way, the response of the indicator, unmodified electrode serves as a common blank for all experiments.

(a) Preparation of Hydrophobic Indicator Electrodes. Methanol, 1.5 mL (Futarom, Laboratory Chemicals, Haifa), 1.0 mL of methyltrimethoxysilane, and 0.05 mL of hydrochloric acid (11 M) catalyst were mixed for 2 min and then 3.75 g of carbon powder was added and the resultant mixture shaken for an additional 1 min. A 3-mm length of a 1 mm inside diameter capillary was filled with the sol-gel carbon mixture, and the mixture was then dried overnight under ambient conditions ($\sim 25\ ^\circ\text{C}$). Additional water for the hydrolysis step is provided by air humidity. Base or neutral catalyses failed to produce rigid monoliths (or films) and yielded only silica-covered carbon powder. After drying, the electrode was polished with emery paper and wiped with a

weighing paper before use. Electrical contact was made by silver paint (Bio-Rad, A1208 Q-D colloidal silver). The resulting electrode was rigid, black, and the solid graphite particles were observable under an optical microscope. After polishing, the electrode became smoother and shiny though not mirrorlike. The electrodes were formed in the shape and dimensions of the molding vessel, and the adhesion of the CCE material to the capillary was excellent. Similar adhesion was observed in the low-pH preparation of thick ($10\text{--}20\ \mu\text{m}$) sol-gel films that were recently introduced for planar chromatography.³⁰ The conductivity of the carbon-silica composite material was $\sim 1.0\ \Omega^{-1}/\text{cm}$. No additional electrochemical pretreatment was required before use.

(b) Preparation of Organic Redox Modified CCE. Quinone (quinhydrone, *p*-benzoquinone, 9,10-phenanthrenequinone) and ferrocene modified electrodes were prepared by using the indicator electrode preparation procedure, with one exception: 0.014 g of organic modifier (quinhydrone (BDH Chemicals), benzoquinone (Aldrich), or ferrocene (Sigma)) or 0.007 g of 9,10-phenanthrenequinone was incorporated along with the sol-gel precursors.

(c) Preparation of Silver-Silver Chloride Modified CCEs. Silver nitrate, 0.012 g (Riedel-de Haen) was dissolved in a solution containing the sol-gel precursors: 1.5 mL of methanol, 1.0 mL of tetramethoxysilane, and 0.05 mL of 60% HNO_3 (nitric acid catalyses was preferred here in order to prevent silver chloride precipitation by HCl). Then, the electrode was prepared according to the previous preparation protocol. But hydrophilic electrodes were preferred in order to increase the active surface area of the electrode. In order to increase the concentration of the doped silver, the electrode was soaked further in 2.5 M silver nitrate solution for 1 h, air-dried for 12 h, and then soaked in 6 M aqueous hydrazine (Merck) solution for 30 min in order to reduce the silver. AgCl was deposited electrochemically from 0.5 M KCl solution (5 min at 0.25 V SCE). The electrodes were soaked in water to wash excess impurities and then dried overnight before use. The resulting electrode was identical in shape and color to the indicator electrodes, but when these electrodes were immersed in aqueous solution, the water, driven by capillarity forces, eluted through the porous hydrophilic carbon-silica matrix. After drying, the upper side of the electrode was sealed with conductive carbon cement (A-1216, Bio-Rad), which served here as an electrical connection in order to prevent contact of the penetrating solution with silver paint or the copper lead. For practical applications silver paint contact can be used. In these experiments, carbon paint was used in order to ensure that bulk modification of the electrode by the silver-silver chloride couple controls its response.

(d) Preparation of Glucose Oxidase Modified CCE. Carbon powder, 100 mg, was mixed with 25 mg of glucose oxidase (EC 1.1.3.4 type VII-S from *Aspergillus niger*, Sigma Chemicals Co.) and 0.5 mL of triply distilled water. Approximately 0.02 mL of the suspension was applied on the surface of a glassy carbon electrode and allowed to dry for 2-3 h. Then, another drop of 0.02 mL of freshly prepared sol-gel solution (composed of 1.5 mL of methanol, 0.5 mL of tetramethoxysilane, and 0.02 mL of 11 M HCl) was applied

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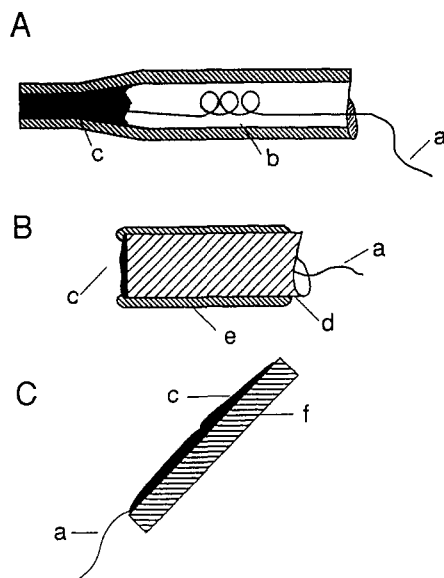


Figure 1. Configurations of CCEs: (A) monolithic; (B) film on conductive substrate; (C) film on insulator. (a) copper lead; (b) glass capillary; (c) silica-carbon material; (d) glassy carbon; (e) insulating epoxy; (f) microscope slide.

on the carbon surface. The electrode was left to gel and dry in ambient conditions for a few hours before a final washing in pH 5.6 phosphate buffer.

(e) Preparation of Composite Carbon Microelectrodes. A tapered end 2 mm, inside diameter, capillary was drawn by a micropipet puller. The thick end of the capillary was dipped into a paste containing the same precursors that were used in the preparation of the indicator CCEs. The glass capillary containing the sol-gel precursors was centrifuged in order to drive the sol-gel precursors into the narrow tip of the capillary. Finally, the microelectrode was allowed to gel and dry overnight in ambient conditions and then was polished gently. Electrical contact was made by silver paint.

(f) Preparation of Carbon Electrodes. Two types of carbon electrodes were used. (1) Glassy carbon: a 3 mm diameter glassy carbon rod was placed in a glass tube and sealed by Torr-Seal epoxy (Varian, Lexington, MA). The electrode was polished with Emery paper followed by a 0.05- μm alumina slurry on a woolen polishing cloth (Buehler, IL). (2) Carbon paste electrodes: 0.3 g of carbon powder was mixed with 0.1 mL of paraffin oil and filled in 0.3 mm (inside diameter) glass capillaries. The electrode was wiped with a weighing paper.

RESULTS

CCEs can be prepared in a variety of geometrical configurations, including silica-carbon matrix molded into an insulating capillary (depicted in Figure 1A), thin films of composite material applied on conductive supports (e.g., graphite rod or platinum foil, Figure 1B) or on insulating (e.g., microscope slide) supports (Figure 1C), and in the form of monolithic rods or disks. In addition, CCEs can be prepared in virtually any required dimension including, for example, miniature electrodes.

Indicator Electrodes. Indicator (inert) electrodes are used for studies of chemical kinetics and for electroanalytical applications such as FIA and LC electrochemical detectors. Mandatory requirements for such electrodes include large

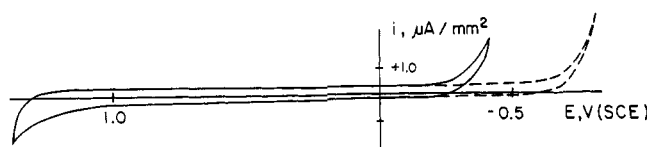


Figure 2. Cyclic voltammogram of an indicator composite carbon electrode in 1 M HCl ($A = 7.85 \times 10^{-3} \text{ cm}^2$), 100 mV/s sweep rate before (solid line) and after (dotted) oxygen removal from the bulk of CCE.

operational voltage window, in which low and constant background current prevails, operational and storage stabilities, and low interaction (e.g., by adsorption) of the electrodes with the reactants and poisoning chemicals. Monolithic composite graphite electrodes made of a methyltrimethoxysilane (or diphenyldiethoxysilane) precursor exhibited a hydrophobic surface before and after polishing, and water was rejected and did not penetrate through their porous structure. The indicator CCEs remained hydrophobic and repelled water even after prolonged periods (weeks) in aqueous solution. The monolithic CCEs were too small for a reliable water contact angle measurement. Therefore, contact angle measurements were conducted with a thin layer ($\sim 0.2 \text{ mm}$) of polished composite carbon-silica material applied on a microscope slide. These electrodes were prepared according to the same preparation protocol of the indicator electrode. The water contact angle was $78 \pm 2^\circ$ determined by four repeated measurements. The water contact angle was not affected by the thickness of the composite ceramic-carbon layer. Other organic solvents such as acetonitrile and methanol penetrated the electrodes. Similar unmodified and hydrophilic Ormosil electrodes made with tetramethoxysilane or (2-cyanoethyl)triethoxysilane exhibited hydrophilic surface, water penetrated through them, and contact angle measurements were irrelevant.

A cyclic voltammogram of a composite methyl-modified silica-carbon electrode in 1.0 M HCl is depicted in Figure 2. When a regular indicator electrode is immersed in deoxygenated 1 M HCl solution, the working potential window ranges between -400 and 1200 mV/SCE . However, by clearing the oxygen from the porous bulk of the electrode (e.g., by passing nitrogen above the composite porous material, or by a few minutes of oxygen reduction, when the upper side of the electrode is sealed), the cathodic range is extended to $\sim -700 \text{ mV/SCE}$ (dotted line in Figure 2). The overpotential for oxygen evolution is similar to that exhibited by other carbon electrodes. The hydrogen overpotential is somewhat lower than the hydrogen evolution overpotential of polished glassy carbon, better than that of graphite rod electrodes ($\sim -400 \text{ mV/SCE}^{31}$) and carbon epoxy composite ($\sim -350 \text{ mV/SCE}^{32}$), and much larger than the overpotential of the platinum group electrodes.

The observed capacity of the indicator CCE can be calculated from eq 2

$$C = I/Sv \quad (2)$$

where I is the current, S is the geometric area of the electrode (measured by an optical microscope), and v is the scan rate.

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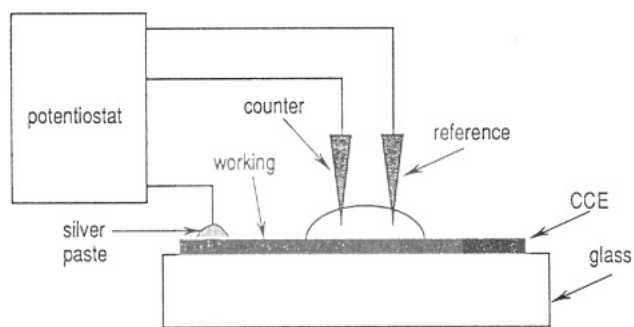


Figure 3. Electroanalysis of an aqueous drop on a flat hydrophobic CCE.

The background current is attributed to surface charging and faradaic surface reactions and is discussed in ref 33. The current was nearly uniform over the whole working potential range, and despite the rough surface it is $\sim 100 \mu\text{F}/\text{cm}^2$. The observed capacity is somewhat smaller than the observed capacity of polished glassy carbon electrodes ($= 120 \mu\text{F}/\text{cm}^2$,³¹ measured by 100 mV/s scan rate CV) though much larger than the observed capacity of carbon paste electrodes ($\sim 4.0 \mu\text{F}/\text{cm}^2$ ³¹ using the above preparation procedure). Similar electrochemical studies were conducted on a drop of 1 M HCl solution applied on the surface of the thin-layer electrode (Figure 3). The electrode was prepared by spreading an ~ 0.2 mm thick layer of the CCE precursors on a microscope slide (followed by the above-mentioned electrode preparation procedure). A miniature reference electrode and a small counter electrode, immersed in a ~ 3 mm diameter drop, were used. The thin-layer electrode revealed the same voltammogram and identical current characteristics as that of the composite carbon electrode, thus confirming that the contact angle studies that were conducted on the flat electrode configuration are also relevant for the composite rod electrodes.

Ormosil-carbon composite electrodes made of other hydrophobic glass precursors such as diphenyldiethoxysilane or (chloroethyl)trimethoxysilane exhibited similar behavior, while hydrophilic composite electrodes made of tetramethoxysilane or (2-cyanoethyl)triethoxysilane precursors exhibited a large background signal, precluding the possibility of applying hydrophilic carbon-silica as indicator electrodes in aqueous solutions. Detailed comparative studies of the characteristics of indicator CCEs are presented elsewhere.³¹

Parts A and B of Figure 4 compare the cyclic voltammograms of the composite carbon electrode in 1 M HCl + 1 mM potassium ferricyanide solution with that of the carbon paste electrode. The indicator CCE exhibited a reversible electrochemical reaction with ~ 60 -mV separation between the potentials of the anodic (E_{pa}) and the cathodic peaks (E_{pc}). The superior stability of the CCE is clearly diagrammed on the dotted curves in Figure 4A,B, which demonstrate the response after 24 h in the same solution. The signal of the composite carbon electrode remained virtually unchanged during this period. Both electrodes regained their original signal after surface renewal by mild mechanical polish. CV studies (at 100 mV/s) reveal a linear dependence of the cathodic peak

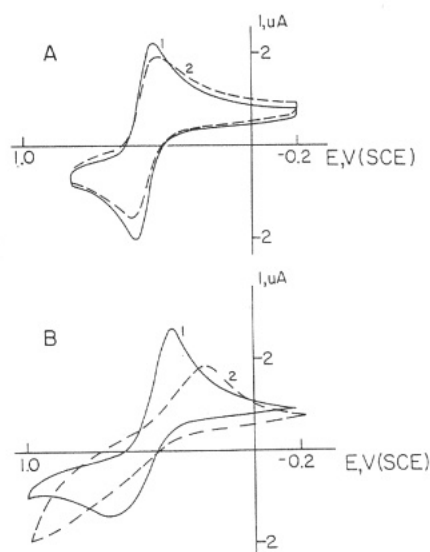


Figure 4. Cyclic voltammograms: (A) CCE and (B) carbon paste electrode, in 1 M HCl + 1 mM hexacyanoferrate, (1) immediately after immersion and (2) after a 24-h period.

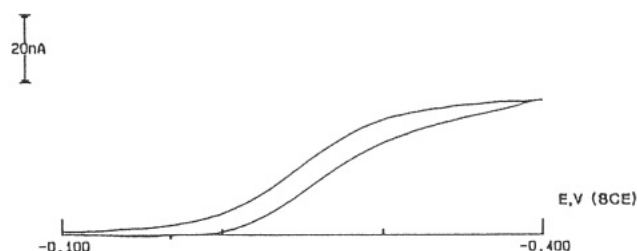


Figure 5. Cyclic voltammogram of a microcomposite silica-carbon electrode in 5.0 mM hexamineruthenium(III) chloride (0.2 M acetate buffer + 0.3 M sodium sulfate, pH 4.7; sweep rate 50 mV/s).

current (slope $1.61 \mu\text{A}/\text{mM}$; correlation coefficient, $R = 0.997$) over two decades of hexacyanoferrate concentrations (0.1–10 mM). The calculated diffusion coefficient ($D = 5.8 \times 10^{-6} \text{ cm}^2/\text{s}$) falls within 5% of that calculated by the $I-v^{0.5}$ dependence (slope $5.02 \mu\text{A}/(\text{V}/\text{s})^{0.5}$; $R = 0.998$; $D = 5.6 \times 10^{-6} \text{ cm}^2/\text{s}$, at 1 mM solution). Despite the ion exchange characteristics of silanol groups, the calibration curve was independent of the direction of changes in concentration. This was true even after prolonged time of immersion in the hexacyanoferrate solution (Figure 4A) and even at high pH, when a larger fraction of the surface silanol groups is deprotonated. This surprising feature is believed to be contributed by a combination of (a) the small percentage of silica at the surface of polished electrodes, (b) the smaller amount of surface silanol groups in acid-formed Ormosils (which has relatively small surface area⁷), and (c) the hydrophobic surface (comprised of hydrophobically modified silica and graphite) which hindered deep penetration of the inorganic compound into the porous structure.

Miniature Electrodes. Figure 5 demonstrates a cyclic voltammogram (scan rate 50 mV/s) of 5.0 mM hexamineruthenium(III) chloride (STEM Chemicals) in 0.2 M acetate buffer (pH 4.7) and 0.3 M sodium sulfate supporting electrolyte. Assuming a flat electrode configuration, the effective radius of the electrode can be calculated by eq 3³⁴ giving a 12- μm radius (r)

$$I = 4\pi r n F D c \quad (3)$$

where n is the number of stoichiometric electrons, D is the

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diffusion coefficient (taken as $D = 5.4 \times 10^{-6} \text{ cm}^2/\text{s}^{34}$), and c is the concentration of $\text{Ru}(\text{NH}_3)_6^{3+}$. One disadvantage of the sol-gel process is the shrinkage of the monolith during gelation. The fact that it is possible to form miniature electrodes demonstrates that the shrinkage of the CCE material is very small and the CCE can be molded to fit the exact dimension of complex molding vessels.

Quinone Modified Electrodes. The immobilization of reagents in polymer-coated electrodes is a well-established method to tailor their chemical characteristics.³⁵ The porous structure of the composite carbon-silica electrode allows for bulk modification. This permits the electrode to benefit from the mobility of the reagents in the monolith. Additionally, unlike polymer-coated electrodes, the surface of the modified electrodes can be renewed easily. Quinone compounds were selected for presentation, despite their complex and still disputed charge-transfer mechanisms,³⁶⁻³⁸ due to their popularity as charge-transfer mediators and model redox compounds and their strong adsorption on graphite, which provides a way to probe the structure of the modified electrodes,^{39,40} and finally quinone modified electrodes may have practical use as pH indicators.

Figure 6A demonstrates typical voltammograms of 9,10-phenanthrenequinone (PQ) modified hydrophobic electrodes (PQ/CCE) in 1.0 M HCl solution at different scan rates. The anodic and cathodic peak separation of PQ/CCE ranged between 8 (at 10 mV/s) and 115 mV (at 10 V/s), indicating a dominant adsorption mechanism. The cyclic voltammograms of a blank and a PQ modified indicator electrode (impregnated electrode) are depicted in Figure 6B for comparative reasons. The impregnated electrode was prepared by immersing an inert indicator electrode for 24 h in an aqueous solution containing $15 \mu\text{M}$ PQ. The electrode was then washed with distilled water. The E_0' ($= (E_{\text{pa}} + E_{\text{pc}})/2$) of the modified inert CCE and the PQ doped CCE was 0.180 ± 0.003 . Peak separation and peak shape were also similar at low scan rates due to the strong adsorption of PQ on graphite surfaces. However, the doped CCE also exhibited a long tail of diffusion current, which was not observable in the PQ impregnated electrode. The similarity between the response of modified electrodes and inert CCEs (exposed to aqueous solution containing the same modifiers) was also observed for other (less strongly adsorbed) modifiers. For example, quinhydrone modified CCE exhibited $E_0' = 0.454$, which is close to the standard electrode potential ($E_0 = 0.458 \text{ V/SCE}^{41}$) and the $E_0' = 0.454$ of inert CCE in quinhydrone 1 M HCl solution.

Figure 7 depicts the dependence of the anodic charge of the PQ modified indicator and the PQ doped CCEs as a function of the scan rate. The charge of the PQ impregnated CCE was almost independent of the sweep velocity over more

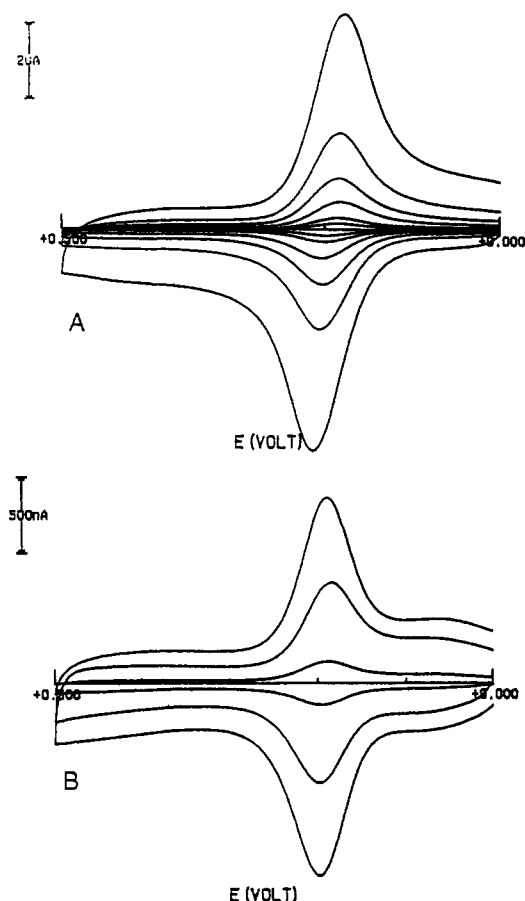


Figure 6. Cyclic voltammograms of (A) 9,10-phenanthrenequinone modified hydrophobic CCE in 1 M HCl solution (scan rates 10, 20, 50, 100, 200, and 500 mV/s) and (B) PQ modified indicator CCE in 1 M HCl solution (scan rates 10, 50, and 100 mV/s).

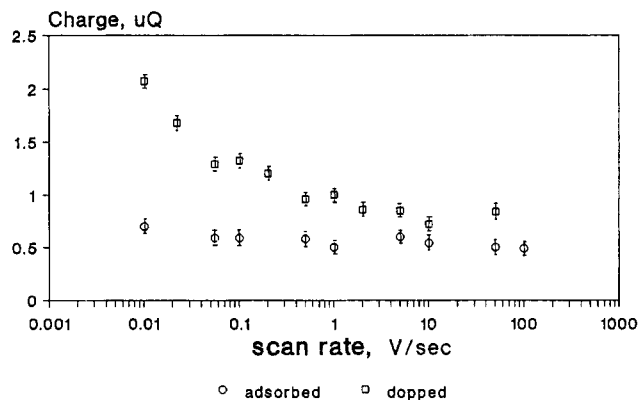


Figure 7. Cumulative cathodic charge exchanged by a modified PQ/CCE and a PQ impregnated CCE in 1 M HCl as a function of scan rate.

than four decades of scan rates, while the charge of the modified PQ/CCE decreased to less than 25% over the same range of scan rates. At high scan rates ($> 5 \text{ V/s}$), the exchanged charge was independent of the scan rate. At such high scan rates the diffusion layer becomes very small and the solution contributes only a small amount of reactive species compared with the adsorbed layer.

The amount of adsorbed PQ on modified CCE can be used to estimate the active area of the electrode. The quantity of adsorbed PQ was $\sim 400 \text{ pmol/cm}^2$. McCreery³³ reported a value of 170 pmol/cm^2 for a monolayer of adsorbed PQ on a polished glassy carbon electrode. Thus, the ratio of active

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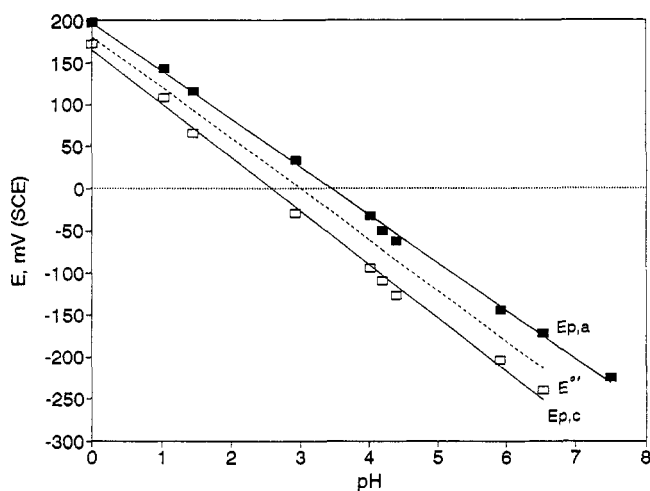


Figure 8. pH dependence of the peak potential of 9,10-phenanthrenequinone modified CCE in citric-phosphate buffers (scan rate 100 mV/s).

surface area to the geometric area (postulating that the specific adsorbance of graphite powder is similar to that of glassy carbon) is approximately $a = 2.5 \text{ cm}^2/\text{cm}^2$ (where $a \equiv$ active area/geometric exposed surface).

Quinone Modified pH CCEs. Voltammetric electrodes often exhibit a faster response and a lower level of interferences than potentiometric sensors. Voltammetric polymer-coated (e.g., Nafion⁴² or poly(ethylenimine)⁴³) pH electrodes and microelectrodes^{43,44} have recently been reported. The quinone modified CCEs demonstrate a new class of voltammetric pH sensors with renewable surface. Figure 8 shows the dependence of the potential of the cathodic and anodic peaks of 9,10-phenanthrenequinone modified carbon-silica electrode on the pH of a buffer solution. An almost Nernstian dependence of the anodic peak current on pH is found over a wide pH range (0–7): $dE_0'/dpH = 60.2 \text{ mV}$ ($R = 0.9996$). At higher pH, deprotonation of the quinone interferes. Quinhydrone modified electrodes exhibited a larger linear pH range (0–9) which is only violated near the pK_a of hydroquinone ($pK_{a1} = 9.85$; $pK_{a2} = 11.4$ ³⁸). Small leaching of the quinones from the electrode during prolonged continuous cycling does not affect its accuracy since the pH determination depends on potential shifts and is not sensitive to the absolute value of the peak current.

The stability of organically doped CCEs depends on the type of modifier. Open circuit 9,10-phenanthrenequinone and quinhydrone and ferrocene modified CCEs did not lose any activity even after long duration in aqueous solution. The ferrocene did not lose activity even after extensive voltammetric cycling while PQ/CCE and quinhydrone/CCE lost ~5–10% activity during 3 h of cycling between –0.2 and 1.2 V (SCE) (after a 30-min pretreatment of continuous cycling to leach externally adsorbed dopants). The stability of the organically doped electrodes depends on the leachability of the modifiers from the electrodes. Leaching of dopants from sol-gel silica matrices is well studied and was found to depend on the interaction of the immobilized species with the supporting

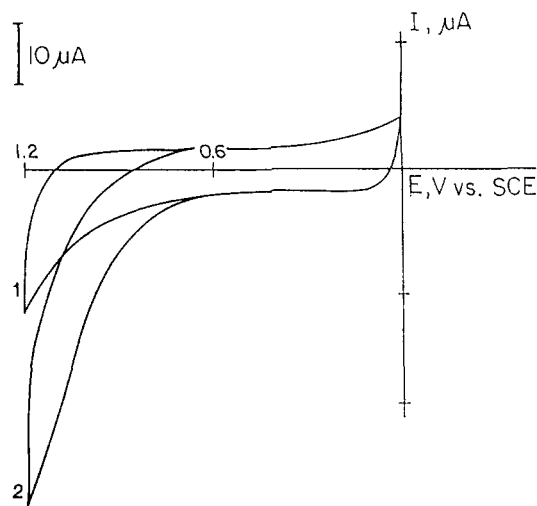


Figure 9. Cyclic voltammogram (100 mV/s) of a composite carbon-silica glucose biosensor in 0.1 M phosphate buffer (pH 5.6): (1) blank and (2) 9.8 mM glucose.

matrix, size exclusion (which depends on the sol-gel preparation procedure), and solubility of the compound.¹⁸

Hydrophilic Silver-Silver Chloride CCEs. Modified electrodes are frequently used in potentiometric devices as reference electrodes or as ion-selective electrodes. Sol-gel derived carbon-silica composite electrodes modified by a silver-silver chloride couple demonstrate both reference and selective ion applications. The Ag-AgCl couple was chosen as a demonstrative example due to its popularity as a reference electrode and its excellent halide selectivity. Therefore, although more useful (especially in aprotic) applications exist, the silver-silver chloride modified composite electrode is demonstrated here.

Silver-silver chloride CCEs were prepared according to the procedure depicted in the Experimental Section. The electrode potential (measured relative to standard calomel electrode) was stable for at least several days. A pH change over the range 4–10 did not alter the electrode response. A logarithmic dependence (range 1–100 mM; slope 49 mV/Cl[–] decade; $R = 0.997$) of the electrode potential on chloride ion concentration was observed. The reference (and halide-selective) electrode retained its signal even after surface renewal by polishing with emery paper. This confirms that the bulk of the porous electrode was modified by the silver-silver chloride couple and the modification was not confined to its outermost surface.

Biosensing. Braun and co-workers¹³ demonstrated the possibility of protein immobilization in sol-gel derived silica matrices and recently this ability was extended to antibodies.⁴⁵ This class of bioceramic materials was applied to produce silica-based photometric^{46,47} and flow injection analysis detectors.⁴⁸ Electrochemical biosensing applications of composite carbon-silica electrodes should be especially attractive due to the high conductivity of the composite electrodes. Figure

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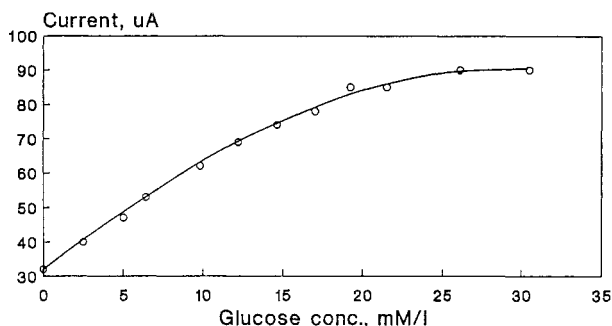
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Table 1. Demonstrated Classes of Composite Ceramic Electrodes (CCEs)

class of CCEs	demonstrated configuration	active surface	composition of ceramic network	active compound	mode of immobilization	demonstrated application
indicator electrode	1. rod 2. microelectrode 3. film	external	C/[≡Si—CH ₃] or C/[≡Si—C ₆ H ₅]	hydrophobic functional groups	covalent bonding	electrosensing
organically modif	rod	external	C/[≡Si—CH ₃]	hydroquinone or ferrocene	sol-gel doping	pH sensing
inorganic modif	rod	bulk	C/[SiO ₂] _n	Ag/AgCl	1. doping 2. impregnation + reduction	1. reference electrode 2. halide-selective electrode
biochemical modif	coated layer	bulk	C/[SiO ₂] _n	glucose oxidase	doping	glucose sensing

**Figure 10.** Calibration curve of composite carbon-silica glucose biosensor (scan rate 100 mV/s; pH 5.6; $E = 1.0$ V/SCE).

9 depicts the cyclic voltammograms (scan rate 100 mV/s) of the carbon composite electrode immersed in a blank solution (buffered at pH 5.6 by phosphate buffer) and in a 9.8 mM glucose solution. The increased anodic current, which becomes apparent at ~ 700 mV (SCE), is caused by oxidation of the hydrogen peroxide that was formed during the enzymatic conversion of glucose to gluconolactone. This was verified by nitrogen bubbling, which recovered the blank response. Figure 10 demonstrates a typical glucose calibration curve depicting the dependence of the current at 1.0 V (SCE) on glucose concentration. The biosensors described here show relatively low stability in dry storage. This phenomenon was also observed in sol-gel derived optical biosensors.⁴⁶

CONCLUSIONS

Table 1 summarizes the classes of CCEs that were demonstrated in this article. Some of the more important characteristics of CCEs include the following. (1) Electrode configuration: CCEs enjoy the inherent versatility of the sol-gel molding technology and it is possible to cast silica-carbon matrices in virtually any desired geometrical configuration. (2) Active surface: CCEs are made of porous material and thus can operate as flow-through or large surface area electrodes where the bulk of the electrode is available for charge transfer. On the other hand, in hydrophobically modified CCEs only the outermost surface is electrochemically active. However, even when only the external surface is wetted the electrodes can be bulk modified, and thus polishing exposes a new surface area. (3) Surface polarity: The use of a modified silica network (Ormocel) provides an ability to tailor electrode surface attributes such as ion exchange, size exclusion, polarizability, surface polarity, and hydrophobic nature. (4) Type of immobilization: Modification of electrode structure is not confined to a selection of the silica precursors.

Impregnation by physical or chemical adsorption on prepared electrodes can be used. Sol-gel doping, i.e., incorporation of the modifiers along with the sol-gel reaction precursors, facilitates the entrapment of heat-sensitive reagents in the bottleneck structure that is formed during sol-gel doping.¹⁸ Adsorption of modifiers on carbon grains prior to their incorporation in the starting sol-gel solution is still another method that may be used to protect sensitive (e.g., biochemicals and enzymes) compounds from the aggressive sol-gel solution.

The silica-carbon matrices combine some additional favorable characteristics which were less emphasized in this article: high electrical conductivity ($>1 \Omega^{-1}/\text{cm}$); physical rigidity; negligible swelling in aqueous and organic solvents; chemical inertness, which implies low interaction with analytes and slower poisoning by irreversible side reactions; high photochemical, biodegradational, and thermal stability especially at low pH; and excellent adhesion to glass supports.

CONCLUDING REMARKS

A new class of carbon-ceramic electrodes is introduced, and its electroanalytical applications were demonstrated by amperometric biosensing (glucose sensing) and indicator electrodes, potentiometric reference and ion-selective electrodes, and voltammetric pH sensors. The electrodes can be manufactured in virtually any dimension and geometrical configuration including flat plates, metal-coated electrodes, monolithic rods and disks, and even microelectrodes. The bulk and external surface of the electrodes can be modified by covalent bonding, impregnation, or sol-gel doping. Such versatility has traditionally been attributed exclusively to organic polymers, but the evolution of sol-gel technology changed these (once) accepted notions.

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