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Electrochemical Applications of Silica-Based Organic−Inorganic Hybrid Materials

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A comprehensive overview is presented on the implication of silica-based organic−inorganic hybrid materials in electrochemical science. It involves composite materials of both class I (weak bonds between the organic and inorganic components) and class II (strong chemical bonds). Starting with a description of the common designs of electrodes modified with these hybrids, the review then reports their applications in the various fields of electrochemistry, illustrating the diversity of the organically modified silicates used for this purpose. The mild chemical conditions allowed by the sol−gel process provide very versatile access to these electrochemical devices. They have found many applications in electroanalysis, including preconcentration associated with voltammetric detection, permselective coatings, electrochemical sensors, electrocatalysis, and detectors for chromatography. They were also applied as redox and conducting polymers, as solid polymer electrolytes for batteries, for the design of spectroelectrochemical and electro-chemiluminescence devices, and in the field of electrochemical biosensors.

1. Introduction

The elaboration of hybrid materials by bridging organic and inorganic chemistry at a molecular level is now a wide field of investigation. A major appeal of such research activities is probably linked to a synergistic effect carrying advanced properties to the organic−inorganic hybrid materials, which can even be improved in comparison to the own unique properties of each component (organic and inorganic). With this respect, the renaissance of sol−gel chemistry[1−3] during the past decade has played a prominent role by providing a versatile method to prepare various solids with well-controlled composition, displaying a wide range of attractive properties. Plenty of well-documented reviews are available describing the methods of preparation, characterization, physical and chemical properties, and selected uses of these advanced materials.[4−44] Some of them were specifically directed toward practical applications, like enzyme immobilization and biosensors,[9,10,12,36,38,39] the chemical modification of crystalline mesoporous materials with organic moieties,[32,42] the exploitation of materials science in designing sensing devices[23,27−29,35] or optical devices,[40,41] and electrochemistry involving sol−gel materials.[22,24]

On the other hand, the chemical modification of conventional electrodes has attracted much attention during the past 25 years because it provides a powerful means to bring new qualities to the electrode surface that can be exploited for electrochemical purposes. Chemically modified electrodes can be obtained (1) by attaching molecules on electrode surfaces (adsorption, covalent binding, self-assembled monolayers, etc.), (2) by immobilizing multimolecular layer films on electrodes (mainly polymers), and (3) by designing heterogeneous and spatially defined layers and microstructure onto electrode surfaces or within the bulk of the electrode material.[45] They found applications in various fields, including electrocatalysis, electroanalysis, polymer science, protective coatings, surface analysis, electrosynthesis, molecular electronics, and some others.[45−48] Among the wide range of electrode modifiers, the inorganic materials have been the focus of attention for electrochemists[49] because of advantageous features such as mechanical stability and durability, two- or three-dimensional rigid structure, possibility for molecular recognition or discrimination, or intrinsic catalytic properties. They include metal oxides,[46] polynuclear transition metal cyanide derivatives,[50] clays,[51−53] zeolites,[53−59] polyoxometalates,[60] or sol−gel-processed materials.[22,23,29,35,39,44]

The growing interest in coupling the attractive properties of organic−inorganic hybrids with electrochemical science is briefly reviewed in this paper by providing a comprehensive coverage of the various applications of such silica-based materials in electrochemistry. The silica-based organic−inorganic hybrid materials considered here are both of class I (weak bonds between organic and inorganic counterparts) and of class II (stronger covalent or iono-covalent chemical bonds in the hybrid system), as defined by Sanchez and Ribot.[8] They include silica samples covered with adsorbed organic moieties or biomolecules, sol−gel silicates comprising organic and/or bioorganic species by physical entrapment, interpenetrating ceramic−organic copolymers, and organic−inorganic nanocomposite materials prepared by co-condensation of alkoxysilanes and

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organo-alkoxysilanes. These materials exhibit chemical and physicochemical features that might be readily exploited when used to modify electrode surfaces. Moreover, the versatility of sol–gel chemistry offers advantages in the design of electrode devices and microscopic electrochemical reactors. Applications have been described in various fields, that is, chemical and biological sensors (electrocatalysis, preconcentration, enzyme electrodes, etc,), spectroelectrochemistry, electropolymerization, batteries, and fuel cells. They represent about 200 papers, 85% of them being published during the past 5 years and 50% during the 1999–2000 period, which illustrates the recent character of these research activities. Notwithstanding the comprehensive aspect of this short review, particular attention will be focused on summarizing the most recent advances to avoid overlap with some previous overviews dealing (at least in part) with the topic of silica-modified electrodes.[22,29,35]

2. Preparation and Electrochemical Behavior of Electrodes Modified with Organic–Inorganic Hybrid Materials

2.1. Preparation Methods. Because of their intrinsic properties and the ease to be synthesized by the versatile sol–gel technique, the organic–inorganic hybrids are basically interesting materials with respect to their use in connection to electrochemistry. Most of these materials, however, are electronic insulators so that they must be coupled to an electrical source to study or to exploit their influence on electrode reactions. With the exception of solid polymer electrolytes (most often sandwiched between planar electrodes), nearly all the silica-modified electrode designs rely on either bulky conductive composites or silicate films coated on solid electrode surfaces. Nevertheless, various strategies were applied to prepare electrodes chemically modified with silica-based organic–inorganic hybrid materials, depending on the concerned application.[61–252] Table 1 lists the means by which such materials have been incorporated into electrode assemblies and includes the electroactive species (or ionic conductor) and/or target analytes involved in the application. The chemical specifics were detailed to highlight the key role of the preparation method and that of the electrode configuration in the achievement of their advanced applications (described below). They also bring to the reader a rapid and detailed survey on the various kinds of silica-based organic–inorganic hybrids that have been the subject of research thus far in electrochemical science.

A simple course to prepare electrodes modified with these hybrids is achieved by the dispersion of the as-synthesized materials into carbon paste.[61–92] This approach was mainly considered by the groups of Kubota, Gushikem, Hernandez, and Walcarius, with using (1) silica particles coated with inorganic layers supporting adsorbed catalysts for applications in electrocatalysis, (2) silica gels grafted with organic groups applied to accumulate electroactive analytes prior to their voltammetric analysis, and (3) silica-based materials with immobilized enzymes for biosensing applications.

Competing with the silica-modified carbon paste is the ceramic–carbon composite electrode (CCE), first proposed by Lev and co-workers in 1994,[93–95] which consists of graphite powder entrapped in a hydrophobically modified silica network obtained by the sol–gel process. These electrodes offer better mechanical stability than carbon paste. They are amenable to chemical modification by physical encapsulation or covalent binding of various complexing ligands, catalysts, or biomolecules, with applications mainly in electrocatalysis, as biosensors, or as detectors in flowing streams.[96–103,105–101,118–141] They can be manufactured in several configurations as monolithic rods, bulky cylinders, flat plates, or thin films.[93,118] An alternative to this last approach was developed by Wang's group by coupling the sol–gel chemistry with the screen-printing technology, resulting in the production of single-use electrochemical sensors.[104,112–116] Metal–ceramic composite electrodes were also described.[107,114,123,125]

The most common approach is the surface modification of solid electrodes (mainly glassy carbon, platinum, and indium–tin oxide) by applying a thin silicate film prepared by the sol–gel method. Many examples are available[142–198] dealing with the preparation of organically modified silicate films combining the rigid structure of the silica network with the specific function(s) of the organic or organometallic modifier (i.e., ion exchange or redox polymer, preconcentration agent, catalyst or charge-transfer cofactor, ionophore or chromophore, structure templating agent, active biomolecule, etc.). These modifiers were comprised in the silica network either via physical entrapment by doping the starting sol with an appropriate molecule or biomolecule or by way of covalent bonding between the organic and inorganic part by using organo-alkoxysilane(s) in the starting sol or as interpenetrating organic–inorganic polymers (Table 1). The major challenges in this approach are (1) to obtain stable films strongly adherent to the electrode surface, (2) to ensure high rates of charge and mass transfer into the film, (3) to prepare homogeneous coatings without cracks, and (4) to prevent leaching of the doping agent into the external solution. Even if good adhesion of silicates to electrode surfaces was generally observed,[22] there is a lack of detailed investigation on the interaction occurring at the electrode/silicate interface. There is no doubt that better knowledge of this interface would promote the fabrication of durable silica-modified electrodes. In contrast, the optimization and control of charge and mass transfer across the film were largely investigated. Charge transfer was often promoted by the presence of a mediator (encapsulated or covalently bonded) within the silicate network (i.e., refs 148, 155, 166, 175, 181, and 194) or via a conducting or redox polymer interpenetrating the silicate network (i.e., refs 143, 148, 235–237, and 253). Mass transfer can be controlled by an appropriate modulation of the permeability of the coating by tailoring the structure of the organic–inorganic material (i.e., refs 162, 165, 174, and 183) or by inducing permselective properties.[154,174] Efforts have been otherwise directed to the formation of crack-free films: they can be obtained by introducing an appropriate additive in the starting sol such as poly(ethylene)glycol, poly(vinyl) alcohol-grafted-poly(vinyl) pyridine, cetyl-trimethylammonium, and *N*-methyl-*2*-pyrrolidone (i.e., refs 126, 149, 168, and 254). These additives limit the shrinkage effect generally observed during the gel-to-xerogel tran-

Table 1. Preparation Methods for Electrochemical Devices Containing Organically Modified Silica-Based Materials

Methods and electrode configurations[a]	Electroactive species[b]	Target analytes[c]	References
DISPERSION OF AS-SYNTHESIZED MATERIALS INTO CARBON PASTE ELECTRODES			
A. Silica coated with inorganic layer(s) supporting adsorbed catalysts			
1. CP + [FeTsPc/TiO_2 coated on silica gel], (carbon-to-mineral ratio: ¾)	Iron phtalocyanine		71
2. CP + [NiTsPc/TiO_2 coated on silica gel], (carbon-to-mineral ratio: ¾)	Nickel phtalocyanine	Hydrazine	80
	Nickel phtalocyanine	Cysteine	81
3. CP + [Ru(edta)/ZrO_2 coated on silica gel], (carbon-to-mineral ratio: ¾)		Dissolved oxygen	72, 73
4. CP + [MeB/titanium phosphate coated on silica gel], (carbon-to-mineral ratio: ¾)	Methylene Blue		79
5. CP + [MB/titanium phosphate coated on silica gel], (carbon-to-mineral ratio: ¾)	Meldola's Blue	NADH	74
		Hydrazine	91
6. CP + [CoHMP/Nb_2O_5 coated on silica gel], (carbon-to-mineral ratio: 1:1)	Cobalt porphyrin	Dissolved oxygen	89
7. CP + [CoTmPyP/titanium phosphate coated on silica gel]	Cobalt porphyrin	Dissolved oxygen	90
B. Silica gels grafted with organic groups			
1. CP + 50% C_{18}-bonded silica gel		Tifluadom	62
		Methyl parathion, Nitrophenols	65
		Bendiocarb	66
		Ephedrine	69
2. 43-58% graphite + 37% nujol + 5-20% silica gel grafted with 2-mercaptobenzimidazole		Hg^{II}	67
3. 60% graphite + 30% nujol + 10% silica gel or MCM-41 grafted with aminopropyl groups	Cu^{II}		85, 92
4. CP + sol-gel silica containing Cu^{II}-aminopropyl groups, (carbon-to-mineral ratio: 1:1)	Cu^{II}		84
5. CP + silica gel grafted with propylpyridinium groups, (carbon-to-mineral ratio: ¾ or 1:1)	$Fe(CN)_6^{3-/4-}$,		68
	$FeTSPc^{4-}$	Dissolved oxygen	88
6. CP + silica gel grafted with 3-n-propylimidazole groups	$CoTSPc^{4-}$	Oxalic acid	86, 87
C. Silica-based materials with immobilized enzymes			
1. Enzyme adsorption			
• CP + [Fc and GOD immobilized on TiO_2 coated on silica gel] (carbon-to-mineral ratio: ¾)		Glucose	75
• CP + [HRP immobilized (via cross-linking by GluA) on TiO_2 coated on silica gel]		Phenol	83
• CP + FDH or SH + [MB immobilized on titanium phosphate coated on silica gel]		Fructore or salicylate	76-78
2. Enzyme entrapment			
• CP + microreactor (CPC-silica+ GOD + DMDHP or PMS or BQ + $Fe[EDTA]^-$ or $Fe(CN)_6^{3-}$)		Glucose	82
D. Other			
1. CP + hybrids based on Polypyrrole/Siloxane networks	PPy		70
2. CP + Fc- or DMFc-modified siloxane polymers + GOD	Fc	Glucose	61, 63, 64

Table 1 (Continued)

Methods and electrode configurations[a]	Electroactive species[b]	Target analytes[c]	References
CERAMIC-CARBON COMPOSITE ELECTRODES (CCEs)			
A. CCEs based on pure methyltrimethoxysilane			
1. 1.25-3.75 g graphite + [1.0 ml MTMOS + 1.5 ml MeOH + 0.05 ml HCl (11 M)]	$Fe(CN)_6^{3-}$, PAQ, ...		93, 94
2. [1.0 ml MTMOS + 1.5 ml MeOH + 0.05 ml HCl (11 M)] + graphite, ketjenblack, or AcB	$Fe(CN)_6^{3-}$		95
3. 2.0 g graphite + [500 μl MTMOS + 750μl EtOH + 50 μl HCl (11 M)]		Neurotransmitters	109
4. 0.5 g graphite + [0.4 ml MTMOS + 350μl H_2O + 25 μl HCl (1 M)]		Carbohydrates	130, 132, 133
		Neurotransmitters	131, 132
B. CCEs doped with inorganic materials			
1. 1.25 g graphite + [1.0 ml MTMOS + 1.5 ml MeOH + 0.05 ml HCl (11 M) + $PdCl_2$]		Oxygen	96, 105, 124
3. 0.5 g graphite + 0.05 g Cu_2O + [0.4 ml MTMOS + 350μl H_2O + 25 μl HCl (1 M)]		Carbohydrates	130, 132, 133
		Neurotransmitters	131, 132
4. 1.87 g graphite + [3.75 mg P_2Mo_{18} + 0.25 ml MTMOS + 0.75 ml MeOH + 0.025 ml HCl (11 M)		Bromate	137
5. 1.87 g graphite + [3.75 mg $SiMo_{12}$ + 0.25 ml MTMOS + 0.75 ml MeOH + 0.025 ml HCl (11 M)		Nitrite	138
6. 1.87 g graphite + [2.8 mg PMo_{12} + 0.25 ml MTMOS + 0.75 ml MeOH + 0.025 ml HCl (11 M)]		Ascorbic acid,bromate	139, 141
7. 1.87 g graphite + [2.8 mg Mo_8O_{26} + 0.25 ml MTMOS + 0.75 ml MeOH + 0.025 ml HCl (11 M)]		Nitrite	140
C. CCEs modified with small organic or organometallic species			
1. [graphite + MB] + [0.8 ml MTMOS + 0.1 ml H_2O + 0.1 ml HCl (0.1 M)]	Meldola's Blue		120
2. [120 mg graphite + 15 mg Me_2phen] + [0.2 ml MTMOS + 0.2 ml EtOH + 0.1 ml H_2O + PEG (50 μl of 1:1 PEG/ H_2O) + 50 μl HCl (3 M)]		Fe^{II}	126
3. 2 g carbon powder + [1.0 ml MTMOS + 1.0 ml MeOH + 1.5 ml Rh_2POM + 0.01 ml HCl (cc)]		Peptides	119, 134
4. 380 mg [graphite + Co-TMMP] + [1.0 ml MTMOS + 1.5 ml MeOH + 0.05 ml HCl (11 M)]	Cobalt porphyrin	Gaseous oxygen	98
5. 50 mg [KB + FePc] + [1.0 ml MTMOS + 1.5 ml MeOH + 0.1 ml HCl (11 M)]		Nitrite	126
6. 2 g graphite + [300 mg DMG + 0.5 ml MTMOS + 1.5 ml EtOH + 50 μl HCl (11 M)]		Ni^{II}	110
7. 2 g graphite + [83.5 mg CoPC + 0.5 ml MTMOS + 1.5 ml EtOH + 50 μl HCl (11 M)]	Cobalt porphyrin	H_2O_2, hydrazine, cysteine, oxalic acid	111
8. 2 g carbon powder + {[1.0 ml MTMOS + 1.0 ml MeOH + 0.01 ml HCl (cc)] + 40 ml Ru^{II}Den		L-Met, L-Cys, As^{III},	136
or Ru^{II}tpy}		CN^-	135
D. CC film electrodes			
1. On titanium foil: 4 g graphite + [2 ml "MTMOS, PTMOS, TMOS or PTEOS" + 7 ml MeOH + 0.1 ml HCl (38%)]			118
2. On copper foil: 1 g graphite + [1 ml MTMOS + 6 ml MeOH + 50 μl HCl (11 M) + 0.2 ml H_2O]			121, 122
3. On glassy carbon: bilayer [(TMOS + HRP + graphite)/(TMOS + GOD)]		H_2O_2, Glucose	108

Table 1 (Continued)

Methods and electrode configurations[a]	Electroactive species[b]	Target analytes[c]	References
E. Enzyme-containing CCEs			
1. [100 mg graphite + 20 mg GOD] + 0.3 ml [0.8 ml MTMOS + 0.5 ml H_2O + 0.5 ml MeOH (either with or without 4 mg ml^{-1} TTF or Fc) + 0.1 ml HCl (0.1 M)]		Glucose	97, 99, 100
2. 1 g C + [1 ml MTMOS + 0.8 ml MeOH + APTS + TESP-Fc + 20 μl HCl (10 mM) + 0.1 g GOD]		Glucose	101, 102
3. 160 mg C + 20 mg vinylferrocene + 20 mg GOD + 0.3 ml [0.8 ml MTMOS + 0.5 ml MeOH + 1 ml H_2O + 0.1 ml HCl (1 mM)]		Glucose	127
4. 3 × [8% BV on graphite + XOD] + 2 × [4:2:1 mixture of MTMOS, H_2O, 0.05 M HCl]		Hypoxanthine	128, 129
5. 0.1 g [graphite + $PdCl_2$ or $RhCl_3$ + GOD, LOD, or L-AAOD] +0.6-0.7 ml [0.8 ml MTMOS + 0.5 ml H_2O + 0.5 ml MeOH + 0.1 ml HCl (0.5 M)]		Glucose, lactate, amino acids	103, 106
F. Metal-ceramic composite electrodes			
1. 0.025 ml [1.0 ml MTMOS + 1.5 ml EtOH + 0.05 ml HCl (11 M)] + 0.160 g gold powder	$Fe(CN)_6^{3-}$, Fc, H_2O_2, DA, AA, UA, acetaminophen		114
2. [EDAS + APTS + HCl (0.1 M) + $HAuCl_4$], (gold reduction by $NaBH_4$), with or without GOD		Glucose	107, 123, 125
G. Screen-printed silicate-containing electrodes			
1. Ink: 300 μl enzyme solution (30 mg GOD or HRP) + 1 ml [3 ml TEOS + 0.66 ml H_2O + 0.66 ml EtOH + 50 μl HCl] + 0.80 g graphite (+ 0.10 g CoPC) + 500 μl of 4% hydroxypropyl cellulose		Glucose, H_2O_2, 2-butanone peroxide	104
2. Idem 1., but with 0.9-1 g graphite and 30 mg DMFc or RuO_2 (instead of 0.10 g CoPC)		Glucose, H_2O_2	112, 113
3. Ink: 200 μl enzyme solution (30 mg GOD) + 0.5 ml [1.5 ml TEOS + 1 ml H_2O + 1 ml EtOH + 0.1 ml HCl (1.0 M)] + 0.5 g gold powder		Glucose	114
4. Ink: [0.5 ml TEOS + 0.7 ml EtOH + 0.2 ml HCl (11 M)] + 0.9 g graphite + 0.5 ml of 4% hydroxypropyl cellulose		β-NADH	115
5. Ink: 1 ml [AOT:TMOS:H_2O (1:50:200, molar ratio)] + 0.6 g graphite + either [2.5% Fc + 5% GOD], or 5% CoPC, or 10% DPT		Glucose, GSH, Pb^{II}	117
6. Ink: 5 mg RIgG + 1 ml [4.5 ml TEOS + 2.7 ml H_2O + 1.0 ml EtOH + 0.1 ml HCl (0.05 M)] + 1 g graphite + 500 μl of 4% hydroxypropyl cellulose		IgG	116
THIN SILICATE FILMS (SOL-GEL) DEPOSITED ON SOLID ELECTRODES			
A. Silicate film encapsulating small electroactive organic species			
1. 30 μl {1.8 ml [5 ml TMOS + 8.6 ml MeOH + 4.2 ml H_2O + 1 ml HCl (0.1 M)] + [5.9 mg $Fe(CN)_6^{3-}$, or 7.0 mg $FcCH_2OH$, or 48.5 mg $Ru(bpy)_3^{2+}$]} spin-coated on GC	$Fe(CN)_6^{3-}$, $FcCH_2OH$, $Ru(bpy)_3^{2+}$		153

Table 1 (Continued)

Methods and electrode configurations[a]	Electroactive species[b]	Target analytes[c]	References
2. 100 μl {1 ml [2.2 ml TEOS + R-TMOS (R = Me, *i*Bu, or Ph), in 2:1 or 1:1 ratio + 1 ml EtOH + H_2O (silane:H_2O ratio = 1:5) + 0.75 ml HCl (0.1 M)] + 3 mg BcG or CR} spin-coated on glass		H^+/OH^-	173
3. [70 μl APTS + 20 μl ETHETS + 50 μl H_2O + 5 μl HCl (0.1 M) + 5 mg FcCA] coated on Pt	Fc	K^+	175
B. Interpenetrating organic-inorganic polymer films			
1. Nafion-silica composite spin coated on graphite rods (composite: 4.0 ml TEOS + 1 ml H_2O + 0.1 ml HCl (0.1 M) + Nafion solution to get Nafion:sol ratios of 4:1, 3:1, 2:2, 3:2, 4:3)		MV^{2+}	162
2. Nafion- or-poly(styrenesulfonate)-silica composite spin coated on graphite rods or dip-coated on carbon fiber (composite: 1.0 ml [TEOS:H_2O:HCl] + 5% Nafion solution)	$[Re(DMPE)_3]^+$		163, 183, 185
3. Nafion-silica or polyammonium-silica composites coated on ITO (composite: 2.0 ml TEOS + 4.0 ml H_2O + 0.1 ml HCl (0.1 M) + 5% Nafion or 20% PDMDAAC solution)	$Ru(bpy)_3^{2+}$, $Fe(CN)_6^{3-}$ $Ru(CN)_6^{4-}$, $Fe(CN)_6^{4-}$		159-161, 184, 186-189
4. Nafion-silica composite spin coated on GC (composite: 0.5 ml TMOS + 0.43 ml H_2O + 0.1 ml HCl (0.1 M) + Nafion solution and 0.1 M NH_4OH, to get Nafion:SiO_2 ratios from 53 to 88%)	$Ru(bpy)_3^{2+}$		190
C. Organically-modified silicate film displaying ion exchange and/or permselective properties			
1. 10 μl [TEOS + H_2O + HCl + 1% PVSA or 2% PDMDAAC] spin-coated on graphite rods	$Ru(bpy)_3^{2+}$, $Fe(CN)_6^{3-}$	$Ru(NH_3)_6^{3+}$, MV^{2+}	158
2. 100 μl [1 ml TMSPedat + 1 ml MTMOS + 2 ml MeOH + 1 ml H_2O + 0.2 ml HCl (12M)] on GC	$Fe(CN)_6^{3-}$	$Fe(CN)_6^{3-}$	154
3. 100 μl [2 ml APMDES + 0.5 ml MTMOS + 2 ml EtOH + 1 ml H_2O] on GC	$Ru(NH_3)_6^{3+}$, MV^{2+}	DA, AA	154
4. 100 μl [1 ml DETESPM + 4 ml EtOH + 2 ml H_2O + 0.2 ml HCl (0.02 M)] on GC	$Ru(NH_3)_6^{3+}$, MV^{2+}		154
5. [SIS + DMF + H_2O + 0.1 M HCl] on GC or ITO, followed by oxidation with HNO_3	PB	K^+, H^+/OH^-	172
6. [laponite clay + oligosilasesquioxane (TMSPTEAI or DMAPTS) on GC or Pt	$Ru(NH_3)_6^{3+}$, $Mo(CN)_8^{4-}$		164
7. Silesquioxane 3-n-propylpyridinium chloride polymer coated on graphite rods		H^+/OH^-	197
D. Organically-modified silicate film with ligand properties			
1. 30 μl [APTES:(BTMOS, PhTMOS, TMOS, or MTMOS) in ratios varying from 4:1 to 1:4 + MeOH + *i*PrOH + H_2O + HCl (with silane:water:alcohol = 1:3:23)] spin-coated on GC	$Ru(NH_3)_6^{3+}$, $Fe(CN)_6^{3-}$		174
2. 10 μl [5% SIS in ethanol + H_2O (SIS:H_2O = 1:8) + 0.1 M HCl] spin-coated on GC		Hg^{II}	179
3. 50 μl { 1.7 ml [3 ml TMOS + 0.37 ml PhTMOS + 0.30 ml MTMOS + 3 ml EE + 0.7 ml H_2O + 1 ml HCl (0.1 M)] + 19 mg dopamine} spin-coated on GC		Dopamine	165
E. Organically-modified silicate film with electroactive moieties covalently attached to the material			
1. 50 μl [0.205 g TMOS-Fc + 0.073 g TMOS + 10 ml MeOH + 2.4 mmol H_2O + 1 mmol NH_4F] on Pt	Fc in the gel		144, 145, 148
2. 30 μl [50 μl TMOS + given amount of FDAH (FDAH:TMOS ratios = 1:50, 1:35, 1:25, 1:10) + 60 μl MeOH + 40 μl H_2O + 140 μl acetonitrile + 30 μl HCl (0.1 M)] spin-coated on GC	Fc in the gel		166
3. Copolymer of vinylferrocene and methylhydrosiloxane-dimethylsiloxane coated on Pt electrodes	Fc in the copolymer		142, 143
4. Copolymer of OEG and PROXYL-COOH coated on GC electrodes	PROXYL		147

Table 1 (Continued)

Methods and electrode configurations[a]	Electroactive species[b]	Target analytes[c]	References
F. Silicate film encapsulating an enzyme or another biomolecule			
1. Pt coated with {TEOS + MTEOS + APTS + GOD (+ EtOH + H_2O)}		Glucose	157
2. {TEOS + EtOH + H_2O + GOD} mixture dip-coated on Pt (microsensor device) / Nafion		Glucose	167
3. GC coated with {TEOS + PVA-g-P(4-VP) + GOD (+ EtOH + H_2O + HCl)}		Glucose	168
4. GC coated with {TEOS + PVA-g-P(4-VP) + SPOD (+ EtOH + H_2O + HCl)}		H_2O_2	180
5. GC coated with {TEOS + PVA-g-P(4-VP) + HRP (+ EtOH + H_2O + HCl)}		H_2O_2	193
6. GC coated with {TEOS (with or without MTMOS + APTES) + PVA-g-P(4-VP) + Tyrosinase (+ EtOH + H_2O + HCl)}		Phenols	195, 196
7. 50 μl [1 ml TEOS + 5 ml HCl (2.4 mM) + 4 ml urease solution] casted on Pt		Urea	182
8. Pt coated with {APTS + EETMS + GOD (+ HCl + H_2O) + eventually PEG and/or graphite}		Glucose	176, 177
9. 5 μl [3-5 ml TMOS + 1 ml H_2O + 50 μl HCl (0.1 M) + 4-6 ml urease solution] casted on Pt- or Au-IDA		Urea	191, 192
10. GC covered with {(MTEOS + GluA) + (cytochrome P_{450} + DDAB + BSA)}	P450	PAHs	198
G. Silicate film encapsulating an enzyme and a mediator			
1. Pt coated with {TEOS + MTEOS + APTS + GOD (+ EtOH + H_2O) + Fc + CTAB}		Glucose	157
2. Gc coated with {SSS + MB + HRP + PVA-g-P(4-VP)}; SSS + MB: [0.4 ml MTMOS + 1.6 ml MPTMS + 8 ml H_2O], further oxidised by HNO_3 and ion-exchanged with MB cations		H_2O_2	181
3. GC covered with a [Nafion – MG] film, coated with {TEOS + PVA-g-P(4-VP) + HRP (+ EtOH + H_2O + HCl)}		H_2O_2	194
H. Silicate and enzyme (and mediator) in multilayered film configuration			
1. Electrode / {enzyme layer} / {silicate film}			
• CPE / {5 μl [5 mg HRP in 200 μl PBS (pH 7) + 5 μl glycerol]} / {10 μl [50 μl TMOS + 10 μl CTAB (3.8%) + 600 μl MeOH + 60 μl H_2O + 10 μl NaOH (5 mM)]}	$Fe(CN)_6^{4-}$	H_2O_2	149, 169
• Idem above-mentioned, with tyrosinase as the enzyme (instead of HRP)		Phenolic compounds	170
2. Electrode / {mediator layer} / {enzyme layer} / {silicate film}			
• GC / {3 μl Os-polymer (1% in MeOH)} / {3 μl GOD or LOD (in PBS (pH 6.4))} / {4.5 ml MTEOS + 1.6 ml H_2O + 0.03 ml HCl (50 mM)]}	H_2O_2	Glucose, lactate	150, 151
• Idem above-mentioned, with HRP as the enzyme (instead of GOD or LOD)		CN^-, H_2O_2	152, 171
3. Electrode / {silicate film 1} / {enzyme layer} / {silicate film 2}			
• ITO / {200 μl [4.5 ml TEOS + 1.4 ml H_2O + 0.1 ml HCl (0.1 M) + 1 ml MeOH]} / {0.5 ml GOD (20 mg l^{-1} in PBS (pH 6))} / {silicate film 2 = silicate film 1 without MeOH}		Glucose	146
• Pt / {20 μl [70 μl APTS + 20 μl EETMS + 700 μl H_2O + 5 μl HCl (0.1 M) + eventually graphite (2 g l^{-1})]} /{5 μl [GOD (20 mg l^{-1})]} / {20 μl of silicate film 1 with PEG (2 g l^{-1})}		Glucose	178

Table 1 (Continued)

Methods and electrode configurations[a]	Electroactive species[b]	Target analytes[c]	References
• CPE / {10 μl [50 μl TMOS + 10 μl CTAB (3.8%) + 570 μl MeOH + 30 μl H_2O + 10 μl NaOH (5 mM) + 5 mM Fc]} /{5 μl [GOD or HRP (25 mg l^{-1} in PBS (pH 7)) + 5 μl glycerol]} / {10 μl of silicate film 1 without Fc}	Fc in the gel	Glucose, H_2O_2	155, 156
MEMBRANES AND SOLID POLYMER ELECTROLYTES			
A. Membranes for potentiometric analysis			
1. [silica gel grafted with propylpyridinium groups] coated on an epoxy-graphite membrane		ClO_4^-	199, 200
2. {2.5 g [3.08 g 1,4-butanediol + 16.9 g iCPTES] + 15 ml DMF + 80 mg TDMAC + 4.6 ml HCl (0.15 M)} coated on PET surface		Cl^-	207, 209
3. Composite: carbon powder + silica gel + epoxy resin		H^+/OH^-	225
B. Membrane films on field effect transistor devices			
1. [1 mg alkoxysilyl bis(12-crown4), or 16-crown-5, + 0.2 mg tetraphenylborate derivative + 22 μl TEOS + 62 μl DEDMS + 69 μl EtOH + 21 μl HCl (0.1 M)] coated on ISFET device		Na^+	203, 210
2. [29 mg TOMAC + 44 μl TEOS + 124 μl DEDMS + 138 μl EtOH + 42 μl HCl (0.1 M)] or [58 mg TDDTAC + 94 μl TEOS + 88 μl DEDMS + 174 μl EtOH + 122 μl HCl (0.1 M)] coated on ISFET device		Cl^-	219
3. [0.75 mg KTFPB + 0.5 mg DMPAP + polysiloxane PSX 851 (from Petrarch Systems)] coated on a FET device covered with poly-HEMA		NH_4^+	220
4. [4 mg $DBSO_4$ + 10 mg $TOHDANO_3$ + {TEOS + DEDMS + BDMO + 0.2 M HCl}] coated on ISFET device		SO_4^{2-}	226
5. [PMHS + α- or β-cyclodextrin] spin-coated on EIS device, or dip-coated on ISFET device		Cd^{2+}, Pb^{2+}	227
C. Ionic conductor films based on organic-inorganic solid polymer electrolytes			
1. [MPGSC + TEOS + PEG + $LiCF_3SO_3$ + DMF + EtOH + HCl] spin-coated on ITO	(Li^+)		202, 208
2. [AMF + fumed silica + $LiClO_4$ in EC/DMC] sandwiched between Li anode and C composite electrode	(Li^+)		211, 228
3. [PVA or SEBS + $HClO_4$ or H_3PO_4 + TEOS + EtOH] sandwiched between two C composite electrodes	(H^+)		212, 221
4. [GLYMO + epoxy + $LiClO_4$ or $LiCF_3SO_3$] coated on nickel foil	(Li^+)		213
5. [GLYMO + MEMO-S or MEMO-SA + TEOS] sandwiched between stainless steel electrodes	(H^+, Li^+)		201, 214, 229
6. [Nafion + SiO_2 Aerosil-200 + Pt powder] pressed between two PTFE foils	MeOH		204, 222
7. [TEOS + SiO_2 + HCF_3SO_3 + Li_2CO_3 + crown 12-O-4 + PEO] coated on Teflon	(Li^+)		223
8. [PEO + ICS + MPH + MDP] casted on PS substrate	(H^+)		224
9. Nafion membrane comprising silicon oxide synthesized in situ by sol-ge processing of TEOS	(H^+)		230
10. Composite membrane: PEEK-S + silica	(H^+)		231

Table 1 (Continued)

Methods and electrode configurations[a]	Electroactive species[b]	Target analytes[c]	References
D. Ionic conductor monoliths based on organic-inorganic solid polymer electrolytes			
1. [12.5 ml TEOS + 4 ml H_2O] + PEG + $LiClO_4$	(Li^+)		205, 206, 234
2. [TrEOS-PEG-TrEOS or TrEOS-PPG-TrEOS] + $LiClO_4$ + NH_4F + EtOH + H_2O	(Li^+)		215-217, 234
3. Composite: TrEOS-PPG-TrEOS + W-PTA (sandwiched between two ITO electrodes)	(H^+)		218
4. Composite polymer electrolyte: PEO + lithium salts + fumed silica	(Li^+)		232
F. Solid electrolyte with embedded electroactive species			
1. [TMOS + H_2O + HCl] + [0.005 M Fc in 1 M $LiClO_4$] + propylene carbonate	Fc		233
OTHER			
1. Electrodeposition: ITO (E = -0.3 to -1.5 V vs. Ag/AgCl) in 1.25 ml MTMOS + 5 ml EtOH + 5 ml KNO_3 (0.2 M) in phosphate buffer (1 mM, pH = 3.5)	$Fe(CN)_6^{3-}$		244
2. Electropolymerization: ITO (E = 2.3 V vs. Ag/Ag^+): 1 M pyrrole and 1 M TsONa in 10 ml EtOH + 2 ml DMF + 8 g TEOS + 0.2 g HCl	PPy		238
3. Alkylsilane monolayer by silanization: OTMS (4% v/v solution in toluene) on ITO	$Fe(CN)_6^{3-}$		252
4. Ormosil monolith including a microelectrode assembly: {(TEOS or TMOS + H_2O + MeOH + HCl) + [$Ru(bpy)_3$]Cl_2 or $FcCH_2OH$ or $Fe(CN)_6^{3-}$} in a glass or PS vial housing the microelectrode assembly	$Ru(bpy)_3^{2+}$, $Fe(CN)_6^{3-}$, $FcCH_2OH$		247-251
5. $Ru(bpy)_3^{2+}$-containing ormosil (TMOS:MTMOS) entrapped in poly-HEMA coated on Pt-IDA	$Ru(bpy)_3^{2+}$	codeine	245
6. $Ru(bpy)_3^{2+}$ complex-modified chitosan, covered by a sol-gel silica film (TMOS), coated on Pt		oxalic acid	241
7. Epoxy-carbon composite containing AChE (or BChE) enzyme immobilized on silica gel grafted with aminopropyl groups		Organophosphorous pesticides	239
8. Oligonucleotides immobilized on Si/SiO_2 chips via a silane layer (APTS or GPTS)		DNA	246
9. Polyelectrolyte/polymer layers coated on ITO via an organically-modified silane layer (APTS or GPTS)	$Ru(bpy)_3^{2+}$, $Fe(CN)_6^{3-}$ $Ru(CN)_6^{4-}$		242, 243
10. Electrodeposition of a poly(methylsiloxane) polymer containing side chains coordinated to Fc moieties	Fc		237
11. NQ/BV/Siloxane copolymers electrodeposited on GC or ITO electrodes	NQ, BV^{2+}		240
12. Electroprecipitation of a siloxane-paraquat redox polymer on Pt electrode	PQ^{2+}		235, 236

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[a] When not specified otherwise, all the "%" values given here are expressed as "weight percent". Abbreviations: CP, carbon paste; FeTsPc, iron tetrasulphophtalocyanine; NiTsPc, nickel tetrasulphophtalocyanine; Ru(edta)/ZrO_2, ruthenium-(ethylenediamine tetraacetic acid) immobilized on zirconium oxide; MeB, methylene Blue; MB, Meldola's Blue; CoHMP, cobalt hematoporphyrin IX; CoTmPyP, cobalt tetrakis(1-methyl-4-pyridyl)porphyrin; C_{18}, octadecyl; Fc, ferrocene; GOD, glucose oxidase; HRP, horseradish peroxidase; FDH, fructose 5-dehydrogenase; SH, salicylate hydroxylase; DMDHP, 5,10-dimethyl-5,10-dihydrophenazine; PMS, *N*-methylphenazonium methyl sulfate; BQ,

Table 1 (Continued)

o-benzoquinone; MTMOS, methyltrimethoxysilane; P_2Mo_{18}, 2:18-molybdodiphosphate; $SiMo_{12}$, 1:12-silicomolybdic acid; PMo_{12}, 1:12-phosphomolybdic acid; Mo_8O_{26}, isopolymolybdic anion; Me_2phen, 4,7-dimethyl-1,10-phenanthroline; PEG, polyethylene glycol; Rh_2POM, bis(acetato)dirhodium-11-tungstophosphate; Co-TMMP, cobalt tetramethoxymesoporphyrin; KB, Ketjenblack; FePc, iron phtalocyanine; DMG, dimethylglyoxime; CoPC, cobalt phtalocyanine; Ru^{II}Den, ruthenium dendrimer; Ru^{II}tpy, ruthenium terpyridil; PTMOS, propyltrimethoxysilane, TMOS, tetramethoxysilane; PTEOS, phenyltriethoxysilane; TEOS, tetraethoxysilane; TTF, tetrathiafulvalene; TESP-Fc, *N*(3-trimethoxysilylpropyl)-ferrocenylacetamide; BV, butylviologen; XOD, xanthine oxidase; LOD, lactate oxidase; L-AAOD, L-amino acid oxidase; EDAS, *N*-[3-(trimethoxysilyl)propyl]-ethylene diamine; APTS, 3-aminopropyltrimethoxysilane; DMFc, 1,1'-dimethylferrocene; AOT, bis(2-ethylhexyl) sulfosuccinate (sodium salt); DPT, diphenylthiocarbazone; RIgG, rabbit immunoglobulin; $FcCH_2OH$, ferrocenemethanol; $Ru(bpy)_3^{2+}$, ruthenium(II) tris(2,2'-bipyridyl); R-TMOS, alkyl-trimethoxysilane; BcG, bromocresol green; CR, cresol red; ETHETS, 2-(3,4-epoxycyclohexyl)-ethyltrimethoxysilane; FcCA, ferrocene carboxaldehyde; Nafion, perfluorinated ion-exchange polymer; ITO, indium tin oxide; PDMDAAC, poly(dimethyldiallylammonium chloride); GC, glassy carbon; PVSA, poly(vinylsulfonic acid, sodium salt); TMSPedat, *N*-[3-(trimethoxysilyl)propyl]ethylenediamine-*N,N',N'*-triacetic acid trisodium salt; APMDES, 3-aminopropyl-methyl-diethoxysilane; DETESPM, diethyl(triethoxysilylpropyl) malonate; SIS, bis[3-(triethoxysilyl)propyl] tetrasulfide; DMF, *N,N*-dimethylformamide; TMSPTEAI, (trimethoxysilylpropyl)trimethylammonium iodide; DMAPTS, 1-1'-dimethyl-(3-aminopropyl)trimethoxysilane; BTMOS, isobutyltrimethoxysilane; PhTMOS, phenyltrimethoxysilane; EE, ethoxyethanol; TMOS-Fc, 1,1'-bis(trimethoxysilyl)ferrocene; FDAH, (ferrocenylmethyl)dimethyl(*w*-trimethoxysilyl)alkylammonium hexafluorophosphate; OEG, oligo(ethylene glycol); PROXYL-COOH, 2,2,5,5-tetramethyl-3-carboxy-Δ3-pyrroline-1-oxyl; MTEOS, methyltriethoxysilane; PVA-g-P(4-VP), poly(vinyl alcohol) grafting 4-vinylpyridine; SPOD, soybean peroxidase; EETMS, 2-,3,4-epoxycyclohexyl-ethyltrimethoxysilane; IDA, interdigitated array; GluA, glutaraldehyde; DDAB, didodecyldimethylammonium bromide; BSA, bovin serum albumin; CTAB, cetyltrimethylammonium bromide; SSS, sulfonated silica sol; MG, methylene green; MPTMS, 3-mercaptopropyltrimethoxysilane; CPE, carbon paste electrode; PBS, phosphate buffer solution; Os-polymer, $[Os(bpy)_2(PVP)_{10}Cl]Cl$; PVP, polyvinyl pyridine; iCPTES, (3-isocyanopropyl)triethoxysilane; TDMAC, tridodecylmethylammonium chloride; PET, poly(ethylene terephtalate); Alkoxysilyl bis(12-crown4), bis(2,5,8,11-tetraoxacyclododecylmethyl) 2-[3-(triethoxysilyl)propyl]-2-methylmalonate; 16-crown-5, 15-triethoxysilylmethyl-16-crown-5; Tetraphenylborate derivative, sodium triphenyl{4-[3-(triethoxysilyl)propyl]phenyl}borate; DEDMS, diethoxydimethylsilane; ISFET, ion selective field effect transistor; TOMAC, trioctylmethylammonium chloride; TDDTAC, tetradecyldimethyl(3-trimethoxysilylpropyl)ammonium chloride; KTFPB, potassium tetrakis[3,5-bis(trifluoromethyl)phenyl] borate; DMPAP, 2,2'-dimethoxyphenyl-acetophenone; FET, field effect transistor; poly-HEMA, polyhydroxyethyl methacrylate membrane; $DBSO_4$, Dibekacin sulfate; $TOHDANO_3$, Trioctylhexadecyl ammonium nitrate; BDMO, Barium dimethoxide; PMHS, polymethylhydro-siloxane; EIS, electrolyte insulator semiconductor structure; MPGSC, 3-triethoxysilylpropylcarbamate; AMF, Poly(acrylonitrile-co-methyl methacrylate-co-styrene); EC/DMC, ethylene carbonate/dimethyl carbonate; PVA, polyvinylalcohol; SEBS, styrene-ethylene-butylene-styrene copolymer; GLYMO, 3-glycidoxypropyltrimethoxysilane; MEMO-S or MEMO-SA, (methacryloxypropyl)trimethoxysilane-sulfonic or –sulfonamide; PTFE, polytetrafluoroethylene; PEO, poly(ethylene oxide); ICS, 3-isocyanatopropyltriethoxysilane; MPH, monophenyltriethoxysilane; MDP, monododecylphosphate; PS, polystyrene; PEEK-S, sulfonated polyethetetherketone; TrEOS-PEG-TrEOS, O,O' Bis (triethoxysilyl)polyethyleneglycol; TrEOS-PPG-TrEOS, O,O' Bis (triethoxysilyl)polypropyleneglycol; W-PTA, peroxopolytungstic acid; TsONa, sodium p-toluenesulfonate; OTMS, octadecyltrimethoxysilane; AChE, acethylcholinesterase; BChE, butyrylcholinesterase; GPTS, glycidoxypropyl-triethoxysilane; NQ, naphtoquinone; BV, benzylviologen.

[b] Abbreviations: $FeTSPc^{4-}$, iron tetrasulphophtalocyanine; $CoTSPc^{4-}$, cobalt tetrasulphophtalocyanine; Ppy, polypyrrole; Fc, ferrocene; PAQ, 9,10-phenanthrenequinone; DA, dopamine; AA, ascorbic acid; UA, uric acid; $FcCH_2OH$, ferrocenemethanol; $Ru(bpy)_3^{2+}$, ruthenium(II) tris(2,2'-bipyridyl); DMPE, 1,2-bis-(dimethylphosphino)ethane; MV^{2+}, methylviologen; PB, Prussian Blue; PROXYL, 2,2,5,5-tetramethyl-3-carboxy-Δ3-pyrroline-1-oxyl; NQ, naphtoquinone; BV^{2+}, benzylviologen; PQ^{2+}, paraquat.

[c] Abbreviations: NADH, dihydronicotinamide adenine dinucleotide; Tifluadom, N-[5-(2-fluoro-phenyl)-2,3-dihydro-1-methyl-1H-1,4-benzodiazepine]-2,4-methyl-3-thiophene carboxamide; Methyl parathion, *O,O*-dimethyl-*O*-*p*-nitrophenylthiophosphate; Bendiocarb, 2,3-isopropylidenedioxiphenylmethyl carbamate; Ephedrine, (1R,2S)-(-)-a-(1-methylamine-ethyl)benzyl-alcohol; L-Met, L-methionine; L-Cys, L-cysteine; GSH, glutathione (reduced form); IgG, immunoglobulin G; MV^{2+}, methylviologen; DA, dopamine; AA, ascorbic acid; PAHs, polyaromatic hydrocarbons; DNA, desoxyribonucleic acid.

sition.[19] Finally, a basic requirement for the proper operational working of chemically modified electrodes is their long-term stability, implying a durable confinement of the modifying reagent on the electrode surface. To prevent reagent leaching into the external solution, several methods were proposed: (1) the most powerful approach is the covalent bonding that can be achieved with using a selected organo-alkoxysilane (i.e., refs 154, 158, 164, and 179); (2) the physical entrapment during the formation of the film by the sol−gel process might be efficient only in the case of a bulky modifier (i.e., biomolecule or large organometallic complex) (i.e., refs 154, 175, 180, and 195) or when controlling the porous structure of the material (by templating or imprinting);[165,173] (3) the last possibility is to exploit the strong interaction liable to occur between the organic−inorganic matrix and the reagent, which can induce substantial partitioning of the reagent into the film[157,158,181] or to use a nanoglue (i.e., glutaraldehyde)[198] to retain the reagent on the electrode surface.

The sol−gel process was also exploited to prepare ceramic membranes doped with ionophores, either covalently bonded to the material or simply encapsulated within it, for designing ion-selective devices (i.e., refs 207, 210, and 219). Various proton and lithium ion conductor films based on organic−inorganic solid polymer electrolytes were manufactured, most of them being made of interpenetrating poly(ethylene or propylene)-glycol and sol−gel silica doped with an inorganic acid or a lithium salt (Table 1). Finally, some other scarce methods were described, that is, electro-assisted film generation (i.e., refs 244, 237, 238, and 240) to combine the organically modified silicates with electrochemistry.

2.2. Electrochemical Characterization. The basic characterization of a newly fabricated silica-modified electrode system was often performed via a thorough examination by cyclic voltammetry. Without entering into the details, some general trends and some specific recent observations are briefly mentioned hereafter.

Kubota, Gushikem and co-workers[71,73,79,81,86−91] have examined the voltammetric response of several catalysts and charge-transfer cofactors (metal phthalocyanines, porphyrins, methylene or Meldola's Blue) adsorbed on silica gels coated with inorganic layers (mainly titanium oxide or titanium phosphate), as a function of various experimental parameters like pH or the nature of the electrolyte. They have recently reported the strong binding of these electroactive species, preventing leaching into the external solution,[86−91] and have provided a factorial design optimization by searching the conditions for the best reversibility of the redox processes.[79]

The ceramic−carbon composite electrodes (CCEs) and the corresponding metal-doped CCEs were fully characterized by Lev's group (i.e., refs 22, 93−96, and 124). An interesting feature is the possible control of the thickness of the electrochemically active portion of the electrode by monitoring the hydrophobicity of the CCE by a proper choice of the started organo-alkoxysilane.[124] This kind of bulk-modified electrode generally provides higher sensitivity than carbon paste or glassy carbon[95] and display sometimes an intrinsic electrocatalytic effect (i.e., lowering the overpotential by 300 mV with respect to glassy carbon for the detection of NADH),[120] similar to CCEs made of other metal oxides.[255]

Cyclic voltammetry (CV) was also applied to characterize the associated charge and mass-transfer reactions within the organically modified silicate films coated on solid electrode surfaces. For electrode-confined siloxane polymer films containing redox subunits, the following has been allowed: to distinguish between diffusion control and thin-layer behavior, to highlight a pH dependence, to discuss the influence of the nature and electrolyte concentration of the soaking solution, or to evidence a catalytic effect.[143,236,240,256] For organically modified silicate films containing electroactive species (adsorbed, liganded, or ion exchanged), the CV technique was often used to characterize the accumulation-leaching processes or to quantify the partitioning of selected analytes (i.e., refs 68, 84, 85, 162, and 183). CV was also used to demonstrate the feasibility of biosensing applications involving organic−inorganic hybrid materials containing encapsulated biomolecules, despite the fact that amperometry was mostly employed in practice (refs 35 and 39 and references cited therein). A recent investigation on electrochemically produced Pt particles on sol−gel-modified carbon film has revealed a new kind of morphology for Pt, which holds great promise for Pt-catalyzed reactions.[257]

Another aspect is the exploitation of the electrochemical techniques for either probing the sol to gel to xerogel transition or characterizing the porosity of sol−gel-derived materials or even evaluating the extent of interaction between a redox probe and the internal surface of the silicate.[22,153,233,248,250,258−262] The general principle is based on the fact that the voltammetric response of the electrode is dependent on the apparent diffusion coefficient of the redox probe, which can be related to its mobility into the porous structure of the sol−gel material. This approach was initiated by Audebert and co-workers[259−262] to follow the sol−gel−xerogel evolution by means of electroactive probes in silica (and other transition metal) oxide based gels. Recent advances in this field were reported by Collinson et al.[247−251] By coupling cyclic voltammetry and chronoamperometry applied to an organically modified silica monolith comprising an ultramicroelectrode assembly, they were able to obtain a calibration-free evaluation of the apparent diffusion coefficient of redox probes encapsulated within the monolith.

3. Emerging Applications

Before describing the various electrochemical applications involving organic−inorganic hybrid silica-based materials, it should be emphasized how the target application determines the particular choice of the modified electrode design. Besides the large amount of information provided in Table 1 dealing with the preparation methods of silica-modified electrodes, it is possible to connect roughly the target applications to a type of electrode configuration, depending on class I or II hybrids, as gathered in Table 2. This would help the reader to obtain a rapid survey of the various applications, linked to a brief description on the corresponding electrochemical devices.

3.1. Preconcentration−Permeation Associated with Voltammetric Detection. A common practice with chemically modified electrodes is to exploit the binding properties of the modifier to accumulate a target

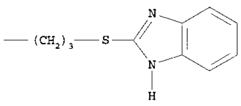
Table 2. Target Applications versus the Most Common Electrode Designs

Electrochemical applications[a]	Class of hybrids	Electrochemical devices – electrode configurations
PRECONCENTRATION-PERMEATION PRIOR TO VOLTAMMETRIC DETECTION		
# Accumulation by adsorption or complexation	Classes I & II	Silica-modified CPE or CCE
# Accumulation by ion exchange	Class I	Interpenetrating organic polyelectrolyte – inorganic lattice coated on solid electrodes
# Permselective coatings	Class II	Ormosil film coated on solid electrodes
# Selective accumulation via molecular imprinting	Class II	Sol-gel-derived ormosil film coated on solid electrodes
CHEMICAL SENSORS		
# Detection by electrocatalysis	Class I	Organic catalysts adsorbed on metal oxide coated silica (dispersed into CPE)
	Class II	Catalysts encapsulated within CCEs
# Gas sensors	Class II	CCEs
# Ion sensors	Classes I & II	Organically modified membranes (often deposited on FET devices)
# Disposable sensors	Class I	Interpenetrating sol-gel silica and cellulose-based polymer comprising C particles
# Detectors in chromatography	Class II	CCEs
ELECTROPOLYMERIZATION AND LONG-RANGE CHARGE TRANSFER		
# Charge transfer in redox polymers based on ormosil	Class II	Electroactive organically-modified silane or siloxane films coated on solid electrodes
# Interpenetrating silica networks and conducting polymers	Classes I & II	Conducting polymers – ceramic films coated on solid electrodes
# Electro-assisted generation of silicate films	Class II	Ormosil films grown on solid electrodes
SPECTROELECTROCHEMISTRY AND ELECTROGENERATED CHEMILUMINESCENCE		
# Spectroelectrochemical sensing	Class I	Interpenetrating organic polyelectrolyte – inorganic lattice coated on solid electrodes
# Electrochemiluminescence	Class I	Chemiluminescent precursor dispersed into silica monolith comprising UME
BIOSENSORS		
# First generation	Class I	CCEs or sol-gel silica films on solid electrodes containing encapsulated biomolecules
# Second generation	Class I	CCEs or sol-gel silica films coated on solid electrodes containing an encapsulated biomolecule together with a charge transfer mediator
	Class II	Ormosil films or monoliths containing encapsulated biomolecules (sometimes with C)
BATTERIES AND FUEL CELLS	Classes I & II	Ormolyte or ormocer films coated on one (or sandwiched between two) electrode(s)

Abbreviations: CPE, carbon paste electrode; CCE, ceramic-carbon composite electrode; Ormosil, organically modified silicate; FET, field-effect transistor; UME, ultramicroelectrode; Ormolyte, organically modified electrolyte; Ormocer, organically modified ceramic.

analyte prior to electrochemical quantification. Improvement with respect to the corresponding unmodified electrodes is expected in both sensitivity and selectivity. Sensitivity should be enhanced by the chemical preconcentration and selectivity would arise from the proper choice of a modifier liable to interact preferentially with the target analyte while rejecting the interferent species. For this purpose, organic−inorganic hybrid materials look promising because the organic part can be selected on the basis of its particular affinity to a target analyte, and the inorganic network can be tailored with multiple structures displaying large open spaces of tunable porosity that would impart easy access to the binding sites and therefore a high preconcentration efficiency.

3.1.1. Accumulation by Adsorption or by Complexation. Both class I and class II organic−inorganic hybrid silica-based materials were employed for this purpose. The concept of using an organic ligand immobilized within a ceramic−carbon composite electrode for the detection of metal species in the preconcentration/voltammetry strategy was demonstrated by Wang et al. (Ni^{II}−dimethylglyoxime)[110] and Ji and Guadalupe (Fe^{II}−dimethylphenanthroline).[126] Hernandez and coworkers have exploited the binding properties of C_{18}−silica gel, a common stationary phase in chromatography, for the determination of various drugs and pesticides.[62,65,66,69] Other class II hybrids were then prepared and applied for electroanalytical purpose, with durable retention capabilities due to the covalent bond between the silica network and the organic ligand, which was achieved by using an organoalkoxysilane. Examples are available for the analysis of mercury[67,172] and copper,[85,92] the grafted reagents and sol−gel precursors being 3-(2-mercaptobenzimidazolyl)propyl groups (**1**), 3-aminopropyl moieties (**2**), or bis[3-(triethoxysilyl)-propyl] tetrasulfide, SIS (**3**).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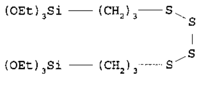
$-(CH_2)_3-NH_2$

2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3.1.2. Ion Exchange. Most of the work in this field was performed with interpenetrating organic−inorganic polymer composite films, where the organic component was a long-chain polyelectrolyte displaying cation (**4**−**6**) or anion (**7**, **8**) exchange properties.[158,161−163,185]


$-(CH_2-\underset{SO_3H}{CH})_n-$

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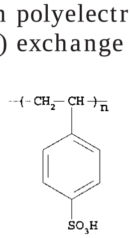
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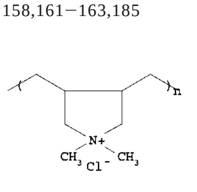
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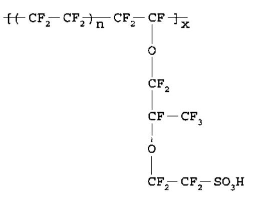
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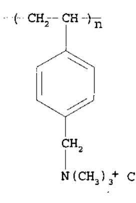
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Their analytical utility as electrode modifiers was illustrated by the Heineman's group.[158,162,163,185] It was demonstrated that cationic analytes (as methyl viologen or $[Re^{I}(DMPE)_3]^+$ with DMPE = 1,2-bis-(dimethylphosphino)ethane) partitioned much more quickly in a sol−gel−Nafion composite electrode compared to the corresponding pure Nafion (**6**)-modified electrode.[162,163] This improvement was ascribed to the rigid three-dimensional open structure of the composite film, which was induced by its inorganic component (silica network), leading to enhanced mass transfer to and from the ion-exchange sites located inside the film. Enhancing diffusion processes in Nafion by dispersing the polymer into a sol−gel-derived silica matrix was otherwise evidenced by electrochemical impedance spectroscopy and other techniques.[34,263] This behavior was exploited for electrochemical sensing of $[Re^{I}(DMPE)_3]^+$ at both a planar graphite electrode and carbon-fiber microelectrode covered with a sol−gel-Nafion film, lowering by 10000 times the detection limit compared to that of unmodified electrodes because of the substantial preconcentration of the analyte in the film.[163,185] The use of other ion exchangers (**4**, **7**) embedded in a sol−gel glass resulted in similar improvements for the analysis of both cations and anions ($Fe(CN)_6^{3-/4-}$, $Ru(NH_3)_6^{3+}$, and $Ru(bpy)_3^{2+}$).[158]

3.1.3. Permselective Coatings. As expected from the above observations, if polyanionic systems are liable to accumulate cations (and polycationic electrolytes would concentrate anions), one can easily imagine that anions and cations would be rejected respectively by polyanionic and polycationic polymers. This kind of permselective behavior, applied to electroanalytical chemistry, was investigated by Collinson et al.[154,174] by coating on glassy carbon electrodes an organically modified silicate film containing either $-NH_2$ or −COOH groups covalently linked to the silica backbone. Whereas the silicate−COOH electrode resulted in large voltammetric currents for cationic analytes such as methyl viologen or ruthenium hexaamine, nearly complete suppression of the electrochemical response was observed with using the silicate−NH_2 electrode. Complementary behavior was exhibited for the negatively charged ferricyanide analyte.[154] The magnitude of the phenomenon was found to depend strongly on the amount of ion-exchange sites, the type of modifier, and the structure (more or less open) of the organic−inorganic hybrid.[174] Another approach to modulate the permeability of organic−inorganic layered coatings on electrode surfaces was proposed by Coche-Guérente et al.:[164] it consists of the intercalation of polycationic silasesquioxane oligomers into a Laponite clay film deposited on platinum or glassy carbon, which induces mesoporosity in the resulting clay-modified electrode.

3.1.4. Molecular Imprinting. A striking field in materials chemistry is the search for integrated systems allowing recognition/discrimination at the molecular level. An elegant way to reach this goal is provided by the molecularly imprinted polymers, which have already found some sensing applications.[264−266] However, their implication in electrochemistry was rather limited because they often suffer from long response times due to slow diffusion of the analyte into the material. One possibility to overcome this limitation was suggested by

Makote and Colinson.[267] They have fabricated an organic−inorganic hybrid sol−gel material, by a template-based approach, which was found to be selective to dopamine over ascorbic acid. They have further exploited this selectivity in electrochemistry by the way of a dopamine-templated film electrode, which displayed an increased molecular permeation of dopamine through the material over that of structurally related molecules, resulting in the selective voltammetric analysis of this species.[165]

3.2. Chemical Sensors. Commonly with what has occurred for many studies on chemically modified electrodes, the electrochemists working with the organic−inorganic silica-based hybrid materials are sometimes grappling with transferring the fundamental research of chemically sensitive interfaces from concept to the practical application. And the sensor field is a favorite domain where the fundamental levels could be coupled to the needs of real-world applications and to a broad range of scientific disciplines outside chemistry.

3.2.1. Electrocatalysis. Perhaps the straightforward way from fundamental electrochemistry to the elaboration of sensing devices is encountered with systems displaying electrocatalytic properties, at least when they are not coupled to a preconcentration step and when they can operate without any sample pretreatment.

Kubota, Gushikem, and co-workers[71−74,80,81,87−91] have largely exploited the electrocatalytic properties of various organometallic compounds adsorbed on modified silica gel surfaces (hybrids of class I). These latter were previously coated with a metal oxide layer prepared by the reaction of a metal chloride, MCl_x, with the surface silanol groups, ≡SiOH (eq 1) followed by hydrolysis of the remaining chloride moieties (eq 2). The metal was

$$n{\equiv}\mathrm{SiOH} + \mathrm{MCl}_x \Rightarrow ({\equiv}\mathrm{SiO})_n\mathrm{MCl}_{(x-n)} + n\mathrm{HCl} \quad (1)$$

$$({\equiv}\mathrm{SiO})_n\mathrm{MCl}_{(x-n)} + (x-n)\mathrm{H_2O} \Rightarrow ({\equiv}\mathrm{SiO})_n\mathrm{M(OH)}_{(x-n)} + (x-n)\mathrm{HCl} \quad (2)$$

mainly Ti (but also Zr or Nb) because of the enhanced conductivity of TiO_2,[268] and the layer was sometimes overcoated with phosphate because of its favorable interaction with many common charge-transfer mediators used in electrocatalysis.[269] For example, they have reported attractive sensors for dissolved oxygen,[72] NADH,[74] hydrazine,[80] and oxalic acid,[86] with ruthenium−(ethylenediamine)−tertraacetic acid, Meldola's Blue, nickel and cobalt phthalocyanines, respectively, as the mediators. Analysis of natural samples, such as lake water[72] or spinach,[86] was also performed with such modified electrodes, and long-term stability (6 months) was reported.[80]

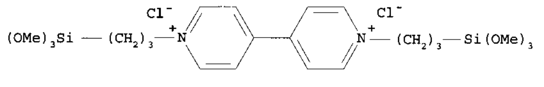
The hydrophobic matrix of ceramic−carbon composite electrodes, CCEs, was also exploited to immobilize catalysts. Wang et al.[137−140] have constructed amperometric sensors for inorganic anions (NO_2^- and BrO_3^-) and for ascorbic acid, made of CCEs containing encapsulated phospho-, silico-, or isopolymolybdic compounds. They report short response times, long-term stability, and good reproducibility. Cox's group[119,134,136] has utilized other polyoxometalates based on rhodium(II) as well as ruthenium(II) metallodendrimers encapsulated in a CCE matrix, for the amperometric sensing of proteins and peptides. The robustness of the CCE allowed effective use in flowing streams. Similar performance has been reported by Wang et al.[111] for sol−gel-derived cobalt phthalocyanine-dispersed carbon composite sensor, applied in flow injection analysis of hydrogen peroxide, hydrazine, oxalic acid, cysteine, and thiourea.

3.2.2. Gas Sensors. Tsionsky and Lev[98] have proposed a prototype electrochemical oxygen sensor for which the sensitive device was made of a homogeneous dispersion of a cobalt porphyrin catalyst and carbon powder into a sol−gel-derived organically modified silica. The role of the organically modified silica is essential because the porous inorganic network provides a rigid open structure permitting gas permeability while the organic part induces hydrophobicity at the electrode surface and thus minimizes effects of liquid-side mass transfer. Later on, the same group replaced the organometallic catalyst by metal palladium clusters and examined this new inert metal-modified CCE by providing a characterization of the wetted section of this kind of gas sensor.[124] Amperometric sensing of gaseous oxygen was also performed with membrane sensors using propylene carbonate electrolytes gelled by highly dispersed silica.[270] It should be reminded here that other gas sensors based on silica-modified electrodes were reported,[49,271−273] exploiting the versatility of the sol−gel technology, but they did not involve the organic−inorganic hybrids.

3.2.3. Ion Sensors. Various potentiometric sensors based on organic−inorganic hybrid silicates were reported.[199,200,203,207,209,210,219,220,225−227] Most of them described already in recent reviews,[22,35] they will not be detailed here but are listed in Table 1. Basically, these systems involve the fabrication of membranes comprising selected ionophores, which were then used as prepared or coated on field-effect transistor devices. To prevent leaching of the active ionophore, most of the authors used covalently bound reagents or even bulky ionophores physically entrapped within the membrane. Recent investigations in this field were directed to the formation of organically modified silica films on conventional electrodes and applied either to pH measurement[173,197] or as devices sensitive to K^+ ions.[175,172] For example, Guo et al.[172] have produced a Prussian Blue sol−gel composite via post-chemical-derivatization of a functionalizable sol−gel thin film based on the SIS compound (**3**), which was found to be a robust all solid-state ion-selective potentiometric sensor for K^+ ions.

3.2.4. Disposable Sensors. Decentralized electrochemical monitoring is another efficient possibility for transfering the results of fundamental studies to the needs of real-world applications, and the use of disposable sensors is one way toward on-site clinical or environmental monitoring.[274,275] Wang's group[104,112−116] has pioneered the field of screen-printed organically modified silicate containing electrochemical sensors. These are made of interpenetrating sol−gel silica and cellulose-based polymer comprising carbon particles. The fluid character of the starting sol is compatible with the thick-film technology. After having reported several biosensing applications based on enzyme electrodes,[104,112−115] they provide the first example of disposable immunosensor, showing that a rabbit immunoglobulin G antigen immobilized within the organically modified ceramic−carbon matrix retains its affinity and specificity to the antibody.[116] An alternative route to thick-film sol−gel graphite composites, proposed by Guo and Guadalupe,[117] is based on surfactant-induced sol−gel synthesis that does not require the use of either a cosolvent or a cellulose binder or an acid catalyst or a thermal curing step. Its applicability was demonstrated for biosensing, electrocatalysis, and voltammetric analysis after chemical preconcentration.

3.2.5. Detectors in Chromatography. Two major requirements for detectors (i.e., electrochemical), when applied in flowing conditions, are their physical robustness and their specific chemical sensitivity. The organically modified silicates combines these two properties, the silica backbone ensuring a rigid structure while the tuning of chemical reactivity can be modulated by a suitable choice of the organic moieties. These materials, associated with the versatility of sol−gel processing, look therefore promising for this purpose. The first example was described by Pamidi et al.[109] who evaluated the performance of CCE in a wall-jet configuration as an amperometric detector for liquid chromatography. Later on, Hua and Tan[131,133] adapted a similar composite material for the amperometric detection of dopaminergic compounds in capillary electrophoresis. They extended the principle to the detection of carbohydrates by incorporating a catalyst (Cu_2O) in the electrode material.[130,132] Cox et al.[134] detected peptides, after separation by reverse-phase HPLC, by using a dirhodium-substituted polyoxometalate as the catalyst in CCE. The same group recently introduced an electrocatalytic amperometric detector based on CCE doped with a ruthenium(II) metallodendrimer and applied it to the analysis of cyanide by Donnan dialysis coupled with ion chromatography.[135]



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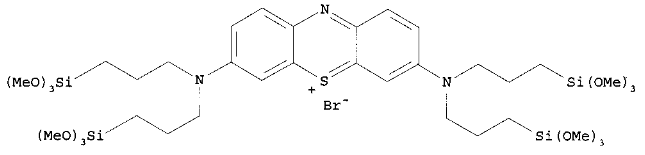

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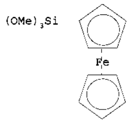

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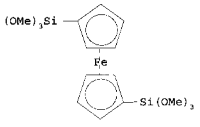

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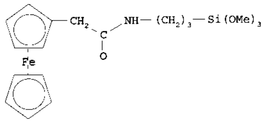

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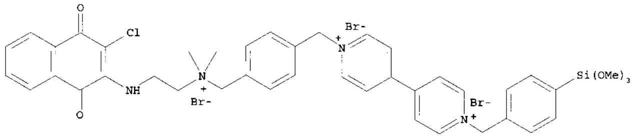

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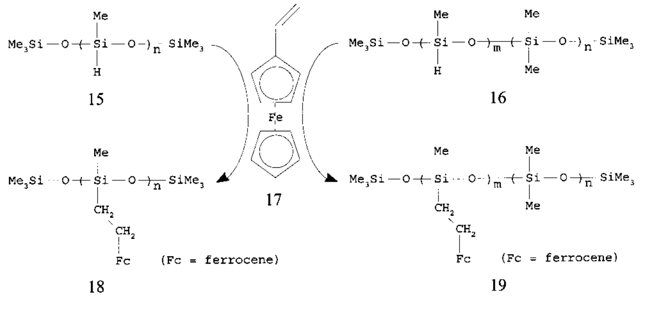
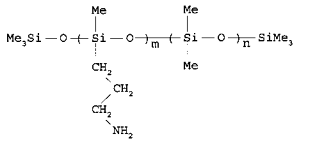
3.3. Electropolymerization and Long-Range Charge-Transfer Films.

3.3.1. Redox Polymers Based on Organically Modified Silicates. The earliest implication of organic−inorganic silica-based hybrid materials in electrochemistry is that involving redox-active groups covalently linked to a polysiloxane macromolecule, to form what was called a redox polymer,[276] in which the charge transfer usually occurs via electron hopping between the adjacent electroactive groups. Two main synthetic routes to produce these redox polymers were reported: (1) the hydrolysis and condensation of organoalkoxysilanes containing the redox moieties and (2) the hydrosilylation of a molecule containing a vinyl function attached to a redox-active group with one alkylhydrosiloxane homopolymer or copolymer. An alternative to this last case is the amidation reaction between a COOH or COCl function attached to a redox-active group and an aminopropyl(alkyl)siloxane polymer. Examples of organosilane precursors are *N*,*N*′-bis[3-(trimethoxysilyl)propyl]-4,4′-bipyridinium dichloride (**9**),[236] 3,7-bis-[bis(trimethoxysilyl-3-propyl)amino]phenothiazin-5-ium bromide (**10**),[277] (trimethoxysilyl)ferrocene (**11**)[148] or 1,1′-bis(trimethoxysilyl)ferrocene (**12**),[144,145] *N*-[3-(trimethoxy-silyl)propyl]ferrocenylacetamide (**13**),[101] 2-chloro-3-[[2-{dimethyl[[[[*N*′-[[4-(trimethoxy-silyl)-phenyl]methyl]-4,4′-bipyridinium]methyl]phenyl]-methyl]ammonium}ethyl]amino]-1,4-naphthoquinone (**14**).[240] Except for **9** and **10** where the polymer was electrodeposited from the pure organotrimethoxysilane,[236,277] the organosilanes **11**−**14** were usually copolymerized with other alkoxysilane(s) acting as cross-linking agent(s), leading to less flexible and more robust surface-confined polymers. This process inducing a “dilution” effect of the redox centers within the redox polymer film, it is therefore not surprising that the highest rate of charge transport was observed with the film prepared from the pure redox-active-linked silane (observed effective diffusion coefficients of about 0.3−3 × 10^{-9} cm^2 s^{-1}).[236,277] Systems based on benzyl viologen/naphthoquinone/siloxane copolymers (prepared from **14** and other analogues) were found to display charge-trapping properties.[240] The second method for preparing silica-based redox polymers was mainly applied to the production of ferrocene−siloxane films. Basically, the methylhydrosiloxane homopolymer (**15**) or the methylhydrosiloxane−dimethylhydrosiloxane copolymer (**16**) were allowed to react with vinylferrocene (**17**) to give the corresponding methyl(2-ferrocenylethyl)- and methyl[2-(dimethylferrocenyl)ethyl]siloxane polymers (**18**, **19**). When coated on a solid electrode surface, these polymers display nonideal thin film behavior (dependence of peak currents, i_p, on scan rate, ν, in the form of $i_p = \nu^{0.8} - \nu^{0.9}$).[142] This can be attributed to the diffusion of the electrolyte anion into the film to maintain charge balance during the oxidation of the ferrocene moieties;



the stability of the film upon continuous potential cycling was also found to be strongly dependent on the nature of the electrolyte anion.[143] Such ferrocene–polysiloxane compounds are efficient electron-transfer relay systems, which were exploited for biosensing applications.[61,63,64] Other allyl-terminated redox catalysts (PROXYL[147] and porphyrin[256]) were covalently attached to polysiloxane derivatives and further applied in electrocatalysis. An alternative to preparing analogue structures was given through the chemistry of silicon-based ferrocenyl dendrimers.[276] Typically, (aminopropyl)methylsiloxane–dimethylsiloxane (**20**) is reacting with (chlorocarbonyl)ferrocene (**21**) or 1,1′-bis(chlorocarbonyl)ferrocene (**22**)[237] or the corresponding carboxylic forms to give the corresponding ferrocenyl–silica polymers. The electrochemistry of polysilane copolymers with pendent ferrocenyl groups was also reported.[278]



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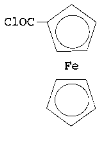

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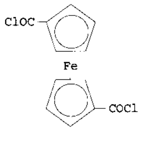

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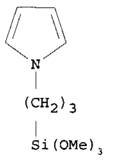
3.3.2. Interpenetrating Silicate Networks and Conducting Polymers. Both the preparation and chemistry of conducting polymer nanocomposites, including those involving silicates, were recently overviewed,[253] and the electrochemistry of hybrid interpenetrating conducting polymer–metal oxide materials was also treated in a more general review.[22] Because very few new electrochemical investigations have appeared recently, only the preparation mode of these hybrids in connection to electrochemistry will be briefly treated here, the interesting reader being directed to the above reviews. Conducting polymer silica-based composites can be prepared via the electrochemical polymerization of a selected monomer (i.e., pyrrole, aniline, or thiophene derivative) in the presence of a silica source (as-synthesized inorganic particles)[253] or a silica precursor (tetra-alkoxysilane),[169,238] this latter case corresponding to a coupled organic–inorganic copolymerization reaction. An alternative to this approach is the electrochemical synthesis of the conducting polymer within the porous structure of a preformed sol–gel silica, as demonstrated for polyaniline.[279] A second method is the hydrolysis–condensation of a silanized monomer, followed by its chemical polymerization. Examples of monomers used for this purpose are *N*-[3-(trimethoxysilyl)propyl]pyrrole (**23**) or 2,5-bis(trimethoxysilyl)–mono-, bi-, and terthiophene (**24**). While Sanchez et al.[70] used a starting gel doped with the pyrrole monomer (together with (**23**)), Corriu et al.[280] reported polymerization in the thiophenylene-bridged gels without added monomer species. Both composites gave a voltammetric response. Finally, conducting polymer–silica composites were also obtained by doping as-synthesized polymers with a silica sol that was then allowed to gel, giving a silica network after aging.[281]



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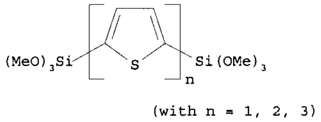

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3.3.3. Electro-Assisted Generation of Silicate Films. Besides the electro-assisted polymerization reactions described above (in sections 3.3.1 and 3.3.2), an interesting approach was proposed by Shacham et al.[244] to produce methylated sol–gel films on conducting substrates. It involves the potentiostatic generation of OH^- species by water reduction, which catalyze the sol–gel condensation near the electrode surface. The formation of the silicate layer on the electrode does not result from the electron transfer by itself, but the latter is acting locally (i.e., at the electrode/solution interface) on one key parameter (pH) affecting the sol–gel process. Coatings of variable thicknesses can be obtained by appropriate control of the deposition potential and/or time.[244] This constitutes a novel method in the field of electro-assisted synthetic routes to produce ceramic thin films.[282]

3.4. Spectroelectrochemistry and Electrogenerated Chemiluminescence. 3.4.1. Multimode Selectivity in Spectroelectrochemical Sensing. A new type of spectroelectrochemical sensor demonstrating multimode selectivity was recently introduced,[159,160] and then largely developed,[184–189] by the group of Heineman, Seliskar, and co-workers. It consists of an optically transparent electrode (i.e., indium tin oxide) coated with an organic–inorganic hybrid made of interpenetrating organic polymer and silica network produced by sol–gel technology. Upon a proper choice of the organic polymer, selective permeation of target analytes (or rejection of interferences) can be achieved. This constitutes the first mode of selectivity. Second, the analyte partitioned into the selective coating could be detected, or not, by attenuated total reflection (ATR) chosen as the optical detection mode. This is the second mode of selectivity. Third, the application of a selected potential to the electrode would result in the electrolysis of the previously accumulated analyte(s) that are electroactive at this potential value, leading to the third mode of selectivity. Optical detection was usually performed on the electrolysis product(s). The multimode selective sensing of a target analyte relative to other solution components is therefore achieved by a judicious choice of coating material, electrolysis potential, and wavelength for optical monitoring.[159,160]

The concept was first demonstrated with an anion-selective coating made of sol–gel-derived PDMDAAC–SiO_2 composite, where PDMDAAC = poly(dimethyl–diallylammonium chloride) (**7**), and $Fe(CN)_6^{4-}$ as a model analyte. When partitioned into the film, the analyte was detected by the change in the transmittance of the ATR beam resulting from oxidation of $Fe(CN)_6^{4-}$ to $Fe(CN)_6^{3-}$.[160] Linear calibration was obtained at the permeation equilibrium in the 5–400 μM concentration range.[189] When an $Fe(CN)_6$4-/$Ru(CN)_6^{4-}$ binary mixture, for which both anions are liable to permeate within the PDMDAAC–SiO_2 film, was used, selectivity was achieved either by restricting the electrolysis potential to a range specific to the $Fe(CN)_6^{4-}$ component (selectivity to $Fe(CN)_6^{4-}$) or by recording the ATR signal at a wavelength specific to the $Ru(CN)_6^{4-}$ component (selectivity to $Ru(CN)_6^{4-}$).[159] When an $Fe(CN)_6^{4-}/Ru(bpy)_3^{2+}$ binary mixture was used, selectivity was induced by the choice of a charge-selective thin film: PDMDAAC−SiO_2 was found to accumulate $Fe(CN)_6^{4-}$ species while rejecting $Ru(bpy)_3^{2+}$ and the opposite action was observed with a Nafion (**6**)−SiO_2 composite. Using the couple [Nafion−$SiO_2/Ru(bpy)_3^{2+}$] as a model system, it was shown that the detection limit can be significantly lowered under the condition of continuous potential cycling with concomitant averaging of the optical response.[184] Optimization of the excitation potential waveform was investigated with the same model system by using a simulation program.[186] Moreover, the nonabsorbing analyte can even be detected by this technique if a charge-transfer mediator entrapped in the film is employed: this was exemplified for the indirect analysis of ascorbate with $Ru(bpy)_3^{2+}$ as the mediator.[187] A prototype sensor was constructed by the incorporation of planar waveguide technology into the spectroelectrochemical device.[188] When anion- and cation-exchange polymer blends and a mixture of analytes ($Fe(CN)_6^{4-}$, $Ru(CN)_6^{4-}$, and $Ru(bpy)_3^{2+}$) were used, spectroelectrochemical modulation could be achieved, based on variation in the electrochemical reversibility of the analyte, the effect of the potential window, and the variation in the speed of permeation of the analyte into the polymer film.[243]

3.4.2. Electrochemiluminescence. Collinson and co-workers[247,249] have recently reported that solid-state electrogenerated chemiluminescence (ECL) can be observed from $Ru(bpy)_3^{2+}$ encapsulated within a silica gel host using gel-entrapped tripropylamine as the reductant, which was excited via an immobilized microelectrode assembly. The ECL produced was very stable because of the relative immunity of both the chemiluminescent precursor and the reductant to water and oxygen (due to encapsulation) as well as the use of an ultramicroelectrode assembly.[249] When reductants of various natures and sizes (several tertiary amines and sodium oxalate) were used, it was suggested that the ECL response could be exploited to probe the diffusion in constrained environments and assess surface interactions between the entrapped reagents and the walls of the silicate host.[251] Similar production of ECL can be obtained with Nafion−SiO_2 composite films doped with $Ru(bpy)_3^{2+}$ and coated on a glassy carbon electrode surface,[190] with a $Ru(bpy)_3^{2+}$-modified chitosan/silica gel membrane coated on platinum[241] or with a $Ru(bpy)_3^{2+}$/(polyhydroxyethyl)methacrylate/sol−gel/silica composite film deposited on a silicon chip.[245]

3.5. Amperometric Biosensors. The discovery 10 years ago of the possibility of encapsulating enzymes in the bulk of a silica matrix by the sol−gel process, while maintaining their biological activity,[283] has driven extensive research activities in the development of new optical and electrochemical biosensors, as described in several well-documented reviews.[9,10,12,22,23,29,35,39−41,44] In the same time, advances on bioentrapment procedures were reported.[38,284−291] Wang recently presented a complete overview on sol−gel materials for electrochemical biosensors.[39] Only a brief account on those involving organically modified silicates is given hereafter.

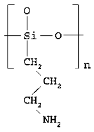
An electrochemical biosensor consists of three components: an active biological system, an electrochemical transducer, and an output system. A successful ensemble displaying high sensitivity, good selectivity, and long-term stability would require the optimization of some key experimental parameters: (1) the proper immobilization of the biomolecule with ensuring no or little loss in its activity and preventing denaturation (biological activity, sensitivity, and stability); (2) charge transport between the electrode material and the electrochemically active centers must be achieved (transduction and sensitivity); (3) overpotentials should be minimized by using a suitable catalyst or charge-transfer mediator (selectivity), which must of course be kept in the neighborhood of the biomolecule and be accessible to the transducer. The sol−gel-derived (bio)-organic−inorganic hybrid materials offer great promise for fulfilling efficiently most of these requirements so that it is not surprising that many biosensing devices based on these hybrids were developed (Table 1).

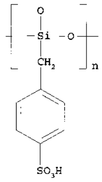
A basic approach is the microencapsulation of an enzyme within a silicate matrix by low-temperature sol−gel processing. This can be performed in the presence of carbon particles to obtain either a bulk-modified ceramic−carbon biocomposite[97,99,100] or a thick-film enzyme electrode.[115,117] Organic mediator or metallic particle catalysts were easily dispersed into these composites by adding them in the starting sol to facilitate communication between the enzyme and the conducting carbon.[103,104,106,112−114,127−129] The advantages of sol−gel-derived materials can also be exploited to prepare bioceramic thin films coated on conventional electrode surfaces. Once again, examples are available for pure enzyme-doped silicate films[157,182,191,192] and for composite films encapsulating the biomolecule together with a charge-transfer mediator.[157,181,194,292,293] The films were applied to the electrode surface by spin or dip coating, and special efforts were directed to produce crack-free materials by adding a suitable organic polymer into the starting sol (Table 1).[168,176,177,180,181,193−196] The versatility of sol−gel technology enables the design of multilayer configurations in which the enzyme is sandwiched between the electrode surface and a silicate layer[149,169,170] or between two silicate layers deposited as a three-layer architecture at the electrode/solution interface.[146,178] These sensing devices are also compatible with the use of a mediator, which can be trapped within a silicate layer,[155,156] or solely constitutes an individual layer, most often located between the electrode surface and the active enzyme.[150−152,171] If class II hybrids (with strong chemical bonds between the organic and inorganic components) were largely employed in electrochemical biosensing applications, they were mainly devoted to controlling the hydrophobic/hydrophilic balance (limited swelling), to structuring the composite (efficient encapsulation), or to favoring the immobilization of the enzyme and/or the mediator at the electrode surface. Yet only few investigations have exploited the organoalkoxysilane chemistry to bind, in a covalent way, a biomolecule or an enzyme to the electrode/ceramic matrix to definitely prevent leaching of the reagents into the external solution. One example is given by Gun and Lev[101,102] using *N*-[3-(trimethoxysilyl)propyl]ferrocenylacetamide (**13**) as a precursor to obtain ceramic−carbon composite biosensors with a covalently attached mediator.

3.6. Batteries and Fuel Cells. Polymer electrolyte fuel cells are promising candidates as power generators for zero-emission vehicles.[294] Polymer electrolytes are also expected to play an important role in the development of improved energy sources, which is required in parallel to the huge development of cellular phones, book-type computers, and many personal digital assistants.[295−297] The classic polymer electrolytes are based on organic macromolecules mostly containing, in the backbone, poly(ethylene oxide) units that are doped with inorganic salts. It is well-established in pure polymer electrolyte that conductivity occurs in the amorphous phase, above the glass transition temperature, via a liquidlike motion of the cations associated with segmental reorientations of the neighboring chains.[295,298] As these electrolytes often contain crystalline regions, leading to low ionic conductivity at room temperature, much effort has been directed to increase the volume fraction of the amorphous domains to enhance conductivity. In this respect, considerable advance was gained recently by designing new polymer electrolytes based on organic−inorganic hybrids or nanocomposite systems, among which silica-based materials hold a prominent place. They were called ORMOLYTEs (organically modified electrolytes) or ORMOCERs (organically modified ceramics) and generally applied as protonic or lithium ion conductors (Table 1).

A straightforward way to these hybrids is the incorporation of silica gel in an organic matrix doped with a suitable acid or lithium salt. Matsuda et al.[212,221] have fabricated electric double-layer capacitors using protonic conductor composites using PVA/$HClO_4^-$ or SEBS/H_3PO_4-doped silica gels hybridized with activated carbon powders, where PVA was a poly(vinyl alcohol) and SEBS a styrene−ethylene−butylene−styrene elastomer. They reported ionic conductivity as high as 5×10^{-2} S cm^{-1} at room temperature.[212] Sulfonated polyetherketone membranes containing 10% amorphous silica were also described, displaying conductivities in the range 0.03−0.09 at 100 °C (100% relative humidity).[231] Composite polymer electrolytes made of $LiClO_4$, silica particles, and various polymeric plasticizers have been prepared.[211,228,232] Room-temperature ionic conductivities of 1.9×10^{-3}, 5.1×10^{-4}, and $>10^{-3}$ S cm^{-1} were observed, respectively, with poly(acrylonitrile-*co*-methyl methacrylate),[228] poly(acrylonitrile-*co*-methyl methacrylate-*co*-styrene),[211] and poly(ethylene oxide)[232] as the plasticizer. Using silica particles grafted with various organic groups, it was possible to tailor the mechanical properties of the composite.[232] Polymer electrolyte fuel cells based on mixed Nafion/silicon oxide membranes were also investigated,[204,222,230] displaying improved performance over pure Nafion. The composite membranes were prepared either by adding SiO_2 colloids to a Nafion solution[204,222] or by filling a preformed Nafion membrane with sol−gel-derived silica.[230] This latter concept was further exploited to prepare organic−inorganic hybrids for lithium battery applications, via the sol−gel synthesis of a silica-based material in the presence of a lithium salt ($LiClO_4$ or $LiCF_3SO_3$) and ethylene oxide oligomers[213] or polymers.[223] This single material can be used as both separator electrolyte and binder electrolyte in the composite cathode of lithium secondary batteries.[213]

Beside these hybrids of class I, class II hybrid materials with strong chemical bonds between the organic and inorganic parts were also used as solid polymer electrolytes for applications in batteries or fuel cells. This field was pioneered by Poinsignon's group[299−301] who prepared protonic polymer electrolytes by polymerization or copolymerization of organoalkoxysilanes, eventually followed by a postsynthesis chemical treatment to obtain the appropriate final products: poly(aminopropyl)siloxane (**25**),[299] poly(benzyl sulfonic acid)siloxane (**26**),[300] and poly(benzyl sulfonic acid-diethylbenzenehexyl)siloxane (**27**).[301] This last copolymer resulted in high ionic conductivity (about 1.6×10^{-2} S cm^{-1}) at room temperature as well as thermal stability up to 250 °C, making it a promising solid electrolyte for practical fuel cell applications.[301] The method was extended by Popall and co-workers[201,214,229] who synthesized proton conductors by co-condensation of γ-glycidyloxypropyltetramethoxysilane (**28**) and γ-methacryloxypropyltetramethoxysilane (**29**) with allyl- or aryl-functionalized trimethoxysilanes containing either sulfonic acid or sulfonamide groups (**30a,b**, **31a,b**). Lithium conductivity can be introduced in these materials by neutralizing the sulfonic acid groups by LiOH, resulting in a decrease in ionic conductivity of the ORMOCER (5×10^{-6} S cm^{-1} for Li^+ and 5×10^{-3} S cm^{-1} for H^+ in the system made from **28**, **29**, and **30a**).[201] For the same purpose, Judeinstein and co-workers have focused their efforts on the preparation of lithium ion-conducting organic−inorganic nanocomposites based on poly(ethylene glycol) or poly(propylene glycol) covalently attached to a silica network comprising a lithium salt.[205,206,215,216,234] The precursors (**32**, **33**) used in the sol−gel process were prepared from *O*,*O*′-bis(2-aminopropyl)poly(ethylene glycol) or *O*,*O*′-bis(2-aminopropyl)poly(propylene glycol) by reaction with (3-isocyanatopropyl)triethoxysilane.[302,303] Interestingly, the authors provide a comparative study of these organically modified electrolytes producing chemical bonds between the organic (polymer) and inorganic (silica) phases, with those obtained from a mixture of tetraethoxysilane poly(ethylene, propylene glycol) that are not chemically bonded.[215,216,234]


25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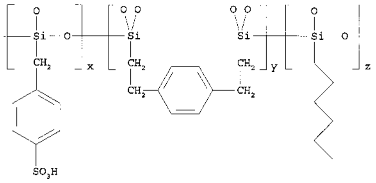
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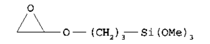
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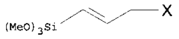
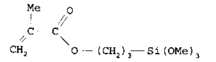
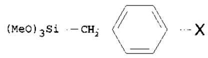
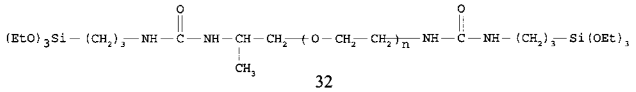

30

a X = SO_3H

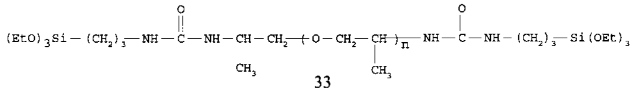
b X = SO_2NH_2


29


31

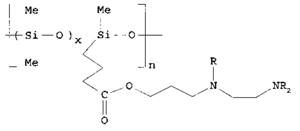

$$\mathrm{(EtO)_3Si-(CH_2)_3-NH-\overset{O}{\overset{\|}{C}}-NH-\underset{CH_3}{CH}-CH_2\!-\!(O-CH_2-CH_2)_n-NH-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_3-Si(OEt)_3}$$

32


$$\mathrm{(EtO)_3Si-(CH_2)_3-NH-\overset{O}{\overset{\|}{C}}-NH-\underset{CH_3}{CH}-CH_2\!-\!(O-CH_2-\underset{CH_3}{CH})_n-NH-\overset{O}{\overset{|}{C}}-NH-(CH_2)_3-Si(OEt)_3}$$

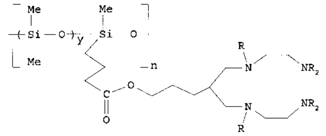
33

In the presence of a lithium salt inside the nanoporous structure, both composites display high ionic conductivities at room temperature and are consequently adequate to be used as lithium-conducting electrolyte in all solid-state electrochemical devices. Ionic conductivity presents a maximum for [O]/[Li] = 8 with class I materials (weakly bonded) and for [O]/[Li] = 15 with class II materials (covalently bonded).[215] The ion mobility was found to be assisted by segmental motion of the polymer.[234] Good mechanical stability of these materials was observed.[208] When replacing the lithium salt by peroxopolytungstic acid[218] or monododecyl phosphate[224] inside the nanoporous structure, a proton conductor solid electrolyte was obtained. Recently, a new type of ionic conducting nanocomposite polymers (i.e., structures **34** and **35**) was synthesized by grafting anion receptors on siloxane polymer backbones.[304] By complexation of these polymers with LiCl salt, room-temperature conductivities in the range of 7×10^{-8} to 4×10^{-6} S cm^{-1} were observed, depending on the structure of the material. The unique feature of these novel materials is that complexation occurs between the attached anion receptors and the anions and there are no ethylene oxide groups in these polymers.



34 (x = 0, 2)

R = CF_3SO_2



35 (y = 2, 5)

4. Conclusions and New Trends

In this review, it was outlined how the development of silica-based organic–inorganic hybrid materials has led to applications in various fields of electrochemistry, including electroanalysis, electrocatalysis, electroactive and permselective coatings, chemically modified electrodes, solid polymer electrolytes, chemical and biochemical sensors, spectroelectrochemistry, and electrochemiluminescence. These applications are a brief illustration of the wide possibilities opened by this class of materials for electrochemical science. Perhaps their greatest interest arises from the synergy exhibited by the organic–inorganic hybrids resulting from the combination in one material of the intrinsic properties of their two components (rigid inorganic matrix with tailored structure and organic groups or macromolecules with specific functionalities). The contribution of the flexible sol–gel technology, though yet complex, is considerable for this purpose.

This field of research is rather young and very promising results claimed for future opportunities. Nevertheless, as shown in Tables 1 and 2, one could be surprised by the high level of diversity in both the applications and the production of materials (i.e., synthetic efforts in preparing new organoalkoxysilanes for the modification of conventional electrodes). This comes probably from the exciting desire to demonstrate the feasibility of new applications involving novel materials, in a first step, rather than a complete understanding of all the parameters affecting the preparation of the devices and their operational working. It might also be explained by the recent interest of electrochemists for this aspect of materials science, which would benefit from collaborative connections between the two scientific communities.

Even if functional porous nanostructures can now be designed with a high degree of complexity,[17,32,42] future work has to deepen the understanding of chemical and polymerization processes on a molecular scale to tailor, in a more controlled way, the properties of organically modified silicates. This would lead to improved and/or additional applications in various fields including electrochemistry. For example, advances would be achieved by better control of the structure of the hybrid material to monitor the diffusion processes, which are often a rate-limiting factor in electrochemistry. Outlook would also result from the covalent bonding of new specific organic derivatives to the silica backbone, which could induce additional properties liable to be exploited in electrochemistry (selective preconcentration, catalysis, electrical wires, host–guest interactions, optical properties, enhanced ionic conductivity, etc.). Practical biosensing applications in vivo (i.e., subcutaneously implantable sensors) would require biocompatibility, which was recently demonstrated for sol–gel matrixes.[305] In my opinion, another trend in the proliferation of silica-based organic–inorganic hybrids in electrochemistry could be observed by bringing ordered mesoporous silicates to an electrode/solution interface, as recently illustrated for pure silica MCM-41.[306–308] There is no doubt that their high surface area, their monodisperse pore size, and their ability to be organically modified (by postsynthesis grafting or by co-condensation with an organosilane) would contribute, in the upcoming years, to the improvement of the performance of many of the electrochemical applications described here.

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