Exciting new directions in the intersection of functionalized sol–gel materials with electrochemistry

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The implications of organically-modified silica-based materials in electrochemical science is reviewed along with some selected recent trends in the field of functionalized and sol–gel silica electrochemistry. These recent trends include the electro-assisted generation of organosilica films on solid electrode surfaces, the preparation and applications of sol–gel derived composite (carbon, gold, nanotubes) electrodes, the electrochemical characterisation of mass transfer reactions in porous functionalized silicas, solid-state electrochemistry and gas sensors involving sol–gel materials, imprinted functionalized silica, and the electrochemical characterisation and applications of ordered mesoporous organosilicas.

1. Introduction: the intersection between functionalized silica chemistry and electrochemical science—a summary

Silica-based organic–inorganic hybrids are attractive composite materials since they combine in a single solid both the properties of a rigid three-dimensional silica network with the particular chemical reactivity of the organic component(s).1–11 These multifunctional materials have found numerous applications in various fields, including chemical and biological sensors, separation sciences, optical devices, and catalysis.12–34 Basically, the organic–inorganic hybrids can be classified into two categories:10 class I materials are characterised by weak interactions between the organic and inorganic components (hydrogen bonding, van der Waals contacts, or electrostatic forces), and class II corresponds to systems where the organic and inorganic components are linked through strong chemical bonds (covalent, ionic-covalent, or Lewis acid–base bonds). This last category is particularly suited to the production of...
leak-free devices because the silicon-to-carbon covalent bond is quite stable toward attack by nucleophilic species (i.e., water, alcohols, hydroxylated ligands). Class II materials can be prepared either by post-synthesis grafting the surface of an unmodified silica with organofunctional alkoxysilanes or chlorosilanes, or in one step by co-condensation of silicon alkoxides and one or more organosilanes. It is noteworthy that the field of organic–inorganic hybrids has exploded during the last decade owing to the versatility of the soft inorganic chemistry processes (i.e., sol–gel), which enables a wide range of organically-modified silica-based materials to be made under mild synthetic conditions.\(^4\) Another important breakthrough in materials science relies on the use of supramolecular templating techniques to build mesoporous silica architectures around self-assembled organic templates; these ordered solids can be also designed in the form of organic–inorganic nanocomposites, once functionalized with suitable organosilane reagents.\(^1\) Of special interest is the versatility of the sol–gel process to produce composite materials in various morphologies (e.g., xerogels, aerogels, thin and thick films, uniform particles, monoliths) displaying tailor-made chemical, mechanical, optical, or electrical properties.\(^4\) This is typically achieved by the use of functional alkoxysilanes (R,Si(OR)\(_n\))\(_{4-n}\), n = 1–3, R = organic group, R’ = alkyl, in mixture with a tetraalkoxysilane (Si(OR)\(_4\)), as one or more of the precursors for the sol–gel reaction. The polymerization mechanism involves hydrolysis and co-condensation processes, leading to the following global reactions for an initial 1 : 1 mixture of alkoxysilane and organoalkoxysilane (eqn. 1a–b).

\[
\text{Si(OR)}_4 + n \text{Si(OH)}_4 + (8 - n)\text{H}_2\text{O} \Rightarrow \text{Si(OH)}_4 + n \text{Si(OH)}_4 + (8 - n)\text{R’OH} \quad (1a)
\]

\[
\text{Si(OH)}_4 + n \text{Si(OH)}_4 + (8 - n)\text{R’OH} \Rightarrow (\text{OH})_{n-1}\text{Si-O-SiR’}_n\text{OH}(3 - n) + \text{H}_2\text{O} \quad (1b)
\]

The “soft” conditions associated with the sol–gel process have been proven to be compatible with the immobilisation of biomolecules (e.g., enzymes) by encapsulation in silica-based materials without preventing their biological activity, leading to various applications in the field of biosensors.\(^4\) From the point of view of electrochemists, the silica-based organic–inorganic hybrids are attractive electrode modifiers for several reasons.\(^16\) They are usually highly porous solids made of a mechanically stable inorganic backbone displaying large specific surface areas (i.e., 200–1500 m\(^2\) g\(^{-1}\)), which are likely to contain a high number of organic functional groups (i.e., in the mmol g\(^{-1}\) content range) accessible to external reagents or analytes (except for some thin films that may not be that porous). Open frameworks enable effective and fast access to active functionalities immobilised at the electrode/solution interface. This fast access is expected to ensure a high sensitivity to the electrochemical response, as most electron transfer processes are diffusion-controlled.\(^5\) On the other hand, an appropriate choice of the organic functional groups would impart additional features to the modified electrode, e.g., recognition/discrimination properties towards target analytes/interferences and electrocatalytic behaviour by means of suitable charge transfer mediators or long-range charge transport in confined media.\(^6\) Ease of dopant entrapment opens up the possibility of electrochemical sensors and biosensors.\(^7\) All these attractive features have contributed to the emergence of (organo)silica modified electrodes in the field of the

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“integrated electrochemical systems”, known as chemically modified electrodes”, which has seen a tremendous expansion during the past decades (see, e.g., ref. 50, 74 and references cited therein).

Notwithstanding the fact that silica-based organic–inorganic hybrids offer a nearly ideal embodiment of most properties desired when designing chemically modified electrode surfaces, most of these materials are electronic insulators so that they must be coupled to an electrical feeder/collector to be exploited in electrode processes. Except for the particular case of composite membranes used in potentiometric experiments,57–74 or monoliths comprising an immobilised microelectrode assembly,56,56,58,61,63,81–126 nearly all the (organo)silica modified electrodes have been prepared according to two general strategies: (1) the dispersion of as-synthesized material particles into a conductive composite matrix, or (2) the deposition of silica-based coatings on solid electrode surfaces. Mostly, the versatility of the sol–gel process was exploited, either to prepare intended materials (with given composition, structure and properties) that are then incorporated in a suitable electrode material, or to build directly the modified electrode (as bulk conductive composites, or coated materials on conventional electrode).22,34,49,51 Of particular interest is the possibility to immobilise a broad range of reagents at the electrode surface, including, for instance, organic functions, selective ligands, (electro)catalysts, biologically active compounds, metal particles, macromolecules, or organic polymers.

Roughly, one can distinguish four kinds of electrochemical devices containing organically modified silica-based materials.34 They include:

1. thin films deposited on solid electrode surfaces,56,56,58,61,63,81–126
2. (organo)silica modified carbon paste electrodes,54,55,57,62,70,127–144,144–152
3. ceramic-carbon and ceramic-metal composite electrodes;54–64,69,124,125,153–180
4. silica-containing membranes and solid polymer electrolytes.

These main categories can be further subdivided with respect to the nature of the organic–inorganic hybrid material and/or the configuration of the electrode/solution interface; some illustrative examples are given in Table 1 together with selected references.

Silica-based organic–inorganic hybrid materials have found numerous applications in electrochemistry. They are only briefly summarised hereafter; the interested reader being directed to more comprehensive reviews or monographs.16–18,21,22,33,34,47,49–53,199,200

Voltammetric detection after open-circuit accumulation

The chemical preconcentration of a target analyte onto the electrode surface prior to its electrochemical quantification enables the detection sensitivity to be dramatically improved. An elegant way to achieve this goal is through the use of chemically modified electrodes for which an appropriate modifier is chosen on the basis of its particular affinity towards the analyte. If the modifier is also likely to reject potentially interfering species, this can also contribute to the enhancement in the selectivity of the detection process. Silica-based organic–inorganic hybrids, most often dispersed in carbon paste electrodes, have been largely used for that purpose. Preconcentration can be performed by adsorption (e.g., on C18-silica gels128,131), by complex formation (e.g., on porous silica grafted with N- or S-containing ligands54,57,62,63,99,134), by ion exchange (e.g., on interpenetrating “sol–gel–silica–organic polymer” composites acting as polyelectrolytes displaying either cation or anion exchange properties56,61,89,201), or by selective recognition based on the molecular imprinting technology (e.g., dopamine-templated hybrid sol–gel materials for the preferential accumulation of dopamine in the presence of structurally related molecules60,202). Of close interest is the design of permselective films that are intended to preconcentrate target species while rejecting interferences (e.g., charge selective polyelectrolytes, as organically modified silica films containing either –NH3+ or –COO– groups,58,63 which are likely to modulate the access of analytes to the electrode surface based on their charge).

Chemical sensors and electrochemical detectors

A huge amount of work has been directed to exploit the versatility of silica-based and sol–gel-derived hybrid materials to immobilise organic or organometallic catalysts for designing electrocatalytic devices. For example, the research groups of Kubota and Gushikem203 have largely studied the electrocatalytic properties of carbon paste electrodes modified with silica particles coated with metal oxide thin films (metal = Ti, Sn, Zr, Sb, Nb) with adsorbed mediators (e.g., nickel phthalocyanine,138,139,204 phenthiazines,142,205 cobalt prophyrrins135,141,206). Charge transfer mediators and other catalysts (e.g., polyoxometallates54,67,69,155,157,207) were also immobilised within the hydrophobic matrix of ceramic–carbon composite electrodes and applied as amperometric sensors for anions (NO2–, BrO3–) or organic compounds (ascorbic acid, peptides). The robustness of such composite electrodes enables their use in flowing conditions as those applied in flow injection analysis163 as well as in detectors for liquid chromatography64,161,208 or capillary electrophoresis.154,209,210 Gas sensors based on catalysts immobilised in hydrophobic ceramic–carbon or ceramic–metal composite electrodes have been also described,66,162 mostly for oxygen detection. Finally, beside these electrocatalytic determinations, one should mention that several potentiometric devices have been constructed on the basis of membranes comprising suitable organic ionophores, either physically entrapped in sol–gel silica matrices or covalently bound to the silica framework, which can be used as such75,78,181,182 or coated on field effect transistors.76,77,183–185

Electrochemical biosensors

Intense research activities have been carried out in the field of electrochemical biosensors involving sol–gel materials47 from the discovery of the possibility to entrap biomolecules (especially enzymes) by physical encapsulation in a silica-based matrix without losing their biological activity, owing to the soft conditions associated to the sol–gel process.42,44,119,211,212 Several devices have been designed by exploiting the
microencapsulation of an enzyme (alone or together with a charge transfer mediator) within a silicate matrix by low temperature sol–gel processing, including the dispersion of bio-organosilica particles in carbon paste electrodes. In an attempt to ensure enough mobility to encapsulated biomolecules and mediators while keeping them in the electrode vicinity (i.e., to avoid leaching of the (bio)reactants in solution, to get leak-free sensors), this last approach was extended to the formation of composite films in multilayer configurations (electrode/ enzyme/silica, electrode/mediator/enzyme/silica, electrode/ enzyme/silica). Note that durable immobilisation by physical entrapment is quite easily achieved for the larger small organic or organometallic moieties used as mediators. An elegant way to improve the long-term stability of mediator-based biosensors is the covalent attachment of the charge transfer cofactor to the silicate framework. In such a case, special care should be taken to ensure the mediator plays its role as an electron shuttle (i.e., sufficiently fast charge transfer should be maintained in the non conductive confined space) while keeping them in the electrode vicinity (i.e., to avoid leaching of the (bio)reactants in solution, to get leak-free sensors). This last approach was extended to the formation of composite films in multilayer configurations (electrode/ enzyme/silica, electrode/mediator/enzyme/silica, electrode/ enzyme/silica). Note that durable immobilisation by physical entrapment is quite easily achieved for the larger biomolecules, such as enzymes but is somewhat difficult for the small organic or organometallic moieties used as mediators.

### Methods and electrode configurations

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### Spectroelectrochemical sensors

Heineman, Seliskar, and co-workers, 87,90–92,94,95,215–218 have introduced and then developed a new class of spectroelectrochemical sensors with three levels of selectivity. Multimode selectivity is achievable in a single device made of a thin film of interpenetrating organic polyelectrolyte and sol–gel silica network coated on an optically transparent indium
tin oxide electrode. The first level of selectivity is due to the permselective properties of the hybrid film (i.e., charge selectivity). The second level is induced by the optical detection mode (by attenuated total reflection), and the third one is related to the electrochemical activity of the target analytes (the accumulated species can be tuned from their oxidation to reduction states, and inversely, by applying a suitable electrolysis potential).

Electrogenerated chemiluminescence

Electrochemiluminescence can be generated from electrodes modified with composite materials containing a chemiluminescent precursor (i.e., Ru(bpy)$_3^{2+}$) and a suitable reductant. This was achieved by exploiting the versatility of the sol–gel process to immobilise the required reactants at an electrode surface, either in the form of silica monoliths comprising an ultramicroelectrode assembly, or as silica–polymer hybrid membranes coated on solid electrode surfaces (e.g., Nafion–silica on glassy carbon or chitosan–silica on platinum).

Long-range charge transfer

The preparation of redox polymers in which charge transfer occurs by electron hopping between adjacent redox centres has been reported in the field of organically modified silica-based electrodes. These systems are made of poly(siloxane) molecules containing covalently attached redox-active groups, which have been deposited on solid electrodes. Examples of functional groups involve ferrocene derivatives, methylviologen, or phenothiazin dyes. Long-range charge transfer in organically modified silica can be also achieved by resorting to conducting polymer nanocomposites. Examples that deal with the electrochemical properties of polypyrrole, polyaniline, and polythiophene silica composites are available.

Solid polymer electrolytes for power sources

The design of new polymer electrolytes based on organic–inorganic hybrid nanocomposites has gained considerable interest in recent years because such systems offer enhanced conductivity in comparison to the purely organic macromolecules, doped with inorganic salts, usually used as solid electrolytes in batteries and fuel cells. Hybrids of both classes I & II have been prepared for that purpose. The first ones are mostly based on interpenetrating organic poly-electrolytes–inorganic silica doped with a suitable acid or lithium salt, while the second category involves ionic conductors prepared by (co)polymerisation of organoalkoxy-silane(s) precursor(s) containing either acid groups (i.e., proton conductors that can be turned to lithium conductors simply by neutralisation with LiOH) or poly(ethylene glycol) moieties.

As plenty of well-documented overviews treating totally or in part the various topics of functionalized silica electrochemistry are available, our goal in this feature article is to offer a view of recent trends in the fields, rather than yet another comprehensive coverage including also older (yet very interesting) aspects. Special emphasis has thus been given to six emerging points, including the ceramic-based composite electrodes, the electrochemical deposition of (organo)silica films, the use of electrochemical methods to study diffusion in functionalized silica, the solid-state sol–gel electrochemistry and gas sensors, molecular imprinting with functionalized silica, and the implication of ordered mesoporous materials in electrochemical science.

2. Composite electrodes based on functionalized silica

2.1. Main features of composite sol–gel electrodes

There are two major ways to add specific functionalities to sol–gel derived silicates: The first and simpler is to add class I and class II molecular modifiers as discussed in the previous section of this review. A second possibility is to introduce a separate, third phase in addition to the void fraction and siloxane networks, i.e., produce a hybrid. It is customary to distinguish two types of hybrids, alloys (blends) and composites. Composites comprise at least two separate phases. The distinction between the two types of hybrids is vague and depends on the length scale employed in the discrimination of the different phases. Blends and composites based on sol–gel technology are widely used by material scientists in order to gain improved stiffness, strength, toughness and to some extent also improve the temperature and corrosion resistance. In electrochemistry, these attributes are of lower importance, and composites are synthesised for different reasons as detailed below.

Increased sensitivity. The response of amperometric sensors and devices depends on the flux of the target solutes to the conductive surface. Eqn. 2—which will be used as illustrative guideline—describes the simplest case of unidimensional mass transport through a film of thickness $b$ under diffusion limited conditions (e.g., for high overvoltage).

$$j = \frac{FD_{eff}K_{partition}C_{solution\ interface}}{b}$$

where $F$ is the Faraday constant, $D_{eff}$ is the effective diffusion coefficient of the analyte and the product, $K_{partition}C_{solution\ interface}$ is the actual concentration of the analyte in the film side of the modified electrode/solution interface. Eqn. 2 shows that the sensitivity (i.e., $jC_{solution\ interface}$) is determined by the product of the effective diffusion coefficient and the partition coefficient, $K_{partition}$. We can now discuss the different ways by which the incorporation of a two-phase film can increase the sensitivity of sol–gel modified sensors in light of eqn. 2.

The first way is the incorporation of polymers with large affinity to the analyte. This mode of charge transport acceleration is driven by increasing $K_{partition}$ in eqn. 2. A dramatic charge-specific permeability is obtained by incorporation of negatively charged polymers that facilitate $H^+$ and other cations’ (e.g., methylviologen) transport. By far, the most useful anionic polymers are the perfluorosulfonic acid polymers and particularly Nafion (Du Pont). Imine containing polymers, such as poly(ethyleneimine) (PEI) or biopolymers...
such as chitosan have been reported to enhance the transport of small anionic species.

The second approach involves the change of accessibility, $D_{\text{eff}}$. There are two ways to increase the effective diffusion coefficient by two phase coatings: the increase of the void fraction or the enlargement of the interfacial area. Incorporation of a second phase into the starting sol–gel solution and leaving off the guest phase after gel formation creates large voids in sol–gel films and monoliths. This concept is indeed widely used in chromatography. Leaching of soluble polymers after electrode coating was also used in order to enhance electrode sensitivity in composite carbon ceramic electrodes. Template formation by introduction of porogens or surfactants, which is another viable way to increase the void fraction in sol–gel silicates, is discussed separately in the context of mesoporous silicate electrodes. Another approach to increase the current density is to incorporate solid fillers in the sol–gel coating. The diffusion rate is increased along grain boundaries and along the volume of the silicate film adjacent to the interfacial area. The way by which the diffusion is accelerated is not entirely clear; in fact, it seems to be counter-intuitive since the diffusion pathway along such interfaces is tortuous, and does not follow the shortest path between the solution and the metal support. It is possible that fast polymerisation of the silicate creates a third phase of macroporous voids or less dense film through which accelerated diffusion takes place. Another possibility is that the segregated phases do not wet each other efficiently, and a third phase with constrained properties is formed near the interface between the phases. Enhanced diffusion can then take place through this phase. The large metal/silicate or graphite powder/silicate interface is probably one of the reasons for the favourable electrochemical characteristics of carbon and metal composite carbon ceramic electrodes described below.

**Biocompatibility.** The encapsulation and stabilisation of biochemicals in sol–gel oxides is one of the most exciting developments in sol–gel science. Sergei Braun and his co-workers, the pioneers of the current wave of sol–gel biochemical encapsulation noted that sol–gel encapsulation stabilises many proteins and protects them against heat denaturation. A dramatic increase of stability was noted by a number of other researchers for a wide range of biochemicals. For example Heller reported a 200-fold stability increase of glucose oxidase by encapsulation in monolithic silica. However, unlike monoliths and powders, the encapsulation of proteins in silicate films is complex. Most successfulencapsulations of active biochemicals were reported for composite films or for sandwich like materials where the biomolecules are entrapped in the interface between a solid support and the sol–gel coating. The incorporation of a second, less crosslinked, organic polymer phase provides modes for stress relaxation and reduces the physical pressure on the encapsulated proteins, probably by creation of flexible microdomains within the silicate matrix. Additionally, the mere adsorption of the proteins onto solid microdomains stabilises the 3D structure of biochemicals. The combination of these two mechanisms is probably responsible for the success of guest fillers such as glycerol, polymers, graphite, metallic particles and nanoparticles, and even inorganic additives such as Prussian blue in enzyme preservation within silicate composite films.

**Electric and ionic conductivity.** Amperometric sensors and at times even potentiometric sensors benefit from increased interfacial area between the ionic and electronic conductors, the area where charge transfer reactions take place. Amperometric applications strive to minimise the mass transport barrier in the ionic conductor, even at the expense of increasing the electric pathway in the electronic conductor, because the former is much slower. A way to attain these goals is to minimise the length of the diffusion pathway of analytes (the term $b$ in eqn. 2) by using thin silicate films. However, a thin layer configuration limits the film capacity to encapsulate reagents, catalysts or enzymes. A way to achieve a thin layer configuration and still obtain a large encapsulation capacity is by the incorporation of a second conductive phase within the silicate. This can be done by coating a porous conductive network (e.g., reticulated vitreous carbon cylinders) with a silicate film or by the incorporation of a second, electron conductive phase made of interconnected particles or conducting polymer. The catalyst or biocatalyst can then be imbedded in the three-dimensional silicate structure. Sol–gel electrochemical applications based on this approach include carbon–ceramic and metal–ceramic sensors and biosensors, in which a network of metallic particles provides large surface area and long-range electron percolation.

A similar approach uses (multi wall) carbon nanotubes encapsulated in silicates in order to obtain electric conductivity at an extremely low volumetric loading of the conductive phase (<0.1 mg ml$^{-1}$). Similar approaches use electrically conductive organic polymers such as poly(aniline) and poly(pyrrole) instead (or in addition to) the conductive metal phase. Electric conduction can also be carried out by a hopping mechanism between adjacent redox sites. This mode of self exchange charge transfer within silicate composites was exploited by the incorporation of redox polymers such as the osmium redox polymer, [Os(bpy)(2)(PVP)(10)Cl]Cl$^{122,252}$ in the silicate backbone. A similar approach utilises redox silicate polymers as a binder in carbon ceramic composite electrodes.

Ionic conduction in silicate sensors and biosensors is important in order to decrease Ohmic drops in amperometric applications. The conductivity of silicates can be improved by surface modification so as to increase the concentration of the surface charges within the porous network or by incorporation of cationic or anionic polymers such as Nafion and poly(ethyleneoxide)–phosphotungstate as mentioned above.

**Crack prevention and adhesion of silicate films to the supporting electrode.** Composite sol–gel silicate–organic compounds can be tailored to have extremely good adhesion to oxide substrates due to the $\equiv$Si–O–M$=\equiv$ bonding (M = metal). The stability of thick composite films is an important property since it is difficult to construct sol–gel films thicker than ca 10 μm. The high surface tension that builds up in partially-filled pores during the drying stage fractures.
sol–gel matrices and limits their usefulness. The inherent heterogeneity of composite electrodes provides routes for stress relaxation and prevents fractures. Indeed, thick polymer/silicate and carbon/silicate films can be successfully deposited without cracking on solid substrates. It was also demonstrated that composite poly(aniline)–silicate coatings have much higher operational stability compared to pure poly(aniline) films.255

Polymeric catalysts were also used in two phase segregated composites rather than as isolated molecules. The main advantage in using two phase systems rather than isolated molecules is to benefit from the higher diffusion coefficient, but sometimes larger catalysts simply perform better. For example the incorporation of crystalline or amorphous ruthenium oxide provided an improvement in catalysis also due to the conductivity of the encapsulated oxide.256

2.2. Classes of composite electrodes

We distinguish three types of silicate composites here, polymer, carbon, and metal–silicate composites.

Nanoporous composite materials—polymer–silicate composite electrodes. This class involves matrices bearing nano-domains of silicate and organic or inorganic guest polymers. The guest polymer can be either of inorganic nature such as Prussian Blue250 or poly(oxyometalate)257 or more often organic polymers (such as poly(imine), poly(pyrrrole), PEG). The organic polymer can be either grafted (i.e., covalently bonded to the inorganic network) or doped (i.e., incorporated without covalent linkage in the silicate network).

Polymer science distinguishes between polymer blends and interpenetrating polymers. The distinction is based on the formation of segregated phases, which are often distinguished from molecularly mixed materials by their opacity due to light scattering. For optical and mechanical applications where transparency or material strength counts, segregation should be avoided because it leads to optical losses and lower material strength. Favourable conditions for the creation of transparent composites include among others, intimate mixing by using inorganic and organic monomers that dissolve in the same solvent, selection of monomers that form hydrogen bonds with each other and preferably also have similar polymerisation rates. However, for the vast majority of electrochemical applications, segregation on an appropriate 50–500 nm scale is favourable since it can provide enhanced diffusion and the segregated composites can provide soft, accommodating nanodomains for delicate proteins along with tough networks that preserve matrix integrity. Additionally, for most electrochemical applications the loss of material strength due to the incorporation of the organic phases is not crucial and can be compensated by the strength of the conductive electrode support. Exceptional cases where intimate mixing of the organic and inorganic phases is essential even for electrochemists include:

1) Conductive alloys for which careful control of stoichiometry is essential for transport. For example the high Na⁺ mobility of NASICONs (\(Na_{1+x}Zr_2Si_3P_3O_{12}\))258 depends critically on intimate mixing of the precursors.

2) Photoelectrochemical applications, electrochemical luminescence (ECL), solar photocells, and dual electrochemical–optical applications rely on light penetration, and thus segregation should be avoided.

3) For corrosion-preventing coatings22 where transport should be minimised, flawless coating is essential and therefore segregated phase composites should be avoided.259

Three methods for the preparation of polymer–silicate composites have already been demonstrated in electrochemical applications.

Polymer doping. Sol–gel polymerisation of the silicate network in the presence of a pre-prepared guest polymer yields an inorganic–organic hybrid copolymer. Both synthetic (PVA, polysiloxane) and natural (chitosan, starch) polymers were used for electro- and bio-sensing. In all these cases the polymer should be sufficiently bulky to prevent leakage from the inorganic–organic film.

Polymer grafting. Sol–gel polymerisation of the silicate network takes place in the presence of a pre-prepared guest polymer that can participate in ester formation with the silicate network. Although the preparation conditions are identical to the previous protocol, here the covalent linkage provides stronger attachment, which becomes important when linear polymers or thin film configurations are involved. The covalent bond between the two polymers is often created by condensation reactions between the silane monomer and OH groups on the polymer. This is indeed the case in the formation of PVA–poly(vinylpyridine) (PVA-g-PVP) and poly(ethylene glycol) and dextran sulfate–silica sol composites which were used for hydrogen peroxide and glucose electro-sensing.260,261 Another synthesis procedure involves linear polymers containing reactive end-groups such as hydroxyl terminated poly(dimethyl siloxane).262

Polymerisation of organic polymers within pre-formed silicate films. Monomers of the guest polymer are first impregnated into a pre-formed porous silicate film, and then polymerisation of the guest polymer is initiated either by ultraviolet irradiation (e.g., for monomers containing oxides) or by chemical oxidation (for example by peroxydisulfate oxidation of aniline and thiophene). This procedure is favourable for the incorporation of linear polymers in silicates, but the procedure eliminates some of the more important advantages of organic–inorganic composites, including good adhesion to the substrate and biocompatibility. Failure of film adhesion and protein denaturation occur before the organic polymerisation takes place. A related method is the electropolymerisation of a conductive polymer within a pre-formed silicate film.228,263 Poly(aniline), poly(pyrrrole), and poly(thiophene) are popular conductive polymers, widely used by electrochemists, and they are used to easily polymerised by electrooxidation within interconnected pores of silicate films. This mode guarantees electro-conductivity by the conductive polymer, material strength provided by the silicate and good adhesion due to surface silanols. However, since long chain polymers are essential for good conductivity the composite exhibits somewhat lower conductivity compared to the pure conductive polymers.
Composite carbon–ceramic electrodes (CCEs). These composites are prepared by mixing different forms of graphitic materials with the sol–gel reactants. A porous, brittle composite matrix is formed after gelation and drying. The composite electrodes benefit from the mechanical properties of the silicate backbone, from electron percolation conductivity through the interconnected carbon grains and from the ability to manipulate the physicochemical characteristics of the matrix by incorporation of suitable monomer precursors or sol–gel dopants.

The preparation protocols of CCEs entail a large number of degrees of freedom in choosing the starting carbon and the silicate, ormosils (ormosil = organically modified silicate) or other inorganic oxides such as titanium, zirconium and ruthenium oxides. Ormosils are usually preferred over purely inorganic networks for several reasons. It is possible to control the exposed surface area of the electrode in aqueous electrolytes by tuning the hydrophobicity of the ormosil binder. Additionally, appropriate organofunctional groups are useful anchors for subsequent covalent modification of the electrodes with desirable functionality. As discussed earlier, the aminopropyl functionality provides a useful anchor for aldehyde and carboxylate reagents. Finally, the silane monomer can contain organofunctional ligands, charge mediators, electrocatalysts or redox groups which can participate in desirable electroanalytical tasks.

It is possible to cast CCEs in a wide range of electrode configurations including supported and unsupported thick films, rods and disks. Since large grain carbon powder CCEs do not shrink during gelation and they adhere very well to metal oxide supports it is possible to cast electrodes and microelectrodes in glass tubes. Fig. 1 taken from a publication of Hua and Tan demonstrates how CCEs can accommodate the complicated shape required for detectors of capillary electrophoresis (CE).

Control of the configuration, conductivity, wetted section, and pore size distribution of CCEs were addressed by changes of carbon type, size, addition of additives, and selection of desirable pH during polymerisation. CCEs are porous and rigid and thus it is possible to synthesise CCEs with controlled thickness of their wet section. A controlled wet porous section of up to 1000 μm was demonstrated. The active section of the CCEs does not clog upon repeated polishing due to their brittleness, and thus the electrode active section can be renewed by mechanical polish after each measurement. The reported relative standard deviations of renewal repeatability or sensor-to-sensor reproducibility by screen printing are usually only a few percent.

Recently, Gong et al. demonstrated an important new class of CCEs in which carbon nanotubes are used instead of a carbon network. In addition to the electrocatalysis and microelectrode ensemble configurations which are demonstrated by Gong, these electrodes may become especially useful for ECL and other opto-electrochemical applications since very low concentrations of carbon nanotubes are needed for conductivity. Single wall nanotube silicate electrodes are especially promising.

Metal–ceramic composite electrodes (metal CCEs). Gold and other metals can be used instead of graphite as conductive networks in CCEs. The specific density of metals is larger than carbon and thus a much larger weight percent of metal is needed to attain electron percolation. This limits the practical application of the metal ceramic electrodes to thin films and microelectrodes. On the positive side, metal ceramic electrodes provide better electrocatalysis, and it is easier to prepare metal nanoparticles of controlled dimensions and configuration and to functionalize metal surfaces.

Procedures for the preparation of metal ceramic electrodes range from simple mixing of fine metal powder with the silicate precursors to more elaborate techniques which involve pre-prepared metallic nanoparticles. Wang and Pamidi used 0.5 μm gold microparticles, tetramethoxysilane and glucose oxidase to cast a sol–gel composite glucose biosensor. Aminosilane stabilised gold nanoparticles (ca. 3–10 nm) were prepared by reduction of gold chloride (AuCl₄⁻) in aminopropyltrimethoxysilane solution. The sol was used to dip-coat electrodes with a thin gold-silicate composite film. One of the major limitations of carbon CCEs is the lack of transparency, prohibiting photometric modes of analysis. The metal nanoparticle–silicate films provide sufficient transparency and overcome this problem. Electrochemical deposition of fold silicate biosensing elements was recently reported.

3. Electro-assisted generation of organosilica films on electrodes

Organosol–gel films made of silica (ormosil) as well as other metals are usually formed by three alternative methods: spin-coating, dip-coating and spraying. These methods are straightforward and allow controlling the thickness of the deposited films. In most cases the thickness achieved by these methods varies between 100 nm to a few μm. The methods are simple to apply and do not require
sophisticated instrumentation, however, they lack at least two important features. Spin-coating and dip-coating can be applied to basically flat surfaces only. In spite of the fact that spraying is applicable to surfaces having complex geometries, it usually covers the surface with much thicker and non-homogenous coatings. The second limitation is the lack of selectivity. That is, the entire surface is covered, which means that if one wishes to coat only parts of the surface, it requires applying multi-step lithography, where those parts will be first covered with a coating that could be removed after coating the entire surface with a sol–gel film.

These two drawbacks can readily be resolved by electrodeposition. Deposition is driven by electron transfer, which occurs in close proximity to the surface, forcing the deposit to follow the intimate structure of the surface. This allows coating and filling of complex geometries having high aspect ratio.\textsuperscript{275,276}

On the other hand, electrodeposition is limited to conducting surfaces and depends on the potential or current applied to the surface. This allows not only control of the areas to be coated but also the rate of deposition.

Nevertheless, the formation of sol–gels does not involve electron transfer processes but rather acid–base reactions. Therefore, it is evident that sol–gel films cannot be electrodeposited in the same manner as metals that are deposited by electrodeposition of their respective ions. Interestingly, the electrodeposition of ceramic materials (i.e., metal oxides) has been reported and is fairly established.\textsuperscript{277–281}

This field has been reviewed by Therese and Kamath\textsuperscript{282} and more recently by Zhitomirsky\textsuperscript{283} and therefore will be mentioned only briefly, emphasising the similarities and differences between the electrodeposition of ceramic and organosol–gel films. Zhitomirsky divides the electrodeposition methods into two; electrophoretic and electrolytic deposition. While electrophoretic deposition is accomplished via motion of charged particles towards an electrode under an applied electric field, electrolytic deposition leads to the direct precipitation of metal oxides as a result of a Faradaic process occurring on the electrode surface. It should be noted that electrophoretic deposition has been quite intensively used for depositing sol–gel films\textsuperscript{284–287} and usually involves the formation of rather large (i.e., sub-micron) particles that are deposited under high voltage (>100 V). The thickness of these films is limited to a few \textmu{}m, although recently studies showed that it was possible to increase the thickness by using nanometer particles.\textsuperscript{288}

Electrolytic deposition can be divided into a few categories according to the mechanism of deposition. Deposition can be driven using cathodic currents by either reducing the metal ions, which causes their deposition (eqn. 3) or by driving a proton-dependent reducing process, such as water reduction, leading to an increase of the pH on the electrode surface and the subsequent metal hydroxide deposition (eqn. 4–5). The essence of this approach lies in the electrogeneration of a strong base (e.g., OH\textsuperscript{−}), that attacks (hydrolyses) the metal ion.

\[
M^{n+}_{\text{(aq)}} + (n - 2x)e^- + xH_2O(l) \rightarrow MO(x) + 2xH^+_{\text{(aq)}} \quad (3)
\]

\[
H_2O(l) + e^- \rightarrow \frac{1}{2}H_2(g) + OH^-_{\text{(aq)}} \quad (4)
\]

\[
M^{n+}_{\text{(aq)}} + nOH^-_{\text{(aq)}} \rightarrow M(OH)_n^{(n+)} \quad (5)
\]

The cathodic deposition of Cu\textsubscript{2}O is an example of utilising the first route,\textsuperscript{289,290} while the widely-used deposition of Ni(OH)\textsubscript{2} upon reducing nitrate or water, and increasing the pH locally\textsuperscript{291,292} shows the feasibility of the second approach.

Alternatively, the deposition of metal oxides and hydroxides can be driven by anodic currents as a result of oxidising the metal ions, thus increasing their oxidation state and usually resulting in the lower solubility of their hydroxide salts. For example, iron(III) hydroxide can be precipitated\textsuperscript{293} upon electrochemically oxidising Fe(II) under conditions where the latter does not precipitate whereas Fe(OH)\textsubscript{3} does.

These various methods have been used for the electrodeposition of different metal oxides from aqueous and non-aqueous solutions. For example, Pauporte\textsuperscript{278} and his coworkers reported on the cathodic electrodeposition of TiO\textsubscript{2}–WO\textsubscript{3} mixed oxide thin films. Gal-Or et al.\textsuperscript{279} have used cathodic electrodeposition quite intensively\textsuperscript{280,281,294–297} for depositing a variety of oxides, such as TiO\textsubscript{2}, ZrO\textsubscript{2} and ZrTiO\textsubscript{4} on platinum substrates via hydrolysis of TiCl\textsubscript{4} and ZrOCl\textsubscript{2}.

Zhitomirsky summarised\textsuperscript{283} the different parameters, such as mass transport, accumulation of particles, coagulation and interparticle forces that affect the formation of cathodic deposits. His review also covered recent developments in the electrodeposition of organoceramic materials.

Since the two basic processes that lead to the formation of organosol–gel materials (i.e., hydrolysis and condensation) are known to be catalysed by acid or base, it was evident that electrolytic deposition should be applicable to these processes as well, in spite of the fact that organometallic species are involved rather than inorganic species.

The first study was reported by Shacham et al.\textsuperscript{298} who proposed a new approach for sol–gel film formation, which involved the electrochemical control of the pH near a conductive surface. They described the electrodeposition of methyltrimethoxysilane (MeTMOS) on indium–tin oxide (ITO) and gold surfaces. The method was based on the “two-step” sol–gel preparation procedure in which the MeTMOS was first pre-hydrolysed and then polycondensed. The polycondensation rate was accelerated by applying a constant negative potential, thus increasing the pH of the hydrolysed solution in the vicinity of the electrode surface. The authors showed it was possible to deposit \textmu{}m-thick films by applying either a negative or a positive potential. Fig. 2 shows the dependence of the film thickness on the applied potential. Other parameters that influenced the thickness of the deposit were the time of applying the potential and the nature of the electrode material, i.e., its overpotential for hydrogen reduction. They reported that a less negative potential was required in order to deposit a sol–gel film (of the same thickness) on a gold surface.

This approach benefited from three major advantages: the pH varied only close to the electrode surface unchanging the bulk solution; the thickness and other properties of the deposit were controllable by the electrochemical parameters; the deposition of films was restricted to the conducting part of the surface and was controlled by the kinetics of the electrochemical process, thus opening the way to selective deposition of sol–gel films on conductive patterns.

In this respect it should be noted that controlling the pH on the electrode surface by amperometric (constant potential) or
galvanostatic (constant current) techniques has been examined previously by Kuhn and Chan\textsuperscript{299} and used as mentioned above for depositing metal hydroxides and metal oxides.

The electro-assisted organosol–gel deposition has been explored by other researchers as well. For example, Walcarius and Sayen\textsuperscript{300} prepared thiol-functionalized silica films on gold surface by applying a negative potential to the electrode. They varied the ratio between the two monomers used \( (i.e., \text{mercapto}）\text{propyltrimethoxysilane and tetraethoxysilane})\) and formed very stable and highly mechanical films due to the strong affinity of the thiol moieties to the gold surface. The porosity of the films alluded from the cyclic voltammetry of hexacyanoferrate(III), depended on the amount of mercapto-propyl groups in the composite layer. These groups played also a key factor influencing the sensitivity of \( \text{Hg(II)} \) detection for depositing metal hydroxides and metal oxides.

Collinson and her coworkers reported also on the electro-assisted organosol–gel deposition.\textsuperscript{300,301} In one study they electrodeposited sol–gel films from a solution consisting of tetramethoxysilane. A negative potential was applied to a glassy carbon electrode that drove the reduction of oxygen to hydroxyl ions \( (\text{at potentials less than 1.0 V vs. Ag/AgCl})\) and enhanced the hydrolysis and condensation of the silane monomer. The deposition was followed \( (\text{Fig. 3})\) by a quartz microbalance and cyclic voltammetry using the redox hexaamineruthenium(III). Films were also deposited on Pt, Au and ITO but always under negative potentials \( (+2.5 \text{ to } -1.5 \text{ V vs. SHE})\) on conducting surfaces immersed in a 2-propanol solution of zirconium tetra-n-propoxide using minute quantities of water \( (\text{water–monomer molar ratio values in the range of 10}^{-5} \text{ to } 10^{-1})\). The electrodeposition of organosol–gel films is not limited to silica-based films as was demonstrated by Shacham et al.\textsuperscript{302} \( \text{ZrO}_2 \) thin films were electrodeposited on ITO. The films, 50–600 nm thick, were obtained by applying moderate positive or negative potentials \( (+2.5 \text{ to } -1.5 \text{ V vs. SHE})\) on conducting surfaces immersed in a 2-propanol solution of zirconium tetra-n-propoxide using minute quantities of water \( (\text{water–monomer molar ratio values in the range of 10}^{-5} \text{ to } 10^{-1})\) making water the limiting reagent. The magnitude of the applied potential and its duration provided a convenient way of controlling the film thickness. The films exhibited an amorphous phase as revealed from XRD measurements. The effect of different parameters, such as the potential applied and its duration, the amounts of added water and the current-time characteristics, were studied. The films were exceptionally smooth as was evident by AFM. Fig. 4 shows bare, dip-coated and electro-deposited \( (\text{coated at } -0.9 \text{ and } -1.4 \text{ V vs. Ag/AgBr})\) ITO samples. The mechanism, which was proposed, was similar to that commonly accepted for \( \text{ZrO}_2 \) sol–gel formation, catalysed under acidic or alkaline conditions. The electrochemical processes generated eventually either \( \text{H}^+ \) or \( \text{OH}^- \) even in cases where the solvent was also oxidised or reduced. Yet, the presence of water was crucial for film deposition suggesting that water was involved not only in the electrochemical reaction but also in the condensation itself. The authors suggested that water served as the nucleophile that attacked

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**Fig. 2** Thickness of a methyltrimethoxysilane film deposited on an indium–tin oxide surface as a function of the potential applied for 30 min. (Reproduced from ref. 298, with permission.)

**Fig. 3** Current–time and change of frequency–time plots obtained at a gold electrode in a tetramethoxysilane sol following a potential step from 0.0 to \(-0.8 \text{ V vs. Ag/AgCl}\). (Reproduced from ref. 301, with permission.)

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\( \text{Ru(NH}_3\text{)}_{6}^{3+} \)
zirconia species under both oxidative (acidic) and reductive (basic) conditions.

In their recent study Shacham et al. applied the electro-assisted electrochemical method for the deposition of titania thin films. Moreover, they demonstrated the feasibility of entrapment a variety of organic and inorganic molecules and ions in the course of the electrodeposition. Four dyes (basic blue 41, methylene-blue, Fe(bpy)$_3^{2+}$ and Ru(bpy)$_3^{2+}$ were incorporated in the titania films, which were electrodeposited between 2.0 to 2.1 V vs. Ag/AgBr on ITO from alcoholic solutions consisting of titanium tetra-n-propoxide as the monomer. The film thickness was controlled by the applied potential and its duration and varied between 20–1000 nm.

Electroencapsulation of redox molecules and organic dyes was also reported by Collinson within a silica network. Cyclic voltammograms for the gel-entrapped ferrocene methanol and Ru(bpy)$_3^{2+}$ exhibited the characteristic redox behaviour of the molecules. Using angle-resolved XPS it was concluded that the entrapped species are homogeneously distributed in the silica matrix. The electroencapsulation of organic dyes in their “native” form proved to be more difficult because these species typically contain reducible functionalities that change the structure of the dye. Most of the examined dyes were irreversibly reduced or strongly adsorbed during the electrodeposition.

Entrapment of biologically active molecules by the electrodeposition of a sol–gel was recently reported by Luo et al. They showed that an amperometric biosensor for the quantitative measurement of glucose can be constructed by electrodeposition of chitosan hydrogel, glucose oxidase, and gold nanoparticles onto an Au electrode. The resulting biocomposite electrode provided a shelter for the enzyme to retain its bioactivity at considerably extreme conditions, and the decorated gold nanoparticles in the biocomposite offer excellent affinity to the enzyme. The biosensor exhibited a rapid response (within 7 s) and a linear calibration range from 5.0 μM to 2.4 mM with a detection limit of 2.7 μM for the detection of glucose.
Furthermore, and as Collinson pointed out, since gelation by the potential or the current has many implications of the surface and the rate of deposition can be well-controlled. The fact that deposition occurs only on the conducting parts work carried out so far it seems to offer several significant. Different electronic and mechanical properties to be very promising for designing tailor-made coatings with the titanium monomer and the copper ions. This method seems depended primarily on the ratio between the concentration of the sol–gel in the solution can be controlled independently of each other it allows the formation of films with greater porosity.

In conclusion, the electro-assisted approach is a new and versatile method for the formation of sol–gel films. It is evident that this route has not been fully explored, however, from the work carried out so far it seems to offer several significant advantages over the classical methods of spin and dip-coating. The fact that deposition occurs only on the conducting parts of the surface and the rate of deposition can be well-controlled by the potential or the current has many implications. Furthermore, and as Collinson pointed out, since gelation and drying proceed in this method independently of each other it allows the formation of films with greater porosity. Finally, the concentration of the sol–gel in the solution can be substantially lower than used in spin or dip-coating, making it an attractive approach for the formation of composites that consist of biologic and inorganic substances, which could be incorporated in the course of the electrodeposition without being affected by the mild conditions.

4. Diffusion in functionalized silica

The rate at which reagents enter and leave the silica host matrix is critically important to the development of sol–gel based chemical sensors, catalysts, and solid state devices. This rate dictates the response time of the device and influences its sensitivity and selectivity. The rate at which an entrapped receptor leaches from the matrix is also important. This rate impacts the usability of the device and controls the length of time it can be used. Diffusion in silica materials will be more complex relative to diffusion in a liquid as it will depend on the pore structure (pore size, pore size distribution, tortuosity) and the extent of intermolecular interactions between the guest and the host. Understanding how reagents move into and out of the sol–gel derived solid is vitally important, as is the ability to control this process.

Diffusion in sol–gel based materials has been studied using a number of different techniques, including time dependent methods, Raman spectroscopy, fluorescence correlation spectroscopy (bulk and single molecule), and electrochemical methods. Electrochemical methods have primarily been used to study diffusion in monoliths, but the information obtained is applicable to thin films as well. Electrochemical methods are particularly useful because they provide direct information about the diffusion of an assortment of different size and charged species both before and after gelation as well as through the early stages of drying in both functionalized and nonfunctionalized materials.

One of the first “electrochemical” studies was done by Murray and Zhang. In this work, an electrode was placed in a silica sol doped with supporting electrolyte and a redox active ferrocene derivative. Cyclic voltammograms of the encapsulated redox species were recorded before, during and after gelation. From the observed Faradaic current, they were able to obtain some information about diffusion. The research group of Audebert also used a similar set up and looked at the diffusion of entrapped ferrocene derivatives as well as ferrocene modified alkoxysilanes. The latter studies have been used to obtain information about the polycondensation kinetics in acid- and base-catalyzed gels.

Work in the Collinson group and the Cox group has focused on the use of ultramicroelectrode electrochemistry to measure the diffusion coefficient of a variety of different redox active dopants in gels prepared from TMOS or from functionalized alkoxysilanes. The advantage that ultramicroelectrodes provide over the more traditional microelectrodes are three fold: (1) their small size reduces gel cracking, (2) the diffusion coefficient of the entrapped redox probe can be obtained independent of concentration (important because concentration increases as the gel dries), and (3) the time scale of the experiment, and hence the diffusion layer distance, can be changed over a large range (important because the silica monolith is a rigid structure and can crack near the electrode interface). The apparent diffusion coefficient of a variety of different redox active molecules varies from their approximate value in solution (10^-6 cm^2 s^-1) to an order-of-magnitude or two smaller (10^-7 to 10^-8 cm^2 s^-1).

In hydrated monoliths, it appears diffusion depends more on the extent of intermolecular interactions between the host and guest than it does on pore size. One of the many advantages that functionalized silica provides is that the walls of the silica host can be very easily modified. Changes in the interfacial region of the host can significantly alter the degree at which the dopant interacts with the matrix, and hence diffusional rates. For example, the addition of just a small amount of organic modifier (i.e., CH₃) can cause the diffusion coefficient of gel-entrapped cobalt (II).
tris(bipyridine) (Co(bpy)₃²⁺) to increase a factor of ca. 3.³²³ Addition of a quaternary ammonium functional group can cause the apparent diffusion coefficient of Co(bpy)₃²⁺ to increase by one order of magnitude and the apparent diffusion coefficient of Fe(CN)₆³⁻ to decrease by one order of magnitude relative to those measured in an unfunctionalized silica gel.³²² Functionalizing silica with organic groups provides a fascinating approach to control diffusion in hydrated monoliths.³²２

Another electrochemical method that can be used to obtain indirect information about diffusion in solids is electrochemical luminescence (ECL).⁷⁹,²¹⁹,²²⁰,³²³ In this work, ECL reagents (ruthenium(II) tris(bipyridine) and either tertiary amines or oxalate) were introduced into the sol along with an ultramicroelectrode.⁷⁹,²¹⁹,²²⁰,³²³ After the sol turns into a gel, it was placed in a light-tight box and the ECL generated through application of a sufficiently positive potential. The magnitude of luminescence provides information about the diffusion and the reactivity of the entrapped guests. Functionalized silica hosts have also been shown to significantly increase the amount of light production for the Ru(bpy)₃²⁺–TPA system due to a decrease in the extent of intramolecular interactions between the co-reactant and the silica walls.²²⁰,³²³

5. Solid-state electrochemistry with silica sol–gel matrices and their application to electrochemical gas sensors

5.1. General considerations and background

Sol–gel systems that are processed at ambient temperature retain sufficient pore electrolyte and water content to support conventional electrochemical measurements such as cyclic voltammetry and amperometry. The scope of application of these sol–gel electrolytes is enhanced because they can be fabricated to have a variety of sizes and shapes, are amenable to coupling electrochemistry by a variety of methods including optical spectroscopy and mass spectrometry, and can possess a range of such properties as hydrophobicity and internal structure, which are accomplished by chemical modification of the solids by methods that include organic modification of the backbone structure. Among the potential and reported applications of solid-state voltammetry of sol–gels are electrochromic displays, gas sensors, and charge storage systems. In addition, they provide media for fundamental studies of charge transport, electrocatalysis, and sol–gel processing.

Initial reports on solid-state electrochemistry are typified by investigations of charge transport with mixed-valence systems. For example, Prussian Blue (PB) bridged between two electrodes using a cell such as that described in Fig. 6b yielded dc conductivity related to the rate of electron self-exchange between Fe(II)–Fe(III) lattice sites and voltammetric behavior that was influenced by potassium ion transport through the solid matrix.³³¹ A finding in a study of PB that is significant in studies of electrochemical processes in sol–gels in the absence of a bulk liquid phase is that for an appreciably Faradaic current at ambient temperature some liquid electrolyte must be present.³³² Sol–gel processing can lead to mixed-valence redox systems, most notably V₂O₅, that are partially reduced in the presence of Li⁺ to form an energy storage electrode; however, this material is typically employed in contact with propylene carbonate that contains LiClO₄,³³³ rather than as a redox-active solid in the absence of a bulk liquid phase.

Early studies on solid-state electrochemistry with silica sol–gel electrolytes used a cell comprising the solid immobilised between two electrodes (Fig. 6a). A potential applied across the cell resulted in current flow when the solid electrolyte contained an oxidizable and a reducible species such an Fe(CN)₆³⁻–Fe(CN)₆⁴⁺ mixture.³³⁴ The mixed state that allows current flow was formed by exposure of a hexacyanoferrate-containing sol–gel, which included alcohol dehydrogenase, to ethanol vapors. As in the case of PB immobilised between two electrodes, this system will yield a cyclic voltammogram with two peaks that are symmetrical around 0 V in that the

Fig. 6 Common solid-state voltammetry cells used for study of sol–gel systems. (a) two-electrode “sandwich” cell; (b) interdigitated microelectrode array; (c) two-electrode cell with a micron-scale working electrode; (d) co-planar disk electrode cell; (e) three-electrode cell with a micron-scale working electrode. (Reproduced from ref. 338, with permission.)
electrodes switch between roles of cathode and anode during cycling and the current at each electrode must be the same at all times.\(^{331}\)

An improved cell design is to use a three-electrode system, with the working electrode area smaller than that of the counter electrode, thereby obviating the need for a mixed-valence system. In one design, the solid was dip-coated over a Pt interdigitated electrode array, which provided the counter and working electrodes (Fig. 6b); a low-flow junction Ag/AgCl electrode was contacted to the sol–gel to provide a reference potential.\(^{335}\) When the solid was a sol–gel doped with Fe(phen)\(^{3+}\), where phen is orthophenanthroline, the cyclic voltammogram had the same general characteristics as that of Fe(phen)\(^{3+}\) in aqueous solution. In both cases the complex was oxidized reversibly at 0.9 V.

Here, our focus is on silica materials, in which case solid-state electrochemistry is limited to applications as an electrolyte rather than an electroactive solid except when a redox site is bonded to the backbone. Moreover, the review will be limited to materials processed at ambient temperature, so residual water will reside in the pores.

### 5.2. Electrochemistry of reagents encapsulated in silica sol–gels

One reason to investigate the solid-state electrochemistry of dopants in sol–gels is to probe the gelation chemistry. The prototypic study was that of Oliver et al.\(^{329}\) By monitoring the voltammetry of ferrocene during the gelation of a sol, the point at which diffusion becomes restricted is manifested by a change in current, which signals the gelation point. Opallo’s group did a similar study but with silica sol–gels in which the aqueous electrolyte was replaced with an organic electrolyte.\(^{336,337}\) Both tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS) were used as precursors. Propylene carbonate or sulfolane that contained lithium or a tetraalkylammonium perchlorate was exchanged for water as the pore liquid; however, residual water still established the negative potential limit of electrochemical measurements. The resulting voltammetry was similar to that in the analogous bulk liquid phase, which supported the model of facile diffusion in these sol–gels. However, as in the study by Oliver et al.,\(^{329}\) the current decreased with age of the solid. Perhaps the most important result in terms of the interpretation of voltammetric measurements in sol–gel electrolytes was evidence that the interface between the working electrode and the solid was stable and that there was not a liquid boundary between them.

As discussed in section 4, interpretation of electrochemical data obtained with sol–gel electrolytes must consider that apparent diffusion coefficients depend both on the pore structure and, particularly with modified silica, on possible interactions between the dopant and the silica backbone. For freshly prepared sol–gels or with those processed with templating agents to have a mesoporous structure, the apparent diffusion coefficients of dopants can approach the values observed in liquids (e.g., 10\(^{-6}\) cm\(^2\) s\(^{-1}\)).\(^{79,80,320,325}\) even in the absence of a contacting liquid phase,\(^{79,325}\) as long as interaction between the redox probe and the backbone does not hinder mass transport of the probe and/or the counterion. A description of the difference between the apparent diffusion coefficient and the physical diffusion coefficient, along with a discussion of related fundamental electrochemical parameter in solid-state voltammetry is provided in a recent review.\(^{338}\)

The pore size and backbone interactions also can influence the pathway of electrochemical reactions in these solid-state electrolytes. An example is the electrochemical reduction of UO\(_2^{2+}\) in silica derived from TMOS or TEOS.\(^{339}\) The sol–gel was cast as a coating on co-planar disk electrodes (Fig. 6d), which were immobilised by epoxy in a cylindrical mold. The working, counter and reference electrodes were 0.2 mm (diameter) Au, 0.5 mm Pt, and 0.5 mm Ag, respectively. The reduction of UO\(_2^{2+}\) was the same as that observed in aqueous solution; specifically, cyclic voltammetry showed a reversible, diffusion-limited process at \(ca.\) 0.6 V. However, the corresponding oxidation was shifted to \(-0.3\) V from the aqueous solution value of about 0.6 V. The change of behaviour was attributed to the disproportionation of U(V) that is the initial product of the reduction. It occurs slowly on the time scale of cyclic voltammetry (25–1000 mV s\(^{-1}\)), in this case in a liquid electrolyte; however, in silica, the disproportionation was apparently accelerated by interaction of UO\(_2^{2+}\) with the partial negative sites of the silica. This hypothesis was supported by results obtained with La\(^{3+}\) included in the silica; the masking of the negative sites restored the voltammetry in silica to that observed in aqueous solution, that is, the oxidation was observed near 0.6 V in the presence of La\(^{3+}\).

Modification of the ion-exchange properties of silica can be exploited in doping of silica electrolytes. Inclusion of generation-4 poly(amidoamine) dendrimer (G4-PAMAM) in the sol leads to a mesoporous structure\(^{340}\) with a cation-exchange property related to the amine sites of this dendrimer. The resulting material can be doped homogeneously by high levels of PB by first incorporating Fe(CN)\(_6^{3-}\) from an external solution followed by contact with Fe\(^{2+}\).\(^{341}\) Profiling by Raman microspectroscopy demonstrated homogeneous distribution of PB throughout a 1.0-mm monolith. Cyclic voltammetry at a Pt electrode using a cell similar to that in Fig. 6e gave current–voltage curves that agreed with those for films in contact with a liquid electrolyte (Fig. 7). Notably, the redox process near 0.85 V was diffusion-limited, which was attributed to the easy motion of counter-ions in this mesoporous matrix along with rapid electron transfer at the working electrode. When the PB
FeFe(CN)$_6$ was attributed to the mesoporous structure. The incorporation of vanadia in a composite sol–gel, SiO$_2$–V$_2$O$_5$.342 The silica was microporous but contained residual water (10–15% by weight) and electrolyte. Because of the smaller pore size as compared to the PB studies, the cyclic voltammetry of the V IV,V couple in the composite was less perturbed during continuous cycling of the potential. In addition, the current was limited by resistance when the composite was used.

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Pore size also influenced the voltammetry of the V IV,V couple of vanadial in a composite sol–gel, SiO$_2$–V$_2$O$_5$.342 The silica provided a network more stable than that of vanadial alone during continuous cycling of the potential. In addition, the redox of the V IV,V couple in the composite was less perturbed by resistance when the composite was used.

A case where pore size can be hypothesised to have an important influence on the electrochemistry of a dopant in a silica matrix is when the product of the electron-transfer reaction at the electrode undergoes subsequent chemical reaction, particularly where multiple pathways leading to final products of highly disparate physical size are possible. An example is the oxidation of indoles. The cation radical that is produced at the electrode can form a dione of approximately the same size as the indole, or it can dimerize. For indoles that are neurotransmitters, such as 5-hydroxytryptophan (5-HTPP), this difference in pathway is of importance in biological systems.343 A test of whether the pathway can be changed by performing redox in silica matrices with a varying pore structure was performed with 5-HTPP doped by addition to the TMOS precursor to silica.344 With a mesoporous solid electrolyte, the cyclic voltammetry was similar to that obtained with aqueous solution. In both cases, an irreversible oxidation was observed at 0.4 V. When the experiment was repeated in microporous silica, the oxidation was quasi-reversible; the ratio of the anodic to cathode peak currents approached 1.0, signifying that the rate of any coupled chemical reaction that consumes the product of the electron-transfer reaction, presumably a cation radical, was slow on the time scale of the experiment.

To verify the hypothesis that the dimer is formed by oxidation of 5-HTPP in mesoporous silica and that the dione is formed in microporous silica, identification of the products of oxidation was required. Because the oxidation of indoles passivates electrodes, the oxidation was performed chemically using air oxidation over a 3-week period. A matrix-assisted laser desorption/ionization (MALDI) mass spectrometry method was developed to determine species in sol–gels.345,346 The MALDI results verified the formation of the dimer and dione in mesoporous and microporous silica, respectively. The agreements of the masses with the hypothesis were 0.15% (dimer; mesoporous) and 0.04% (dione; microporous).

The passivation of the working electrode is not the only concern in the generation of high levels of electrolysis product in a silica matrix; in cells such as those in Fig. 6, the product of the oxidation at the working electrode can diffuse to the counter electrode and be reduced, and conversely. To prevent this reversal of reaction, the analogue of using a counter electrode isolated from the sample by a salt bridge in liquid systems was explored; the method was to use a bilayer sol–gel for solid-state electrochemistry in which the layer in contact with the counter electrode contained a depolarizer other than the test substance. This design involved casting an acidified silica layer, which support the counter electrode process (the reduction of hydrogen ions) on a dried sol–gel that contained the test species in contacting with the working electrode (an anode, in the case that was studied). The example that was reported was the oxidation of glutathione at a glassy carbon electrode modified with an electron- and oxygen-transfer catalyst, mixed-valence ruthenium oxide, RuO$_x$.347 As in the analogous aqueous-solution study, the product that was identified by MALDI was cysteic acid.

The oxidation of aniline in silica sol–gels has been investigated, primarily as a means of “wiring” the matrix with a conducting polymer. Ita et al.348 chemically oxidised aniline with peroxydisulfate during the processing of a TMOS-derived sol–gel in the presence of surfactant, sodium dodecyl sulfate. Evidence of aggregates of the emeraldine form of poly(aniline) (PANI) was obtained. Their attempt to form PANI chemically...
after the sol–gel dried was not successful. The formation of a silica–PANI composites using PANI dissolved in organic solvent has been reported.255,349

The formation of PANI by solid-state electrochemistry of aniline in the sol–gel is complicated by the influence of the pore size. With microporous silica, electrochemical oxidation yielded the dimer, whereas with mesoporous silica, short-chained polymers were formed.263 A route to addressing the problem of not obtaining long-chained PANI was described.350 The aniline was bound to the silica as a component of an organosilane precursor to the solid, 3-aminophenyl-[3-(triethoxysilyl)propyl]urea. Combinatorial chemistry was used to optimise the ratio of organosilane to TEOS in the gelling mixture that was subsequently oxidised to PANI. A 1 : 12 mole ratio was identified as the optimum value. When the oxidation is performed by scanning between −0.2 and 0.8 V, the initial product is not PANI; the onset of formation of the polymer after ca. 30 cycles at 50 mV s⁻¹ was suggested by the shapes of the current–voltage curves.

5.3. Application to electrochemical gas sensors
Sol–gel materials, especially those such as SnO₂ that are semiconductors, often have been employed to determine gas-phase analytes on the basis of conductance changes in response to the surrounding gas composition (see ref. 351 and citations therein). In contrast, few sensors for gas-phase analytes that are based on an electron-transfer reaction in a sol–gel matrix in the absence of a bulk liquid phase have been reported even though this general approach has been used frequently with organic ionomers (e.g., Nafion) as the electrolyte.235,338,352 A problem with the use of organic ionomers as the solid electrolyte is that in order to obtain a consistent response the water content must be controlled by contact with a reservoir, for example via a wicking system. As described below, the chemistry of silica sol–gels permits inclusion of an internal humidistat to obtain consistent results.

A gas sensor that represents a transition between those based on semiconducting sol–gels and those clearly based on semiconducting sol–gels and those clearly based on semiconductors, often have been employed to determine gas-phase analytes on the basis of conductance changes in response to the surrounding gas composition (see ref. 351 and citations therein). In contrast, few sensors for gas-phase analytes that are based on an electron-transfer reaction in a sol–gel matrix in the absence of a bulk liquid phase have been reported even though this general approach has been used frequently with organic ionomers (e.g., Nafion) as the electrolyte.235,338,352 A problem with the use of organic ionomers as the solid electrolyte is that in order to obtain a consistent response the water content must be controlled by contact with a reservoir, for example via a wicking system. As described below, the chemistry of silica sol–gels permits inclusion of an internal humidistat to obtain consistent results.

A gas sensor that represents a transition between those based on semiconducting sol–gels and those clearly based on the redox of the analyte is one that responded to ammonia.353 The cell was similar to that in Fig. 6b, except that the interdigitated array was a three-electrode assembly. The electrodes were coated with vanadia. The working electrode was coated with RuOₓ, a known catalyst of electrochemical oxidations.347 Quantitative measurements were made on gases containing various quantities of ammonia; Coulombs were measured by applying 1.0 V for 60 s comprised the signal. The array electrode was suspended in the vapor over a chemical humidistat to maintain the water content of the sol–gel. The electrode process was uncertain. Although the electrochemical oxidation of ammonia with a comparable catalyst is known,354 the interaction between ammonia and the vanadia cannot be discounted as a source of the current increase over background levels.

A carbon monoxide sensor was developed using a TEOS-derived sol–gel as the coating over the array electrode (Fig. 9).355 Signal generation was the oxidation of CO at a Pt electrode. The linear scan voltammetry was the same as that observed with CO dissolved in solution except that a potential difference related to the use of a quasi-reference electrode in the gas sensor and an Ag/AgCl reference in the liquid experiment was observed. Specifically, using the cell in Fig. 9 in the static mode, after a 2-min equilibration with 3.3 pptv CO, the peak potential was 0.42 V whereas in pH 0.5 aqueous solution saturated with CO, the peak potential was 0.88 V. With the TEOS-based sensor, the sensitivity was 0.4 nA ppm⁻¹, and the detection limit when used in the flow injection mode, which results in dilution of the CO in the carrier gas, was 5 ppmv. Perhaps the most important results were that the sensitivity was independent of humidity over the range 9–76% and the results were unchanged by aging of the sol–gel for at least 40 d.

An approach similar to that for the CO sensor was used for determination of hydrogen peroxide356 and monomethyl hydrazine.357 The hydrogen peroxide sensor used a base-catalysed sol–gel process (using TEOS) to cast the film over a three-electrode assembly. The working electrode was Pt. A challenge was to develop a base-catalysed procedure that retained a high level of pore water. Inclusion of 1.3 M MgCl₂ in the sol and using 0.02 M NH₃ as the catalyst resulted in a film that was ca. 60% water over the range 3–11 d. The MgCl₂ served as an internal humidistat in the silica, thereby providing long term stability. Triton X-114 was included to template the sol–gel into the mesoporous domain. The electrodes were co-planar disks, as shown in Fig. 6d. The reason for using base-catalysed processing was to obtain a pH of the sol–gel that led to extraction of hydrogen peroxide into the silica as HO₂⁻. The sensor responded linearly over the range 0.096–5.4 ppmv and had a detection limit of 0.01 ppmv with a 60-min preconcentration and differential pulse voltammetry as the signal-generating step.

The monomethyl hydrazine (MMH) sensor was the same as that for H₂O₂ except that acid-catalyzed processing was used. RuOₓ-coated Pt was the working electrode, and the cell design had the working electrode extending through the silica so that a three-phase boundary among the gas, solid electrolyte, and electrode surface was formed.357 This design obviated the need to preconcentrate the analyte into the silica. The Pt was in the form of a grid, which increased the surface area. With this design, steady-state currents at 0.65 V were developed, the magnitude of which was linearly related to the MMH concentration in a gas flow cell (Fig. 10).
A limitation of these gas sensors is that they are not selective. They are potentially useful on controlled systems such as leak detectors, but a wider scope of application will require coupling them to a separation system such as a gas chromatograph. But this application will require a provision to maintain at least 5% humidity at the detector. A promising extension of the concept used in the sol-gel gas sensor with the three-phase boundary cell is to electrochemically monitor solutes in non-polar liquids that lack electrolyte. This method is easy. One of the first examples of this approach was demonstrated by Collinson and Makote using dopamine. PTMOS was lyzed and condensed in the presence of dopamine. TMOS, methyltrimethoxysilane, and TMOS were hydrolysed and condensed in the presence of dopamine. PTMOS was chosen because of its likely affinity toward the aromatic group template via the hydrolysis and condensation of TMOS (or TEOS) often in the presence of organoalkoxysilanes. Relative to organic polymerisation techniques, sol–gel processing has many advantages. Most notably:

1. Mild reaction conditions allow for almost any “template” to be introduced into the polymerising network.
2. Enormous flexibility associated with material fabrication. Thin films, high surface area powders, or porous monoliths can easily be prepared. Thin films, in particular, are most beneficial for chemical sensor applications because of the short path length for reagent diffusion into the matrix.
3. Large selection of commercially available organoalkoxysilanes that can be incorporated into the inorganic framework to improve chemical specificity toward a given template.
4. Potentially faster diffusion and reduced non-specific binding.

Traditionally there have been three approaches to imprinting: the covalent approach, the noncovalent (self-assembly) approach, and surface imprinting. In this section, these three concepts will be described as they pertain to functionalized silica.

In the covalent approach, the print molecule is derivatized with the polymerisable groups (silicon alkoxide groups) such that it will be “covalently attached” to the polymeric framework. The covalent bonds that lock the template in place are then cleaved and the template subsequently released. An excellent example of this approach is the work performed by Davis and Katz. In this study, an aromatic ring was derivatized with either 1, 2, or 3, aminopropyltriethoxysilane side groups. This template was reacted with TEOS to produce the imprinted bulk materials. The C–N bond was cleaved and the resulting aromatic core removed from the framework. The resulting cavities had either one, two, or three spatially arranged aminopropyl groups and have been shown to “act as shape-selective base catalysts”.

In another intriguing example, the covalent approach was used to imprint estrone in sol–gel derived nanotubes formed from nanopore alumina template membranes. The estrone was modified by reacting the phenol group on the estrone with the isocyanate group of 3-(triethoxysilyl)propyl isocyanate. The urethane bond can be cleaved at elevated temperature to remove the template from the nanotube host. Due to the open framework, these materials showed a fast uptake of the imprinted molecule into the host.

In the self-assembly approach, the cavity is created via noncovalent interactions between the template and the polymeric network. Examples of noncovalent interactions include van der Waals interaction, π-stacking, electrostatic attractions, and hydrogen bonding. This method is more routinely used because it does not require the synthetic modification of the template with polymerizable groups. The availability of organosilanes with phenyl, amino, carboxyl, etc. functionalities makes the selection of monomers relatively easy. One of the first examples of this approach was demonstrated by Collins and Makote using dopamine as the template. In this work, phenyltrimethoxysilane (PTMOS), methyltrimethoxysilane, and TMOS were hydrolysed and condensed in the presence of dopamine. PTMOS was chosen because of its likely affinity toward the aromatic group.

Fig. 10 Chronoamperometry of monomethyl hydrazine at a silica-based gas sensor with a RuOx coated Pt working electrode. Currents corresponding to regions a–f correspond to incremental increases of concentration of 50, 100, 300, 133, 150, and 150 ppmv, respectively. (Reproduced from ref. 357, with permission.)
in dopamine. The composite sol was cast on an electrode, the dopamine removed by soaking in buffer, and the selectivity of the templated film for dopamine evaluated using cyclic voltammetry.60,202 Fig. 11 depicts this approach. In more recent work, Avnir and co-workers have created specific chiral cavities in thin sol–gel derived films by utilising PTMOS, TEOS, and 3-aminopropyltriethoxysilanes as the functionalized monomers and (R),(S)-propranolol, (R),(S)-2,2,2-trifluoro-1-(9-anthryl) ethanol, or D,L-3,4-dihydroxyphenylalanine as templates.366

Another facet to molecular imprinting involves “surface imprinting.”359 By focusing on just the surface of a support or a thin layer on a surface, fast uptake/release of the target analyte can be achieved. An early example of “surface imprinting” was demonstrated by Moshbach and coworkers. In this work, organoalkoxysilanes and a given template were combined and the resultant sol used to coat the surface of porous silica particles to create recognition sites on a solid support for chromatographic applications.367 Dai and coworkers have also eloquently shown that the cavities of mesoporous silica can be imprinted by utilising organoalkoxysilanes (i.e., 2-(2-aminoethylamino) propyltrimethoxysilane) that have an affinity for metal ions.368 This group has also demonstrated that uptake kinetics can be also increased by combining traditional metal based coordination imprinting with micellar templating.369,370 When the micelles are removed from the host, a large number of “pores” remain in the host to allow faster access and transport kinetics.

In chemical sensing, it is necessary to attach a selective material, for example, imprinted functionalized silica, to a suitable transducer to detect the magnitude and extent of binding. Fluorescence,371,372 piezoelectric,373,374 radioactive,366 and electrochemical60,202,375,376 based detection has been reported.359 Electrochemical based methods have not received as much attention as, for example, piezoelectric methods, because it often requires that the template be electroactive and accessible to the electrode surface. This potentially limits the types of compounds that can be targeted and materials made. A few examples, however, have been appeared in the literature. A templated film selective toward the electroactive neurotransmitter, dopamine, has been described by Collinson and Makote (vide supra).60,202 Mandler, Marx and co-workers have made thin sol–gel films from organoalkoxysilanes using parathion as the template.375 Parathion exhibits well defined cyclic voltammograms in aqueous solution. Cyclic voltammetry was used in part to prove that the template is in the film, the template can be removed from the film, and the template can repartition back in the film.375 Electrochemical sensing using molecularly imprinted materials is still new even for the more widely studied organic polymers.377 There is still much work to be done in the coupling of functionalized silica with potentiometric, conductometric, capacitive, and voltammetric detection.

7. Electrochemistry of ordered mesoporous organically-modified silicas

A new class of silica-based materials was discovered in 1992,378 arising from the inorganic polymerisation of sodium silicate or silicon alkoxide(s) in the presence of a liquid crystal-forming template (ionic or non-ionic molecular surfactant, block copolymer).379,380 These are made of amorphous silica walls spatially arranged into periodic arrays that often mimic the liquid crystalline phases exhibited by templates, displaying regular cylindrical mesopores of monodisperse size (typically in the range from 20 to 100 Å in diameter). The mesostructure is usually maintained after template removal (by calcination or solvent extraction), leading to highly porous ordered solids with extremely high surface area (up to 1400 m² g⁻¹), mesopore volume greater than 0.7 mL g⁻¹ and narrow pore size distribution. An illustration of the preparation of the most widely used mesoporous silica, the so-called MCM-41, made of a regular hexagonal packing of mesopore channels, is depicted on Fig. 12. These solids can be derivatized with a wide range of organic groups to give mesoporous organic–inorganic hybrids, which bring additional physical and chemical properties that might be readily exploited for new applications.339,40 Functionalization can be performed according to two main

![Fig. 11](image1)

**Fig. 11** Simplified “cartoon” of the sol–gel imprinting approach as it pertains to the templating of dopamine in functionalized silica.

![Fig. 12](image2)

**Fig. 12** Schematic representation of the synthesis of hexagonal MCM-41 silica materials by the template route, involving the hydrolysis and condensation of tertaethoxysilane (TEOS) in the presence of surfactant molecules; the final solid is obtained after extraction of the surfactant from the mesoporous structure.
routes: the post-synthesis grafting of as-prepared mesoporous silicas (reaction of organosilanes on pre-fabricated mesoporous supports\(^{41,379}\)) or in one step by co-condensation of a tetraalkoxysilane and one or more organoalkoxysilane(s) (sol–gel synthesis in the presence of surfactant\(^{381,382}\)). This second approach has led to a better control of the amount of incorporated species\(^{383}\) and to a more uniform distribution of the organic functional groups within the mesopore channels,\(^{384}\) but may suffer from some loss in structural order, especially at high organic content.\(^{383,385}\) Finally, the versatility of the sol–gel process enables the preparation of mesostructured organosilicas in various morphologies, including micron- and nano-size particles, films, monoliths, regular spheres, etc.\(^{2,386,387}\)

Several strategies were applied to confine mesoporous silica-based materials on electrode surfaces.\(^{388}\) One can basically distinguish 4 categories: (1) the dispersion of as-synthesised particles into carbon paste electrodes;\(^{48,54,55,144–146,389–392}\) (2) composite electrode devices based pressed materials (MCM + graphite or SnO\(_2\) particles) on Pt or as pellets;\(^{193–196}\) (3) composite films made of mesoporous particles embedded in an organic polymer, with or without mixed graphite particles, deposited on the surface of a solid electrode;\(^{397–402}\) (4) the \textit{in situ} generation (spin casting) of mesoporous films on a solid electrode by the sol–gel process, applied in the presence of a surfactant template.\(^{403–408}\) The choice between one approach or another relies mostly on the target application.\(^{388}\)

It is now well-established that ordered mesoporous organosilicas offer significant advantages over the related amorphous organosilica gels in terms of enhanced accessibility to the organic functional groups. This has been recently pointed out in the solid–liquid extraction of heavy metals,\(^{409,410}\) in the secondary transformation of the organic functions,\(^{411,412}\) and in heterogeneous catalysis.\(^{413–415}\) The uniform pore structure allows easier access to the active centres in comparison to hindered or even blocked sites in an amorphous material made of non regular porosity (Fig. 13). Such an advantage has been especially demonstrated for mercury(II) binding to thiol-functionalized mesoporous silica samples, obtained either by post-synthesis grafting or by the co-condensation route. In fact, an effective access to all the binding sites (100% of SH groups complexed with Hg(II) was achieved in micelle-templated mesostructures with pore diameters larger than 2.0 nm, whereas incomplete filling was always observed when the corresponding amorphous silica-based adsorbents were used.\(^{410,416,417}\) Possible increase in selectivity of the binding process was also reported due to confinement effects in the regular mesostructure.\(^{418,419}\) but functionalized sol–gels for mercury(II) extraction displayed the same performance in terms of distribution coefficient and residual concentration in solution independently of whether they were prepared with or without surfactant templates.\(^{420}\) It should be mentioned, however, that the beneficial effect of the uniform pore structure might be less if the reaction involves the formation of charged moieties on the mesopore walls, which results in a local electric field possibly restricting the further ingress of charged species of the same sign (e.g., protonation of aminopropyl-grafted MCM-41\(^{416}\) or Hg\(^{2+}\) binding to thiol-functionalized mesoporous silicas in acidic media\(^{134}\)).

Even more interesting, mass transport kinetics in ordered mesoporous organosilicas were superior over those in related amorphous solids, as first pointed out for proton diffusion in silica-based materials grafted with amine groups.\(^{416,421}\) More detailed studies were conducted with the mercury(II)–thiol-functionalized mesoporous silicas system, involving a wide range of materials obtained by post-synthesis grafting or co-condensation and displaying various structure, pore size, and density of functional groups.\(^{385,416,421–424}\) Kinetics investigations were first made from batch experiments involving the continuous in situ monitoring of Hg(II) consumption from an aqueous suspension containing thiol-functionalized mesoporous silica particles, by using a rotating disk electrode operating in stationary diffusion conditions. Some typical results are summarised in Fig. 14a. As shown, the uptake of Hg(II) species was faster in mesostructured materials compared to amorphous gels. Some distinction can also be made between mesoporous organosilicas obtained by post-synthesis grafting or by the co-condensation route, the latter giving rise to faster mass transfer processes at the beginning of the adsorbent filling while slower diffusion was observed at higher loadings. Diffusion rates were usually found to decrease by increasing the filling levels because less and less place was available to ensure fast mass transport,\(^{385,416}\) except in case of large MCM-41 spheres for which acceleration of the binding process has been reported.\(^{422}\) The density of functional groups in the hybrid materials was also reported to play an important role in affecting the apparent diffusion coefficients measured for Hg(II) in the mesopores, the highest values being achieved for an optimum content of 20% organosilane in the starting sol (and 80% of tetraalkoxysilane) leading to mesoporous organic–inorganic hybrids with wormhole framework structures.\(^{385}\) Comparing the binding rates of Hg(II) in thiol-functionalized SBA-15 and SBA-16 materials has revealed faster mass transport in the hexagonal SBA-15 structure than in the cubic SBA-16 sorbent.\(^{424}\) As expected, the rate of access to the binding sites was also much higher in materials of larger pore size.\(^{385,416,421,423,424}\)

Recently, we have shown that the incorporation of ordered mesoporous particles into carbon paste electrodes (CPEs) enables one to get a rapid evaluation of mass transfer rates of Hg(II) (used as a target electroactive probe) in the thiol-functionalized materials.\(^{55,144}\) This is illustrated in Fig. 14b.

![Fig. 13 Schematic and comparative illustration of grafting (a) an amorphous silica gel and (b) an ordered MCM-41 silica material. (Adapted from ref. 410, with permission.)](image-url)
where the voltammetric response of CPEs modified with various types of thiol-functionalized silica particles have been compared after open-circuit accumulation of Hg(II) species from a dilute solution: as shown, the intensity of the electrochemical response can be directly related to the speed at which Hg(II) species are likely to reach the binding sites in the materials as this process constitutes the rate-determining step of the "open-circuit preconcentration–voltammetric detection" sequence.

A direct consequence of the above features is the possibility to exploit such modified electrodes in preconcentration electroanalysis, with better performance expected with ordered mesoporous adsorbent in comparison to amorphous functionalized gels (Fig. 14b). Indeed, tuning the sensitivity of electrodes modified with an organic–inorganic hybrid was reported to be possible by tailoring the structure of the nanocomposite material, as exemplified for Hg(II) sensing at thiol-functionalized silica-modified electrodes\textsuperscript{44,55,425} or for the detection of Cu(II) at electrodes modified by polysiloxane-immobilized amine ligands\textsuperscript{446} or carnosine moieties\textsuperscript{426} in agreement with what was otherwise observed for sensing heavy metal species at CPEs comprising unfunctionalized MCM-41 particles.\textsuperscript{48,389} Other examples involve the simultaneous determination of Pb\textsuperscript{2+} and Cd\textsuperscript{2+}, Cu\textsuperscript{2+} and Pb\textsuperscript{2+}, or uranium sensing\textsuperscript{391,426} at carbon paste electrodes modified with either thiol or carbamoyl phosphonic acid self-assembled monolayer on mesoporous silicas, with detection limits in the ppb concentration range. The generation of mesoporous thin films on gold and their subsequent functionalization with mercaptopropyl groups was also applied to the adsorptive stripping voltammetry of Pb\textsuperscript{2+}.\textsuperscript{408,426} Finally, ion exchange voltammetry was successively applied to the detection of Cu\textsuperscript{2+} and Ru(NH\textsubscript{3})\textsubscript{6}\textsuperscript{3+} cations at CPEs modified with sulfonic acid-functionalized mesoporous silica particles, with the highest sensitivity achieved with materials meeting the best compromise between a high density of organofunctional groups and sufficiently high porosity to maintain an easy and fast access of guest cations to the ion exchanging sites.\textsuperscript{145}

By bringing mesoporous materials to an electrode/solution interface, one can characterise the electrochemical behaviour of electroactive guests that had been introduced in the mesopore channels either by simple impregnation, by ion exchange, by complexation to organic ligands present in the material, or even by covalent attachment to the silica walls. Examples are available for cobalt(II)-based Schiff base complexes impregnated in MCM-41\textsuperscript{393,394} for copper- and manganese-phenanthroline complexes impregnated and/or complexed to aminopropyl-grafted MCM-41 samples,\textsuperscript{395} or for ferrocene-based dendritic guest molecules in highly ordered mesoporous silica.\textsuperscript{398} In general, the more mobile electroactive species gave rise to the more sensitive electrochemical responses, while a great part of the redox probes immobilised deeply and strongly in the bulk of the mesostructure were electrochemically silent,\textsuperscript{393} except when intra-MCM-41 electron transfer was favoured by electron hopping between closely associated (i.e., ferrocenyl) moieties in the mesopore channels.\textsuperscript{398} More intense electrochemical signals have been obtained for redox cations bound to MCM-41 particles via electrostatic interactions (e.g., Cu(NH\textsubscript{3})\textsubscript{4}\textsuperscript{2+} or Hg(NH\textsubscript{3})\textsubscript{2}\textsuperscript{2+} in pure silica MCM-41\textsuperscript{389} or Ru(bpy)\textsubscript{3}\textsuperscript{2+} in Al-hexagonal mesoporous silica\textsuperscript{402}, for which easy desorption can occur
prior to the redox transformation on the electrode surface. On the other hand, a permeable behaviour of dense MCM-41 films prepared by spin-coating on indium–tin oxide substrates was reported on the basis of charge selectivity as only the positively charged redox probes \((i.e., \text{Ru(bpy)}_2^{2+}, \text{Fe(bpy)}_3^{3+}, \text{Os(bpy)}_2^{2+})\) were allowed to cross the membrane to reach the electrode surface whereas the negatively charged species \((i.e., \text{Fe(CN)}_6^{3-}, \text{Ru(CN)}_6^{3-}, \text{Mo(CN)}_6^{3-})\) were excluded.\(^{405}\)

The support/guest properties of mesostructured silica-based materials used in connection to electrochemistry began to be exploited in several sensor applications. Among them, electrocatalysis holds a prominent position because of the wide possibilities offered by mesoporous \((\text{organo})\text{silicas}\) to host a wide range of catalysts and/or charge transfer mediators. Their implication in electrochemistry involves \(\text{ClO}_3^-\) and \(\text{BrO}_3^-\) sensing with CPEs comprising amine-functionalized-MCM-41 particles doped with \(1:12\) phosphomolybdic acid,\(^{427}\) the catalytic oxidation of 1,4-dihydrobenzoquinone by \(4,4'\)-bipyrindinium units covalently attached within MCM-41 particles,\(^{399}\) or the electrocatalytic applications of \(\text{Pd}_n\) nanoparticles immobilised in SBA-15 in the presence of \(\text{CO.}^{401}\) Another promising field is that of bioelectrochemistry, which exploit the regular confined environment if mesopore channels to immobilise biomolecules while maintaining their biological activity. This field is rather young, but one can already mention electrochemical biosensors based on glucose oxidase immobilised within a mesoporous silica or \(\text{TiO}_2\) hosts,\(^{428,430}\) and two studies on the electrochemical behaviour of cytochrome \(\text{C}^{431}\) and hemoglobin\(^{397}\) immobilised by impregnation in mesoporous silicas. It is noteworthy that silylation of the mesopore openings is sometimes necessary to prevent leaching of the biomolecule in the solution.\(^{431}\) Finally, mesoporous silica films or particles were also involved in gas sensing devices (for water, alcohols, \(\text{NO}_x\), \(\text{CO}, \text{H}_2\), or \(\text{CH}_4\)), but they were most often based on non-functionalized materials.\(^{396,403,404,406,407}\)

### 8. To be continued?

Notwithstanding the numerous successful investigations and exciting results presented above, it is likely that the area of sol–gel and organic–inorganic hybrid materials is still underdeveloped/underrepresented in electrochemical science. We are confident that future works in this field could take benefit from a closer contact between materials scientists and electrochemists to enable a rationalization of the modified electrodes preparation (composition, structure, long-term stability) to bring “on demand” properties directed to improve the performance of target advanced applications.

Of course it is not easy to predict what the future would be, but one can assume that the two major challenges are the control of the architecture of the electrode material (sol–gel composite matrix or hybrid film coated on a conductive support) and the design of integrated electrochemical systems enabling fast charge and mass transfer processes. The molecular or supramolecular templating approaches are promising avenues for these purposes, at the conditions to be able to get materials displaying reproducible characteristics with mechanically and chemically stable structures over prolonged times. The electrochemical manipulation of chemical parameters \((i.e., \text{pH})\) would also be helpful, either by participating in the generation of the sol–gel materials or by monitoring the reactivity of the modifying layers. Another critical point that appears as a real challenge, is the need to increase the long term stability of hybrid films on electrode surfaces. To this end, special attention should be paid to provide both a durable rigid structure to the porous film and to ensure its good adhesion to the electrode surface, \(e.g.\) via a “nanoglue” layer, without preventing or limiting to great extent the electron transfer processes. One can also expect that electrochemical impedance spectroscopy (EIS) would be useful for characterisation of these novel electrode materials, as already exploited for the determination of bulk resistance variations in silica sol-gels during the gelation and aging stages,\(^{332,434}\) as well as for the development of impedancemetric sensors.

Biohybrid formation will no doubt continue to attract the attention of sol–gel scientists and consequently inspire sol–gel electrochemists. Particularly, the recent evolution of gentle techniques for encapsulation of genetically engineered and native microorganisms in sol–gel electrodes is expected to reach also the electrochemical arena opening new prospects in fuel cells and biosensing.

As we live in the “nano” era one would anticipate that nanotechnology will also play a major role in the future prospects of sol–gel. The “nano” mania is likely to be expressed in both dimensions, namely, in the thickness of the sol–gel films as well as in the lateral ability to form well-ordered nanometric structures of sol-gel materials. The advantage of reducing both dimensions is evident: while nanometer thick films will bridge between monolayers and traditionally polymeric films enabling fast mass and charge transfer, nanometric features organized laterally on the electrode surface will be the future building blocks of almost any interfacing device.

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